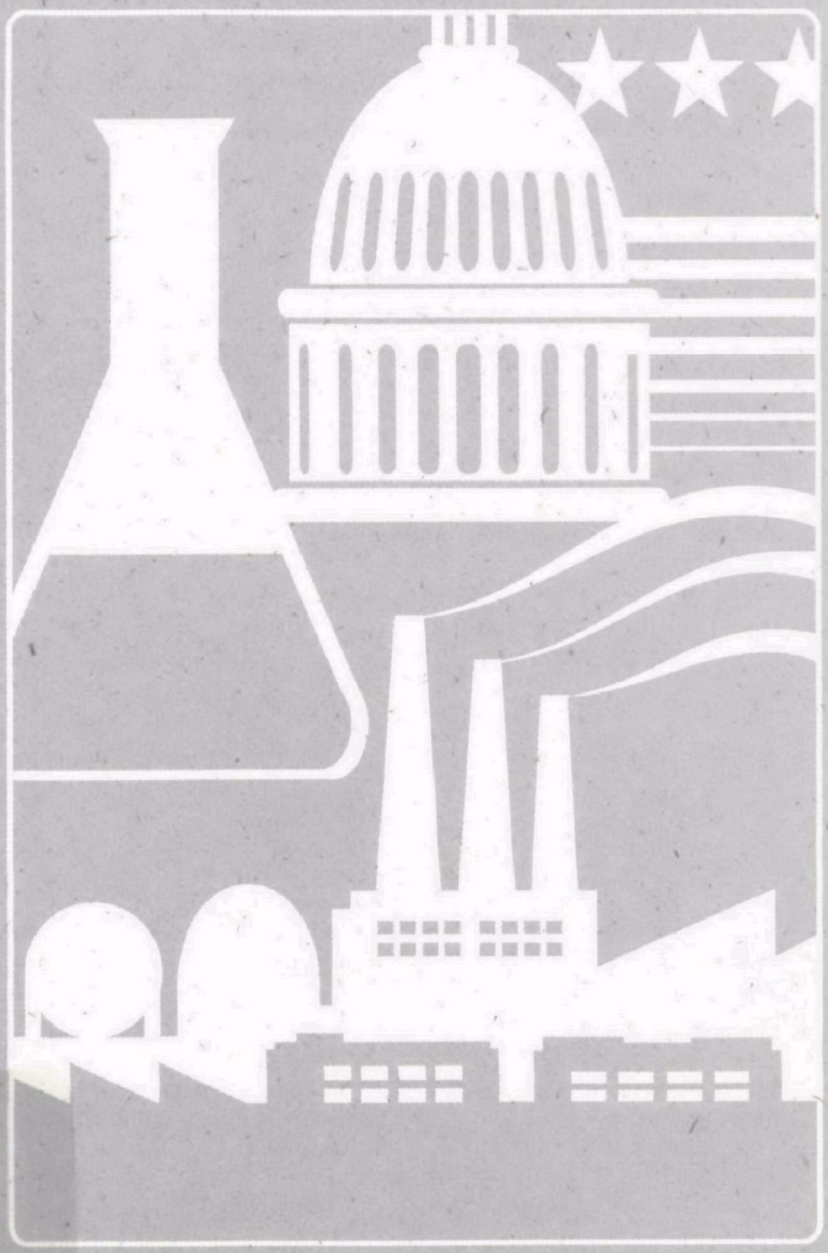
The Twelfth Annual

Waste Testing & Quality Assurance Symposium



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July 23–26, 1996

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Washington, DC

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SAMPLING & FIELD

Sampling Strategies: Impact of Heterogeneity on Waste Characterization

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ABSTRACT

The US Environmental Protection Agency (EPA) Office of Solid Waste is in the process of revising Chapter 9 of SW-846[1]. To support this effort, the Office of Solid Waste is working with the American Society for Testing and Materials (ASTM) to accelerate the development of ASTM standards needed for these revisions. Under this mandate, Task Group D34.01.12 was assigned the task of authoring guidance on sampling strategies for heterogeneous wastes. The resulting standard has passed sub-committee and main committee and final changes have been submitted for main committee balloting.

The standard is a practical non-mathematical discussion and guide for heterogeneous waste sampling which is consistent with particulate material sampling theory as well as inferential statistics and can serve as an introduction to the statistical treatment of sampling issues. The standard approaches the sampling of heterogeneous wastes in a generic sense while leaving project specific details to a planning process such as the Data Quality Objective process.

The annex to the standard contains an introductory discussion of homogeneity, practical homogeneity, random heterogeneity, non-random heterogeneity, stratification and the relationship of samples to populations. The main body of the standard focuses on the sampling of highly stratified wastes, which are usually very difficult to characterize. An appendix applies the guidance to a storage area containing 4000 drums.

INTRODUCTION

The first edition of EPA Publication SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods was announced in May of 1980. Around 500 to 1000 copies of the first edition were distributed. The first edition included a limited discussion of sampling issues. The second edition of SW-846 which included an expanded discussion of statistical issues was announced in September of 1982. Approximately 5000 copies of this edition were distributed. The third edition of SW-846 was announced in the Federal Register in March of 1987. Chapter Nine of the third edition which is entitled, "Sampling Plan" incorporated the earlier version of the statistical discussion along with an expanded discussion of sampling plan implementation. Chapter Nine has remained unchanged since it was authored in 1986.

EPA recognized that Chapter Nine must be updated to reflect the increased understanding and complexity of waste sampling issues. As part of its strategy to update Chapter Nine,

[1] Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Third Edition.

EPA has worked within the ASTM consensus standard process. EPA sponsored several accelerated standards on issues pertinent to waste sampling, including a standard guide on Sampling Strategies for Heterogeneous Waste, which is the subject of this paper.

In January of 1994, a task group defined a scope for the accelerated standard guide on heterogeneous waste. In response to EPA's request, the task group agreed that the standard would address the more extreme cases of heterogeneity that can be encountered during waste characterization. Since it was an accelerated standard, the task group met on a quarterly basis for a period of 2 years. A number of drafts were completed and balloting has progressed such that a Society approved standard is expected this year.

The focus of the Standard Guide on Sampling Strategies for Heterogeneous Waste and of this paper is four fold: 1) to describe the causes and types of heterogeneity; 2) to discuss the relationship between samples and populations; 3) to discuss the impact of heterogeneity on the sampling process and 4) to present a guide for sampling heterogeneous wastes. This paper addresses issues presented in the standard as well as related issues that the author believes further develops aspects of heterogeneity and their impact on sampling.

HETEROGENEITY

The following subsections discuss sampling in terms of populations, samples and characteristics. The following definitions should facilitate this discussion.

Characteristic— a property of items, a sample or population which can be measured, counted, or otherwise observed. A characteristic of interest may be the cadmium concentration or ignitability of a population.

Heterogeneity— the condition of the population under which all items of the population are not identical with respect to the characteristic of interest.

Homogeneity— the condition of the population under which all items of the population are identical with respect to the characteristic of interest.

Item— a distinct part of a population, (e.g. microscopic particles, macroscopic particles and twenty-foot long steel beams).

Population— the totality of items or units under consideration.

Practical Homogeneity— the condition of the population under which all items of the population are not identical. However, for the characteristic of interest the differences between individual physical samples are not measurable or significant. That is, for practical purposes the population is homogeneous.

Random—lack of order or patterns in a population whose items have an equal probability of occurring.

Sample— a portion of a population which is taken for testing or for record purposes.

According to the prior definitions, sampling of an abandoned property would be a simple task if it was a homogeneous population. Being homogeneous, all items of the abandoned property would be identical for the characteristic of interest. Thus sampling and measuring any item from the property would allow one to evaluate the entire property. Unfortunately, homogeneity is a theoretical state and actual populations don't consist solely of identical items.

Since heterogeneity is the norm, the items of the abandoned property would be dissimilar to some degree. The degree of heterogeneity can range from that of a population whose items are so similar that for practical purposes the population can be considered homogeneous (Practical Homogeneity) to a population whose items are all dissimilar. Usually, the greater the degree of heterogeneity, the greater the sampling difficulty.

Due to the identical nature of items, no distributional differences can be detected within a theoretical homogeneous population. However, the different items of heterogeneous populations can be distributed differently to create distinctly different types of heterogeneity.

Random heterogeneity— occurs when dissimilar items are randomly distributed throughout the population.

Non-random heterogeneity — occurs when dissimilar items are non-randomly distributed resulting in the generation of strata.

Strata— are subgroups of the population which are separated in space or time from the remainder of the population and are internally consistent with respect to the characteristic of interest and different from adjacent portions of the population.

Figure 1 is a graphical depiction of homogeneous, randomly heterogeneous and non-randomly heterogeneous populations. The drum-like populations portray different types of spatial distributions while the populations being discharged through the waste pipes represent the different types of temporal distributions. No spatial or temporal distribution is identifiable between the identical items of a homogeneous population. Identifiable spatial and temporal distributions are present in the heterogeneous populations, with the existence of strata in the non-randomly heterogeneous populations. It is important to note that the perception of a population's homogeneity or heterogeneity is relative to analytical sample size, population size, sampling objectives and at times the analytical methods.

For example, pure silver nitrate, some of which is powder and some of which is in the form of large crystals would be considered heterogeneous by the analyst concerned with particle size while the analyst concerned with leachable silver content would find the material to be homogeneous.

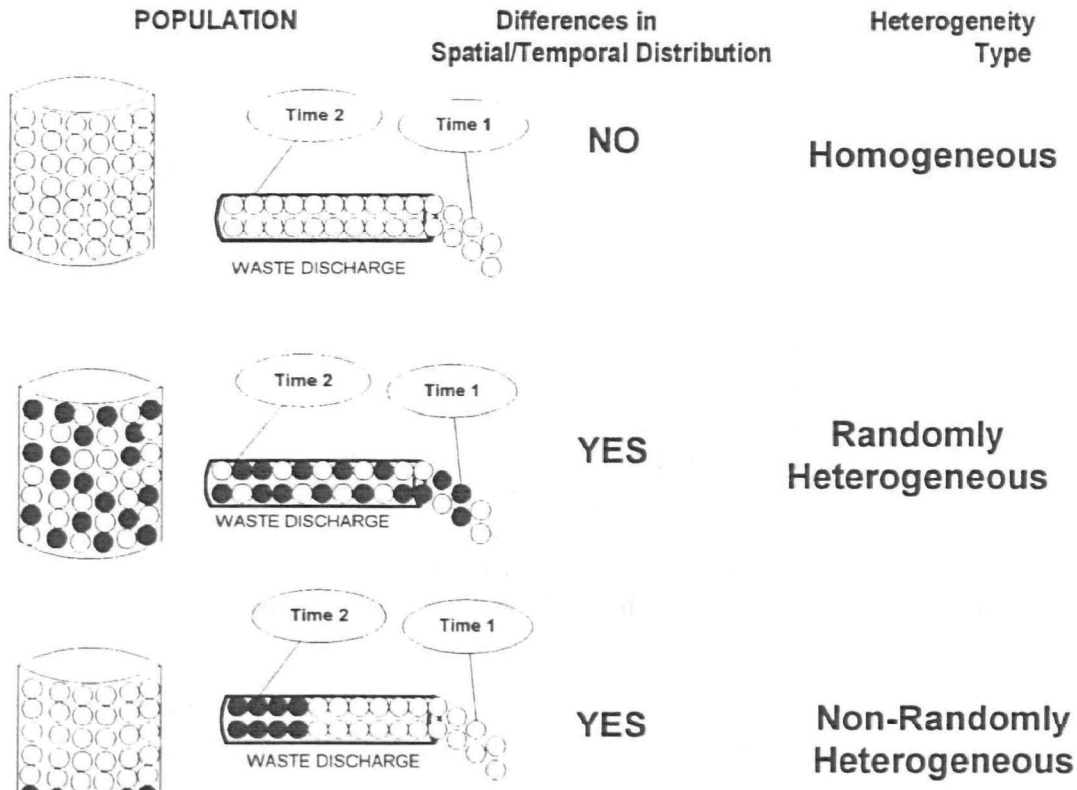
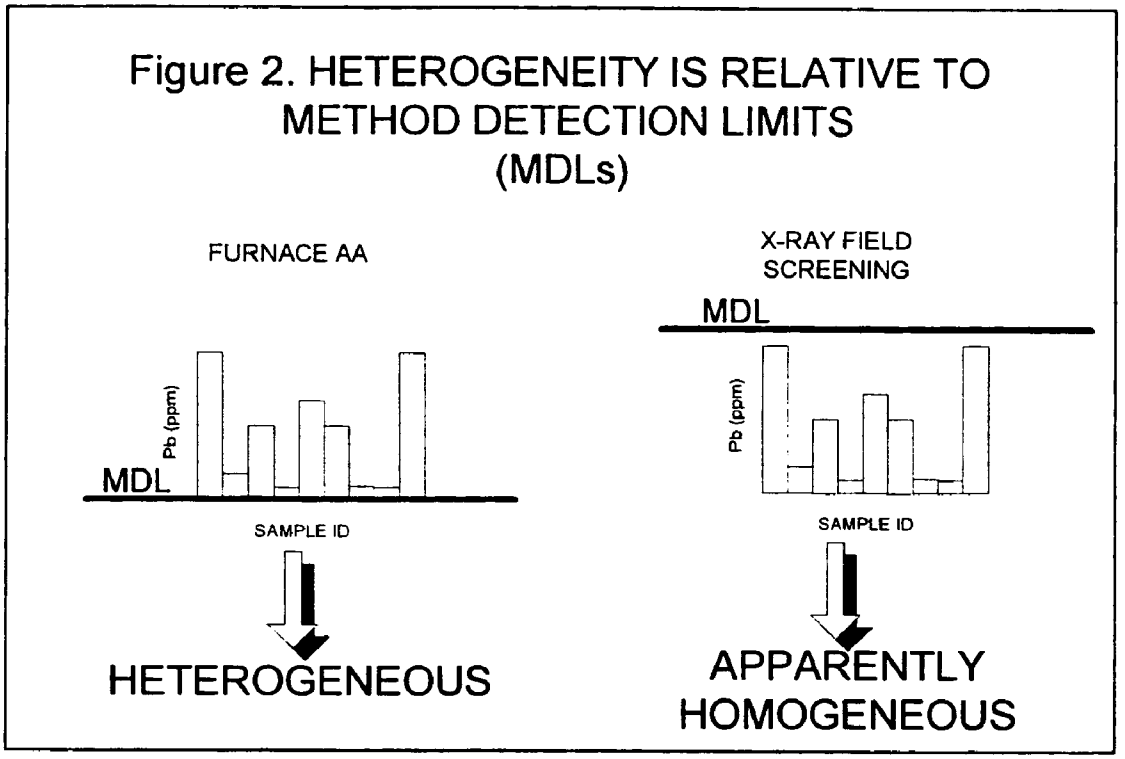


Figure 1 Types of Heterogeneity

Figure 2 displays how the perception of homogeneity can be dependent upon the sensitivity of the analytical method. Subjecting the same samples to two methods having different method detection limits (MDL) can lead to different classifications. The samples analyzed in the field using a less sensitive screening technique result in a series of non-detects indicating that the material is homogeneous. The data for the same samples subjected to a sensitive fixed laboratory method lead to the opposite conclusion of heterogeneity. However, if the action level for the site represented by these samples is a factor of 100 times the less sensitive MDL, then one can conclude even using the more sensitive graphite furnace data that the material is practically homogeneous.

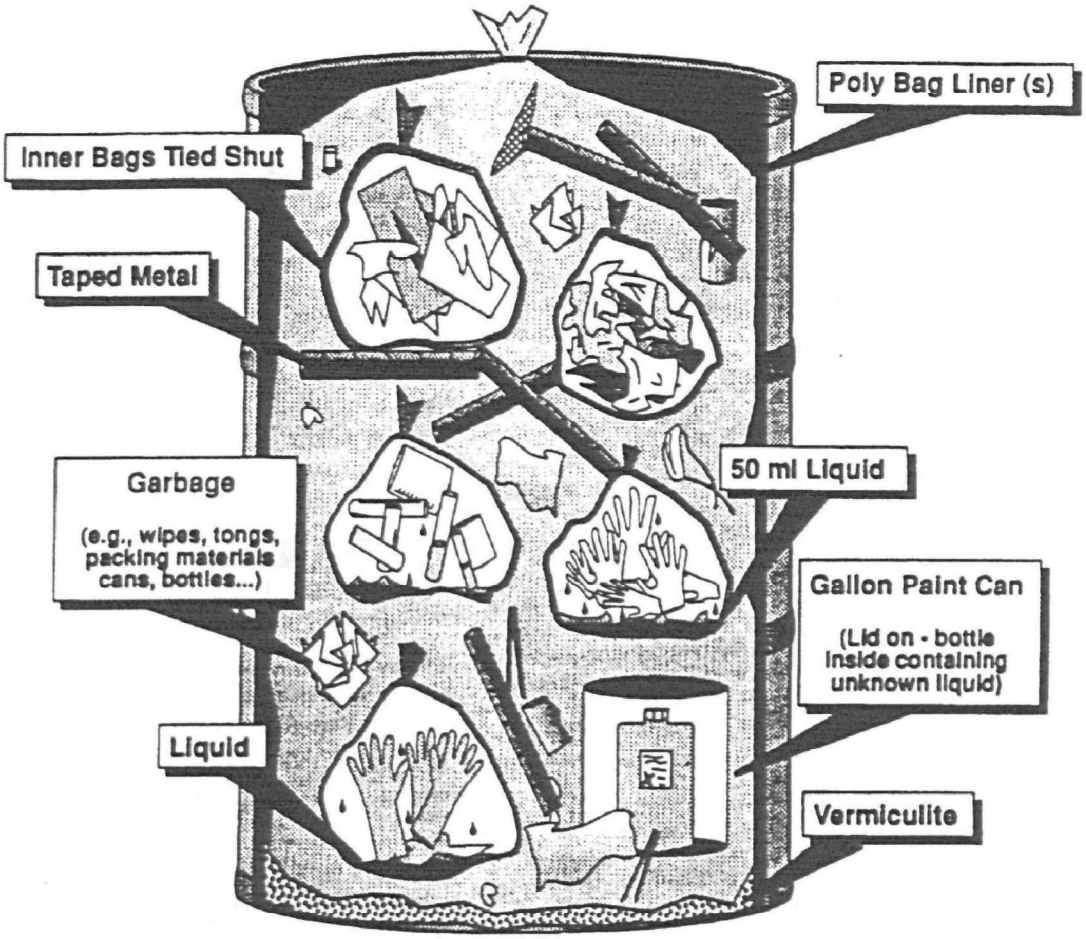
As mentioned, the focus of the standard guide is on those wastes which display the more extreme types of heterogeneity. These types of wastes have proven the most difficult to characterize. Figure 3 displays an example of a "worst case drum of heterogeneous waste" as defined in a report for an EPA work shop on heterogeneous waste. Although, extremely heterogeneous wastes are usually thought to contain variously shaped and sized components of a multitude of different compositions, a single contaminant in an otherwise



homogeneous matrix can be distributed in such a stratified manner that it creates an extremely heterogeneous waste[2]. A common factor for these extremely heterogeneous wastes is their large number of strata. Thus these wastes which are very difficult to characterize will be referred to as "Highly Stratified" wastes. Highly-stratified wastes which are a type of non-random heterogeneous wastes have so many strata that they become difficult to sample and characterize. Classifying a waste according to its level of stratification is a relative issue. It is relative to the persons planning and performing the sampling, their experience, available equipment, budgets, the characteristic of interest and sampling objectives. Highly-stratified wastes are such that it is not practical or effective to employ conventional sampling approaches to generate a representative database. Nor would the mean concentration of a highly-stratified waste be a useful predictor (i.e. the level of uncertainty is too great) for an individual subset of the waste that may be subjected to evaluation, handling, storage, treatment or disposal.

[2] S. Feenstra, Soil Sampling for Environmental for Environmental Studies: Matching Methods with Objectives, ASTM Symposium on Sampling Environmental Media, Denver, CO., April 5, 1995

Figure 3. Highly Stratified Waste



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asbestos gloves, respirator cartridges,
photographic materials

Characterizing Heterogeneous Wastes
EPA 600/R-92-033

Strata are different portions of a population separated in time or space with each portion having internally similar concentrations or properties which are different from adjacent portions of the population

- A landfill may display spatially separated strata, since old cells may contain different wastes than new cells (stratification over space).
- A wastepipe may discharge temporally separated strata, if night-shift production varies from the day shift (stratification over time)

- Lead-acid batteries will constitute a strata separate from commingled soil, if lead is the characteristic of interest (stratification by component).
- Drums from an inorganic process may constitute a different strata from those co-disposed drums generated by an organic process (a sub-type of stratification by component referred to as stratification by source).

Different strata are often generated by different processes or a significant variant of the same process. The different origins of the strata usually result in a different concentration or property distribution and mean concentration or properties.

While stratification over time or space is widely understood stratification by component is less commonly employed. Some populations lack obvious spatial or temporal stratification yet display extreme levels of heterogeneity. If these populations contain easily identifiable components such as large crystals, rods, blocks, gloves, pieces of wood or concrete then it may be advantageous to consider the population as consisting of a number of component strata. An advantage of component stratification is that it can simplify the sampling and analytical process and allow a mechanism for making inferences to a highly stratified population. Component stratification shares many similarities with the gender or age stratification applied to demographic data by pollsters.

POPULATIONS & SAMPLES

This section discusses the interrelation of populations and samples, how samples are used to make inferences about populations and the resulting implications on sampling activities.

Populations can be homogeneous, randomly heterogeneous or non-randomly heterogeneous. Populations possess a mean, a mode and median concentrations as well as a distribution of the characteristics of interest. Environmental professionals often need to know these population attributes to determine if contamination has occurred, the magnitude and breadth of contamination, the suitability of waste for incineration or stabilization, or the health/environmental risks associated with a certain population. To meet these informational needs, the environmental professional will study the population. Ideally, he/she would study the entire population. However, this is often not possible and almost always is not practical, cost or time effective. Thus, in most instances the environmental professional will study portions of the population (samples) and use information from these samples to make inferences about population attributes. These samples are the windows through which the environmental professional views the population.

The population and its boundaries will be a function of sampling objectives. Examples of populations that may be subjected to sampling are a 1-gallon bottle, a waste drum, a parking lot, a pond and a city block. Definition of the population's physical and temporal boundaries are key to defensible decision making. Population attributes can change as the boundaries of the population are changed. For example, the middle population in Figure 3 is clearly randomly heterogeneous. However, if the population was to be re-defined such

that it contained only the four items in the top left-hand corner of the population, the new population would be non-randomly heterogeneous with a layer of black items on top of a layer of white items. Although, changing population boundaries can change a perspective, the re-defining of a population into smaller more manageable exposure or remediation-sized units may be advantageous from a cost savings or waste management perspective.

Samples may be representative of a population, or may not be representative of a population. Samples may be similar to other samples or display significant intersample differences for the characteristics of interest (intersample variance). The differences in the measured characteristics of samples may not be correlated with space or time (i.e. randomly heterogeneous) or the differences in the measured characteristics may be correlated with time or space (i.e. a non-random heterogeneous waste stratified over time or space). Table 1 summarizes how samples can be used to identify a population's heterogeneity type.

Table 1. Population and Sample Attributes

POPULATION ATTRIBUTE	SAMPLE DESCRIPTION	SAMPLE ATTRIBUTE	INFERENCE
Homogeneous (Theoretical Homogeneity)	All samples contain only identical items	No Significant intersample variance. No correlation of concentration or properties with time, space, component or waste source.	Samples are representative of a homogeneous population
Practical Homogeneity	All samples contain dissimilar items, but each sample contains same proportions	No Significant intersample variance. No correlation of concentration or properties with space, time, component or waste source.	Samples are representative of a homogeneous population
Random Heterogeneous	All samples contain dissimilar items, each sample has different proportions, but these proportions are not correlated with time, space or components	Significant intersample variance. No correlation of concentration or properties with space, time, component. or waste source	Samples are representative of a random heterogeneous population
Non-random Heterogeneous (Stratified)	All samples contain dissimilar items, each sample has different proportions and these proportions are correlated with time, space, components or source	Significant intersample variance. Correlation of concentration or properties with space, time, component, or waste source	Samples are representative of a non-random heterogeneous population

INFERENCES

The accuracy of inferences regarding a population will be a function of how well the samples represent the characteristic of interest. The Resource Conservation and Recovery Act (RCRA) defines a representative sample as a sample of a population which can be expected to exhibit the average properties of the population. The use of the singular form of the word "sample" can be misleading to the non-statistician. The varying characteristics of a heterogeneous material are usually better reflected in more than one sample, while measurements of mode, median and variance require the collection and analysis or more than one sample.

It is better to think of representative sample(s) as those sample(s) that are collected in such a manner that they accurately reflect the population characteristic of interest. Figure 4 depicts how samples collected in the field as well as subsamples generated in the laboratory, as a group, must physically and chemically reflect population characteristics for the resulting data to accurately represent the population.

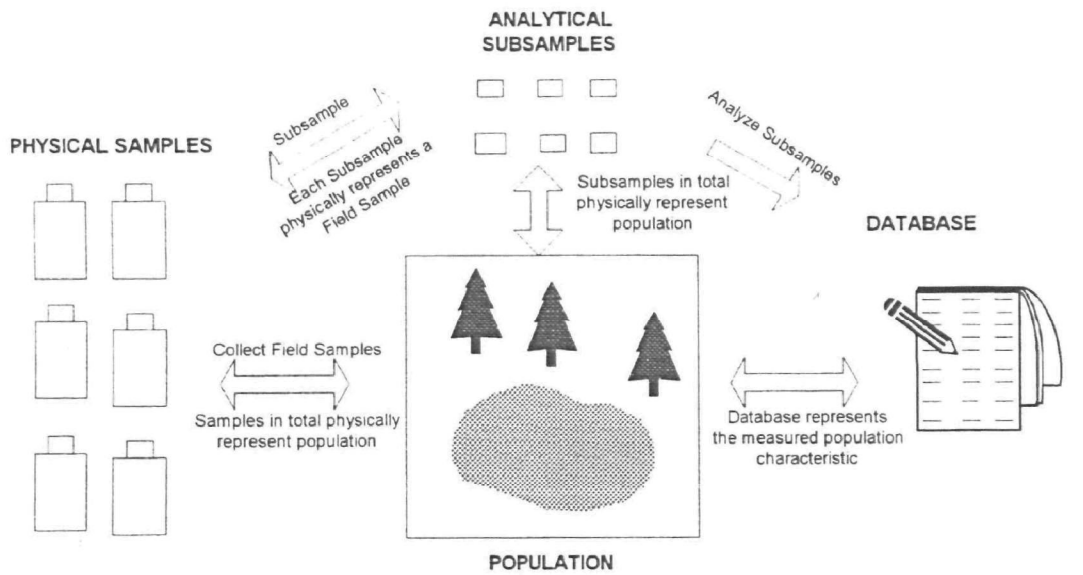


Figure 4 Samples Representing a Population Characteristic

The representativeness of samples and the associated inferences are dependent upon sample collection considerations such as sampling strategy, sampling locations, sample mass, number of samples, sampling equipment and sample handling. Figure 5 shows how the mass/volume of a sample and sampling locations can affect the representativeness of samples. The inferences listed in the middle and right-hand columns are based on sets of different samples masses. One sample of each set was taken from the top of the population while the second sample was taken from the bottom of the population.

As expected, sampling of a homogeneous population (top population in the left hand column) is simplified by the fact that any item accurately represents the population. However, sampling of the randomly heterogeneous population depicted in the center of the far left column is more complicated and different inferences can be made depending on the sample size and the luck of the draw. The large mass samples give a consistent picture of the population, correctly infer that the population is randomly heterogeneous and would yield a representative measure of population characteristics. Different and incorrect inferences regarding population characteristics can be made when collecting the smaller mass samples. If the randomly heterogeneous population consisted of a 50/50 mix of white and black items and only two of the small samples were collected, there would be a 50% chance of inferring that the population was randomly heterogeneous, a 25% probability of inferring that the population was homogeneous and consisted only of white items and a 25% probability of inferring that the population was homogeneous and consisted only of black items.

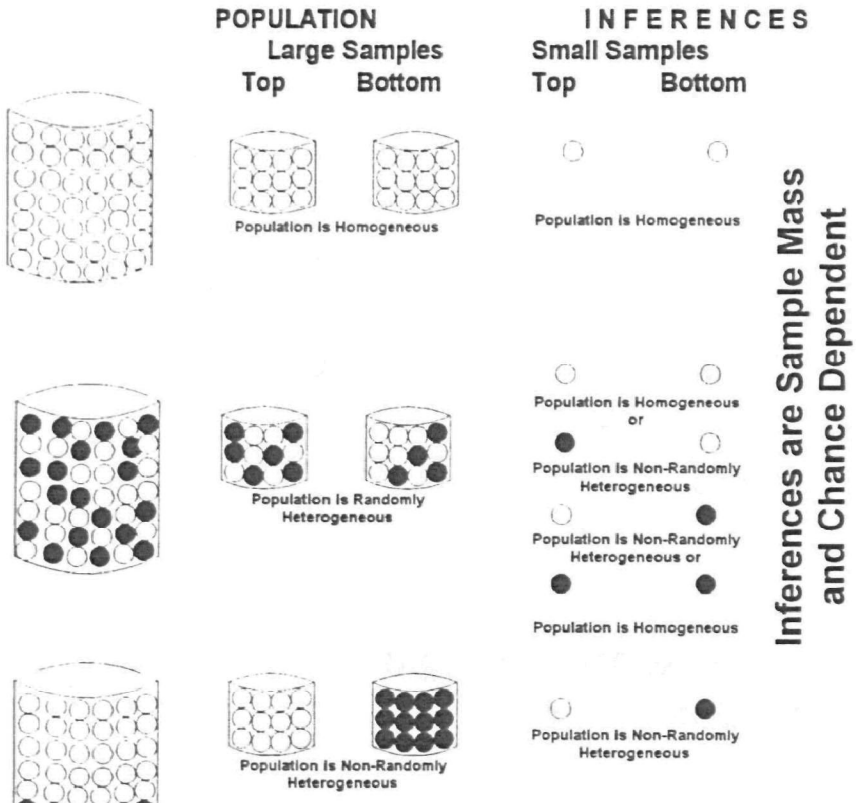


Figure 5 Population Inferenes

The inferences for the non-randomly heterogeneous population depicted as the bottom population in Figure 5 are consistent regardless of sample size. However, this

similarity of inferences for different sample masses would decrease if the samples were collected from random locations within the population, as opposed to the top and bottom locations specified by the figure.

The homogeneous and heterogeneous populations depicted in Figure 5 are greatly simplified, however the lessons learned from studying these simplified populations can be extrapolated to actual populations. For example, in the above example, inferences were based on two samples. After studying the figure, it becomes apparent that as the number of samples increases, the accuracy of inferences can be expected to improve. Also, regardless as to whether the depicted populations represented a drum or a landfill, if the sample consisted of a vertical core from top to bottom, there would be increased confidence that any existing horizontal strata would be represented in the collected sample.

The relative proportions of sample mass to population mass are much smaller in actual sampling situations. The actual percentage of population sampled is usually infinitesimal. All other conditions being the same, the fewer the samples and the smaller the sample mass, the greater the likelihood that the characteristics of a population will not be properly represented.

Equally important is the relationship of item size to sample size. As item size becomes smaller with respect to sample size and the number of items per sample increase the greater the likelihood that a representative sample will be collected.

As the relative size of items increases, the fewer items in a sample and the greater the likelihood of collecting less representative samples. The worse case scenario occurs when item sizes are too large to be accommodated by sampling equipment. Referring back to Figure 5, assume that black items are twice as large as the white items and that the chosen sampling device was only large enough to accommodate the smaller white marble. This sampling scenario could lead to substantial errors if the characteristic of interest differed from white to black items. Considering a more concrete example, 500 g samples collected with a properly designed scoop may be appropriate for collecting granular material. However a 500 g sample mass would not be appropriate if the designated population consisting of a mixture of fine sand and chromium-plated automobile bumpers was to be investigated for chromium. Sampling theory as described by Pitard, discusses methods for using the maximum item size to calculate optimum sample masses that will accommodate all items.

CHARACTERIZATION OF HETEROGENEOUS WASTES

The standard offers strategies for sampling and characterizing different types of highly stratified wastes. Wastes can be heterogeneous in particle size and/or in composition, allowing for the existence of;

- Strata of different sized items of similar composition
- Strata of similar sized items of different composition

- Strata of different sized items and different composition

The last two highly stratified waste categories include the wastes that are usually the most difficult to characterize. Figure 6 describes an approach that is applicable to the characterization of highly-stratified wastes. The standard guide suggests modifications to conventional waste characterization to accommodate the complexities presented by highly stratified wastes. Prior to implementing these modifications the following information should be collected as part of a structured planning process (e.g. ASTM D5792-95 or EPA QA/G-4);

- Is the characteristic of interest correlated with time, space, item size, component or source
- Does any waste component not contain the characteristic of interest be
- Do small items represent a stratum as well as large cumbersome items
- Is the characteristic of interest innate or absorbed to surfaces

This information regarding the distribution of the characteristic of interest can be used to modify sampling and laboratory subsampling, All assumptions used to modify sampling must be justified and well documented. When possible the validity of assumptions should be periodically confirmed by sampling and analysis.

Suggested modifications to the sample preparation step include;

- Increasing the analytical sample mass/volume
- Generation of homogeneous extracts and digestates
- Component elimination and surrogates
- Surface wiping
- Particle Size Reduction

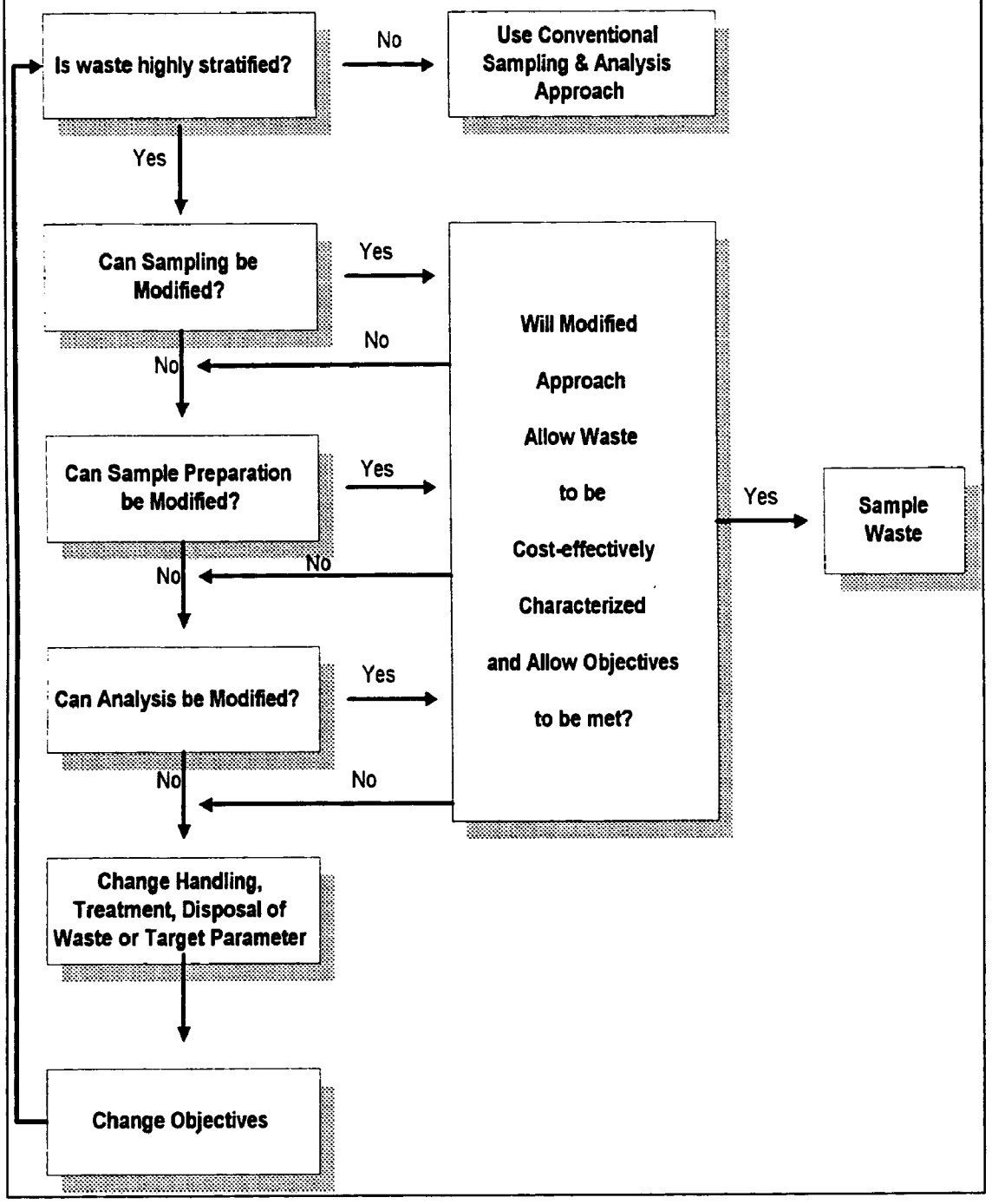
Alternate analytical methods that may allow for the analysis of larger sample mass/volumes and more samples per budget due to decreased analytical costs are summarized.

If modification of sampling, sample preparation or analytical methods do not allow the objectives to be met, the standard suggests review of the reasoning behind the original plan and possible modification of waste management or even of the objectives themselves.

CONCLUSION

The ASTM "Standard Guide on Sampling Strategies for Heterogeneous Wastes" and the cited references should give the experienced scientist a review and the less experienced scientist a background in the significance of heterogeneity when employing samples to make inferences regarding populations of interest.

FIGURE 6. Approach for the Characterization of Heterogeneous Wastes



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DATA QUALITY OBJECTIVES AND THE OPTIMIZATION FOR DESIGN

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ABSTRACT

The objective of the paper is to provide an overview of the latest standard practices developed by EPA and ASTM under a joint effort. These standard practices have been developed to provide guidance focused to project managers using the Data Quality Objective Process and Optimizing Sampling Designs supporting waste management activities.

Environmental data are often required for making waste management and regulator decisions. Both the government and public sector decision makers of the environmental community, have continued to wrestle with 1) mechanisms to define the purpose of an environmental waste management activity and 2) the criteria by which to judge whether or not that activity has been successful.

The development of Data Quality Objectives (DQOs) is the first step in data generation and includes, the development of the criteria on which to base the success of the environmental activity. The other two aspects are 1) implementation of the sampling and analysis strategies and 2) data quality assessment. The seven steps of the DQO process are as follows:

1. Stating the problem
2. Identifying possible decision
3. Identifying inputs to decisions
4. Defining boundaries
5. Developing decision rules
6. Specifying limits on decision uncertainty, and
7. Optimization of sampling and analysis design

After establishing the acceptance criteria via steps four through six, for the problem and decisions, a sampling and analysis design is selected, implemented and ultimately evaluated against the criteria. The sampling design and output of the DQO process, is the blue print by which the data collection activities are implemented. The focus of the Design Optimization strategies presented includes practical and implementable designs, recommendations for evaluation of design and methods for presenting designs to decision makers.

ASTM documents must be balloted and extensively reviewed prior to acceptance as a standard practice. ASTM in conjunction with US EPA have completed development of the DQO document. The Optimization of Design Standard Practice is under development.

INTRODUCTION

The EPA published initial guidance regarding the Data Quality Objective Process (DQO) in 1987 and followed with EPA Guidance for Planning for Data Collection in Support of Environmental Decision Making Using the Data Quality Objective Process (EPA QA/G-4, September 1994). The goal of these documents is to provide a planning method which balances risk including health, ecological and risk of making an incorrect decision with resources including time and budget. A secondary goal was to identify the quality and quantity of data needed to make decisions.

One of the implementation problems in the DQO process is providing sufficient guidance in sampling design. Some organizations believe that defensible statistical designs result in collection of too many samples while other organizations never use a statistical approach. EPA recognized this problem and is working with ASTM D34.01, Waste Management Committee, Subcommittee-Sampling and Monitoring to generate a document for the non-statistician that explains the elements of design and the optimization methods. The optimization allows one to choose logical statistical designs which balance data needs with risk and resources.

This standard guide is one in a three part series of ASTM documents focusing on DQOs (ASTM D5792), quality assurance (ASTM D5283) and design optimization which is currently in the ballot process. The ballot process should be completed early next year.

The DQO process is briefly described with emphasis on the information generated from the process which is needed for design optimization. The last section of this paper describes three major sections of the ASTM document sampling design criteria, design selection, and optimization.

DQO Process

Step 1 - Problem

Problem statements are clearly written after historical knowledge and data are compiled and understood by the stakeholders. Historical data are compiled and summarized and given to the decision makers. The decision makers agree on information which is known, not known and situations that result in problems. Prior to beginning the process, the task lead identifies the team of technical support staff and the appropriate decision makers from DOE, EPA, and Ecology who will perform the planning.

Step 2 - Decisions

For one or more critical problems, decisions are identified. These decisions result in actions which will correct the problem. The focus of the DQO process is on decisions requiring collection or evaluation of data.

Step 3 - Inputs

The inputs are the data and information necessary to make the project decisions. Prior to completing the process the quality, and quantity of data required are agreed upon by the stakeholders. A description of how the data will be used in the decision is agreed upon by the stakeholders. This assures that no unnecessary data are requested.

Step 4 - Boundaries

The spatial and time boundaries associated with the decisions are specified. The boundaries may be physical, practical, or have agreed upon characteristics. Large areas should be subdivided depending on characteristics. For example, each cylinder of grouted sediment will be tested and decisions made from each test. An example of a time boundary is the time required for grouted material to solidify prior to testing or storage. Sampling must be done after the grouted waste is solidified.

Step 5 - Decision Rules/Logic

Decision rules are the criteria upon which decisions will be based. These may be stated as "If..then" statements or presented in logic diagrams. The essential requirements are that the situation be identified

followed by the associated action which should occur. For example, "If the average of three measurements of lead in the grout exceeds 5 mg/l, then the waste will be disposed as a hazardous waste." If measurements are made, the logic should contain the parameter, the mode of comparison (i.e. average) and the resulting action. Logic should be complete by describing actions which occur if the limits are met or are exceeded.

Step 6 - Limits on Decision Uncertainty

The decision makers must agree on the acceptable probability of making an incorrect decision. In order to assess the acceptable probability, the consequences of making an incorrect decision at various concentrations should be understood. Decision error probabilities are based on the:

- number of samples,
- variance or standard deviation,
- level of false positives and negatives, and
- action, risk or regulatory level

Step 7 - Optimization of Sampling and Analysis Design

The data collection activity can be optimized using the above information. Using this information, the technical team develop and document the sampling and analysis plan. Multiple designs are typically presented to decision makers and the decision makers agree upon the resulting plan.

The presentation to the decision makers must include the trade offs in risk and resources. This balance is the greatest factor in optimization.

Table 1.1 - Inputs to Optimization of Design

DQO Step # and Title		Information Used in Optimization of Design (Step 7)
1	Problem	Technical staff and decision makers, resources, conceptual site and risk models, historical data
2	Decision	Decision, actions resulting from the decision, consequences of actions, priority of decisions, questions which allow one to make decisions
3	Inputs	Lists of data and information needed to make each decision, whether the data exists or must be obtained, data generation activities, use of the data, contaminants of potential concern, potential sampling and analysis methods, standard deviations or variance of historical data, typical detection limits by matrix, sample size/volume, holding times, turn around times, in-situ methods, traditional analysis methods
4	Boundaries	Spatial areas for sampling, division of areas by matrix, division of areas by potential level of contamination, division of area based on process knowledge, future use of land or facility, receptors of risk, risk area or exposure unit, time of sampling and project/decision schedule

Table 1.1 - Inputs to Optimization of Design

DQO Step # and Title		Information Used in Optimization of Design (Step 7)
5	Decision Rule	Action or regulatory limits, consequences of each action, statistic to be used (e.g. mean, upper limit, etc.), logic diagram or If..then... statements
6	Decision Uncertainty	Number of samples, variance or standard deviation based on past data or similar data by matrix, level of false positive and negatives, action level, expected level of contaminant, risk or regulatory level, area where consequences of a wrong decision has less consequence, consequence of a wrong decision by concentration level

OPTIMIZATION OF SAMPLING DESIGN

The development of alternate sampling designs requires a knowledge of

- the information generated in the DQO process,
- sampling design selection criteria,
- commonly used and alternative sampling designs.

With the development of sampling plan alternatives, the process of optimization begins. The resultant sampling design should strive to be: practical, objective and technically defensible. Figure 1.1 - Process for Optimization of Sampling Design provides a two dimensional view of the process outlined in the ASTM Guide, which includes descriptions of the inputs needed to select an appropriate sampling design and the subsequent process for optimization.

Decision makers need to consider all of the information available. The following general trends are a good rule of thumb.

- Usually the greater the number of samples, the shorter the confidence interval on the environmental parameter of interest.

- More sophisticated analytical chemistry methods can achieve lower detection limits. However, this may mean higher costs per sample and an increase in sample size mass/volume.

- Composite samples may not identify point source contaminant locations or hot spots.

- If something is known about the expected heterogeneity of a waste site, the non-random sampling designs, such as stratified sampling or a combination design may be the most effective.

- For containerized waste, both the within container and between container sampling error should be considered.

- Usually sampling errors are larger than the analytical errors. However, it may be more difficult to quantify sampling errors.

Optimization is an iterative process of assessing the design alternatives and determining the most resource-effective design which satisfies all of the project objectives or DQOs. For a small project, the entire selection and optimization process may be conducted at the same time. The lack of a formal assessment does not necessarily indicate that an assessment has not taken place. For a large Corrective Action, the process may bear some resemblance to the order the flow chart, however, the "steps" for the assessment and optimization can be and are followed in the most practical order.

It is important to assess the sample design(s) selected with respect to the project objectives. If a resource-effective design is not included in the sampling design alternatives, it may be necessary to modify the closest design alternative or revise the project objectives, returning to the Planning Process and a review of the Project Objectives.

Once the initial set of sampling designs are established, the design alternatives and resources required for each are reviewed by the decision makers. Careful consideration of each alternative allows for an understanding of the benefits and resource commitments needed for each sampling design. The design alternatives may include both directed and statistically based approaches.
Each design is re-evaluated against the project objectives, with respect to the following design constraints, which can be grouped into general categories. Some of these overlap or fall into more than one category and as previously stated, criteria may be applied in any order:

Technical
- Identification of the sampling unit(s)
- Optimum number of samples
- Regulatory or Action Levels

Practical, such as
- equipment limitations
- site considerations - cross contamination potential
- field and laboratory resources
- the experience of the field sampling team
- special analytical needs (low level analyses, dioxin)
- special analytical concerns (interferences, multiple phases, incompatibility)
- safety considerations
- resistant matrices (solidified material)
- investigation derived waste (IDW) generation
- limits on access to sampling locations (buildings, refusals)
- transitory events (start-up, shut-downs)
- special site concerns (unexploded ordnance)

Cost Estimates

Statistical
- Sensitivity analysis
- Statistical Power Curve
- Statistical hypothesis test
- Measurement error

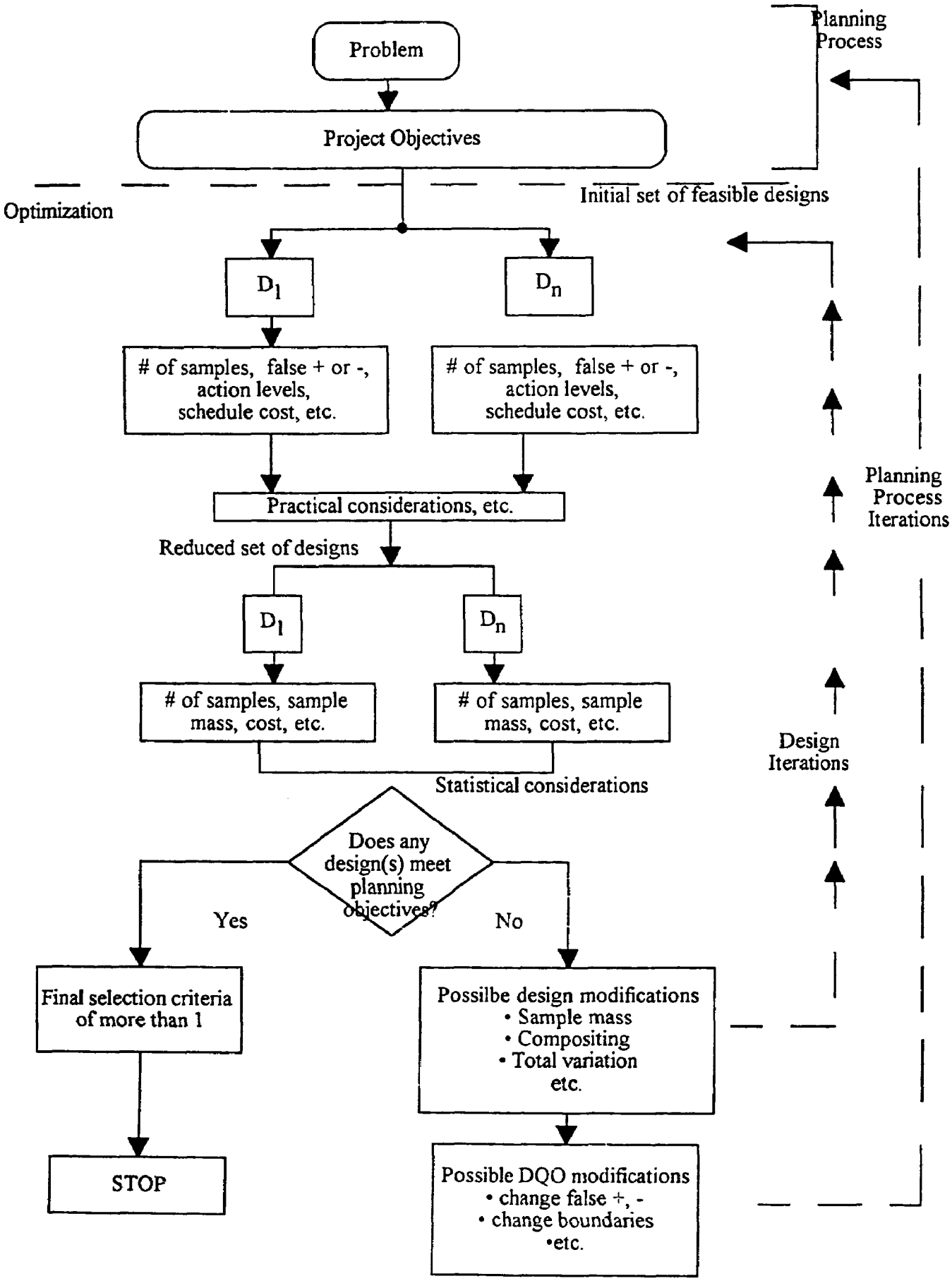
The assessment step of each design constraint will result in a reduced set of designs. Following the completion of the design constraints, final selection of the most resource-effective design occurs. However,

if no design meets the requirements of the project objectives, then either the sampling design or the project objectives will need to be modified.

Design modifications include increasing the number of samples, using design tools such as compositing, or satisfying practical limitations. If significant changes are made, then the "new" alternate designs would require a repeat of the optimization process with a re-calculation of the number of samples, re-development of the cost estimate, and a final review of the potential practical constraints.

Modifications to the project objectives may include a change in the study boundaries, an increase in the tolerable design errors, a relaxation of project constraints, or modifications in the initial hypotheses. A change in the project objectives would necessitate a complete cycling through the optimization process. The efforts to achieve an optimized sampling and analysis design ensure a defensible sampling design and subsequently a successful project.

Figure 1.1–Process for Optimization of Sampling Design



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COMPOSITING AND SUBSAMPLING OF MEDIA RELATED TO WASTE MANAGEMENT ACTIVITIES

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ABSTRACT

The American Society for Testing and Materials (ASTM) has been working with the U.S. Environmental Protection Agency (EPA) to develop methods for use in the Environmental RCRA/CERCLA program. Two standards being developed are guides to field compositing and laboratory subsampling.

Correctly performed compositing and subsampling are critical in the chain of sampling and analytical events. They must be accomplished in compliance with project objectives and instructions to assure that the resulting data is representative. In a site characterization effort, the collection of composite samples may be used to estimate the mean concentration of a waste analyte in contaminated media. Other reasons to composite include reducing costs, efficiently determining the absence or possible presence of a hot spot, and, when coupled with retesting schemes, locating hot spots. If composite samples are collected, it is necessary to ensure that a representative sample is obtained for analysis. This may mean that samples must be mixed and subsampled using procedures that could include pan mixing and quartering, a mixing square, kneading, sieving and mixing, and particle size reduction. Field subsampling procedures include use of a rectangular scoop, an alternate scoop technique, and the slab-cake methods.

A significant source of analytical error exists in obtaining a representative subsample of a sample delivered to a laboratory. Techniques for obtaining representative subsamples include homogenization, layer analysis, grinding and sieving, mixing, transversal subsampling, cone and quartering, riffling, use of a mixing square, use of mechanical mixers, and particle size reduction. Other techniques include changing the physical state such as digesting, drying, melting or freezing. These methods can be applied to a variety of matrices including solid wastes, single-phased liquids, sludges, and multilayered samples. These techniques are dependent on sample matrix, the type of analysis performed, the characteristic of interest, and the project specific instructions. These subsampling methods are designed to reduce the three major sources of subsampling errors; fundamental errors, grouping and segregation errors, and materialization errors.

Both of these guides are still in the developmental stages at ASTM.. They should soon be available for general use.

INTRODUCTION

Data Quality Objectives are generally dependent on getting data that is representative of the site. The more heterogeneous the site matrix, the more difficult this is to achieve. Two areas that influence the ability to achieve a representative sample are compositing in the field, and subsampling in the laboratory. Due to the

lack of regulatory guidance in these areas, the EPA asked ASTM to write standards addressing compositing and subsampling as part of a cooperative agreement between these agencies.

COMPOSITING

Composite sampling (compositing) is the combining of two or more samples into one. The principle assumption in the decision to composite is that the analytical costs are high relative to the sampling costs. The reasons to composite include:

- improving the precision mean estimation
- reducing costs associated with analysis
- efficiently determining the absence or presence of a hot spot
- when coupled with retesting schemes, locating hot spots
- providing a degree of anonymity where population statistics are necessary.

When estimating the mean concentration, a set of composite samples from a heterogeneous population always provides a more precise estimate of the mean than a comparable number of discreet samples. This is because of the physical process of averaging that occurs which provides a greater level of statistical confidence. The composite samples tend to be more normally distributed than the individual samples. This is an advantage for compositing, since the calculation of the mean, standard deviation, and confidence levels generally assumes the data is normally distributed. Spatial design of the compositing scheme is also important, since compositing can either help determine the spatial variability of a site, or be used to improve the precision of the parameter of interest across the whole site.

Due to the increased precision of compositing, the number of composite samples required to achieve a specified precision is smaller than that required for individual samples. The higher the analytical costs relative to the sampling and compositing costs, the greater the savings to the project budget.

Samples can be composited to determine whether an individual sample exceeds a specified limit as long as the action limit is relatively high compared with the actual detection limit and the average sample concentration. For example, if a site was being analyzed for PCB, the known analytical detection limit is <5 mg/kg of soil, and the action level is 50 mg/kg, then up to 10 samples could be composited to determine if any of the samples are a "hot spot." Depending on the difficulty and probability of having to resample, it may be desirable to retain a split of the discreet samples for possible re-analysis to find the specific spot. This type of composite sampling can only be used as a cost saving measure if the possibility of finding a hot spot is relatively low (<40%).

The principle limitation of compositing is the loss of discreet information achieved from a single sample. However, the following situations may not lend themselves to cost-effective compositing either:

- when the integrity of the individual sample values change due to compositing (e.g., chemical reactions occur between constituents in the samples being combined, or volatiles lost during mixing)
- where the composite sample cannot be properly mixed and subsampled in the field or the whole composite cannot be analyzed

- when the goal is to detect hot spots and a large proportion of the samples are expected to test positive for the characteristic of interest
- when analytical costs are low relative to sampling costs (e.g. field testing equipment)
- when regulations specify that a grab sample must be collected.

In general, the individual samples to be composited should be of the same mass. However, proportional sampling may be appropriate in some cases, depending upon the objective. For example, if the objective is to determine the average contaminant concentration of the waste contained in a group of drums, the volume of each sample to be composited should be proportional to the amount of waste in the drum. Another example would be in estimating the contaminants concentration of soil overlaying an impermeable layer. Soil cores should be collected and composited from the surface to the impermeable layer, regardless of the core length

Frequently, it is necessary to mix an individual or composite sample and obtain a representative subsample(s) for transport to an analytical lab. Even when the entire sample collected is to be submitted to the laboratory, it may be desirable to thoroughly mix the sample to help assure that the laboratory analyzes or extracts a representative aliquot. The thoroughness of mixing needed for subsampling is a function of the proportional size of the subsample. The principle problem is that the smaller the aliquot, the less representative the aliquot may be, unless it is thoroughly mixed, homogenized and subsampled. Compositing samples without adequate mixing can nullify the potential benefits of compositing. Prior to mixing, project specific instructions (e.g., the sampling and analysis plan) should be followed.

Methods that may be applicable to field mixing are dependent on matrix. This includes field mixing and quartering in a pan, sieving, kneading, grinding, particle size reduction, and other mixing equipment (e.g., riffle splitters, cone and quartering, etc.). While it is not always possible to determine if a sample is adequately mixed, following standard operating procedures and observing sample texture, color, and particle size distribution are practical methods. If samples are sieved or large materials are removed, it may be necessary to record the mass of materials removed for later estimation of contaminant concentrations in the original sample.

Once the composite sample is mixed, it may need to be subsampled. The reasons for this include a composite sample that is larger than the sample container, or the need to split the composite into multiple sample bottles. If mixing procedures could assure a homogenous sample, subsampling in the field would be simple. However, particles may segregate according to size during mixing, and improper subsampling would introduce bias. Since homogeneity cannot be assumed, appropriate subsampling procedures in the field should be used by field personnel to achieve representative samples. Methods for field subsampling include riffle splitters, cone and quartering, rectangular scoop, alternate scoop, and slab cake techniques.

LABORATORY SUBSAMPLING

Sources of uncertainty arise from sample heterogeneity and from the actual subsampling procedure used. There are three general sources of error that pertain to the subsampling of environmental samples. These must be understood before choosing a subsampling method. These include:

- fundamental error
- grouping and segregation error
- materialization error.

Fundamental error occurs when the contaminants of interest exist as particles or are attached to particles that are randomly dispersed throughout the matrix while the matrix itself is not contaminated or is contaminated with much lower concentrations of the contaminant of interest. The measured concentration of contaminant in such a waste will depend upon the number of these particles that are in the specimen subjected to analysis. For a given concentration, the greater the particle size, the fewer contaminated particles there are in the subsample, hence the smaller the chance is that the contaminant will be appropriately represented in the specimen.

Grouping and segregation error is a function of the distribution of unlike particles (i.e., size, shape, density) within a sample. Differences in size, shape and density can affect heterogeneity further by the development of different strata upon agitation or vibration of the sample.

Materialization errors are those that result from using incorrect subsampling devices or from the incorrect use of subsampling devices.

Successful implementation of laboratory subsampling depends on effective communication between the data user and the laboratory staff. The selection of optimal procedures by the laboratory depends on the intended use of the data. The data user should submit appropriate instructions with all samples and, when necessary, the laboratory staff should contact the data user for confirmation or further clarification of these instructions. Options should be discussed before initiating any subsampling procedure. These options include:

- removal of artifacts, such as rocks and twigs, from the sample prior to subsampling
- digesting or extracting the contaminant from the outside of the large particles instead of breaking down the entire particle
- digesting or extracting particle sizes separately
- using or forming an emulsion layer so that the material may be treated as a single layer
- separation of layers
- drying the sample
- changing the physical state, such as freezing the material so that it may be treated as a solid, or melting the material so that it may be treated as a liquid
- analysis of only one layer of multilayered samples, such as analyzing only the oil portion of an oil/water mixture for PCBs
- compositing portions of a sample for volatile analysis directly in a purge unit vs individual analysis of these portions
- choice of standard method for solids, such as grinding, mixing, cone and quartering, riffling, sieving, or particle size reduction.

Sampling theory suggests a minimum sample size that increases as the size of the largest particle increases. Often, these minimum sample sizes are larger than the normal sample sizes subjected to environmental analysis. Sometimes, the analytical subsample can be increased, or the size of the subsample subjected to digestion or extraction can be increased and a smaller subsample of the well mixed digestate or

extract can be submitted for analysis. Another approach involves dividing a sample of the requisite size into smaller subsamples, which can be subject to preparation. The resulting digestates or extracts can be analyzed individually or proportionally re-composited and a composite sample analyzed.

Subsampling techniques are different when analyzing for volatile compounds than non-volatile compounds. The differences are included for each sample matrix.

I. Solid Matrices

If the maximum particle size is too large for the specimen used in the laboratory, sampling theory would suggest that either particle size reduction is used, or a larger sample size is digested. If something is known about the scale of the "Contaminant Unit" and the mechanism of contamination, the use of particle size reduction may be avoidable. If the contaminant unit is on the atomic or molecular scale or is a particle much smaller than the maximum particle size of the sample, then alternative approaches can be employed with acceptable bias.

For volatile analyses, the Table 1 sums the alternative subsampling methods, since particle size reduction is not possible.

	Particle Size of Sample	Contaminant Unit in Sample	Subsampling Method
Method A	< Maximum Particle Size Allowed	< Maximum Particle Size Allowed	Mix with minimum disturbance, weigh specimen, place in appropriate solvent.
Method B	> Maximum Particle Size Allowed	< Maximum Particle Size Allowed	If data user can accommodate false high concentration, subsample only smaller particles. Another method is to extract the sample with the appropriate solvent, and analyze the solvent as a single phase.
Method C	> Maximum Particle Size Allowed	> Maximum Particle Size Allowed	An alternative to particle size reduction is to use larger sample sizes, dividing the total amount into manageable sizes, then combine the extracts into the same purge chamber.

Table 1. Subsampling Solids for Volatile Analysis

For non-volatile analysis, Table 2 sums the subsampling methods. Gelatinous samples, such as asphalt, may be cooled with dry ice or liquid nitrogen. This makes it possible to grind gelatins and other semi-solids. It is also important to be knowledgeable about the limitations on each of these subsampling methods.

	Particle Size of Sample	Contaminant Size in Sample	Subsampling Methods
Method D	< Maximum Particle Size Allowed	< Maximum Particle Size Allowed	Transversal Subsampling Cone and Quartering Riffle Splitter Grinding and Sieving Mechanical Methods (e.g., spiral mixer, cement mixer, twin-shell V blender, or mills)
Method E	> Maximum Particle Size Allowed	< Maximum Particle Size Allowed	If the data user can accommodate false high concentrations, large particles can be removed, and the methods listed in Method D may be used.
Method F	> Maximum Particle Size Allowed	> Maximum Particle Size Allowed	Particle Size Reduction, using such devices as cutting mills, micro-mills, grinding mills, or jar mills. Another method is to use larger sample sizes by extracting or digesting several aliquots. The extracts or digestates may be analyzed separately and the results can be weight-averaged, or the extracts or digestates may be combined prior to analysis.

Table 2. Subsampling Solids for Non-volatile Analyses

II. Single-phased Liquids

Aqueous samples for non-volatile compounds may contain settleable solids. If the settleable materials are to be considered part of the sample, they must remain in suspension, or be able to be re-suspended and remain so during the subsampling operation. These samples are then treated as a single-phase liquid. These samples should be gently swirled for 15 seconds or slowly inverted 6 times to assure homogenization. If the settleable materials are not considered to be part of the sample, the liquid subsample or specimen may be obtained by filtering, centrifuging, or decanting the liquid portion from the solid portion. The liquid portion can also be pipetted directly into the analytical vessel.

For volatile compounds, samples should not be mixed prior to subsampling. For low concentration materials, the specimen is pipetted straight into the syringe barrel. For high levels of contaminants, use a microliter syringe to collect the specimen directly, or transfer the subsample into a solvent appropriate for analysis in an air-tight container (dilution process).

III. Sludge

Laboratory samples with significant solids cannot be mixed vigorously enough to suspend a solid phase without the potential of losing volatile components. One method of handling sludge is to freeze it, and then handle it as a solid. Generally, the most practical method is to separate them out into their component phases.

For non-volatile compounds, the liquid subsample can be obtained by filtering, centrifuging, decanting, or by pipetting out only the liquid phase from a solution that has settled. Prior to starting, determine the percentage of the phases either by volume or by weight. After separating the liquid from the solid, analyze separately, and weight average the results.

For volatile compounds, gentle centrifuging, or settling can be used to separate the phases. After the liquid subsample is removed, using the methods described in single-phased liquids, the liquid is decanted into a separate container. The solid phase can then be weighed and added directly on the purge unit as quickly as possible.

IV. Multilayered Samples

Multilayered samples are those with two or more distinct visual layers of material. These layers may be the result of differences in density, such as liquid/liquid layers (e.g., chlorinated solvents and water, or water and oil), liquid/solid layers (e.g., sludge), solid/solid layers (e.g., small rocks and large rocks), or combinations of these layers (e.g., water, oil, and dirt). These layers may also be the result of depositional layering, such as green clay and sandy loam from a coring sample.

The methods used in the discussion on sludges will also work for multilayered samples. This includes the use of dry ice or liquid nitrogen to freeze the sample, or separating these samples into their component phases.

For liquid/liquid layers, a separatory funnel may be helpful in separating the phases, if the analysis is for non-volatile compounds. These phases can then be

proportionally recombined in the analytical vessel. For volatile compounds, they can be recombined directly on the purge unit to form a representative sample.

One or more of the previous methods mentioned in this paper can be utilized to subsample a multilayered sample, depending on how many layers are encountered in the sample.

SUMMARY

In a sampling plan, the collection of composite samples may be used to improve the estimation of the mean contaminant levels, reduce analytical costs, determine the absence or presence of a hot spot, and, when coupled with retesting schemes, locate hot spots. While discreet sample information is lost in compositing, collection of multiple composite samples from a grid cell permits estimation of within cell sampling error. There are several mixing and field subsampling techniques available to ensure that the sample sent to the laboratory is representative of what is in the field..

After the field sample arrives at the laboratory, proper subsampling is a key to ensuring that the data meets the data quality objectives. Subsampling must be completed only after a review of the appropriate instructions, or after discussing the options with the data user. Subsampling should then proceed in a manner dependent on the sample matrix, the type of analysis required, and the characteristic(s) of interest.

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4

SAMPLE REPRESENTATIVENESS: A NECESSARY ELEMENT IN EXPLOSIVES SITE CHARACTERIZATION

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ABSTRACT

Explosives-contaminated sites are generally characterized by collecting discrete grab samples of surface soil and shipping them to off-site laboratories for analysis. Decisions as to whether or not site remediation is needed are made based on the results of these analyses, assuming they represent site conditions over fairly large grids. This study was conducted to assess the degree of short-range heterogeneity in analyte concentrations present at explosives-contaminated sites. This information is essential if sampling methods are to be established that provide representative samples on which informed decisions can be based.

Soil was sampled at nine locations on three installations. At each location seven discrete grab samples were collected in a wheel pattern of radius 61 cm (one sample from the center and six equally spaced around the perimeter). Each of the seven samples was homogenized in the field and duplicates were analyzed by an on-site colorimetric method (SW846 Method 8515) as well as being sent for off-site analysis using SW846 Method 8330. Portions of the seven discrete samples were also used to form a composite sample which was analyzed on site using the colorimetric method as well as being analyzed off site using Method 8330.

On-site results from seven of the nine sampling locations indicated that TNT was the contaminant present at highest concentration. This was confirmed by results from Method 8330. TNT concentrations varied substantially at all seven sampling locations; TNT concentrations obtained from both types of analysis varied by as much as 2 1/2 orders of magnitude within a sampling wheel. Partitioning of overall variances for data indicated that sampling error dominated over analytical error. Therefore, the probability of collecting discrete samples that represent average analyte concentrations is very unlikely with these levels of heterogeneity. In order to represent this case using discrete sample collection and analysis, many more samples would have to be used. Results from analysis of composite samples, however, had mean concentrations representative of the average condition, as well as low RSDs, indicating that field homogenization was adequate for characterization. On-site analyses using the EnSys colorimetric method gave results essentially equivalent to those from off-site analysis with Method 8330. Similar results were obtained for the other two sampling locations, where 2,4-DNT and ammonium picrate were the contaminants present at highest concentration. A combination of composite sampling, on-site homogenization, and on-site colorimetric analysis provided an inexpensive and rapid site-characterization procedure that was accurate and precise, and provided results that were representative of site conditions.

INTRODUCTION

Historically, the location and quantification of contamination sources at hazardous waste sites has been conducted by collecting a series of discrete soil samples followed by shipment of these materials to off-site analytical laboratories for characterization. Potentially contaminated areas were often divided into grids of various dimensions, with the dimensions of the grids determined by the per sample cost and the size of the analytical budget allocated for that project. An implicit assumption in this approach is that the distribution of contaminants is sufficiently homogeneous that results from the analysis of these discrete samples can be used to represent average site conditions within the grid. In general, the number of discrete samples collected is insufficient to address the short-range distribution of contaminants and practically speaking all samples are automatically assumed to be representative of average site conditions within the grid from which they were collected.

Explosives are solids at ambient temperature, dissolve slowly and sparingly in aqueous solution and have low vapor pressures. These properties limit modes of mobility compared to other contaminants such as fuels or solvents. Thus the areas of high concentrations which serve as sources for contamination of ground water remain at or near the surface where deposited, unless the soils themselves are moved. Thus characterizing the contamination distribution for explosives will often be possible using samples of near surface soils.

Inexpensive, on-site, analytical methods for the most common explosives in soil have been developed and are now in common use. These procedures appear to be sufficiently accurate and precise to enable their use in mapping locations of contamination and, if a sufficient number of samples are analyzed, provide estimates of short-range contaminant heterogeneity. Intensive sampling combined with on-site analysis is an attractive means of evaluating the degree of representativeness that can be attained using collection and analysis of discrete grab samples to represent site contamination within grids at explosives contaminated sites.

OBJECTIVES

The major objective of this work was to characterize the short-range heterogeneity of contaminants at explosives contaminated sites. This was done by conducting field sampling and analysis studies at a number of explosives contaminated sites that varied in the type of explosives analytes present, mode of contamination, soil type, and geohydrology. Statistical analyses of the results were conducted to determine the following:

1. analytical error which was estimated from the pooled variances from duplicate analyses of seven grab samples collected within a localized area. Short-range sampling error was estimated from the variance computed from the differences of mean values of the seven grab (soil) samples.

2. the degree to which some form of composite sampling could be used to reduce sampling error.

3. whether an inexpensive, colorimetric field screening method (SW846 Method 8515) could be used to provide an accurate description of contaminant distribution and a reliable estimate of sampling error.

EXPERIMENTAL

Sampling sites

Sampling studies were conducted at three explosives-contaminated sites. The Monite site is a small, former industrial site near Sparks, Nevada, that has about 1.5 acres of land contaminated with TNT and DNT. The second installation sampled was Hawthorne Army Ammunition Plant (AAP), which is located in Hawthorne, Nevada, and was a load, assemble and pack facility operated by the Navy until 1977 when it was transferred to Army control. The third installation sampled was Volunteer AAP near Chattanooga, Tennessee. This installation is a TNT and DNT production facility, although it has not actively produced these munition compounds since 1977. Three sampling locations were selected at each facility which varied the major contaminant present, concentration, and mode of contamination as much as possible.

Soil sampling procedure

A common sampling pattern was used for soil sampling at all three installations. A plastic template was placed on the ground with the center at the selected sampling location, and seven samples were collected in a wheel pattern, with sample number 1 in the center. The radius of the wheel was 61 cm and samples arranged around the wheel were separated by 61 cm.

All seven soil samples were collected at the surface from 0 to 15 cm using a manual 5.6-cm-diameter stainless steel hand auger. Vegetation when present was removed. Cores were transferred to plastic zip-lock bags and taken to a processing area.

Soil processing and analysis

Soil samples from the Monite site and Hawthorne AAP were dry and mostly consisted of a mixture of sands and gravels. Soils from Volunteer had a higher moisture content and were composed of a higher percentage of finer-grained material. Individual samples from all three sites were homogenized in the field and subsamples for field and laboratory analysis removed prior to preparing composites for each location. Details on the processing and subsampling techniques used are presented elsewhere (Jenkins et al. 1996).

Soil samples from all sampling locations were extracted with acetone as described in detail elsewhere (Jenkins and Walsh 1992) and analyzed on site using the EnSys colorimetric TNT method (SW846 Method 8515, EPA 1993). The major deviations from the protocol specified by EnSys were as follows: (a) 20 g of field-moist soil was extracted with 100

mL of acetone rather than 10 g of dried soil with 50 mL of acetone, and (b) concentration estimates were calculated by subtracting twice the initial absorbance at 540 nm (rather than four times the initial absorbance) from the final absorbance at 540 nm.

Soil samples for laboratory analysis were returned to the laboratory in coolers by overnight carrier. Upon receipt they were maintained at 4°C until processed. Samples were air dried and processed as described in detail elsewhere (Jenkins et al. 1996). Duplicate 2.00-g subsamples from each discrete soil sample and seven replicate 2.00-g subsamples from composites were extracted and analyzed using SW846 Method 8330 (EPA 1995).

SUMMARY AND DISCUSSION

Because of the large volume of data collected and the similarity of results from site to site, only the individual sample results for the field screening and laboratory analyses for one sampling location at the Monite site are presented here (Table 1). TNT was the major analyte present at this location with concentrations varying from sample to sample over 2 1/2 orders of magnitude. Acetone extracts for field analysis were highly colored even before reaction with the EnSys reagent. Reaction of the acetone extracts with the EnSys reagent resulted in the development of red-colored solutions indicative of the presence of TNT. Substantial dilutions (as high as 1:2000) were required to obtain absorbances after reaction with the EnSys reagent in the linear range (absorbance less than 1.0 A.U. at 540 nm).

Duplicate field analyses for a given soil at sampling location 1 were in excellent agreement (mean RSD was 3.9%), indicating that field sample homogenization was adequate. Duplicate laboratory analyses varied to a greater extent than field analyses (mean RSD was 11.2%), probably due to the smaller sample size used for lab analysis (2 g versus 20 g).

TNT concentrations varied by a large amount from sample to sample and were not normally distributed. In addition, absolute variances were not homogeneous. Thus, in order to perform analysis of variance (ANOVA), data were transformed by taking the logarithm of individual values for both the field and laboratory results. ANOVA was performed on both sets of log transformed data. For the field analyses, the F ratio was 233 indicating that a significant difference was detected among the seven discrete samples at greater than the 99.5% confidence level. Results of a least significant difference test indicated that all seven discrete samples were significantly different from each other. Nearly identical results were obtained when ANOVA was conducted on the laboratory results. For sampling location 1, therefore, identical conclusions were reached regarding the magnitude of TNT concentrations and the nature of the analyte distribution using either the results of field screening or results of laboratory analyses.

Because the mean concentrations and absolute analytical variances for various samples from site 1 differ so drastically, we were not able to compare the uncertainties introduced by sampling with those from analysis by partitioning variances of untransformed data using normal distribution statistics. This was also true for four other sampling locations. Another simple way to compare sampling and analytical uncertainties is to compare the

ratios of mean concentrations obtained for various samples with those for duplicate analyses from the same sample. For location 1, the ratio of highest mean concentration to lowest mean concentration was 243 for the field analyses and 304 for the laboratory analyses. The highest ratios for duplicates were 1.16 for the field analyses and 1.47 for the laboratory analyses. Thus for this location, and the other four where distributions were extreme, sampling error contributes many times more uncertainty than analytical error for either field or laboratory analysis.

Results of the analyses of the composite samples at sampling location 1 were also quite interesting. The mean of the seven field screening analyses for the composite was 13100 ± 532 µg/g in comparison to the mean of the seven discrete samples, which was 13500 µg/g (Table 2). Clearly, analysis of the composite provides a good estimate for the mean concentration of the area sampled.

ANOVA was conducted to compare the laboratory and field screening results for the composite samples. The F ratio of 3.05 indicated that the results of the laboratory and field analyses for this sampling location were not significantly different at the 95% confidence level. This is true even with the good precision (RSDs of 4.1% and 10.1% for field and laboratory) obtained for the analyses of these composite samples. Therefore, a good indication of the degree of contamination could be obtained using a combination of composite sampling and colorimetric field screening analysis.

Results from the other eight sampling locations were very similar to those presented for sampling location 1. A summary of the ranges of concentrations for these data is presented in Table 2. For four of these locations the analyte distributions were sufficiently normal to enable fractionation of variances to get a direct comparison of analytical and sampling variances. In all four cases, sampling error overwhelmed analytical error whether on-site or laboratory results were used.

Results from analysis of composite samples for sampling locations 2–9 were quite similar to those from location 1 (Table 2). In all cases composite results were a good representation of the mean of the discrete samples making up that composite, and the relative standard deviations were small indicating that on-site homogenization was adequate for characterization. Thus a combination of composite sampling, on-site homogenization, and on-site colorimetric analysis provided an effective, inexpensive and rapid site-characterization strategy.

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Table 1. Analytical results for TNT at Monite site, sampling location 1

Sample	On-site Analysis EnSys (EPA 1993) µg/g	Laboratory Analysis (µg/g) RP-HPLC (EPA 1995) TNB	TNT	24DNT	Total
Discrete Samples					
1a	42700	107	37500	70	37700
1b	36900	104	45000	----	45100
2a	492	30	390	----	420
2b	507	30	382	----	412
3a	174	12	113	20	145
3b	154	11	116	----	127
4a	28000	97	44400	----	44500
4b	27600	----	41200	----	41200
5a	24400	----	33000	----	33000
5b	24400	----	22400	----	22400
6a	1240	42	1170	----	1210
6b	1310	33	1200	----	1230
7a	327	23	305	----	328
7b	334	17	227	----	244
Mean	13500				16300
Composites					
C1	12900	----	11800	----	11800
C2	12900	----	13400	----	13400
C3	13300	----	13600	----	13600
C4	14200	----	15200	----	15200
C5	13000	----	13900	----	13900
C6	13200	----	15000	----	15000
C7	12500	----	16100	----	16100
Mean	13100				14100
St Dev	532				1420

Table 2. Summary of on-site analytical results from sampling locations 1–9

Location	Major Analyte	Concentrations (µg/g) Maximum	Minimum	Discrete Mean	Composite Mean
1	TNT	39800	164	13500	13100
2	DNT	37000	3490	16100	23800
3	TNT	115	2.3	19.8	12.6
4	TNT	5880	85.1	1970	1760
5	TNT	373	12.9	156	139
6	Ammon. Picrate	4200	6.1	869	970
7	TNT	82000	21700	57500	55200
8	TNT	30800	580	9920	11300
9	TNT	34.4	4.2	13.7	16.6

GUIDANCE FOR CHARACTERIZING EXPLOSIVES CONTAMINATED SOILS: SAMPLING AND SELECTING ON-SITE ANALYTICAL METHODS[1]

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ABSTRACT

A large number of defense-related sites are contaminated with elevated levels of secondary explosives. Levels of contamination range from barely detectable to levels above 10% that need special handling due to the detonation potential. Characterization of explosives-contaminated sites is particularly difficult due to the very heterogeneous distribution of contamination in the environment and within samples. To improve site characterization, several options exist including collecting more samples, providing on-site analytical data to help direct the investigation, compositing samples, improving homogenization of samples, and extracting larger samples. On-site analytical methods are essential to more economical and improved characterization. On-site methods might suffer in terms of precision and accuracy, but this is more than offset by the increased number of samples that can be run. While verification using a standard analytical procedure should be part of any quality assurance program, reducing the number of samples analyzed by the more expensive methods can result in significantly reduced costs. Often 70 to 90% of the soil samples analyzed during an explosives site investigation do not contain detectable levels of contamination. Two basic types of on-site analytical methods are in wide use for explosives in soil, colorimetric and immunoassay. Colorimetric methods generally detect broad classes of compounds such as nitroaromatics or nitramines, while immunoassay methods are more compound specific. Since TNT or RDX is usually present in explosive-contaminated soils, the use of procedures designed to detect only these or similar compounds can be very effective. Selection of an on-site analytical method involves evaluation of many factors including the specific objectives of the study, compounds of interest and other explosives present at the site, number of samples to be run, sample analysis rate, interferences/cross-reactivity of the method, skill required, analytical costs per sample, and the need for and availability of support facilities/services. Other factors to be considered are the precision and accuracy of the on-site analytical method, but it should be remembered that the analytical error is generally small compared to field error and that the precision and accuracy of a method are dependent on the site (compounds present and relative concentration) and the specific objectives. Modifications to on-site methods may improve method performance including extracting a larger soil sample to improve the representativeness of the analytical sample, ensuring that the shaking/extraction phase of all methods lasts at least three minutes, and evaluating the rate of extraction for heavy soils by conducting a simple kinetic study. With appropriate use, on-site analytical methods are valuable tools for characterization of soils at hazardous waste sites and monitoring soil remediation operations. This paper summarizes an Issue Paper prepared for the EPA's Federal Facility Forum through the EPA's Technology Support Center for Monitoring and Site Characterization, Characterization Research Division, Las Vegas.

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INTRODUCTION

Historical disposal practices from manufacturing, spills, ordnance demilitarization, lagoon disposal of explosives contaminated wastewater, and open burn/open detonation (OB/OD) of explosive sludges, waste explosives, excess propellants, and unexploded ordnance, often results in soil contamination. Facilities that may be contaminated with explosives include active and former manufacturing plants, ordnance works, Army ammunition plants, Naval ordnance plants, Army depots, Naval ammunition depots, Army and Naval proving grounds, burning grounds, artillery impact ranges, explosive ordnance disposal sites, bombing ranges, firing ranges, ordnance test and evaluation facilities, etc. A number of these facilities have high levels of soil and groundwater contamination, although waste disposal was discontinued 20 to 50 years ago. Because of such extensive contamination, the EPA's Federal Facilities Forum determined that remedial project managers need guidance regarding field sampling and on-site analytical methods for detecting and quantifying secondary explosive compounds (Table 1) in soils.

Under ambient environmental conditions, explosives are highly persistent in soils and groundwater, exhibiting a resistance to naturally occurring volatilization, biodegradation, and hydrolysis. Site investigations indicate that TNT is the least mobile of the explosives and most frequently occurring soil contamination problem. RDX and HMX are the most mobile explosives and present the largest groundwater contamination problem. TNB, DNTs, and tetryl are of intermediate mobility and frequently occur as co-contaminants in soil and groundwater.

The frequency of occurrence of specific explosives in soils was assessed (Walsh et al. 1993) using analytical data on soils collected from 44 Army ammunition plants, arsenals, and depots, and two explosive ordnance disposal sites. Of the 1,155 samples, a total of 319 samples (28%) contained detectable levels of explosives. The frequency of occurrence and the maximum concentrations detected are shown in Table 2. TNT was detected in 66% of the samples and 80% of the samples if the two explosive ordnance disposal sites are excluded. Overall, TNT or RDX or both were detected in 72% of the samples containing explosive residues, and 94% if the ordnance sites are excluded. Thus, by screening for TNT and RDX at these facilities, 94% of the contaminated areas could be identified (80% if only TNT was determined). This demonstrates the feasibility of screening for one or two compounds.

OVERVIEW OF SAMPLING AND ANALYSIS FOR EXPLOSIVES IN SOIL

The environmental characteristics of munitions compounds in soil indicate that they are extremely heterogenous in spatial distribution. Concentrations range from non-detectable levels (<0.5 ppm) to percent levels (>10,000 ppm) for samples collected within several feet of each other. In addition, the waste disposal practices at these sites, such as OB/OD, exacerbate the problem and may result in conditions ranging from no soil contamination up to solid "chunks" of bulk high explosives, such as TNT or RDX. Secondary explosives concentrations above 10% (>100,000 ppm) in soil are of concern because of potential reactivity that affects sampling and materials handling processes during remediation.

Reliance on laboratory analyses only for site investigations may result in poor characterization and high analytical costs ($250-350/sample), especially when a large percentage of the samples (up to 80%) contain non-detectable levels of explosives. Because of the extremely heterogeneous distribution of explosives in soils, on-site analytical methods are a valuable, cost-effective tool to assess the nature and extent of contamination. Since costs per sample are lower, more samples can be analyzed, the availability of near-

real-time results permit redesign of the sampling scheme while in the field and on-site screening also facilitates more effective use of off-site laboratories.

DATA QUALITY OBJECTIVES

EPA's Data Quality Objectives process is designed to facilitate the planning of environmental data collection activities by specifying the intended use of the data (what decision is to be made), the decision criteria (action level), and the tolerable error rates. Integrated use of on-site and laboratory methods for explosives in soil facilitate achieving such objectives as determining the horizontal and vertical extent of contamination, obtaining data to conduct a risk assessment (EPA 1992), identifying candidate wastes for treatability studies, identifying the volume of soil to be remediated, determining whether soil presents a potential detonation hazard (reactive according to Resource Conservation and Recovery Act regulations), determining when sufficient excavation has occurred, and determining whether remediation activities have met the cleanup criteria (typically 10 to 100 ppm).

UNIQUE SAMPLING DESIGN CONSIDERATIONS FOR EXPLOSIVES

Heterogeneity Problems and Solutions - In a recent study, Jenkins et al. (1996) collected and analyzed seven soil cores within a radius of 2 ft from nine locations. Results showed extreme variation in concentration in five of the nine locations and in all cases, only a small fraction of the total error was due to analytical error; field sampling error dominated total error. To improve site characterization , the major effort should be to increase sampling densities and composite samples to reduce sampling error. There are several practical approaches to reducing overall error during characterization of soils contaminated with explosives, including increasing the number of samples or sampling density, collecting composite samples, using a stratified sampling design, and reducing within sample heterogeneity.

One simple way to improve spatial resolution is by collecting more samples on a finer sampling grid such as a 5-m instead of a 10-m spacing. This approach has been rejected in the past because of the higher costs but when inexpensive on-site analytical methods are used, this approach becomes feasible.

Samples are always taken to make inferences to a larger volume of material, and a set of composite samples provides a more precise estimate of the mean than a comparable number of discrete samples. This occurs because compositing is a "physical process of averaging." Decisions based on a set of composite samples provides greater statistical confidence than for a comparable set of individual samples (Gagner and Crockett 1996). In Jenkins' study, composite samples were much more representative of each plot than the individual samples that made up the composites. Using a composite sampling, it is possible to reduce costs and the total number of samples collected while improving characterization.

Stratified sampling can also be effective in reducing field and subsampling errors. Using historical data and site knowledge or results from preliminary field screening, it may be possible to identify areas where contaminant concentrations are expected to be moderately heterogeneous (pond bottom) or extremely heterogeneous (open detonation sites). Different compositing and sampling strategies can be used to characterize different areas that can result in a more efficient characterization. Another means of stratification is based on particle size. Since explosive residues often exist in a wide range of particle sizes (crystals to chunks), it is possible to sieve samples into various size fractions which may reduce heterogeneity.

Within sample heterogeneity is frequently observed during field screening when duplicate subsamples are analyzed and results differ by an order of magnitude. To reduce within sample heterogeneity and obtain a representative analytical sample, two methods can be employed: homogenization and extraction or analysis of a larger sample. The smaller the subsample, the more homogeneous the sample should be and this may require sample drying, grinding, and riffle splitting (Gagner and Crockett 1996).

While sample-mixing procedures such as sieving to disaggregate particles, mixing in plastic bags, etc. should be used to prepare a sample, extracting a larger sample is perhaps the easiest method of improving representativeness. CRREL recommends extraction of 20 g of soil, and the same approach can easily be used to improve results with most field screening methods.

Sample Holding Times and Preservation Procedures - Based on spiking clean soils with explosives in acetonitrile, Maskarinec et al. (1991) recommended the following holding times and conditions: TNT-immediate freezing and 233 days at -20°C; DNT-107 days at 4°C; RDX-107 days at 4°C; and HMX-52 days at 4°C. Grant et al. (1993, 1995) spiked soils with explosives dissolved in water to eliminate any acetonitrile effects and also used a field-contaminated soil. The results on spiked soils showed that RDX and HMX are stable for at least 8 weeks when refrigerated (2°C) or frozen (-15°C). When nitroaromatics are of interest, spiked samples should be immediately frozen as some results showed significant TNT and TNB degradation within 2 hours. However, both compounds and 2,4-DNT can be adequately preserved for 8 weeks or longer by freezing. The results on field-contaminated soils did not show the rapid degradation of TNT and TNB observed in the spiked soils and refrigeration appeared satisfactory. Presumably, the explosives still present in the field soil after many years of exposure are less biologically available than in the spiked soils. Explosives in air-dried soils are stable at room temperature if kept in the dark. Acetonitrile extracts of soil samples are expected to be stable for at least 6 months under refrigeration. Acetone extracts are also thought to be stable if stored in the dark under refrigeration.

Explosion Hazards and Shipping Limitations - EPA regions and the U.S. Army Environmental Center consider soils containing more than 10% secondary explosives (i.e., TNT, RDX, HMX, DNT, TNB, and DNB) by weight to be susceptible to initiation and propagation (EPA 1993). If on-site analyses indicate that soil samples contain less than 10% total secondary explosives by weight, they can be shipped to off-site laboratories as environmental samples. Samples with over 10% explosives must be shipped to an explosives-capable laboratory for analysis, and they must be packaged and shipped in accordance with applicable Department of Transportation and EPA regulations for reactive hazardous wastes and Class A explosives (AEC 1994). For sampling at sites with unknown or greater than 10% by weight of secondary explosives contamination, special sampling procedures must be followed (AEC 1994).

SUMMARY OF ON-SITE ANALYTICAL METHODS FOR EXPLOSIVES IN SOIL

Ideally, screening methods would provide high-quality data on a near-real-time basis at low cost and of sufficient quality to meet all intended uses including risk assessments and final site clearances without the need for more rigorous procedures. While the currently available screening procedures may not be ideal (not capable of providing compound specific concentrations of multiple compounds simultaneously), they have proven very valuable during the characterization and remediation of numerous sites. Currently available field methods that have been evaluated against standard analytical methods and demonstrated in the field include colorimetric and immunoassay methods (Table 1). Each method has relative advantages and disadvantages, so one method may not be optimal for all applications. To assist in the selection of one or more screening methods for various users needs, a fairly comprehensive table (Table 3 in Crockett et al.

1996) has been developed comparing the available colorimetric and immunoassay screening tests for detecting explosives in soil. The selection criteria presented include: method type, analytes determined, detection limit and range, sample preparation and extraction procedure, analytical production rate, interferences and cross-reactivities, recommended QA/QC, suggested storage conditions and shelf life, skill required, availability of training, cost per sample, references to tests evaluating the method against Method 8330, and additional method selection considerations. The table is accompanied by explanatory text.

Interferences/Cross-Reactivity - A major difference among the field methods is with interferences for colorimetric methods and cross-reactivity for immunoassay methods. The colorimetric methods for TNT and RDX are broadly class sensitive, that is, they respond to many other similar compounds (nitroaromatics and nitramines/nitrate esters, respectively). Immunoassay methods are relatively specific for the primary target analytes. The cross-reactive secondary target analytes for TNT are mainly other nitroaromatics but this varies considerably among the four TNT immunoassay test kits. Depending upon the sampling objectives, broad sensitivity or specificity can be an advantage or disadvantage. If the objective is to determine whether any explosive residues are present in soil, broad sensitivity is an advantage. For the CRREL and EnSys colorimetric methods, the color development of the extracts can give the operator an indication of what type of compounds are present in soil. An advantage of some colorimetric methods is they can be used to detect compounds other than the primary target analyte. For example, the colorimetric RDX methods can be used to screen for HMX when RDX levels are relatively low, and for NQ, NC, NG, and PETN in the absence of RDX and HMX.

For colorimetric methods, interference is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte. For TNT methods, the primary target analyte is TNT, and the secondary target analytes are other nitroaromatics TNB, DNB, 2,4-DNT, 2,6-DNT, and tetryl. For RDX methods, the primary target analyte is RDX, and the secondary target analytes are nitramines (HMX, NQ), and nitrate esters (NC, NG, and PETN). If the primary target analyte is the only compound present in soil, the colorimetric methods measure the concentration of that compound. If multiple analytes are present in soil, the field methods measure the primary target analyte plus the secondary target analytes, nitroaromatics for the TNT test kit, and nitramines plus nitrate esters for the RDX test kits. In addition, the response of colorimetric methods to the secondary target analytes are equivalent to that of the primary target analyte, and remain constant throughout the concentration range of the methods.

For immunoassay methods, cross-reactivity is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte. For TNT methods, the primary target analyte is TNT, and the secondary target analytes are nitroaromatics TNB, DNTs, Am-DNTs, and tetryl. For RDX methods, the primary target analyte is RDX, and there is little cross-reactivity, 3% with HMX. If the primary target analyte is the only compound present in soil, the immunoassay methods measure the concentration of that compound. If multiple analytes are present in soil, the immunoassay methods measure the primary target analyte plus some percentage of the cross-reactive secondary target.

Both colorimetric and immunoassay methods may be subject to positive matrix interference from humic substances in soils. For colorimetric methods, this typically occurs below 10 ppm, and is indicated by yellow extracts. These interferences can be reduced by careful visual analysis prior to colorimetric analysis. Nitrate and nitrite, common plant nutrients in soil, are potential interferents with the CRREL and EnSys colorimetric procedures for RDX. An extra processing step can be used to remove these interferents in soils that are rich in organic matter or that may have been recently fertilized.

Comparisons to Laboratory Method, SW-846 Method 8330 - Precision and accuracy of the screening methods are most appropriately assessed by comparison to established laboratory methods such as EPA Method 8330. Methods of comparison that have been used include relative percent difference (RPD), linear regression, correlation, percent false positive and false negative results, analysis of variance and paired t-tests. It should also be remembered that analytical accuracy is generally quite small compared to total error (field error is the major contributor).

Three studies have evaluated multiple methods under slightly different field conditions. Readers consult the original studies for more details; however, some summary conclusions from the three cited studies follow. An EPA (1995) study compared the CRREL, EnSys (colorimetric), D Tech, Quantix, and Ohmicron methods for TNT and concluded that, overall, "no single method significantly out-performed other methods" and that accuracies for all the field screening methods were comparable, with CRREL, EnSys, and Ohmicron being more accurate in the greater-than-30-mg/Kg TNT ranges, and D Tech being more accurate in the less-than-30-mg/Kg range. The same study compared CRREL, EnSys, and D Tech methods for RDX in soil and concluded that they were slightly less accurate than the corresponding TNT methods. Haas and Simmons (1995) evaluated immunoassay kits for TNT (EM Science/D Tech, EnSys/EnviroGard Tube and Plate, Idetek/Quantix, and Ohmicron/RaPID Assay. They concluded that for semi-quantitative screening, all kits have the potential to accurately screen soil samples for contamination at risk-based levels. For quantitative analyses, "several of the assays had significant positive bias compared with HPLC results below 1 ppm," "measurements near the detection limit are often problematic," and "above 1 ppm, the correlation between [immunoassay kits] and HPLC was generally good." Myers et al. (1994) evaluated and compared the EnSys (colorimetric) and D Tech methods for TNT in soil versus EPA Method 8330. "EnSys demonstrated a good one-to-one linear correlation with RP-HPLC that can be attributed to the procedure for extraction, i.e., a large sample size of dried homogenized soil." For the D Tech kit, comparison was more difficult due to the concentration range type data and because "one-to-one linear correlation with RP-HPLC was poorer." The EnSys kit was well suited for studies requiring good quantitative agreement with the standard laboratory method and that the D Tech kit was "better suited for quick, onsite screening in situations where all samples above a certain range will be sent forward to a laboratory for confirmation by the standard method."

Emerging Methods and Other Literature Reviewed - Other screening procedures are being used but limited information is available on them. Emerging procedures include: an antibody-based continuous-flow immunosensor for TNT and RDX and a fiber optic biosensor for TNT are being evaluated by the Navy for use in soil, the U.S. Army is developing a cone penetrometer for *in situ* detection of explosives, ion mobility spectrometry is being evaluated by several organizations, a modified Method 8330 has been used in a mobile trailer, thermal desorption followed by gas chromatography/mass spectrometry analysis has been reported, and work is underway within CRREL to investigate the use of a simple thin-layer chromatographic method for use as a confirmation test following colorimetric-based procedures.

SUMMARY

The heterogeneity of explosive in soils poses significant problems to site characterization. Several options exist including collecting more samples, providing on-site analytical data to help direct the investigation, sample compositing, improving homogenization of samples, and extracting larger samples. On-site analytical methods are essential to more economical and improved characterization. What the on-site methods lack in terms of precision and accuracy in simultaneously identifying specific multiple compounds, they more than make up for in the increased number of samples that can be run.

Modifications to on-site methods may be able to improve method performance. In most cases, a larger soil sample can be extracted to improve the representativeness of the analytical sample. Also, with heavy soils or soils with high organic matter content, it may be useful to conduct a short-term kinetic study to determine whether a 3-minute extraction period is adequate. It is recommended that the shaking/extraction phase of all methods last at least 3 minutes. In all cases, it is recommended that a portion of the on-site analytical results be confirmed using a standard laboratory method.

ACKNOWLEDGMENT

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Table 1. Analytical Methods for Commonly Occurring Explosives, Propellants, and Impurities/Degradation Products.

Acronym	Compound name	Field method	Developer/test kit	Lab. method
Nitroaromatics		Cs	CRREL, EnSys/Ris^{s}®	N
TNT	2,4,6-trinitrotoluene	Cp	CRREL, EnSys/Ris^{s}®	N
		Cp	USACE	
		Ip	EM Science/D-TECH™	
		Ip	Idetek/Quantix™	
		Ip	Ohmicron/RaPID Assay®	
		Ip	EnSys/EnviroGard™	
TNB	1,3,5-trinitrobenzene	Cs	CRREL, EnSys/Ris^{s}®	N
		Is	Ohmicron/RaPID Assay®	
DNB	1,3-dinitrobenzene	Cs	CRREL, EnSys/Ris^{s}®	N
2,4-DNT	2,4-dinitrotoluene	Cp, Cs	CRREL	N
2,6-DNT	2,6-dinitrotoluene	Cs, Is	CRREL, EnSys/EnviroGard™	N
Tetryl	Methyl-2,4,6-trinitrophenylnitramine	Cs	CRREL	N
2AmDNT	2-amino-4,6-dinitrotoluene			N
4AmDNT	4-amino-2,6-dinitrotoluene	Is	EnSys/EnviroGard™	N
NT	nitrotoluene (3 isomers)			N
NB	nitrobenzene			N
Nitramines		Cs	CRREL, EnSys/Ris^{s}®	N
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	Cp	CRREL, EnSys/Ris^{s}®	N
		Ip	EM Science/D-TECH™	
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	Cs	CRREL, EnSys/Ris^{s}®	N
NQ	Nitroguanidine	Cs	CRREL	G
Nitrate Esters		Cs	CRREL	
NC	Nitrocellulose	Cs	CRREL	L
NG	Nitroglycerin	Cs	CRREL	P
PETN	Pentaerythritol tetranitrate	Cs	CRREL	P
Ammonium Picrate/Picric Acid			CRREL	
AP/PA	Ammonium 2,4,6-trinitrophenoxide/	Cp	CRREL ,	A
	2,4,6-trinitrophenol	Is	EM Science/D-TECH™?	

A = Ammonium Picrate/Picric Acid (Thorne and Jenkins 1995).
Cp = Colorimetric field method, primary target analyte(s).
Cs = Colorimetric field method, secondary target analyte(s).
G = Nitroguanidine (Walsh 1989).
Ip = Immunoassay field method, primary target analyte.
Is = Immunoassay field method, secondary target analyte(s).
L = Nitrocellulose (Walsh unpublished CRREL method).
N = EPA SW-846, Nitroaromatics and Nitramines by HPLC, Method 8330.
P = PETN and NG (Walsh unpublished CRREL method).

Table 2. Occurrence of Analytes Detected in Soil Contaminated with Explosives.

Nitroaromatics	% Sample with Analyte Present	Maximum Level (μg/g)
TNT	66	102,000
TNB	34	1790
DNB	17	61
2,4-DNT	45	318
2,6-DNT	7	4.5
2-AmDNT	17	373
4-AmDNT	7	11
Tetryl	9	1260
Nitramines		
RDX	27	13,900
HMX	12	5700
TNT/RDX	72	

Derived from Walsh et al. (1993)

Performance of a new disposable sampling and storage device for soil VOCs.

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A stainless steel volumetric sampling device(the EnCore sampler) has previously been demonstrated to be a very effective device for collecting target volumes of soil and for storing VOCs with limited loss. These sampling devices overcome the limitations that exist with other methods. Handling of solvents in the field is eliminated, subsampling of the soil is not required, and the sample can be easily and quantitatively transferred to standard 40 ml vials in the laboratory.
We report here on the development and validation of a disposable sampling tool that can be used equivalently to the stainless steel sampler. Data will be presented on the inertness of the composite material and its leaching potential when exposed to solvents. Data will be presented to validate the performance of the sampler for short term storage of soil VOCs and on extension of the time of storage stability under freezing conditions(<-15 degrees C) to fourteen days.

FIELD SCREENING OF SOILS CONTAMINATED WITH EXPLOSIVES USING ION MOBILITY SPECTROMETRY

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ABSTRACT

Soils contaminated with explosives constitute a high priority problem at some Department of Energy facilities and many Army installations. Because explosives in soil are often heterogeneously distributed, field screening is essential to characterize sites more quickly, economically and accurately. Current immunoassay and colorimetric field screening procedures have proven useful, but have significant per sample costs and limited throughput. Often, only a single analyte or analyte group determination is possible per sample. At present, several field screening procedures are available for TNT in soil, three procedures for RDX and one procedure for 2,4-DNT and ammonium picrate/picric acid (AP/PA). Ion mobility spectrometry has been used for several years in law enforcement work to detect explosives in air at ppt levels, but very little work has been done to apply the technique to detecting explosives in soils. IMS offers great potential since many compounds (TNT, RDX, PETN, DNT, TNB, NG, etc.) can be quantified simultaneously in an acetone extract within a few seconds and at a cost of under a dollar/sample. This study involved the comparison of IMS screening with EPA's standard method for explosives, Method 8330. The U.S. Army provided a large number of soil samples that had been collected from three locations at each of three explosive contaminated installations. The samples, had been dried, ground, homogenized and analyzed in duplicate by Method 8330. Duplicate two gram aliquots of these samples were extracted with 10 mL of acetone by shaking for three minutes, allowed to settle, and then analyzed by IMS for Method 8330 compounds. Half of the extracts were also analyzed in duplicate by IMS. The results of the statistical comparison between IMS and Method 8330 data will be presented. Based on these results, the intention is to provide adequate validation data to EPA for inclusion of the method as a screening procedure in SW-846. This comparison test was run on specially homogenized samples to reduce subsampling errors and improve the quality of the method comparison. For field application, the extraction procedure should be changed to extract 20 g of moist soil with 100 mL of acetone. The chief limitation of the IMS method is the initial cost for instrumentation (~$50 K).

IDENTIFICATION AND QUANTITATION OF PETROLEUM SUBSTANCES IN ENVIRONMENTAL SAMPLES USING FRIEDEL-CRAFTS/HANBY SPECTROPHOTOMETRY WITH CHEMOMETRICS

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Visible (400-650 nm) spectral signatures of aromatic compounds provided by vigourous Friedel-Crafts reactions of extracts of soil and water samples have been utilized to provide qualitative (identification) analyses as well as quantitative information. Extract solutions were prepared with a broad range of mono- and polynuclear aromatic compounds utilizing a heptane/carbon tetrachloride solvent. Friedel-Crafts reactions were performed on the extracts utilizing stoichiometrically large amounts of $AlCl_3$ (Hanby Method). Precipitates were scanned utilizing a small, portable, reflectance spectrophotometer developed by H.E.L.P., Inc. Spectral information obtained across the range of 400-650 nm utilizing SpectraScope software was then subjected to interpretation by the Mathworks(TM) Matlab program and the Chemometrics and Neural Network toolboxes. Quantitation over a range of 1-1000 mg/Kg was achieved and the neural network software was able to provide identification of the various compounds based on their spectral signature over the 400-650 nm range. Approximately 20 crude and refined oils and fuels as well as the individual compounds have been successfully analyzed with the method in similar contamination ranges (1-1000 mg/Kg). Also, liquid/liquid extracts of aromatic compounds and fuels,etc. have been prepared and analyzed with similar success in the .05 to 50 mg/L range. Portable (notebook) computers have been loaded with the appropriate software providing on-site use of the procedure. Spectral signature information is amenable to interpretation of source and date of contamination with appropriate library data.

Abstract

Site Characterization Technology Demonstrations

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The Consortium for Site Characterization Technology (CSCT), which is coordinated by the U.S. EPA Characterization Research Division in Las Vegas, has developed a Guidance Manual for the Preparation of Site Characterization Technology Demonstration Plans. The CSCT is a partnership between the EPA, the Departments of Defense and Energy (DoD and DOE) and the private sector, all of whom share the goal of increasing the use of innovative characterization technologies in assessing contaminated sites. The CSCT conducts demonstrations to show that new and innovative field-deployable measurement technologies perform as claimed by the developers and to provide a verified data set that confirms the performance of the technology. These demonstrations are intended to give potential users the information needed to determine the applicability of the technology for their uses. This manual was used as guidance for three technology demonstrations during 1995. The three demonstrations, Cone Penetrometer-Laser Induced Fluorescence, Volatile Organic Compounds by Field Gas Chromatography/Mass Spectrometry, and Metals by Laser Induced Breakdown Spectroscopy, will be briefly described. Lessons learned about planning and performing technology demonstrations will be presented. Two major areas of concern include developing specific developers' claims for the technology to be demonstrated and assuring the quality of the data produced by the reference laboratories.

ABSTRACT

A Field Demonstration of Portable Mass Spectrometers

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A field demonstration of portable mass spectrometers was held at two hazardous waste sites. These demonstrations were sponsored by the Consortium for Site Characterization Technology (CSCT). The CSCT is a partnership between the EPA, the Departments of Defense and Energy (DoD and DOE) and the private sector, all of whom share the goal of increasing the use of innovative characterization technologies in assessing contaminated sites. The CSCT conducts demonstrations to show that new and innovative field-deployable measurement technologies perform as claimed by the developers and to provide a verified data set that confirms the performance of the technology. These demonstrations are intended to give potential users the information needed to determine the applicability of the technology for their uses. The demonstrations were held at the DOE Savannah River Site, Aiken, South Carolina in July 1995 and at Wurtsmith Air Force Base in Oscoda, Michigan in September 1995. Instruments demonstrated included the Bruker-Franzen Analytical EM640 mobile gas chromatograph/mass spectrometer, the Teledyne Electronic Technologies 3DQ Discovery ion trap mass spectrometer with a direct injection inlet system (developed by Martin Marietta Energy Systems at Oak Ridge National Laboratory), and the Viking Instruments Corporation SpectraTrak 672 transportable gas chromatograph/mass spectrometer. The demonstration was designed to evaluate whether the instruments met the developers' performance claims for a variety of media and analytes under field conditions. At each location, samples of soil gas, ground water, and soil were analyzed for volatile organic compounds. The instruments were operated by developer personnel. The samples were analyzed by developer-selected methods. Split samples were analyzed by standard analytical methods at commercial laboratories to provide a reference for verifying the performance of the instruments. The study design, execution, and results will be presented.

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Title: Comparison of Soil Gas, Heated Headspace, and Methanol Extraction Techniques for Soil Volatile Organic Compound Quantification

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Abstract:

Three soil volatile organic compound (VOC) measurement techniques were compared at two hazardous waste sites located within different climatic and geologic regions. Dissimilar soil properties found at the sites also allowed for the examination of the influence of the differing soil properties on VOC quantification. A total of 41 soil gas, 52 heated headspace, and 51 methanol extraction/purge-and-trap measurements were obtained on collocated samples. Contaminants present at both sites included the following chlorinated hydrocarbons (CHCs): *cis*-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene. Heated headspace offered the highest sensitivity as indicated by the greatest percentage of detections per number of analyses. The statistical regression between headspace concentrations and methanol extraction concentrations was highly significant ($p<0.001$) with a $r^2 = 0.53$. Headspace concentrations were approximately 20% to 30% of the methanol extraction concentrations indicating that the methanol was able to extract significantly more of the CHCs than the headspace extraction, even in soils with relatively low organic carbon contents (< 0.25%). None of the soil properties, *viz.*, gravimetric moisture content, organic carbon content, percent sand, or percent clay, significantly improved the regression fit. The soil gas responses were unlike either headspace or methanol extraction data. CHC measurement by vapor extraction/soil gas could not be used to predict soil CHC concentrations at these sites.

Notice: The U.S. Environmental Protection Agency, through its Office of Research and Development (ORD), prepared this abstract for a proposed poster presentation. It does not necessarily reflect the views of the EPA or ORD.

EVALUATION OF A STANDARD TEST METHOD FOR SCREENING FUELS IN SOILS

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ABSTRACT

A new screening method for fuel contamination in soils was recently developed as American Society for Testing and Materials (ASTM) Method D-5831-95, Standard Test Method for Screening Fuels in Soils. This method uses low-toxicity chemicals and can be used to screen organic-rich soils, as well as being fast, easy, and inexpensive to perform. Fuels containing aromatic compounds, such as diesel fuel and gasoline, as well as other aromatic-containing hydrocarbon materials, such as motor oil, crude oil, and coal oil, can be determined.

The screening method for fuels in soils was evaluated by conducting a collaborative study on the method. In the collaborative study, a sand and an organic soil spiked with various concentrations of diesel fuel were tested. Data from the collaborative study were used to determine the reproducibility (between participants) and repeatability (within participant) precision of the method for screening the test materials. The collaborative study data also provide information on the performance of portable field equipment (patent pending) versus laboratory equipment for performing the screening method and a comparison of diesel concentration values determined using the screening method versus a laboratory method.

INTRODUCTION

A field method for screening fuel contamination in soils was developed within American Society for Testing and Materials (ASTM) Main Committee D-34 on Waste Management (1). This test method is ASTM Method D-5831-95, Standard Test Method for Screening Fuels in Soils (2). Unlike many of the existing methods for screening fuel contamination in soils, the ASTM method provides a fast, easy, and inexpensive procedure that uses low-toxicity chemicals and can be used to screen organic-rich soils.

The method calls for extracting a soil sample with isopropyl alcohol, filtering the extract, and measuring the absorbance of the extract at 254 nm (3). Calcium oxide is added to the soil as a conditioning agent to minimize interferences from organic materials. If the contaminant fuel is available for calibration, the approximate concentration of the fuel in the soil can be calculated; if the fuel type is known, but a sample of the contaminant fuel is not available for calibration, an estimate of the contaminant fuel concentration can be calculated using an average response factor; and if the nature of the contaminant fuel is not known, the absorbance value is used to indicate the presence or absence of fuel contamination. Fuels containing aromatic compounds, such as diesel fuel and gasoline, as well as other aromatic-containing hydrocarbon materials, such as motor oil, crude oil, and coal oil can be determined.

A collaborative study was conducted to determine the reproducibility (between participants) and repeatability (within participant) precision of the method when applied to two different soil types spiked with various levels of diesel fuel (1). Data generated in the collaborative study also provide information on the performance of portable field equipment versus laboratory equipment for performing the screening method and a comparison of diesel concentration values determined using the screening method versus a laboratory method. The purpose of this paper is to further evaluate ASTM Method D-5831-95 using these data.

DESCRIPTION OF THE WORK

Method Development and Collaborative Study Design

Development of ASTM Method D-5831-95 and the collaborative study design have been previously described (1). As a result, these are briefly summarized below.

The screening method became an ASTM standard test method in September 1995. The method that was approved by ASTM is the same method used by the eight participants in the collaborative study. Because the screening method can be performed in the laboratory using laboratory equipment or in the field using portable equipment, three of the participants used laboratory equipment; three participants used field equipment; and two used a combination of both for their testing. The laboratory equipment included various models of a laboratory stir plate, balance, and spectrophotometer. The field equipment consisted of a soil test kit supplied by In-Situ, Inc. (patent pending). The soil test kit contains a portable, mechanical stirrer, portable balance, and portable photometer that measures ultraviolet absorbance at 254 nm.

Each participant tested seven materials in triplicate. The test materials were a sand spiked with three different concentrations of diesel fuel (test materials A, B, and C), an unspiked sand (test material D), an organic soil spiked with two different concentrations of diesel fuel (test materials E and F), and an unspiked organic soil (test material G). The participants used the absorbance values they recorded for the test materials to calculate both approximate and estimated diesel fuel concentrations in the materials. Calculations to correct those values for concentrations reported in the blank materials (test materials D and G) and statistical evaluation of the collaborative study data were performed by Western Research Institute.

ASTM Practice D-2777-86, Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water (6), and ASTM Practice E-691-87, Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method (7), were used for guidance in statistically evaluating the collaborative study data. Calculations outlined in these standards were used to determine the mean concentration, reproducibility standard deviation, and repeatability standard deviation for the approximate and estimated concentration data determined using both laboratory equipment and portable field equipment.

The collaborative study materials were tested to make sure they met a specified homogeneity criterion prior to being sent to the participants (1). Homogeneity testing involved mixing the bulk materials and analyzing subsamples of them for their diesel concentrations. Analysis was by gas chromatography with flame ionization detection (GC-FID) of methylene chloride extracts using modified EPA Method 8015 (4). These data were used to establish a 95% confidence interval for the concentration of diesel fuel in each test material (5). The bulk materials were then taken through an additional mixing procedure. After additional mixing, two subsamples were withdrawn from each of the bulk materials and analyzed. The criterion for determining homogeneity was if the concentrations of diesel fuel determined in the two subsamples fell within the 95% confidence interval, expanded on both sides by 10%, then the bulk material was homogeneous. The 95% confidence interval was expanded by 10% on both sides to allow for error in the GC-FID method due to extraction, concentration, calibration, GC sample injection, and diesel pattern interpretation.

RESULTS AND DISCUSSION

Comparison of Diesel Fuel Concentrations Determined Using ASTM Method D-5831-95 Versus Diesel Concentrations Determined Using Modified EPA Method 8015

A total of 24 approximate and 24 estimated concentration values were generated for each test material by the eight participants in the collaborative study. In the statistical evaluation of these data, the mean approximate concentration of diesel fuel in each test material and the mean estimated concentration of diesel fuel in each test material were calculated (1). These values can be compared with the concentration values determined in the test materials during homogeneity testing using the laboratory GC-FID method. This comparison is shown in Table 1.

Table 1. Comparison of Collaborative Study Data Versus GC-FID Data, mg/Kg

Material	GC-FID Method	Screening Method Mean Concentration	Percent Difference
A	$\bar{x}$ = 122 95% C.I. = 103-143[a]	Approximate = 156 Estimated = 179	28%[b] 47 %[c]
B	$\bar{x}$ = 384 95% C.I. = 329-443	Approximate = 382 Estimated = 459	0.5% 19%
C	$\bar{x}$ = 841 95% C.I. = 719-972	Approximate = 802 Estimated = 972	5% 16%
E	$\bar{x}$ = 156 95% C.I. = 133-180	Approximate = 103 Estimated = 125	-34% -20%
F	$\bar{x}$ = 826 95% C.I. = 704-957	Approximate = 618 Estimated = 737	-25% -11%

[a]95% confidence interval for the concentration of diesel fuel in the test material expanded by 10% on each side
[b]Percent difference between screening method mean approximate concentration and GC-FID $\bar{x}$ value
[c]Percent difference between screening method mean estimated concentration and GC-FID $\bar{x}$ value

In Table 1, higher absolute percent difference values between the screening method mean concentrations and the GC-FID mean values (20 to 47%) are generally shown for the lower diesel concentrations at approximately 100 to 180 mg/Kg. At diesel concentrations in the spiked sand and organic soil of approximately 380 to 970 mg/Kg, the absolute percent differences between the screening method mean concentrations and the GC-FID mean values range from 0.5% to 25%. Comparison of the screening method mean concentration values to the expanded 95% confidence intervals for the GC-FID analyses shows that seven of the ten mean concentration values determined using the screening method fall within the corresponding expanded 95% confidence interval or are just outside the interval by less than 20 mg/Kg. If the absolute values of the percent differences listed in Table 1 are averaged, the result is 20%. This value can be used to give a general indication of how the results from the screening method and laboratory method may vary.

The concentrations determined using the screening method to test the diesel-spiked organic soil (materials E and F) are lower than the corresponding GC-FID values. This may be due to the spiked-organic soil adhering to the sides of the glass vials in which the material was shipped to the collaborative study participants. During addition of this material to the vials and during testing of the material using the screening method, the spiked organic soil adhered to the sides of the glass vials, and even with significant shaking, not all of the material could be loosened from the glass. It is believed that this may have resulted in lower concentrations of diesel fuel in the spiked organic soil that was removed from the glass vials by the participants for testing. Despite this problem and considering that the ASTM method is a screening method and the EPA method is a laboratory procedure, the variation between the values determined using the two methods would be acceptable in most cases.

Performance of Portable Field Equipment Versus Laboratory Equipment for Performing ASTM Method D-5831-95

As mentioned, three of the collaborative study participants used portable field equipment to perform their testing, and three of the participants used laboratory equipment. The mean concentrations of diesel fuel determined to be present in the test materials using laboratory equipment and field equipment can be compared. This comparison is shown in Table 2.

The maximum absolute percent difference between the mean concentration values determined using laboratory equipment and those determined using the soil test kit is 12%, and for six of the comparisons shown in Table 2, the absolute percent difference is 5% or less. This shows very good agreement between the results of the method when laboratory equipment is used and when portable field equipment is used. From the data shown in Table 2, it appears that at lower diesel concentrations in the spiked sand and organic soil, results from using the method with laboratory equipment and field equipment may vary slightly more than at higher diesel concentrations.

Table 2. Diesel Concentration Comparison: Portable Field Equipment Mean Concentration Values Versus Laboratory Equipment Mean Concentration Values, mg/Kg

Approximate Concentration Determinations

Material[a]	Soil Test Kit Mean Value	Laboratory Mean Value	% Difference
A	143	162	-12%
B	373	383	-3%
C	780	812	-4%
E	95	108	-12%
F	579	646	-10%

Estimated Concentration Determinations

Material[a]	Soil Test Kit Mean Value	Laboratory Mean Value	% Difference
A	170	193	-12%
B	475	452	5%
C	968	962	1%
E	123	127	-3%
F	722	759	-5%

[a] Materials A, B, and C are a diesel-spiked sand, and materials E and F are a diesel-spiked organic soil.

The reproducibility and repeatability standard deviation values were used to express the precision of the screening method. Information given in ASTM Practice E-177-90, Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods (8), was used for guidance in expressing the precision of the screening method. The index used for expressing reproducibility and repeatability of the test method is the 95% limit on the difference between two test results. The 95% limit means that approximately 95% of all pairs of test results from users similar to the participants in the collaborative study can be expected to differ in absolute value by less than 2.8 s (standard deviation) or 2.8 CV% (percent coefficient of variation) (8).

The 95% repeatability and reproducibility limits, expressed as 2.8 CV%, for screening the diesel-spiked sand and diesel-spiked organic soil using laboratory equipment and the soil test kit are listed in Tables 3 and 4, respectively.

Table 3. 95% Repeatability Limits[a] for Testing Diesel-Spiked Sand and Organic Soil Using the Screening Method for Fuels in Soils

Materials: Diesel-Spiked Sand and Diesel-Spiked Organic Soil
Equipment: Laboratory

Test Range, mg/Kg	95% Repeatability Limit (% of the test result)
108-962 (approximate or estimated)	15% (9 to 22%)

Materials: Diesel-Spiked Sand and Diesel-Spiked Organic Soil
Equipment: Soil Test Kit

Test Range, mg/Kg	95% Repeatability Limit (% of the test result)
95-968 (approximate or estimated)	18% (11 to 26%)

[a] Within participant

Table 4. 95% Reproducibility Limits* for Testing Diesel-Spiked Sand and Organic Soil Using the Screening Method for Fuels in Soils

Material: Diesel-Spiked Sand **Equipment: Laboratory**	
Test Range, mg/Kg	95% Reproducibility Limit (% of the test result)
162-962 (approximate or estimated)	15% (10 to 22%)
Material: Diesel-Spiked Sand **Equipment: Soil Test Kit**	
Test Range, mg/Kg	95% Reproducibility Limit (% of the test result)
143 (approximate)	47%
170 (estimated)	58%
373 (approximate)	12%
780 (approximate)	28%
475-968 (estimated)	33% (32%, 34%)
Material: Diesel-Spiked Organic Soil **Equipment: Laboratory**	
Test Range, mg/Kg	95% Reproducibility Limit (% of the test result)
108 (approximate)	65%
127 (estimated)	46%
646 (approximate)	35%
759 (estimated)	28%
Material: Diesel-Spiked Organic Soil **Equipment: Soil Test Kit**	
Test Range, mg/Kg	95% Reproducibility Limit (% of the test result)
95-579 (approximate)	14% (15%, 13%)
123-722 (estimated)	33% (32%, 33%)

*Between participants

The 95% repeatability and reproducibility limits listed in Tables 3 and 4 are specific to the test materials used in the collaborative study. For other soil types and fuel contaminants, these data may not apply. However, using these data to evaluate the precision of ASTM Method D-5831-95 using laboratory equipment versus portable field equipment shows the following.

- There is very good agreement between the repeatability precision of the screening method for testing the diesel-spiked sand and organic soil using laboratory equipment (15% of the test result) and the repeatability precision of the screening method for testing the two materials using the soil test kit (18% of the test result). In terms of repeatability precision, these data show comparable performance of the method using both types of equipment.

- There is variation in the reproducibility precision of the method using laboratory equipment and the soil test kit to screen the diesel-spiked sand and organic soil. For screening the diesel-spiked sand, the reproducibility precision of the method using laboratory equipment is better than when the soil test kit is used. However, for screening the diesel-spiked organic soil, the overall reproducibility precision of the method using the

soil test kit is better than when laboratory equipment is used.

- The reproducibility precision of ASTM Method D-5831-95 using laboratory equipment to screen the diesel-spiked sand is very good. The 95% reproducibility limit equals 15% of the test result for both approximate and estimated concentration determinations.

- For approximate diesel concentrations in the organic soil ranging from 95 to 579 mg/Kg, the 95% reproducibility limit of the screening method using the soil test kit is 14% of the test result; and for estimated diesel concentrations in the organic soil ranging from 123 to 722 mg/Kg, the 95% reproducibility limit is 33% of the test result.

- The 95% reproducibility precision of the method for screening the diesel-spiked sand using the soil test kit and for screening the diesel-spiked organic soil using laboratory equipment varies with concentration for both approximate and estimated concentration determinations. In both cases, at lower concentrations, approximately 100 to 150 mg/Kg, the reproducibility precision of the method is poor at approximately 55% and at higher concentrations, the reproducibility precision of the method is a little better at approximately 33%.

- For the case where laboratory equipment and the soil test kit give better reproducibility precision and for the case where laboratory equipment and the soil test kit give lower reproducibility precision, the 95% reproducibility limits of the method are similar. As a result, neither type of equipment can be judged more suitable for performing the method in terms of reproducibility precision.

CONCLUSIONS

The following conclusions can be made concerning the performance of ASTM Method D-5831-95 for screening the diesel-spiked sand and diesel-spiked organic soil used in the collaborative study.

- The average absolute percent difference between the approximate and estimated diesel concentrations determined using ASTM Method D-5831-95 and the diesel concentrations determined using modified EPA Method 8015 to test the diesel-spiked sand and organic soil is 20%. This value can be used to give a general indication of how results from using the screening method and laboratory method may vary. This variation would be acceptable in most cases.

- Average diesel concentrations determined using laboratory equipment and the soil test kit to screen the diesel-spiked sand and diesel-spiked organic soil using ASTM Method D-5831-95 are very comparable. In all cases, they vary by 12% or less. In terms of test results, this shows comparable performance of the method using both types of equipment.

- There is good agreement between the repeatability precision of ASTM Method D-5831-95 for testing the diesel-spiked sand and organic soil using laboratory equipment (15% of the test result) and the repeatability precision of the screening method for testing the two materials using the soil test kit (18% of the test result). In terms of repeatability precision, these data show comparable performance of the method using both types of equipment.

- There is variation in the reproducibility precision of ASTM Method D-5831-95 using laboratory equipment and the soil test kit to screen the diesel-spiked sand and organic soil. However, for the case where laboratory equipment and the soil test kit give better reproducibility precision and for the case where laboratory equipment and the soil test kit give lower reproducibility precision, the 95% reproducibility limits of the method are similar. As a result, in terms of reproducibility precision of the method, neither type of equipment can be judged more suitable for performing ASTM Method D-5831-95.

ACKNOWLEDGMENTS

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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DETECTION OF PESTICIDES AND PCBs IN THE VAPOR PHASE FOR SITE SCREENING

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ABSTRACT

Pesticides and polychlorinated biphenyls (PCBs) are well known as hazardous environmental contaminants. Assessing sites for the presence of these and other organic pollutants typically involves collecting soil and/or ground water samples and analyzing them by one or more analytical methods. A cost effective alternate approach to traditional intrusive subsurface site characterization techniques is the analysis of organic compounds in the vapor phase (soil gas). However, detection of pesticides, PCBs, and other semi-volatile organic contaminants using traditional soil gas techniques (active) has been difficult due to low vapor pressure of compounds, tendency of compounds to adsorb onto organic and mineral components in soil, and the short sampling intervals associated with active soil gas methods.

Detection of pesticides and PCBs utilizing a unique soil gas screening technology known as GORE-SORBER® Screening Surveys has been examined. This technology has been successfully used over the past four years by W. L. Gore and Associates, Inc. to screen for a variety of organic contaminants in the field. The collector is constructed of a patented, hollow insertion/retrieval cord made of GORE-TEX® membrane. This membrane, which is made of expanded polytetrafluoroethylene (ePTFE), is chemically inert, microporous, and hydrophobic. The node and fibril structure of ePTFE allows unimpeded vapor transfer, while preventing liquid water and soil particles from impacting sample integrity. Inside the insertion/retrieval cord are smaller ePTFE tubes sealed at both ends and filled with sorbent material. Analysis of the sorbent filled ePTFE tubes is performed by thermal desorption/ gas chromatography/ mass spectrometry.

The purpose of this study was to determine which pesticides and PCBs from EPA SW846 method 8080 could be successfully detected using the GORE-SORBER® technology. The study included both bench scale experiments and field work. The pesticides that were detected included aldrin, BHC isomers (including lindane), DDD, DDE, dieldrin, endosulfan I, endrin, heptachlor, and heptachlor epoxide. Individual PCB congeners that were detected ranged from monochlorinated biphenyls to pentachlorinated biphenyls.

INTRODUCTION

Success of soil gas screening depends on the physical and chemical characteristics of the compound being monitored and the availability of soil pore space. For compounds to be detected, sufficient amounts of the compound must be available in the soil pore space during the collection time.

Properties such as vapor pressure, solubility in water, and adsorption onto soil organic matter and minerals directly affect the amount of the compound that will exist in the soil gas. The tendency of a compound to adsorb onto the soil organic matter can be expressed using the organic distribution coefficient (K_{OC}) or estimated using the octanol water partition coefficient (K_{OW}). K_{OC} is used to relate the ratio of the amount of compound adsorbed onto the soil organic matter to the amount in the soil solution. K_{OW} is the ratio of the amount of material that will preferentially dissolve into octanol verses water. Table 1[1,2,3] shows the vapor pressure (VP), solubility, and K_{OW} or K_{OC} for selected organic compounds. Data for K_{OW} [1,2] and K_{OC} [3] are noted in their logarithmic form in the references. To better illustrate differences, data from references have been converted from their logarithmic form to the actual number for use in this table. All vapor pressures are noted for substances in their liquid states.

Table 1.
Constants for a Selection of Common Organic Contaminants

Compound	*VP, Pa*	*Solubility, g/m³*	K_{OW} (K_{OC})
Benzene	12700	1780	135
1,1,1-Trichloroethane	16500	1495	309
Toluene	3800	515	490
Tetrachloroethane	2415	150	759
Undecane	52.2	0.04	8710000
Monochlorinated biphenyls	0.9 - 2.5	1.21 - 5.50	20000 - 40000
Trichlorinated biphenyls	0.003 - 0.22	0.015 - 0.40	320000 - 790000
Pentachlorinated biphenyls	0.0023 - 0.051	0.004 - 0.020	1600000 - 3200000
Hexachlorinated biphenyls	0.0007 - 0.012	0.0004 - 0.0007	5000000 - 20000000
Lindane (gamma-BHC)	0.00839	7.3	(1290)
Dieldrin	0.000659	0.25	(12000)
DDT	0.0000134	0.0012	(245000)

The darker shaded region of the table indicates compounds which can typically be detected using active soil gas methods. Undecane, which is lightly shaded, can be detected by active soil gas methods, but not as readily as the others. The unshaded region contains pesticides and PCBs, compounds which have significantly lower vapor pressures, significantly greater affinity for organic material and are not readily detectable by active soil gas methods.

To increase the chances of detecting pesticides and PCBs the collection time must be increased over that of active sampling. Passive sampling, using a sorbent based soil gas collector, allows time integrated sampling. The collector can be placed in the soil subsurface or saturated zone for an extended period of time allowing the compounds of low concentration to concentrate on the sorbent material.

To maximize chances for detection, the collector design must not inhibit exposure of adsorbent to the soil gas and the collector must protect the adsorbent from soil particulates and water. Also, the analytical technique chosen must be highly selective and sensitive.

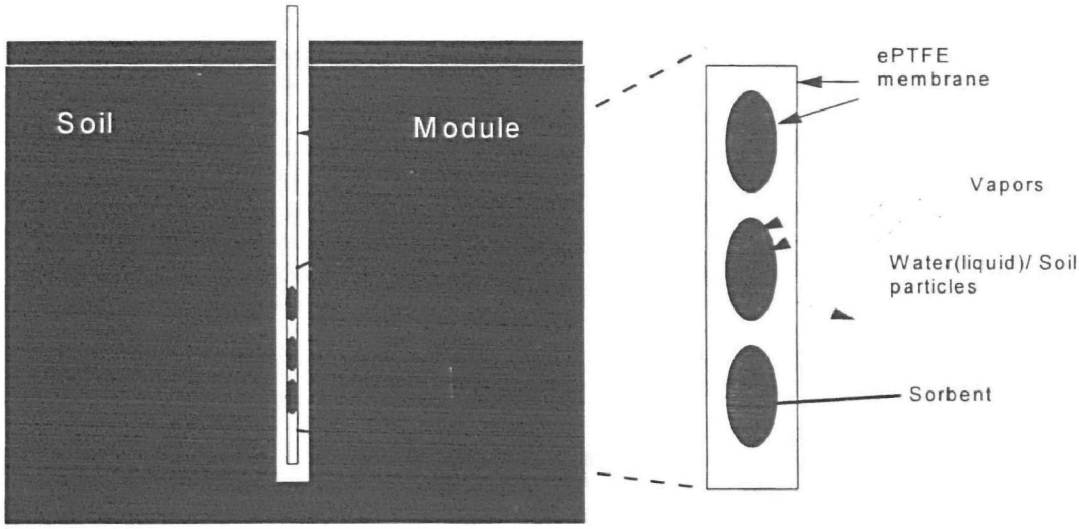
COLLECTOR DESIGN

Figure 1 shows the design and placement in the soil subsurface of the passive soil gas collector utilized in this work. The insertion/retrieval cord and the protective housing of the sorbent packets are made completely of expanded polytetrafluoroethylene (ePTFE). The membrane is chemically inert, microporous, and hydrophobic. The node and fibril structure of the membrane allows unimpeded vapor transfer onto the sorbent material, while preventing liquid water and soil particles from contacting the sorbent.

The collector design enables the use of differing sorbent materials within the same module, allowing for selective adsorption of a broad range of organic compounds. For this study a porous polymer sorbent material was used in the collector.

The design also allows for easy installation. Installation is performed by making a narrow pilot hole with simple hand tools and inserting the module into the hole using an insertion rod.

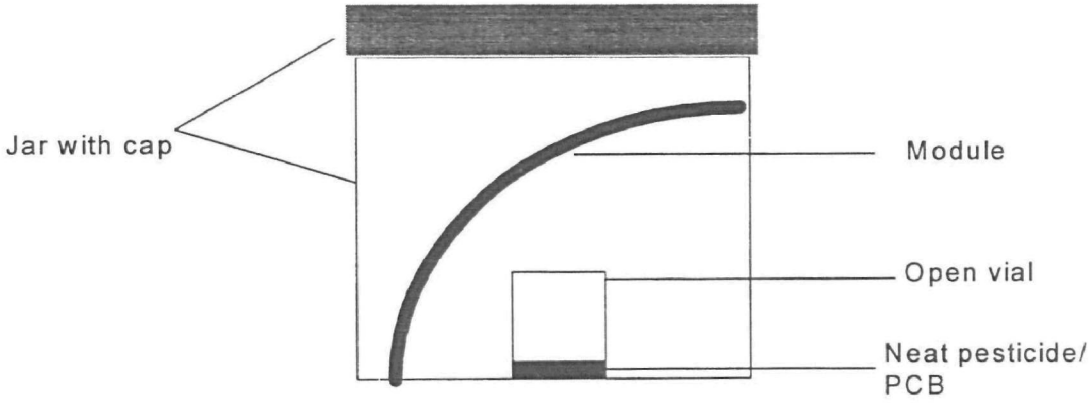
Figure 1.
GORE-SORBER® Soil Gas Module



BENCH SCALE EXPERIMENTS

Bench scale experiments were designed to determine which pesticides and PCBs could possibly be detected using the passive soil gas collector (Figure 2). Compounds chosen for examination were from EPA SW846 method 8080 and were obtained from Chem Service, Inc., West Chester, PA. Collectors were placed in jars containing neat pesticide and PCB materials. A control sample was also prepared by placing a collector in an empty jar. The collectors were protected from direct contact with pesticides and PCBs by using small open vials to hold the neat materials. The outer jars were capped and placed in a fume hood for a two week time period (manufacturer's recommended time period for exposure in the field). After the exposure period, one sorbent packet was removed from each collector and analyzed using thermal desorption/ gas chromatography/mass spectrometry (TD/GC/MS).

Figure 2.
Setup for Bench Scale Experiment



Pesticide Results

Analysis results for pesticides are found in Table 2. Pesticides are listed in GC retention time order. The 'µg detected' column shows the amount of the pesticide detected on the sorbent packet analyzed. Results are meant to show relative amounts detected and are not intended to indicate absolute amount of compound present in the vapor space.

Typical method detection limits for this technology are between 0.02 and 0.2µg. Using 0.2µg as a practical cut off for determining which compounds are suitable candidates for this technology, assignments can be made for the probability of detection. The darker shaded portion of the table indicates compounds which have the greatest probability of being detected in the field (compounds with detected amounts greater than 0.2µg). The lightly shaded compounds are those which are considered to have some possibility of being detected in the field (compounds with detected levels near 0.2µg). The unshaded region of the table contains compounds which are probably not detectable using passive soil gas sampling techniques (compounds not detected or detected well below 0.2µg). Since GC retention times give a rough estimate of relative boiling points and vapor pressures, a possible vapor pressure cut off for readily detectable pesticides can be seen in the region of heptachlor epoxide and endosulfan I and a possible vapor pressure cut off for potential detection can be seen in the region of endrin and 4,4'DDD.

Table 2.
Results of Bench Scale Experiment for Pesticides

Pesticide (amount)	*Retention Time (min.)*	*µg Detected*
A-BHC (100mg)	9.38	17.12
Lindane (1g)	9.66	19.43
D-BHC (100mg)	9.85	6.49
Heptachlor (100mg)	10.27	18.33
Aldrin (100mg)	10.57	27.64
Heptachlor Epoxide (50mg)	10.88	0.23
Endosulfan I (100mg)	11.18	1.23
4,4' DDE (100mg)	11.30	0.19
Dieldrin (50mg)	11.38	0.19
Endrin (1g)	11.56	0.24
4,4' DDD (1g)	11.63	0.05
Endosulfan II (100mg)	11.62	0.00
Endrin Aldehyde (10g)	11.76	0.00
4,4' DDT (1g)	11.91	0.00
Endosulfan Sulfate (50mg)	11.94	0.00
Methoxychlor (1g)	12.31	0.00

(B-BHC was investigated but results are suspect and under investigation)

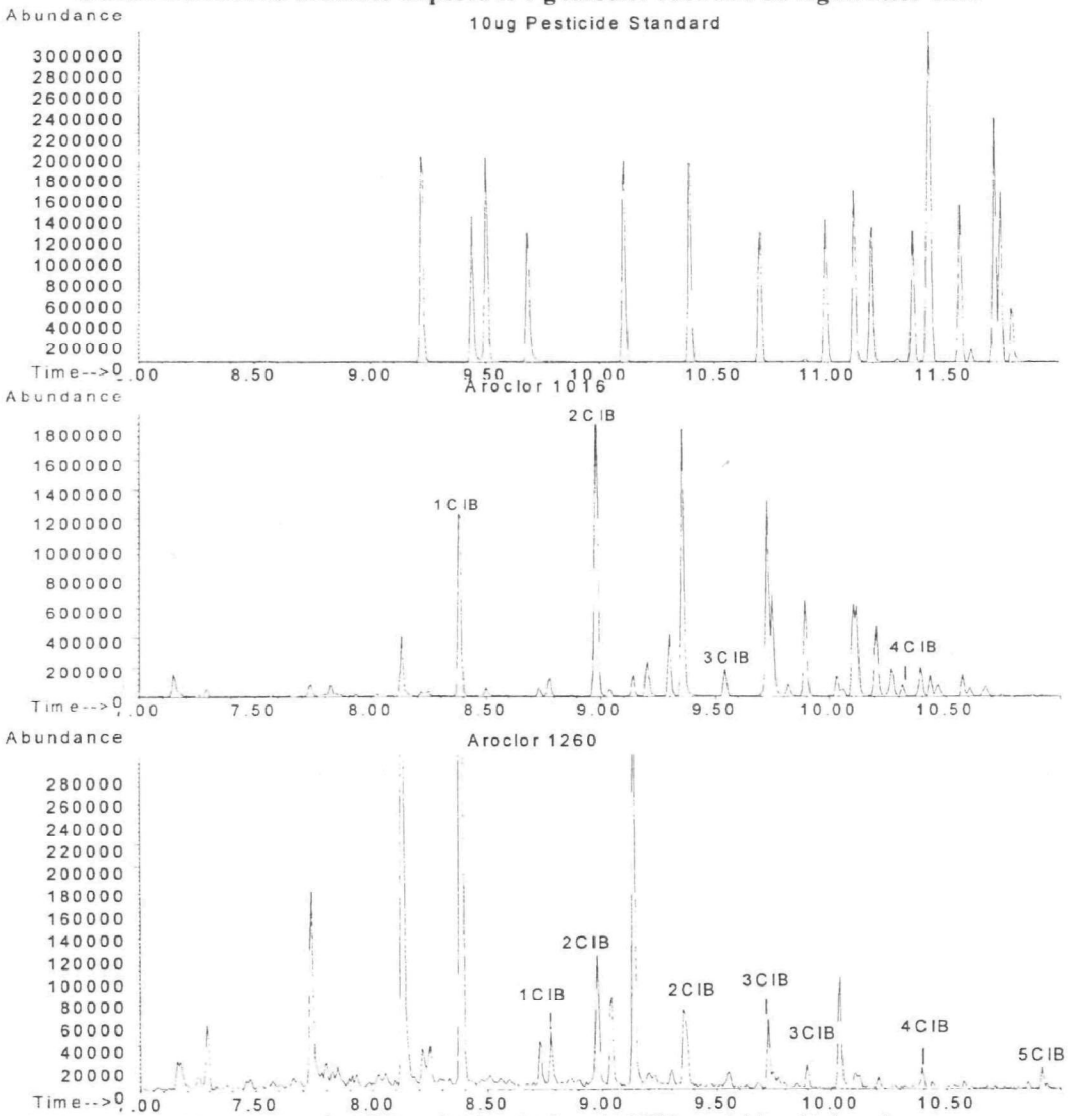
PCB Results

Collectors exposed to PCBs were not analyzed along with calibration standards, therefore no quantitative data is available. However, chromatograms from the analysis of the exposed collectors show a very strong response relative to the pesticide standard examined. Figure 3 shows chromatograms from the analysis of a 10µg pesticide standard and collectors exposed to 1 gram of Aroclor 1016 and 50mg Aroclor 1260.

Collectors were exposed to Aroclors 1242, 1254, 1221, 1232, 1248, 1260, and 1016. Individual congeners up to pentachlorobiphenyl were detected in the exposed modules.

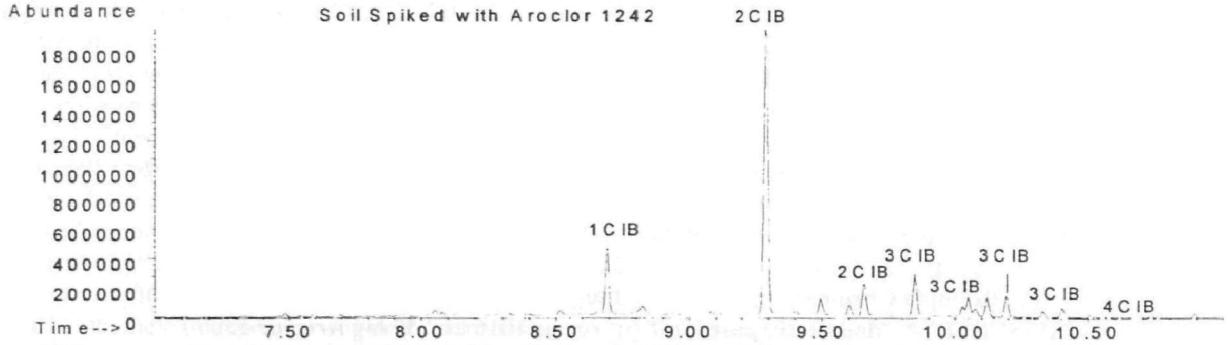
In addition to experiments using neat Aroclor mixtures, a similar experiment was setup using 50g of soil spiked with 39.4mg/kg of Aroclor 1242 (approximately 2mg of aroclor 1242). A soil gas collector was placed in a glass jar containing the spiked soil and an empty jar (control sample). The jars were then capped and placed in a fume hood for 2 weeks. After the 2 week exposure period, one sorbent packet was removed from the module and analyzed by TD/GC/MS. The resulting chromatogram can be seen in Figure 4. Individual congeners up to tetrachlorobiphenyl were detected.

Figure 3.
Example Chromatograms from a 10ug Pesticide Standard and GORE-SORBER® Modules Exposed to 1 g Aroclor 1016 and 50 mg Aroclor 1260



Key: 1ClB = monochlorobiphenyl; 2ClB = dichlorobiphenyl; 3ClB = trichlorobiphenyl; 4ClB = tetrachlorobiphenyl; 5ClB = pentachlorobiphenyl.

Figure 4.
Chromatogram of Module Exposed to Soil Spiked with 39.4mg/kg Aroclor 1242



Key: 1ClB = monochlorobiphenyl; 2ClB = dichlorobiphenyl; 3ClB = trichlorobiphenyl; 4ClB = tetrachlorobiphenyl.

FIELD RESULTS

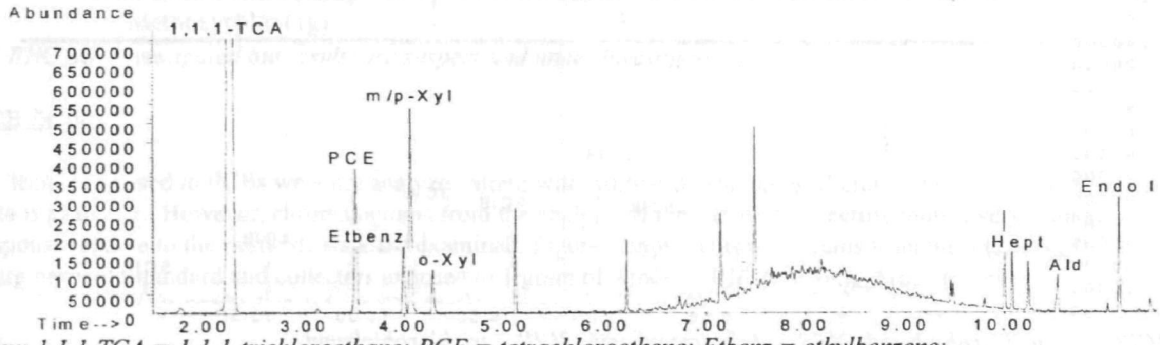
Bench scale experimentation gives a good approximation of what one can expect to be able to detect in the field. However, only field results can give final proof as to whether pesticides and PCBs can be detected in soil gas for site screening, due to the impact of soil permeability and other site specific conditions.

A site belonging to a large pesticide manufacturer was screened for volatile organic contaminants and pesticides in the region of a drum washing area. Sixteen soil gas collectors were installed on a grid at a depth of approximately 2 to 3 feet. Collectors were retrieved after two weeks and returned to the laboratory for analysis..

Aromatic and chlorinated hydrocarbons were detected in the vapor phase as well as several chlorinated pesticides. Pesticides were detected as tentatively identified compounds since calibration standards for pesticides were not used. Pesticides detected included aldrin, heptachlor, endosulfan I, and dieldrin (Figure 5 is an example chromatogram). These results demonstrate the capability of detecting volatile organic contaminants and semi-volatile pesticides in one analytical run using this technology.

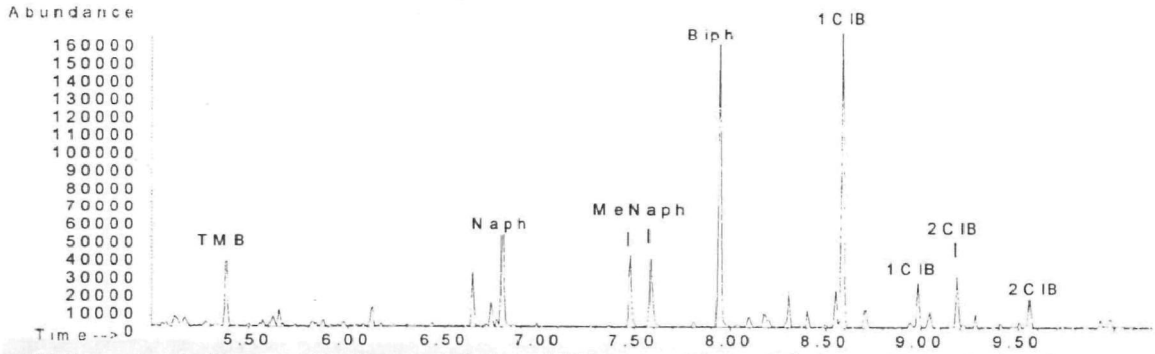
Modules returned from another site showed PCB contamination in the presence of other volatile and semi-volatile organic contaminants. Figure 6 is an example chromatogram showing individual PCB congeners detected.

Figure 5.
Example Chromatogram from Volatile Organic and Pesticide Contaminated Site



Key: 1,1,1-TCA = 1,1,1-trichloroethane; PCE = tetrachloroethene; Etbenz = ethylbenzene; m/p-Xyl = m/p-xylene; o-Xyl = o-xylene; Hept = heptachlor; Ald = aldrin; Endo I = Endosulfan I

Figure 6.
Example Chromatogram From PCB Contaminated Site



Key: TMB = trimethylbenzene; Naph = naphthalene; MeNaph = methylnaphthalenes; Biph = biphenyl; 1ClB = monochlorobiphenyl; 2ClB = dichlorobiphenyl.

CONCLUSION

This investigation has shown that certain pesticides and individual PCB congeners can be detected in the vapor phase using the GORE-SORBER® soil gas collector and TD/GS/MS analysis. Bench scale experiments indicate that using this technology alpha-BHC, lindane, delta-BHC, heptachlor, aldrin, and endosulfan I can be readily detected in the vapor phase and that heptachlor epoxide, 4,4'DDE, dieldrin, and endrin have the potential of being detected in the vapor phase. Analysis of field samples confirms that heptachlor, aldrin, endosulfan I, and dieldrin can be detected in the vapor phase in the soil.

Individual PCB congeners detected in the vapor phase using this technology include mono, di, tri, tetra, and pentachloro biphenyls in bench scale experiments and both monochloro and dichloro biphenyls in field samples.

In addition to the determination of which PCBs and pesticides that can be detected, it was also found that this technology can be used to detect both volatile organic compounds and semi-volatile compounds including pesticides and PCBs in a single analytical run.

GORE-SORBER Screening Survey, GORE-SORBER Module, and GORE-TEX are registered trademarks of W.L. Gore & Associates, Inc.

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RADIOLOGICAL

MONITORING AND METHODOLOGY OF RADIONUCLIDES IN DOMESTIC AND IMPORTED FOODS IN THE U.S.

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ABSTRACT

The U.S. Food and Drug Administration (FDA) is responsible for the wholesomeness of the nation's food supply. The FDA modified its food-monitoring program in January, 1973, to include radioactive isotopes. In 1975, it expanded this program to include selective foods originating in the vicinity of nuclear power stations. It was fortunate that this program was set in place, since over the years it has responded to several nuclear incidents. These include the Three Mile Island incident in Pennsylvania and the Chernobyl accident in the Ukraine of the then Soviet Union. The program at the time of the latter included food products originating from Europe or adjacent areas. In addition, it has responded to concerns over former low-level radioactive ocean waste dump sites off the coast of California and New Jersey. Also, the Massachusetts Bay dump has been surveyed. These were done in cooperation with other federal agencies such as the EPA and NOAA. Recently, a program was set in place to monitor fish from the Arctic Ocean when it was learned that the then Soviet Union had disposed of nuclear submarines in the Aral Sea.

The methodology used to perform analyses on these food products are taken from the standard setting societies such as the AOAC, International, ASTM and APHA/AWWA/WEF. In addition, methods not tested by these societies are taken from the literature or from DOE manuals such as the HASL and also the EPA manuals. These include the methods for long-lived radionuclides such as strontium-90 and cesium-137. The short-lived radionuclides such as iodine-131, the radio cesium and ruthenium.

This paper will show the data from the monitoring of the U.S. food supply, imported foods and some of the special surveys. The interpretation of the results will be discussed in light of the Federal Radiation Council Guidelines and the "FDA Levels of Concern."

INTRODUCTION

The U.S. Food and Drug Administration (FDA) is responsible for the wholesomeness of the nation's food supply. This has been ongoing since 1961, (1-6) when contamination from above ground weapons testing was prevalent. It was suspended in 1969 to avoid duplication of effort. Also, there was a downward trend in fallout following the Test Ban Treaty of 1963. In 1973, the FDA resumed its radionuclide food-monitoring program because of concern of the possibility of food contamination from selective foods originating in the vicinity of nuclear power plants and other sources. It also decided it should maintain a radiochemical capability to detect any upward trend in the radioactive contamination of foods.

In 1975, it expanded this program to include selective foods originating in the vicinity of nuclear power stations. It was fortunate that this program was set in place, since over the years it has responded to several nuclear incidents. These include the Three Mile Island incident in Pennsylvania and the Chernobyl accident in the Ukraine of the then Soviet Union. The program at the time of the latter included food products originating from Europe or adjacent areas. In addition, it responded to concerns over former low-level radioactive ocean waste dump sites off the coast of California and New Jersey. Also, the Massachusetts Bay dump was surveyed. These were done in cooperation with other federal agencies such as the EPA and NOAA. Recently, a program was set in place to monitor fish from the Arctic Ocean when it was learned that the then Soviet Union had disposed of nuclear powered submarines in the Aral Sea.

EXPERIMENTAL SAMPLES

From the fiscal years(FY) 1987 (7) through 1995 (October 1986 through September 1995) 3 types of food collections were examined: Total Diet Study (TDS), reactor survey, and imported. TDS samples represented the general U.S. food supply and were obtained through FDA's TDS program. Portions of all foods comprising one TDS collection were analyzed each fiscal year. During FY87 through FY91, each TDS collection consisted of 234 individual foods selected according to the protocol reported in 1982. The FY92 through FY95 collection included 265 individual foods selected according to a revised protocol (8).

Approximately 300 reactor-survey food test portions, including raw vegetables, food crops (primarily fruits), fish, and milk, were collected in the vicinities of 33 nuclear power reactors (representing 71% of the states having nuclear power reactors). Reactor sites were selected to include many geographical regions and varied from year to year. Reactor-survey food test portions were analyzed for ^{3}H. Half the foods were also analyzed for ^{137}Cs, ^{131}I, ^{106}Ru, and ^{90}Sr.

Imported foods have not been monitored continually since the program began in 1961. Only during the period from 1972-1982 were they previously monitored. However, extensive collection and analysis efforts were initiated in May 1986 to monitor for contamination resulting from the Chernobyl nuclear accident. Samples of food were collected at points of entry during routine import inspections.

Selection of shipments to sample was based on country of origin and food type. All samples were analyzed for ^{137}Cs and ^{134}Cs, which were used as the main indicators of contamination. This monitoring effort is continuing, but on a limited basis, depending upon the product being imported. This is based on the past history of the products.

Other surveys that were undertaken recently were a repeat of the low-level waste dump sites fish survey in that included the Farallon Island area near San Francisco, the coast of New Jersey and Massachusetts Bay. Then again in 1990, the Farallon Island area was sampled. Also, in 1992, the Massachusetts Bay was sampled. The EPA and NOAA took part in this survey.

When, in 1993, it was learned that the then Soviet Union had discarded nuclear powered submarines in the Arctic Ocean, another fishery survey was undertaken. This lasted for two years.

Analytical/Methodology

The methodology used to perform analyses on these food products are taken from the standard setting societies such as the AOAC, International, ASTM and APHA/AWWA/WEF (9-11). In addition, methods not tested by these societies are taken from the literature or from DOE manuals such as the HASL and also the EPA and PHS manuals (12-16). These include the methods for long-lived radionuclides such as strontium-90 and cesium-137. The short-lived radionuclides such as iodine-131, the radio cesium and ruthenium.

Radionuclide analyses were performed at FDA's Winchester Engineering and Analytical Center in Winchester, MA. The basic analytical methods used were described previously (17-20). The activity concentrations of ^{137}Cs, ^{131}I, and ^{106}Ru were determined by using gamma-ray spectrometry with germanium, lithium-drifted germanium, and sodium iodide gamma-ray detectors. The method for the isotopic analysis of plutonium in fish was based on a method for soil and was modified for food ash. The isotopic plutonium content is determined using an alpha spectroscopy system, after the sample is plated.

Limits of detection (LODs) were defined as three times the one sigma analytical uncertainties at low concentrations near the LODs. Uncertainties near the LODs were primarily due to counting statistics. Large variations in food density and, in some cases, the quantities available for analysis, led to wide ranges of LODs. For most foods, LODs were ca 2 Bq/kg for ^{131}I, ^{137}Cs, and ^{106}Ru; 0.1 Bq/kg for ^{90}Sr; and 10 bq/kg for ^{3}H.

More recently the equipment (1992) has been upgraded to include three intrinsic germanium detectors with efficiencies of 40%, 80% and 90% (rated against NaI(Tℓ)). A NaI(Tℓ) detector is still functioning but is not being used. The older 6700 ND system was also replaced with the 9900 ND (Canberra) system. The system handles, in addition to the gamma detectors, two alpha spectrometers. A newer gamma system is being explored.

The FDA/WEAC takes part in the EPA Intercomparison Quality Assurance Program at Las Vegas, NV. It also receives split samples from a DOE contract laboratory. In addition, as part of another quality assurance program, it receives "blind" sources from the NIST.

RESULTS AND DISCUSSION

The Federal Radiation Council (FRC) (21) recommendations are used by the FDA in the interpretation of the analytical results for domestic foods. The FRC gave Radiation Protection Guides (RPGs)(Table 1) and corresponding action ranges for intake rates. Application to FDA's ongoing monitoring was made under the conservative assumption that the daily average consumption of any individual contaminated food (including beverages) would be 1 kg/day. This assumption led to derived-concentration action ranges, also given in Table 1.

No monitoring or actions (other than normal quality assurance exercises) are needed when average activity concentrations are within Range I. Monitoring only (i.e., no control actions) is recommended when average activity concentrations are within Range II or only transient in Range III. Control actions are recommended when activity concentration averages are in Range II but rising toward Range III or are in Range III. Control actions are to be strong and prompt when activity concentrations exhibit a rising trend in Range III. An illustration that detecting capabilities were more than adequate for monitoring the food supply is presented in Figure 1. Relative LODs are given based on the transitions to Range III. where control actions

are recommended, set at 100%. Presented in this way, Range II, which corresponds with monitoring only, extends from 10 to 100%. Range I is below 10%. The radioisotopes presented in Figure I are the main long-range contamination-indicator isotopes that have half-lives of several years and are indicators for the most likely nuclear accident scenarios. The relative LODs are very low. Therefore, contamination from a nuclear event would be very clearly monitored, even if radioactivity concentrations were too low to pose a health concern.

For imported foods, FDA uses the levels of concern (LOCs) recommended by the FDA/USDA Food Safety and Inspection Service Task Force (23), which was set up in May 1986 by the Director of FDA's CFSAN. The radioactivity LOCs in Table 2 were derived from the Preventative Action Guides (24) and use ^{131}I and the combination of ^{134}Cs and ^{137}Cs as indicators of contamination. Shipments of food containing radioactivity concentrations exceeding the LOCs are not allowed into the United States.

Table 2. Radioactivity levels of concern recommended by the FDA/FSIS Task Force[a]

Radionuclide	Infant Foods, Bq/kg (pCi/kg)	Other foods, Bq/kg (pCi/kg)
^{131}I	56(1500)	300(8000)
^{134}Cs + ^{137}Cs	370(10000)	370(10000)

[a]Reported in ref. 15

TOTAL DIET STUDY

The TDS findings in this paper focus on data from 9 fiscal years, FY87-95 when approximately 2100 food test portions were analyzed for ^{137}Cs, ^{131}I, ^{106}Ru, and ^{90}Sr. ^{131}I and ^{106}Ru were below the LODs in all test portions. ^{137}Cs activity concentrations were below the LODs in all but ten test portions; the ^{137}Cs activity concentrations in eight of these ranged up to 4.4 Bq/kg, which is very low in Range I and not unusual (the Range I-Range II transition is 54 Bq/kg).

^{90}Sr findings were consistent with those for previous years. Radioactivity concentrations were below the LODs in most foods (70%), measured and in RPG Range I for 29% of the foods, and low in Range II for 1% of the foods. There was no noticeable increase in ^{90}Sr contamination after the Chernobyl accident.

Dietary intake rates for ^{90}Sr were calculated and are plotted in Figure 2 for all TDS data obtained since the Radionuclides in Foods program began in 1961. Intake rates for 1961-1982 were derived from the TDS protocol for that period and relate to the 16- to 19-year old male age/sex group. For consistency, intake rates for 1982-1995 were derived from the 14- to 16- year old male age/sex group, which, under the protocol, is the closet match to the earlier protocol. In general, ^{90}Sr activity concentrations in the U.S. food supply continued to decline from the high that occurred in FY64 (1.1 Bq/day, very low in Range II), during a period of atmosphere testing of nuclear weapons, to $\leq$0.05 Bq/day after FY87.

IMPORTED FOODS

Since April 1986, imported foods have been monitored for radionuclide contamination resulting from the Chernobyl accident. Extensive sample collection and analysis efforts were begun immediately after the accident and are still in effect. Samples were collected at points of entry during routine import inspections for more than 2600 shipments originating from a total of 48 countries. Food types most likely to have

contamination were given preference during collection, and the practice of routing foods through countries other than those of origin was taken into consideration.

Entry of shipments into the United States was allowed or disallowed on the basis of the LOCs for ^{131}I and Cs (sum of ^{134}Cs and ^{137}Cs) activity concentrations as indicators of contamination. Although other radionuclides also may have been present in contaminated food, the I and Cs isotopes were predicted to pose the greatest health risk resulting from an accident of this type. Because its half life is only 8 days, ^{131}I was useful as a contamination indicator for only a few weeks after the accident. No appreciable ^{131}I activity was found in samples collected after June 1986. Approximately one year after the accident, FDA reaffirmed that the Cs isotopes continued to be the most effective indicators of radionuclide contamination from this accident.

Contamination was found in 705 test portions, most of which were collected within the first two years after the Chernobyl accident. The ratio of ^{137}Cs to ^{134}Cs activity concentrations (decay corrected to the mid-1986 commencement of this monitoring initiative) was approximately 1.5 and was consistent with that predicted for Chernobyl-related contamination. During FY86 and FY87, contamination was found in approximately 40% of the samples collected and indicated that FDA inspectors were successfully targeting contaminated shipments. Since the accident, a total of 23 shipments were denied entry into the United States because their contamination concentrations were above FDA's LOCs. The foods involved were mainly cheeses, mushrooms, pasta, reindeer/elk meat, and spices. Of all the samples collected, only two, cheeses collected shortly after the accident, had ^{131}I contamination concentrations above the LOC.

REACTOR SURVEY

FDA's reactor-survey findings for FY-87-95 were similar to those from earlier years (1-6). Out of a total of approximately 200 test portions analyzed, ^{131}I and ^{106}Ru activity concentrations were below LODs in all test portions. ^{137}Cs activity concentrations were below LODs in all but 7 test portions: 5 fish, a honey and one maple syrup that originated from the vicinities of 4 reactor sites. The ^{137}Cs activity concentrations ranged up to 26 Bq/kg (low in Range I). No definitive control measures are recommended below 540 Bq/kg.

Tritium activity concentrations were below the LODs for all but about 4% of the reactor-survey test portions. For these portions, activity concentrations ranged up to 70 Bq/kg (very low in Range I), primarily in fish and vegetables from the vicinities of 4 reactor sites (Note: These are not the same 4 reactor sites indicated previously for ^{137}Cs). No specific releases of radioactive materials were identified, but the detected tritium probably resulted from routine low-level releases. Ninety-four percent of the reactor-survey test portions had ^{90}Sr activity concentrations in Range I, most (64%) had activity concentrations low in Range II. ^{90}Sr was detected in all types of foods, in foods from the vicinities of virtually all reactor sites, and at activity concentrations up to 5.8 Bq/kg (mid-Range II).

The highest activity concentration was in a maple syrup test portion. Because maple syrup results from a preparation procedure that reduces the matrix volume by a factor of about 40, common contaminants such as those from the 1960s atmospheric testing would be predicted to be concentrated and, therefore, at higher concentrations than found in other foods. No additional surveillance was suggested.

SUMMARY

Analysis of TDS foods showed that the radionuclide content of the domestic food supply during the last nine years was very low and that no control measures were indicated. ^{131}I and ^{106}Ru activity concentrations were below the LODs, and ^{137}Cs activity concentrations were below LOD or at detectable concentrations in Range I in all TDS foods. The highest activity concentration was in an apple juice test portion. The ratio of

^{137}Cs to ^{134}Cs supported the assumption that the contamination came from the Chernobyl accident. A gradual decrease in the ^{90}Sr intake rate has continued since the mid-1960s and has dropped to <0.05 Bq/day. ^{90}Sr activity concentrations were below the LODs for most TDS foods. No other long-range trend was noted for domestic foods.

The radionuclide content of the reactor-survey foods was low and no control measures were indicated. ^{131}I and ^{106}Ru activity concentrations were below LODs in all test portions, and ^{137}Cs activity concentrations were below the LODs in all but 6 test portions, which contained up to 26 Bq/kg. This activity concentration range is very low and, according to FRC recommendations, no control actions would be suggested unless the average activity concentrations approach 540 Bq/kg. ^{90}Sr activity concentrations were comparable to those found in the TDS foods. The activity concentrations were in Range I or Range II of the surveillance and control recommendations of the FRC. Tritium was low in Range I in all reactor-survey foods.

Out of approximately 7 million imported food shipments received by the United States since the Chernobyl accident, approximately 2600 shipments were targeted to be most likely to have Chernobyl contamination and were sampled for analysis. Findings indicated some of the samples had small amounts of contamination, but for the vast majority of foods, contamination concentrations were below FDA's LOC. Only 23 shipments have been detained since the accident occurred. The average contamination concentration and its incidence have declined and this trend is predicted to continue. However, because foods contaminated at levels above the LOCs have been found as recently as FY91, the chances of importing foods with contamination have not yet become negligible. Systematic surveillance for radionuclide contaminants in imported foods will continue, along with the domestic food monitoring of TDS and reactor-survey foods.

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Table 1. Radiation Protection Guides (RPGs) and derived-concentration action ranges for selected radionuclides, as recommended for the general population average

Radionuclide	Target	RPG dose, mSv/year	Derived concentration action ranges, [a]Bq/kg[b]		
			I	II	III
^{131}I	Thyroid	5	0-0.37	0.37-3.7	3.7-37
^{137}Cs[c]	Whole Body	1.7	0-54	54-540	540-5400
^{90}Sr	Bone	5	0-0.74	0.74-7.4	7.4-74
^{3}H[c]	Whole Body	1.7	0-7400	7400-74000	74000-740000

[a] Range I requires no specific action; Range II requires surveillance and routine control of upward trends toward Range III; Range III requires surveillance and controls to reduce exposure to Range II (1); the Range II-Range III transition corresponds with the RPG dose; 1 Bq= ca 27 pCi.

[b] Derived concentrations were calculated on the basis of an average contaminated food intake of 1 kg/day (includes water and other beverages).

[c] ^{137}Cs and ^{3}H were not considered by the FRC. The ranges were derived by using the radionuclide concentrations in water tabulated by the National Committee on Radiation Protection (22) for occupational exposure, x 1/30 to apply to the average of the general population.

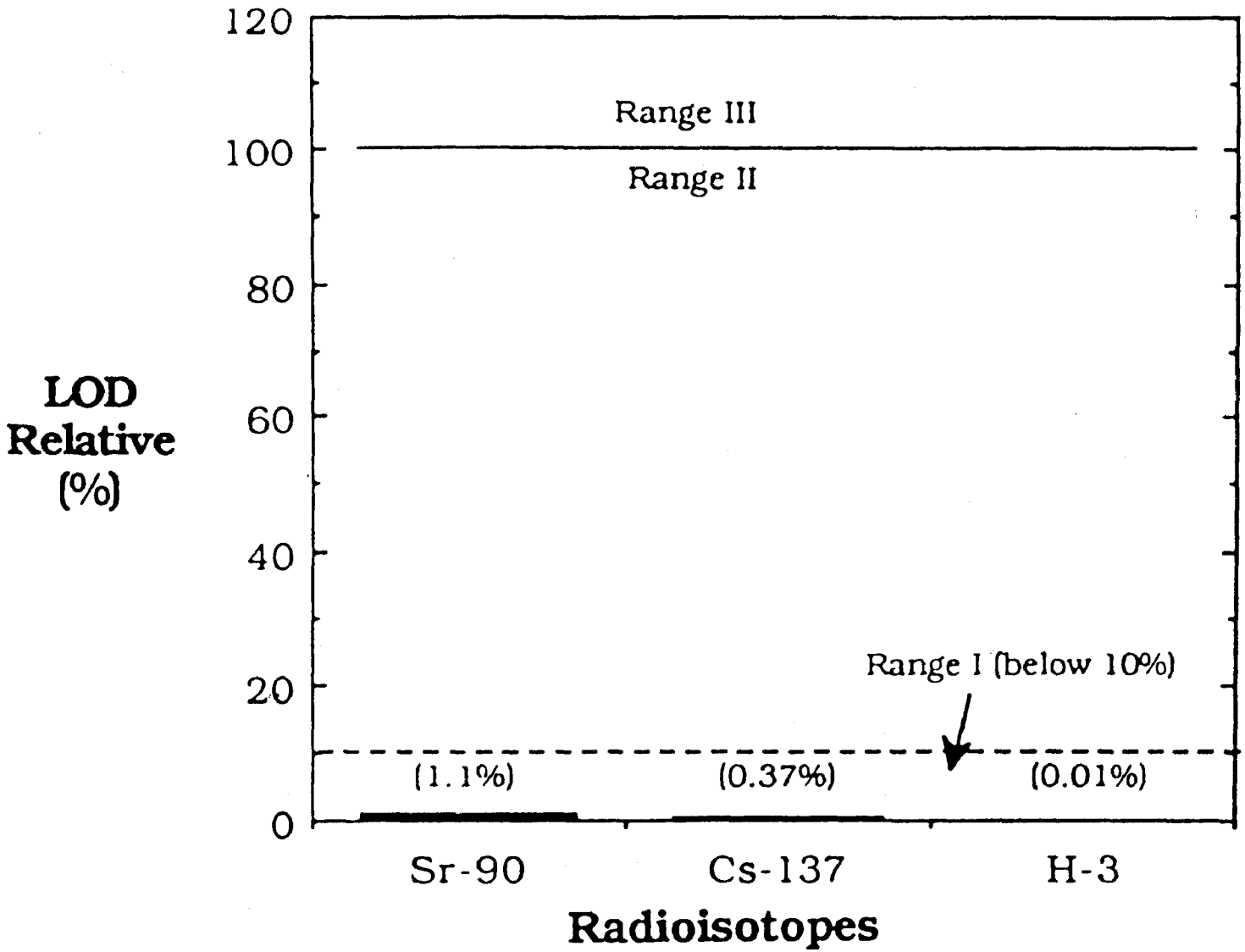
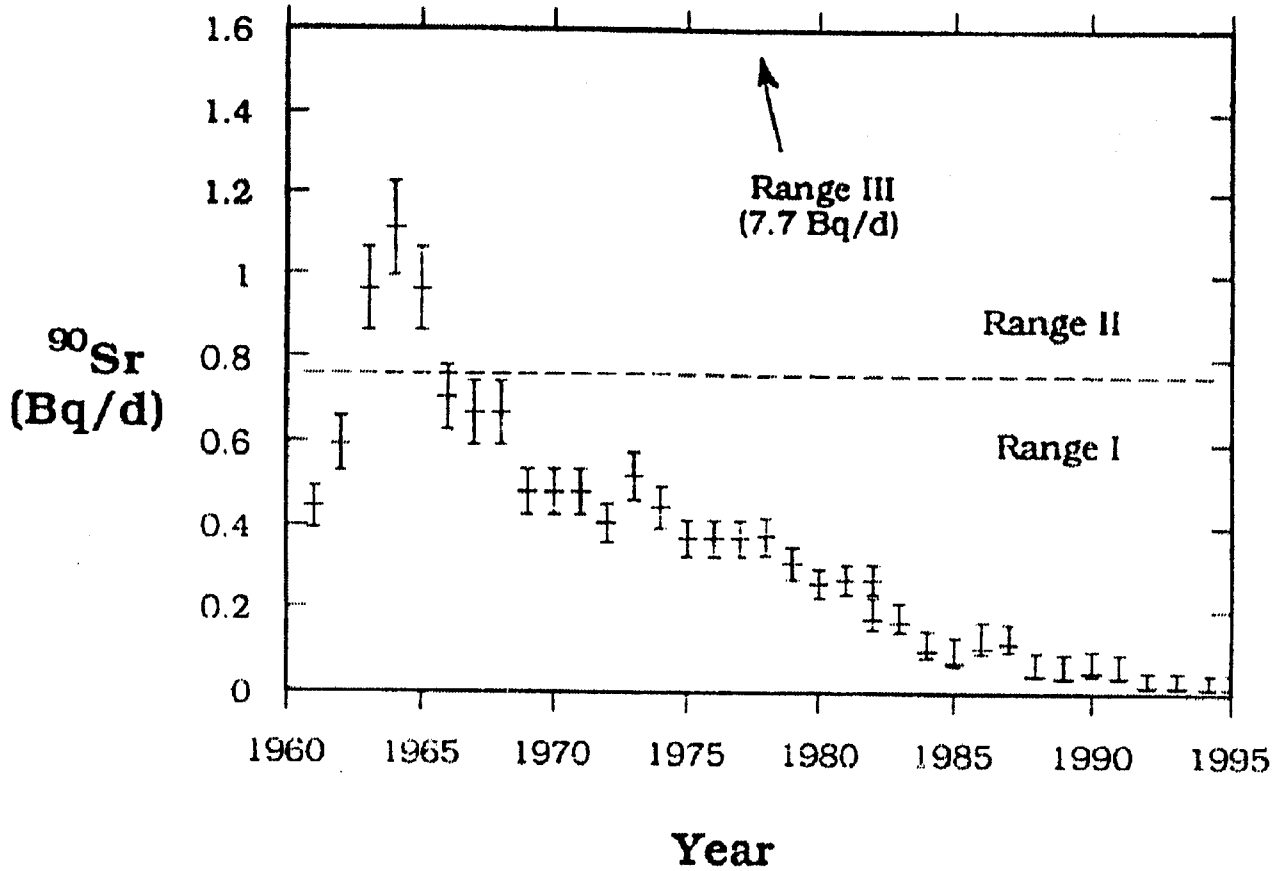


Figure 1. Surveillance LODs for long-term contamination indicators, expressed relative to FRC Action Range II–III cutoff.

Figure 2



U.S. daily dietary intake of ^{90}Sr, 1961-1995

ANALYSIS OF ACTINIDE ELEMENTS IN SOILS AND SEDIMENTS

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Abstract

We have investigated soil dissolution techniques and group separation of actinide elements using a new type of resin in an attempt to make the process simpler and more predictable. We have found that a NaOH fusion gives excellent dissolution results and, with a programmable furnace, can be performed with minimal analyst time. Our approach to avoid troublesome "matrix effects" is to preconcentrate actinides into a common form that would then behave uniformly and predictably during a subsequent separation scheme. A new extraction chromatographic resin based on diphosphonate chemistry called Actinide Resin, exhibits extremely high affinity for actinide elements even in the presence of high concentrations of other, potentially interfering ions. We have documented near-quantitative recoveries of U, Pu, and Am through the preconcentration portion of the procedure by use of natural matrix standards and multiple isotopic tracing techniques. Final recoveries of uranium, americium, and plutonium have been good although thorium yields have been consistently lower for an, as yet, unexplained reason. The quality of the separations themselves have been excellent as judged by peak resolution of the alpha spectra and the complete absence of interfering energies.

Actinide Resin

Recently, a new ion exchange resin based on diphosphonate chemistry was developed at Argonne National Laboratory by E.P. Horwitz and his co-workers (Horwitz et al., 1993; Horwitz et al, 1994). This resin, commercialized as Diphonix® Ion Exchange Resin, and a derivative extraction chromatographic resin called "Actinide Resin" by Eichrom Industries (8205 S. Cass Avenue, Suite 107, Darien, IL), exhibit extremely high affinity for actinide elements even in the presence of macro concentrations of many commonly occurring soil constituents. While Diphonix has been applied to a variety of industrial processes, Actinide Resin has characteristics that make it very attractive for analytical work. Both resins are relatively insensitive to complexing agents such as oxalates, phosphates, and sulfates. Horwitz has shown that for a 1M HCl system, Actinide Resin has K_D's on the order of 10^6 - 10^7 for tri-, tetra-, and hexa-valent actinides with little sensitivity to the presence of HF up to approximately 1M. Tri-valent rare-earth elements (REE) also bind

strongly as does Ti(IV) which could cause a capacity problem should much Ti be present in the sample. Fortunately, the addition of 1M HF to a 1-2M HCl sample load reduces the K_D for Ti about 4 orders of magnitude while actinides are still strongly bound.

We present below a discussion of some our recent results using Actinide Resin for the analysis of U, Th, Am, and Pu in soil samples up to 5.0 grams in size. Because much of the difficulty in obtaining good results for soil samples depends upon the dissolution steps, we first present some background information concerning this issue and discuss how our laboratory handles this problem.

Dissolution, Speciation, and Analytical Problems

The analysis of soils and sediments for environmental levels of uranium, plutonium, and other actinide elements is often hampered by sample-dependent problems involving composition and/or mineralogy. For example, the presence of a refractory actinide-rich yet minor soil component would result in a low bias if this phase is not fully digested together with the remainder of the soil constituents. Clearly, if the actinide-bearing phase is not dissolved, the correct result cannot be obtained. Other problems encountered in soil analysis are often more inexplicable yet very common and tend to be lumped together into so-called "matrix effects." This ill-defined yet persistent type of problem can result in low recoveries or incomplete separations on some samples, while others go through the analysis sequence virtually trouble-free. There is thus some justification for the interpretation that the dilemma has something to do with the specific sample composition.

Many laboratories have adapted a practice of using a strong acid leach for extraction of anthropogenic radionuclides such as transuranic species (Pu, Am, etc.) or fission products (^{137}Cs, ^{90}Sr, etc.). Generally, a total dissolution technique is applied if analysis of naturally-occurring uranium or thorium is required. While acid leaching is thought to be suitable for recovery of fallout-derived nuclides, it may not be suitable in other cases. For example, Oughton et al. (1993) showed that the common laboratory practice of applying a 6M HCl treatment could only recover about 25% of the ^{90}Sr from some soils, even after about 24 hours of leaching. These soils, collected from near Sellafield and Chernobyl, were contaminated with small particles of irradiated uranium oxide from the high-temperature accidents at the two locations. Similar observations have been made for actinide elements over at least the last two decades. Sill et al. (1979), for example, discussed problems dealing with "highly-fired" refractory U/Pu oxides. Some, perhaps many, soils have actinides bound in more than one form. The NIST Rocky Flats standard soil, for example, contains about 90% Pu which is acid leachable and approximately 10% that requires HF treatment to remove (K. Inn, pers. comm.). Soils impacted by the Chernobyl accident show variable amounts of extractable fission products, apparently

reflecting the variable weathering of fuel particles (Salbu et al., 1994). In a recent review of sample dissolution techniques, Sill and Sill (1995) state that "...any procedure that fails to obtain complete sample dissolution for whatever reasons of economy, speed, sample load, or other expediency is untrustworthy at best...". We agree with this assessment and conclude that unless one has reliable prior information concerning the speciation of the analytes in a sample (a rare occurrence), its hard to argue with the approach that dissolving everything before the analysis should be the goal.

As an example of the type of difficulties that may arise, we present frequency distribution plots (**Fig. 1**) for ^{238}U in four soil performance standards issued by DOE's Environmental Monitoring Laboratory (EML) to a few dozen contractor laboratories throughout the country. EML's Quality Assurance Program specifies that all samples will be run blind by whatever methods individual laboratories choose. EML employs a total dissolution via a pyrosulfate fusion in a platinum crucible for U in soil. The data presented in these histograms were taken from the reports issued by EML (eg. Sanderson and Greenlaw, 1996) and are shown as a ratio of the individual lab result to the EML result. Thus, a ratio of 1.0 would be the expected result, assuming that the sample is homogeneous with respect to U and that both the EML and contractor lab have obtained the "correct" result. Note that while the concentration of ^{238}U in the samples varies in a relatively narrow range (25.5 - 33.0 $Bq \cdot kg^{-1}$), the overall quality appears to be much lower in some samples (as 9309) compared to others. While there is some suggestion that the results may be improving, the best mean result (9509) of those presented is still 12% lower than the EML result. There is clearly a low bias in the majority of these U results. We have no way of knowing for certain what caused these differences. For the most part, the same laboratories were participating, most likely with the same methods. We feel that the most likely explanation for the low bias is incomplete dissolution of refractory uranium-bearing phases in these soils. The differences between samples, therefore, must be related to the speciation of U in these soils as well as any improvement in the procedures of the participating laboratories. Interestingly, when the results for Am and Pu in the same soils are examined, there is no indication of bias and there is a definite pattern of improved results at higher concentrations, not surprising as blank corrections become increasingly more important at low concentrations. This is consistent with the interpretation that these contaminants have a soil speciation which, at least in these samples, allowed easier dissolution of Am and Pu then U.

An Approach to the Problem

Soil Dissolution and Preconditioning

We present below a summary of our soil dissolution - actinide preconcentration method as it is currently being applied. The method is still under development and a more

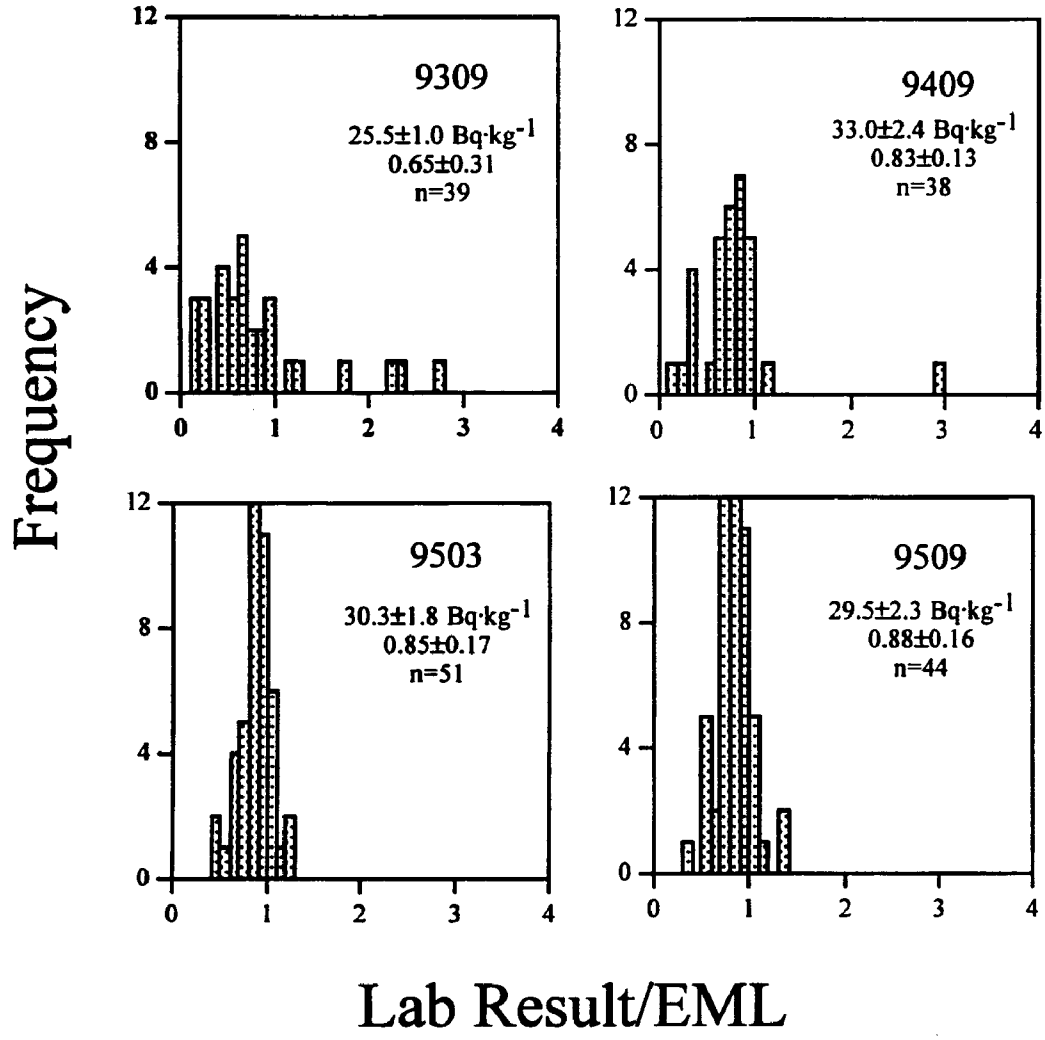

Figure 1. Histograms of reported ^{238}U activities in EML QAP soils. Each histogram also contains the EML reported activity, mean ratio and standard deviation, and number of participating laboratories.

detailed protocol will be published elsewhere and may be requested from the authors. We have tried a number of different soil dissolution techniques in our laboratory. Although the potassium fluoride - pyrosulfate fusion technique is known to be an excellent method for total dissolution of difficult materials like soils, and the fusion can be done fairly quickly (less than one hour for a 10-g sample reported by Sill and Sill, 1995), it requires platinum crucibles and is performed over an open flame which could be hazardous if employed by less experienced personnel. We prefer an approach that is simpler and more amenable to batch work, i.e., can be automated to some degree. A series of tests involving

a few different dissolution techniques on EML soil-9309, a very difficult soil judging by the results discussed above (see **Fig. 1**), shows that the NaOH fusion gave excellent results for U (**Fig. 2**). We use a NaOH-to-sample ratio of 5:1 in an alumina crucible in a programmable muffle furnace. The program is set to ramp the temperature slowly to 160°C and hold for 4 hours (this prevents creep of the flux up the crucible), and then ramp to 550°C where the actual fusion occurs. We have been holding the furnace at 550°C overnight but shorter periods should work equally as well.

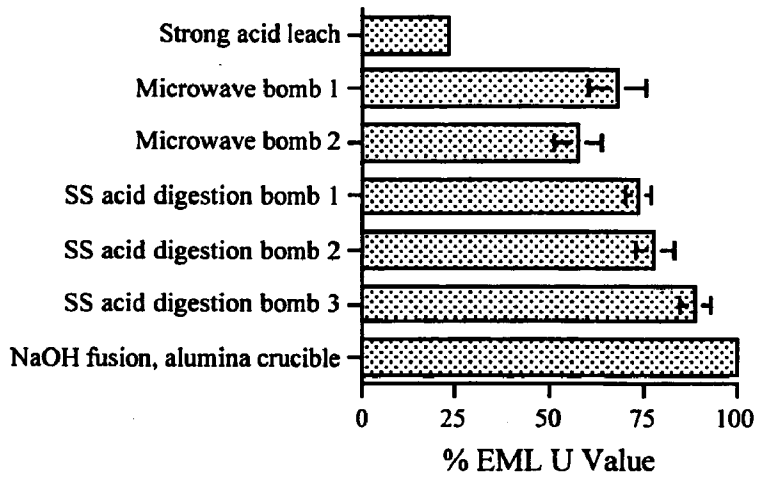

Figure 2. Results for total U, relative to the EML value, for soil 9309 based on several different dissolution techniques. The different runs on the microwave and stainless steel digestion bombs reflect various treatments of the insoluble residues.

After cooling, the resulting cake is dissolved in deionized water, which solubilizes many of the constituent ions while insoluble hydoxides of Fe and other metals remain and should effectively scavenge actinide elements. We add a small amount (~200 mg) of SFS (sodium formaldehyde sulfoxylate; commonly known as "Rongalite") as a reducing agent to ensure no soluble hexavalent species are present which would be lost during the water dissolution and ensuing rinses. After two rinses with a strongly alkaline solution (0.5 - 5M NaOH) to remove some silica and aluminum, the scavenge is rinsed once with deionized water and the insoluble fraction is dissolved in HCl to a final concentration of about 3M. At this point, one may either remove the remaining Si or add HF to the HCl solution to hold the Si in solution while it goes over the column. In the work reported here, we have chosen to remove Si beforehand because of concern that addition of HF would result in losses of actinide elements by co-precipitation with REE fluorides. We thus treated all samples by either fuming the sample in the presence of HF to volatilize Si

as silicon tetrafluoride or by addition of polyethylene glycol (PEG-2000) directly to the 3M HCl sample solution to cause the Si to floc. In the case of the PEG floc, the Si is then centrifuged off, rinsed with 2M HCl - 0.1M PEG, and either discarded or added to the Actinide Resin column later in 2M HCl - 1M HF. We have found that the separated Si floc may contain significant amounts of Th and Am which apparently sorb to the Si surfaces (Corbett et al., 1995). Repeated rinsing with 2M HCl - 0.1M PEG does help, but we consider it safer to either fume off the Si or run the Si fraction through the column as well.

Group Separation via Actinide Resin

After the preconditioning of the hydroxide scavenge and Si removal, we prepare the solution for loading onto the Actinide Resin column by addition of ascorbic acid (make solution about 0.05M AA) to reduce Fe(III) which can bind strongly to the resin. After preconditioning the resin with a few column volumes (~5 mL) of 2M HCl, we load the sample (in about 100 mL 2M HCl) onto the resin bed (0.7g Actinide Resin loaded into 6 x 0.9 cm plastic columns manufactured by Isolab, Inc., Akron, OH). We next rinse the resin with 5 mL 2M HCl followed by another rinse with 2M HCl - 0.5M HF which removes Ti and some Si which often seems to persist through some of the Si removal steps and appears to be partially retained on the column. In some cases we have observed a significant drop off in the flow rate of the column which we believe is due to precipitation of Si gel within the resin bed — the HCl/HF rinse usually clears this up. A rinse with 5 mL of 2M HCl follows to remove the HF from the previous step. The sample load and all rinses through this part of the procedure are collected in a waste beaker and discarded. The actinides may now be eluted off the column as a group. We have been doing this by adding 15 mL of isopropanol which solubilizes the Dipex™ extractant which is collected in a clean alumina crucible. Finally, 5 mL of 1M HNO_3 are added and also collected directly in the crucible. This procedure was found to increase recoveries — presumably because the Amberlite bead supports for the Dipex™ have some ion exchange capacity which sorb charged actinide species (A. Rollins, pers. comm.).

The Dipex™ extractant must now be oxidized in order that the actinide elements will be in a form suitable for chemical separation. Fortunately, the oxidation product of the extractant is phosphoric acid, which upon addition of Ca^{2+}, is a useful matrix for precipitation of basic calcium phosphate ($CaHPO_4$), an excellent scavenger of actinide elements. Although other approaches are possible (eg. wet oxidation, direct high temperature combustion), we have found it convenient to simply add some Ca carrier as $Ca(NO_3)_2$ directly into the crucible, a small amount of NaOH, and then go through another fusion cycle. When that is complete, the $CaHPO_4$ may be readily dissolved in HNO_3 or other acid and then proceed with a chemical separation by whatever approach is

convenient. At this point, the complex soil matrix has been converted to a simple form, $CaHPO_4$, which should make the ensuing separations simpler and much more predictable. While many schemes are possible, we used a tandem set-up of 2 columns packed with Eichrom's UTEVA (U and Th separation) and TRU (Am and Pu) resins for the work reported here. An overview of the entire approach reviewed here is shown in the accompanying flow chart (**Fig. 3**).

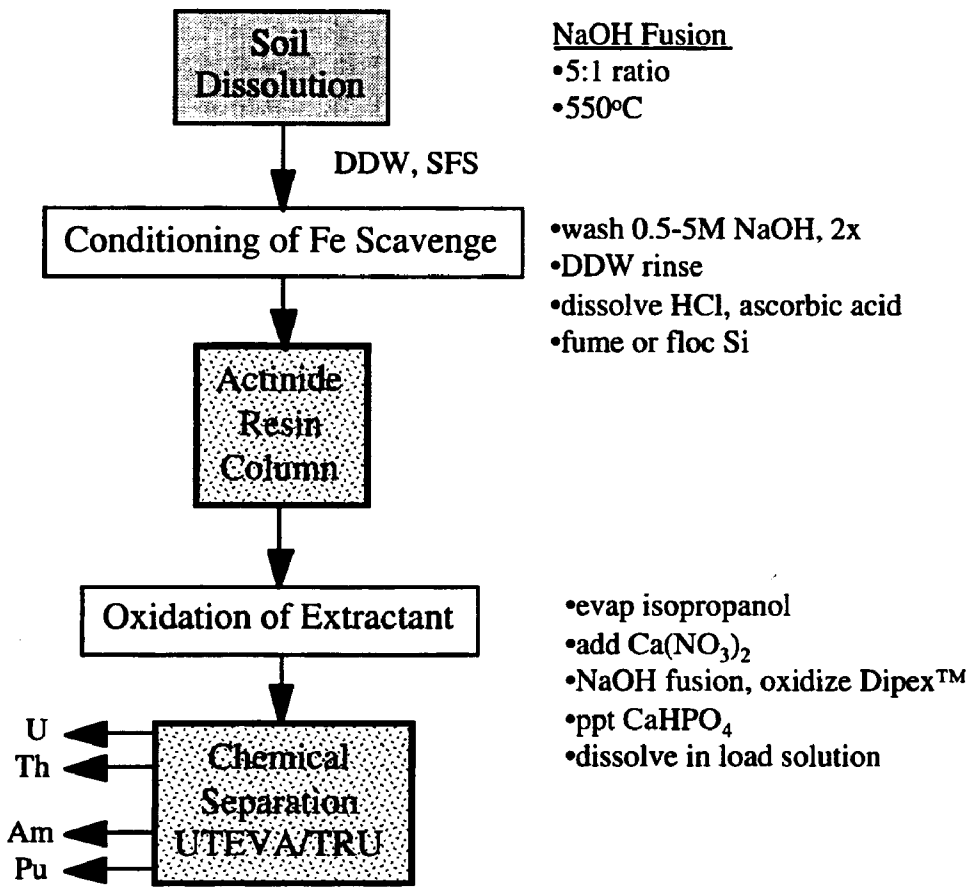

Figure 3. General flow chart of the method for dissolution, group separation and final separation of actinide elements from soils.

Some Results

We described in an earlier report (Corbett et al., 1995) how we were able to verify that actinide recovery through the Actinide Resin part of the procedure was almost quantitative using a standard sediment and multiple tracing techniques. At that time,

difficulties in the conversion process of the Dipex™ extractant to a form suitable for column separation resulted in lower recoveries then desired. Those series of experiments resulted in the change from a simple high-temperature combustion of Dipex™ to the NaOH fusion now employed. In order to evaluate the entire system as now designed, we analyzed a batch of 5 natural matrix soil and sediment standards, each run at 2.5 and 5.0 grams (**Table 1**). These standards were provided by the International Atomic Energy Agency (IAEA) and EML and all have recommended values for U, Am, and Pu while the 2 IAEA standards also have values for Th.

Table 1. Results for U, Pu, and Th isotopes and ^{241}Am from 5 different EML soil and IAEA sediment standards run at two different sample weights.

	IAEA 135			IAEA 300			EML 9309			EML 9409			EML 9509		
	2.5g	5.0g	IAEA	2.5g	5.0g	IAEA	2.5g	5.0g	EML	2.5g	5.0g	EML	2.5g	5.0g	EML
^{238}U Bq·kg^{-1}	29.1	31.3	30.0	60.9	60.9	64.7	26.4	25.5	25.5	29.2	30.0	33.0	29.1	30.4	29.5
^{234}U Bq·kg^{-1}	28.2	29.7	28.3	64.6	65.4	69.0	26.7	25.4	24.8	29.2	30.4	32.6	30.6	30.1	30.4
U Yield (%)	81.7	73.1	--	60.2	66.2	--	62.1	66.1	--	73.4	61.4	--	65.8	84.6	--
^{241}Am Bq·kg^{-1}	353	377	318	1.1	1.3	1.4	0.2	0.3	0.3	2.2	1.3	1.7	1.5	1.6	1.8
Am Yield (%)	98.6	50.8	--	51.2	22.1	--	92.3	51.8	--	59.3	34.0	--	87.3	80.3	--
^{239}Pu Bq·kg^{-1}	204	202	213	3.5	3.3	3.6	1.7	1.6	1.5	8.6	7.2	7.8	5.3	4.9	5.2
^{238}Pu Bq·kg^{-1}	40.3	39.8	43.0	0.2	0.1	0.2	0.2	0.2	--	0.2	0.2	0.3	18.1	15.6	17.5
Pu Yield (%)	75.3	50.0	--	67.3	47.3	--	91.3	49.0	--	59.5	30.6	--	74.5	44.9	--
^{232}Th Bq·kg^{-1}	40.0	44.8	38.2	86.2	94.7	72.4	32.2	32.7	--	35.8	33.0	--	39.3	24.7	--
^{230}Th Bq·kg^{-1}	74.9	81.4	69.1	116	122	88.0	25.8	25.0	24.8[§]	30.2	28.8	32.6[§]	34.2	23.5	30.4[§]
Th Yield (%)	24	21	--	14	6	--	32	25	--	19	20	--	11	6	

[§]Assumed secular equilibrium between ^{234}U and ^{230}Th.

Our results show that there is excellent agreement between our reported U isotope activities and the recommended values. The recoveries for U are good and quite constant with none of the 10 runs outside the range of 60 - 85% yield. The ^{241}Am activities are generally in good agreement with the standard activities, even at very low concentrations. Since we did not include a step to separate REE from the Am fraction (this can be done fairly easily using TEVA Resin), the resolution will deteriorate should there be high REE in the sample. This was the case for IAEA-135 which is why our values are too high. The Am recoveries were generally good although more variable (22 - 99%) than U. We

also note that the Am yield is lower in every case for the 5.0-g sample compared to the 2.5-g run. The Pu isotopic analyses display excellent agreement with recommended values for all samples. The Pu yields were good although somewhat variable (31 - 91%) and also displayed consistently lower recoveries for the larger sample size. An independent experiment was run with 2.5 g of IAEA-300 using exactly the same procedure but with 2 g of the Actinide Resin instead of the usual 0.7 grams. The results showed significantly higher yields for Am and Pu, implying that there may have been breakthrough of these ions in the previous runs. The U recovery remained in the same range as all the other experiments. Unfortunately, we do not have many recommended values for Th isotopes in these standards. Our calculated results agree reasonable well with the recommended values for IAEA-135 but they do not for IAEA-300 which also had very low Th recoveries. While the EML does not include Th in its program, we can assume secular equilibrium between ^{234}U (which is "known") and ^{230}Th to estimate its concentration. If this assumption is correct, a comparison indicates that our ^{230}Th results are in good agreement with that present in these soils. Unfortunately, Th continues to display disappointing recoveries for reasons which we have not been able to discern. A few tracer studies using ^{234}Th indicate that Th behaves as predicted on all the columns used through the procedure. It may be that a large fraction of Th is lost before loading onto the Actinide Resin, either with the silica fraction when forced down with PEG (one tracer test indicated over 50% of the Th was lost in this fraction) or coprecipitation with micro amounts of insoluble sulfates, fluorides, or other compounds. Additional experiments are planned to resolve this problem.

In general, use of the Actinide Resin appears to offer promise as a way to greatly simplify the complex matrices present in natural soils in order to obtain more consistent and predictable results.

Acknowledgments

Although the application of the Actinide Resin to soil analysis should prove useful to the radioanalytical community, the truly innovative work associated with this development was the initial synthesis of the Dipex™ extractant by Phil Horwitz and his group at Argonne National Laboratories. We thank Phil as well as Andy Rollins (Eichrom Industries, now with Motorola) for their helpful advice on our efforts. Additional insights were also gained through numerous communications with Bill McCabe (Institute of Geological and Nuclear Sciences, New Zealand) and Barry Stewart (Environmental Physics, Inc.). Partial financial support for this project was provided by the National Science Foundation (OCE-9214493).

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Quality Control in the Radioanalytical Laboratory: What Do We Really Need to Do? Robert Litman, Chemistry Support Supervisor, Seabrook Station, NAESCO, Seabrook NH, 03874

Environmental radioanalytical laboratories are being pressed to analyze more samples at a higher frequency, and lower detection levels than ever before. Critical to this mission is the performance of the instruments, how we evaluate their performance and when we decide that remedial servicing of our process is required. The process includes not only the instruments themselves but the samples and their preparation for analysis.

Routine quality control analyses will tell us important information about the instruments we are using on a daily basis. However, there are other independent quality *assessments* which are important to the entire sample analysis process. Some of these include background determinations, independent blind analysis, sample splits and spikes. Important to these assessment samples(whether solely instrumental or chemical separation followd by instrumental analysis) is the activity level of the nuclide, the matrix that it is presented in, and the level of interferences present.

The frequency and quantities of these assessments is an analytical decision based on many factors. Do we appropriately challenge the analyst, instrument and method? A discussion of personal experiences in this process of decision making will be presented, and common sense approach to *what we really need to do* will be discussed.

ANSI/ANS Standard for Radioanalytical Data Validation

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In past decades, radioanalytical data was usually accepted from the laboratory and assumed to be correct without questioning its validity, accuracy, or precision. More recently, due to standard protocols put in place by the U. S. Environmental Protection Agency (EPA), laboratory data has undergone increased scrutiny before being used for critical decision making by a process known as data validation. However, no standard EPA protocols have been developed for the validation of radioanalytical data. Therefore, many different protocols with varying criteria have been developed and used. This has led to inconsistency in approach and often to the unnecessary rejection of a large percentage of data for use in decision making.

The American National Standards Institute/American nuclear Society (ANSI/ANS) Radioactive Waste Management Committee is responsible for the development of radioactive waste management and environmental remediation standards that address the generation, monitoring, characterization, treatment, storage, and ultimate disposal of all categories of radioactive waste, including mixed waste, and criteria and operations required for the environmental remediation of nuclear facility sites that have become contaminated. The Subcommittee on Environmental Remediation of Radiation Contaminated Sites manages the development and maintenance of standards that address the cleanup of radioactive materials and radioactivity mixed with hazardous substances. This subcommittee has authorized a writing group to develop a new ANSI/ANS Standard, 41.5, for validation of data from radiological analysis supportive of environmental remediation.

This standard sets forth criteria and processes for demonstrating the validity of radioanalytical results. It addresses the specific measurements and data required to permit the use of the results for environmental remediation activities. This standard will be a consensus standard specifying the essential requirements for accepting radioanalytical data as input to process control, site characterization, waste acceptance criteria, waste certification, litigation, and other applications as deemed necessary. This standard will provide a minimum set of checks and test that will ensure a consistent approach for validation of data produced by any radioanalytical laboratory for waste management, environmental remediation and process control.

The standard is being developed from the assumption that a proper data quality objective (DQO) process has been used to define the quality of data needed for the decision process. Therefore, set limits for the quality control parameters are not being recommended in the standard, but rather qualification of data is to be tied to the DQOs. This allows the qualification to be based on how much the error, bias, lack of precision, lack sensitivity, or lack of selectivity affects the decision that is being made from the data. Furthermore, the standard will provide general guidance for when and how much of the data should be validated.

It is expected that a draft of the standard will be completed this year. This paper will describe the current status of the standard and the philosophies and approaches that the writing committee is currently considering.

Environmental Radiation Monitoring in Venezuela

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Abstract. During the past years, the human population increased considerably in Venezuela. The natural resources suffered deeper the negative consequences of an unplanned explotation contributing to the planet global changes. These included also changes in the radionuclides concentration in the environment. With the purpose to establish the extent of the interference of the human activity with environment and the changes in the radioactivity levels, a monitoring program started in 1990. As an oil producing country, we are aware, that the subsoil material enter the human environment contributing to increase also the radiation level due to the redistribution of natural radioactive substances. In order to determine the environmental radiation changes and to assess the possible human risk the concentration of alpha emitters were measured in potable water and springs including thermal spas. Food and environmental samples (soil, air, sediments and industrial waste) undergo radiation measurements to determine the concentration of both gamma and alpha emitters. Since several recicling programs exist, the ashes produced by oil burning power plants were also studied determining that they are not suitable as an additive material in the construction. Used tecnetium generators were also studied establishing that environmental regulation should be enforced. Results so far obtained are resumed as follows: in the food it was determined the presence of cesium 137 in a low concentration (<10 Bq/Kg), some had a high natural concentration. The radon concentration in most of the water sources is less than 11 Bq/l however more than 5% are well above. Some thermal wells did present around 50kBq/l; that is very unusuall and may be considered as an exception. Gross alpha concentration in drinking water for the 50% of the wells analyzed is less than 0.150 Bq/l and only the 8% has three time this value. The mean out door radon concentration is 36 Bq/m3; In door values have a wide range being the maximum of 400Bq/m3. The natural gas for domestic use contributes to increase the in-door radon concentration by 20% in most of the cases. In some caves we measured radon concentration that exceeds 20kBq/m3. The construction materials other than the natural potassium-40 contained cadmium-109 in the range between 44 and 390 Bq/kg (this isotope has a short lifetime and its identification is uncertain). Oil ashes did show that their content of radioactive substances has a concentration ten times higher than the avarage surface soil. In the south-east region where the human activity is still very limited and restricted by a protected area law, the berilium-7 was measured in tropical plants and fruits.

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Analytical Methodology for Non-normal Distributions of Environmental Data

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Over the past fifteen years, the Radioactivity Group at the National Institute of Standards and Technology (NIST) has certified environmental levels of radionuclide concentrations in River Sediment (SRM 4350B), Human Lung (SRM 4351), Human Liver (SRM 4352), Rocky Flats Soil - 1 (SRM 4353), Freshwater Lake Sediment (SRM 4354), Peruvian Soil (SRM 4355), and Ocean Sediment (SRM 4357). Invariably, the distribution of data for a considerable fraction of the certified nuclides are non-normal. The methodology for the evaluation of the interlaboratory data has evolved over the history of the program and now is fully capable of characterizing the non-normal distributions. The results of the data analysis yields information on: 1) identification of the best choice of statistical distribution; 2) robustness of the statistical distribution; 3) mean values and standard deviation of the means; 4) tolerance limits and their uncertainties at any desired level of confidence. The discussion of the methodology will focus on the analysis of the Ocean Sediment intercomparison data. This methodology could be applied to the analysis of field measurements and to estimate the degree of false positive and negative measurements.

INORGANIC

Method Development Strategies for ICP-MS

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Abstract

Since its introduction as a commercial technique in 1983, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has developed from a research instrument to a routine environmental production tool. Increasing numbers of laboratories have invested in the technology for environmental analyses with much success. However, many laboratories are still concerned about implementation of a performance-based method and the choices that must be made in optimizing method performance.

In this talk we will describe the development of analytical parameters for implementation of RCRA SW-846 Method 6020. The thought processes used in decision making will be outlined to give the user guidance in general method development and in judicious choice of operating parameters for the most rugged performance. Other topics that will be covered include:

- Development of internal standards to give the best performance in complicated matrices. The choice of internal standards will be discussed and the tests performed to optimize the choice described.
- The dissolved solids-handling capability of the nebulizer will be discussed for different types of nebulizers. Certainly, RCRA sample types can be more complicated than those encountered in the analysis of drinking water. The problems with matrices will be discussed and strategies outlined.
- The performance of other elements not included in the current list of method 6020 analytes will be highlighted. Information on several additional elements, such as Se, can be very useful. Instrument and method performance will be evaluated for several types of sample matrices, including soil digests and TCLP extracts.

The final method parameters chosen and the performance on several samples will illustrate the completed development and conclude the discussion.

Introduction

As many laboratories contemplate purchasing an ICP-MS, questions and concerns are raised about the implementation of ICP-MS in their laboratory. Indeed the "comfort factor" with how reliable, easy to use, and the amount of method development time required are usually an important considerations in the ultimate decision. The development of "turnkey" methods for commonly used methodologies such as EPA Method 6020 and Method 200.8 by vendor application specialists has gone a long way to alleviate the new technology anxiety that has been associated with ICP-MS. In this talk, we will describe the development of an instrumental method for the implementation of RCRA SW-846 Method 6020 and discuss the thought processes and decision-making involved.

The first decision to be made in developing a method is what regulatory programs will be supported by the resulting ICP-MS instrumental method. This will help determine which path method development strategies will take. If RCRA SW-846 Method 6020 is the primary method for implementation, then appropriate sample preparation procedures must be selected to go along with that method. In some cases,

only one sample preparation method (e.g., microwave digestion, SW-846 Method 3051) will be used and the overall development scenario is greatly simplified. However, if a laboratory doesn't have the capability to perform Method 3051, more than one sample preparation procedure (e.g., Methods 3010, 3020, or 3050) may need to be investigated. Since most interferences are caused by either the sample matrix or the digestate matrix, some consideration should be given to the impact on analytes of interest. For example, if As and Se are important analytes you may wish to avoid sample preparation methods (such as the ICP digestion in Method 3050) that introduce chloride to the sample so that ArCl interferences on As and Se can be minimized. If avoiding hydrochloric acid in the sample preparation procedure is not possible, isobaric corrections may be used; however, their impact on the data quality objectives (DQO) of the analysis should be evaluated. This can be done by performing preliminary background scans on the sample preparation blanks and evaluating the differences in the overall background between different digestion matrices. This information can then be used in all stages of the method development to help determine what interference corrections, dilution levels, and Method Detection Limits (MDLs) might be possible with each different sample preparation scheme.

Once the sample preparation methods have been decided upon, the real work of method development for the ICP-MS can begin. A confusing point for most ICP-MS novices is setting up the measurement timing on the quadrupole mass spectrometer. Although the measurement time can be an important factor in some applications, for most environmental work, the default dwell and sweep times are generally adequate. For elements where better detection limits may be necessary to achieve the DQOs (such as a particular MDL level) the dwell times can be doubled or tripled to spend more time acquiring data on a particular element. An example of this case is arsenic, which doesn't ionize well in an argon plasma. It may be necessary to measure 3-4 times as long to get count rates similar to those achieved for the more easily ionized elements such as copper.

Other considerations in setting up data acquisition times include sample volume and productivity. In the cases of limited sample volume, the total acquisition time may be determined by the amount of sample. In a production-type environment the DQOs may need to be balanced by productivity concerns. For example, the profitability of an ICP-MS purchase might be based on the need to analyze 250 samples in an 8-hour shift, limiting the data acquisition time for each sample to about two minutes including sample uptake and washout. However, if the lowest possible detection limits are the goal and productivity is not a real concern, then longer data acquisition times can be used to help achieve the necessary detection limits.

In conjunction with measurement time the appropriate choice of data collection mode (i.e., peak hopping or full mass scanning) must be made. This decision is also affected by DQOs and productivity concerns. For example, if you scan 20 points per peak with the same dwell time per amu, you will be spending less time at the point of highest signal to noise than compared to counting on the peak maximum (peak hopped) for the entire dwell time. This difference will ultimately affect your detection limits and the number of samples that can be analyzed in a given time period. It is a simple matter to set up several test data acquisition scenarios and test the differences that might be obtained in detection limits by running a 10-replicate IDL. The use of the data export features of the instrument software can make these calculations automatic by importing the data into an IDL/MDL calculation spreadsheet.

The dissolved solids content of the digested matrix will influence the washout time of the system. Long washout times will prevent build-up and ensure that the system is clean for the next sample. However, long washout times will reduce productivity and may be unnecessary. Several short studies can characterize the system for a representative matrix and determine the optimum washout time. A sample digest, diluted to a representative concentration can be monitored over time for sample build-up by measuring the internal standard recoveries until they deteriorate below the acceptable level. Washout studies will determine how soon the next sample can safely be introduced. Table I shows a representative list of elements introduced at high levels and the washout observed for an instrumental method based on

EPA 200.8. Most elements were rinsed out at or below 10 times the MDL after one analysis cycle, indicating that a 35-second washout was sufficient for this method.

Table I
Estimated Rinse Times (Selected Elements)

Analyte	Tested Conc (µg/L)	Measured Concentration (µg/L)			MDL (µg/L)	10(MDL)
		Cycle 1	Cycle 2	Cycle 3		
V	5000	0.113	0.048	0.041	0.03	0.3
Zn	20,000	0.360	0.189	0.184	0.03	0.3
Se	20,000	0.182	-0.330	-0.169	0.05	0.5
Ba	5000	0.110	0.039	0.025	0.04	0.4
Hg	20	0.125	0.090	0.071	0.02	0.2

Analysis Cycle Time
Rinse time: 35 sec @ 48 rpm
Uptake time: 25 sec @ 48 rpm
Stabilize time: 10 sec @ 24 rpm
Analysis time: 2:06 min @ 24 rpm
Total time: 3:16 min

Next, the choice of which isotopes to monitor for each element must be addressed. If you are modifying a "turnkey" method, this becomes a less cumbersome task than starting from scratch. In the beginning of any method development, the "more is generally better" rule can be used. It is always better to collect too much data and not have to use part of it than to have not acquired enough and find you need it later. Elements with multiple isotopes can be monitored at several masses and the results compared. Interferences in ICP-MS are additive, so the lowest answer is probably more accurate in a situation where isotope results differ. Internal standard elements must be selected after screening typical samples using semiquantitative analysis to determine the presence of any commonly used internal standard elements. A general guideline in choosing specific elements is to keep internal standard elements fairly close in mass (approximately within 50 amu) to the analyte elements and use internal standards that exhibit the same properties in an argon plasma. Sometimes a different internal standard can be used to correct a matrix related problem. For example, during the development of Method 6020 it was observed that suppressed recoveries were obtained for elements with fairly high ionization potentials (As, Se, and Zn) high levels of the alkali metals (e.g., Ca, Na, K, Mg, or Fe) were present. This appeared to be an ionization suppression related interference. A quick study was performed to verify this and then the use of an alternate internal standard with a first ionization potential (see Table II) closer to those of As, Se, and Zn was used. It turned out that by simply switching internal standards to Ge the problem was solved.

Table II
Ionization Potentials

Element	1st Ionization Potential (v)
In	5.76
Y	6.30
Sc	6.54
Rh	7.46
Ge	7.90
Zn	9.34
Se	9.75
As	9.81

Once the best isotopes are determined for a given element the others can be taken out of the method to save time (if this is an issue) and make the method simpler. The best way to test a method for accuracy and isotope selection is the use of certified reference materials in a matrix similar to the samples. Knowing the right answer is a great help in determining which isotopes may have interferences. Table III demonstrates the method performance of RCRA 6020 for an estuarian sediment certified reference material. Other ways to test accuracy include performing spike recovery tests and matrix dilution tests on representative samples. Finally, once method development is completed you can run comparability studies on your own samples and compare results obtained between ICP-MS and other techniques used in the lab such as graphite furnace atomic absorption or optical emission ICP. It is a very important to remember to compare the same sample preparation method for each analytical procedure. It is widely known that each of the EPA weak acid leaching digestions induces method bias into the measured concentrations, so it is important to use the same exact digest for each analytical method you wish to compare. For example, most analyses for lead in soils will yield higher results for method 3050 using the ICP finish (with hydrochloric acid) than if the same preparation method were used with the GFAA finish (no hydrochloric acid).

Once the comparability testing is complete, you can report numbers to your customers that you have confidence in and be able to explain any differences they might observe from past analyses using alternate techniques and sample preparation methods. Indeed, performing quick comparability studies and submitting the data to your clients can go a long way in gaining their acceptance of a new technique that can usually give them more information about their sample with fewer analyses and problems.

Table III
QC Checks - Method 6020
High Purity Estuarian Sediment

Element	Sample Conc. (mg/kg)	% Rec. of Cert. Value	Spike (µg/L)	% Rec. of Spike	% Rec. Limits
Al	548	84.2	NA	NA	75-125
Sb	0.004	98.9	150	103	75-125
As	0.11	112	150	98.4	75-125
Ba	ND	-	150	98.9	75-125
Be	0.02	-	150	117	75-125
Cd	0.0004	104	150	93.6	75-125
Cr	0.78	97.4	150	97.0	75-125
Co	0.12	116	150	97.4	75-125
Cu	0.20	99.6	150	96.0	75-125
Pb	0.31	104	150	102	75-125
Mn	3.64	104	150	90.2	75-125
Ni	0.31	104	150	96.3	75-125
Ag	ND	-	150	94.9	75-125
Tl	ND	-	150	99.6	75-125
Zn	1.52	109	150	98.2	75-125

Conclusion

There are many considerations involved in the method development process. Data Quality Objectives must be balanced with laboratory productivity needs in order to obtain the most cost effective

measurement scheme. Method development must ultimately begin with the sample preparation step, which can greatly affect the overall method development in both time and effort. Once a draft method has been developed, testing procedures should be implemented to test its overall accuracy for the range of sample matrices expected to be analyzed using the method. In addition, the use of comparison studies can be performed to help overcome any client concerns regarding comparability issues with past data and to give them an overall confidence about their sample results using the new analytical technique.

RAPID FIELDABLE ANALYSIS FOR MERCURY

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ABSTRACT

The cost for cleaning-up contaminated sites is often high due to the large number of samples required for site characterization. This process is slow since analyses are performed off-site. A method for rapidly determining mercury concentrations in environmental samples has been developed and tested at the General Electric Company. The analysis uses Anodic Stripping Voltammetry (ASV) to determine mercury concentrations in solution. Mercury is transferred to solution from environmental samples by extraction with an aqueous mixture of potassium iodide and iodine. Analysis requires less than 10 minutes for a 1 ppm detection limit and extraction needs less than 30 minutes per sample. The reproducibility of the electrode surface is enhanced by using an iodine atomically modified electrode. The method can be made fieldable and requires no corrosive acids. The method is also independent of the type of contaminated media and the species of mercury. Recently, this method was part of a screening evaluation for mercury determination technologies conducted by the Energy & Environmental Research Center (EERC) at the University of North Dakota in Grand Forks, North Dakota. A comparison of the data derived from the ASV Method versus the standard EPA Method 7471 laboratory methods for determining mercury content in environmental soils showed an excellent correlation from less than 1 ppm to greater than 10,000 ppm mercury.

INTRODUCTION

Mercury has caused considerable concern when improperly released into the environment [1-2]. The costs associated with contaminated sites are often substantial. A significant portion of the cost is associated with site characterization and assessment. Long delays between acquisition of samples and the analysis of samples leads to long idle periods for personnel and equipment. The development of fieldable analyses has resulted in order to contain costs [3].

Several methods for the determination of mercury in environmental samples while in the field are in various stages of development. Mercury determination is accomplished by the use of x-ray fluorescence [4], immunoassay [5], or vapor analysis [6-7]. While each method is capable of determining the presence of mercury, several serious deficiencies exist including a lack of sensitivity, matrix interferences, limited range, limitations due to the form of mercury, and/or the use of hazardous reagents.

An alternate fieldable method for rapidly determining mercury in environmental samples has been developed at the General Electric Company [8]. The technique utilizes a rapid, selective extraction of mercury from the solid sample. Once mercury is solubilized, it is detected by electrochemical means [9]. The method has been found to have an excellent correlation for total mercury content with the standard laboratory method of sample leaching with strong, hot acid followed by atomic absorption analysis of the leachant [10]. The extraction solution may also be analyzed by chemical reduction of the mercury followed by vapor analysis of the resulting elemental mercury [11].

In addition to site characterization, rapid field analysis can be used in the remediation of contaminated sites [12]. On-site monitoring of the output from decontamination processes can aid in the control of the operation, helping to contain the operating costs.

In this study, the electrochemical methodology was applied to a large number of environmental soil samples obtained from natural gas metering stations. Mercury spills occurred along the natural gas pipeline due to spills and vandalism of manometers containing mercury [13]. Cost containment during site characterization is critical for these sites because of the large number of metering sites and their relatively small size. Thousands of metering sites require characterization. Those sites containing mercury average only 1-2 cubic meters of contaminated soil [14].

Rapid field analysis has been identified as a necessary technical need for these sites [15]. In this study, a comparison of the results produced by the ASV Method and the standard laboratory method for determining total mercury content (EPA 7471) was undertaken.

EXPERIMENTAL

Soil samples were obtained by EERC from a variety of natural gas metering stations in which mercury spillage from manometers had occurred. Three ranges of mercury concentrations in soil were desired; those containing >1000 ppm mercury, those containing 100-1000 ppm mercury, and those containing <1 ppm mercury. Often, samples from the high mercury-containing soils had visible beads of elemental mercury present. Oversized rock and debris were physically removed and the soil blended in a stainless steel mixer. The homogenized samples were then split into 12 sub-samples, two of which were analyzed by EPA method 7471. Samples were submitted as duplicates in a double-blind experiment. Standard soils were obtained from NIST (SRM 2709, 2710 and 2711).

A 1.0 g soil sample was weighed directly into a four-inch threaded Ace pressure tube. To the tube was added 10.0 mL of extracting solution containing 1.0 M KI and 0.5 M I_2. A rubber gasket and Teflon threaded cap were used to secure the vessel. The mixture was shaken, then placed in a boiling water bath for 30 minutes. Next, the sample was removed, shaken, and allowed to cool to room temperature. The mixture was then filtered through a 0.45 micron syringeless filter made of PTFE. The filtrate was saved.

A portion of the filtrate (0.10 mL) was pipetted into a 25 mL glass vial containing 10 mL electrolyte solution (0.25 M K_2SO_4 and 0.1 M KI). The vial was then capped and shaken for solution homogenization. Next, the vial cap was replaced with a special Teflon electrode assembly that was constructed in such a way that once tighten onto the vial, all electrodes were immersed into the electrolyte solution. The assembly consisted of a working electrode (Au disk, 1 mm in diameter), an auxiliary electrode (Pt wire) and a reference electrode (Ag/AgI, 0.1 M KI). Subsequently, the electrodes were connected to a computer controlled potentiostat (Cypress Systems) and a square-wave anodic stripping voltammetric (SW-ASV) experiment was performed. The resulting stripping current was then converted into mercury concentration by comparison with the standards. Deposition time was adjusted to produce a 0.5 ppm detection limit for mercury.

The gold working electrode was initially polished on a polishing pad with alumina slurry, then electrochemically cleaned by the in-situ oxidation-reduction cycling between 1850 mV and -150 mV in 1 M H_2SO_4 solution. The clean gold electrode was then stored in the 1 M H_2SO_4 solution until needed. The electrode was cleaned by in-situ electrochemical cycling once its surface was contaminated based on the decreased stripping current of a standard solution. No additional electrode polishing was required for the remainder of the experiment.

RESULTS

The mercury content of 37 different soil samples is listed in Table 1. The samples were analyzed in duplicate by both General Electric's Anodic Stripping Voltammetry (GE ASV) Method and EPA's Standard Method 7471.

DISCUSSION

A mixture of potassium iodide and iodine dissolved in water serves as the extracting agent. This mixture can thoroughly remove a wide concentration of mercury species from contaminated solids due to the high affinity of iodine for mercury. The combination of an oxidant (iodine) and a solubilizing agent (potassium iodide) give rise to the mixture's exceptional ability to remove a wide variety of mercury species (equations 1-3). The combination of elevated temperature and increased concentration enable through mercury removal in a minimum of time. This extraction mixture has been employed as a means of decontaminating solids containing mercury [16].

$$Hg + I_2 + 2\,KI \rightarrow K_2HgI_4 \qquad \text{(equation 1)}$$

$$HgO + H_2O + 4\,KI \rightarrow K_2HgI_4 + 2\,KOH \qquad \text{(equation 2)}$$

$$HgS + I_2 + 2\,KI \rightarrow K_2HgI_4 + S \qquad \text{(equation 3)}$$

As seen in equations 1-3, no acids or bases are required for the removal of mercury from the soil. Therefore, the extraction process can be conducted without the use of hazardous, corrosive acids.

A measure of precision for the method is illustrated in Figure 1. The amount of scatter in the results between EPA Method 7471 and GE ASV is comparable. The data from GE ASV produced a line with a better linear regression coefficient (R=0.97) than that from the standard method (0.92). A line with a slope of 1 is present to show an ideal correlation of the data. Scatter in the data at high mercury levels in the soil is most likely due sampling. At levels greater than 1000 ppm mercury, elemental mercury was visible. The presence or absence of a bead of mercury can have a dramatic effect on the mercury content of a small sample. Scatter in the data at lower mercury levels may be a better measure of the reproducibility of the methods.

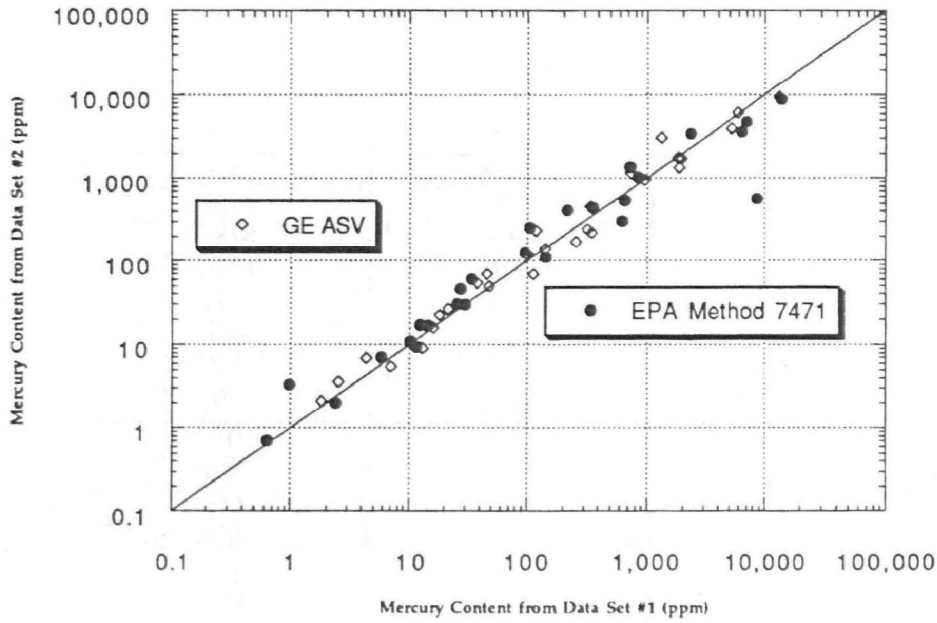
Voltammetric methods often suffer from a lack of reproducibility due to fouling of the electrode surfaces. It is known that both iodine and iodide strongly absorb onto gold surfaces as iodine atoms. This monolayer of iodine protects the electrode from contamination. In the GE ASV Method, gold serves as the working electrode and both

iodine and iodide are present in the electrolyte solution. This results in a reproducible electrode surface. As seen in Figure 1, the reproducibility of the data is comparable to, if not better than, the standard technique.

Table 1
Data Comparison

GE ASV Mercury Content (ppm)		EPA Method 7471 Mercury Content (ppm)	
Set #1	Set #2	Set # 1	Set #2
13500	9400	14100	8830
5850	6200	2330	3420
5200	4000	6950	4780
1950	1730	726	1370
1860	1350	624	300
1840	1748	8670	561
1320	3100	6390	3670
950	950	654	536
730	1150	850	1030
350	220	143	110
340	460	357	445
320	243	218	408
257	170	106	253
142	140	96.3	125
119	234	102	120
113	69	30.1	29.7
47.8	49.5	34.2	60
46	70	27.5	45.7
38	54.3	25.6	30
21.5	26.5	12.4	17.2
18	22.5	10.3	10.9
16	16	14.4	16.7
13	9	11.4	9.43
7	5.5	5.76	7.1
4.3	6.9	0.972	3.29
2.5	3.6	2.4	1.99
1.8	2.1	0.643	0.707
0.5	<1	0.103	0.112
0.5	<1	0.286	0.352
<0.5	2	0.234	0.27
<0.5	1	0.466	0.206
<0.5	<1	0.262	0.202
<0.5	<1	0.056	0.057
<0.5	<1	0.216	0.165
<0.5	<1	0.076	0.275
<0.5	<0.5	0.561	0.438
<0.5	<0.5	0.088	0.137

Figure 1
Comparison of Data Set #1 with Data Set #2 for GE ASV and EPA Method 7471



The data in Figure 2 show a comparison of the average mercury content in the soil samples measured by GE ASV and EPA Method 7471. The error bars in the x direction reflect the scatter in the data from EPA Method 7471 while the error bars in the y direction reflect the scatter in the data produced by the GE ASV Method. The line with a slope of 1 indicates perfect correlation between the two data sets. An excellent correlation between the two data sets exists from 1 ppm to 10,000 ppm mercury content in the soil samples. As seen in Figure 2, the mercury content measured for a majority of the GE ASV data is slightly greater than that measured by EPA Method 7471.

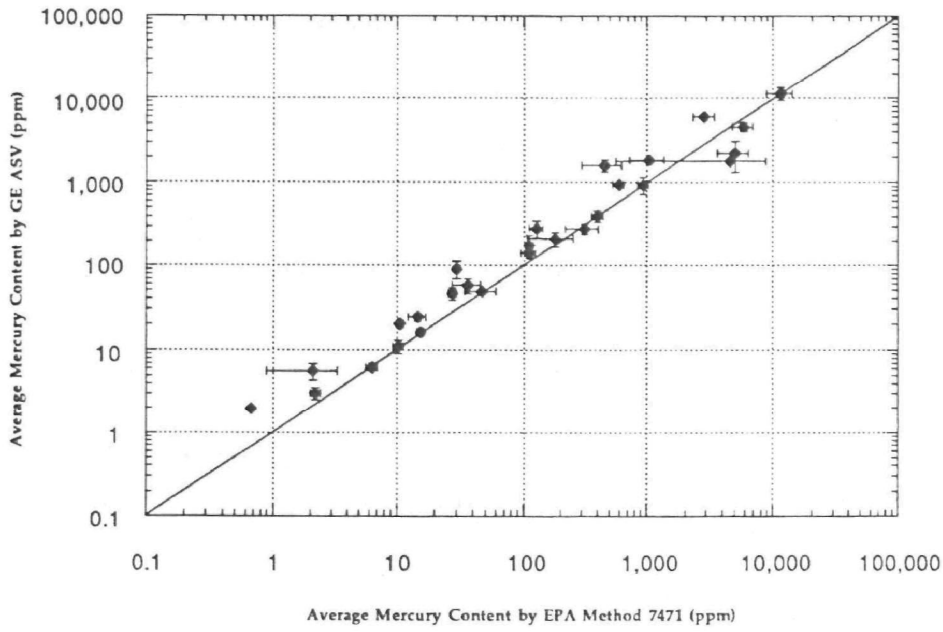
Another way to view the GE ASV Method is as a screening technique rather than a quantitative one. The data in Table 2 show that the GE ASV Method can be used as a screen for mercury in soil. Setting the screen for a content of 1, 10, 100, or 1000 ppm mercury produced no false negative results. The only false results were false positive readings, and these were infrequently encountered.

Table 2
Screening Analysis of 37 Duplicate Soil Samples Using GE ASV*

Screening Level (ppm)	Number of Samples Above Screening Level	Number of Samples Below Screening Level	Number of False Positive Results	Number of False Negative Results
1000	7	30	1	0
100	13	24	0	0
10	23	14	0	0
1	28	9	2	0

*Comparison to Average Mercury Content Determined by EPA Method 7471

Figure 2
Comparison of Average Mercury Content Measured by GE ASV Versus EPA Method 7471



SUMMARY

The method of determining mercury content in soils by first solubilizing the mercury with a mixture of iodine and potassium iodide followed by analysis of the resulting liquid with Anodic Stripping Voltammetry was successfully tested on a wide variety of samples from natural gas pipeline sites. Not only is this new method an excellent screen for mercury, it can yield quantitative data rivaling the standard method of acid digestion followed by

analysis of the extract by atomic absorption. The method yields quantitative results from 1 ppm to 10,000 ppm mercury in soil samples in less than 1 hour. The method is also amenable to field situations.

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EPA METHOD 3052: DEVELOPMENT, CHEMISTRIES AND VALIDATION

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ABSTRACT

EPA Method 3052 has been proposed to meet the EPA's need for analyses requiring total decomposition. This performance based method has the flexibility to allow the analyst to modify the acid digestion chemistry for the particular matrix, analyte, and analytical technique. Due to the methods inherent flexibility, the analyst is encouraged to understand more of the fundamental chemistry of the target analytes and matrix. This paper discusses some of the parameters and unique aspects of this new method.

INTRODUCTION

Due to a recent court decision, acid leaching methods are not sufficient decomposition techniques for ash and other incinerator wastes and fuels. Method 3052 was created to answer the need for a general method for the total analysis of inorganic constituents in a matrix. Total sample decomposition is interpreted to mean the sufficient destruction of the matrix to permit the total analysis to be performed for the elements of interest. The proposed EPA Method 3052, "Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices" is applicable to many solid matrices such as ash, oil, oil contaminated soil, sediment, sludge, soil, and biological tissue. It provides a total digestion of the above matrices for analysis of the 26 RCRA regulated elements. The performance based method involves different combinations of HNO3, HF, and HCl to decompose the matrix. Standard Reference Materials (SRMs) of each matrix type were used to test the proposed method. Method 3052 is a performance-based sample preparation method that has extensive alternatives and more capabilities for adaptation to varied media and matrix applications than previously promulgated methods. It represents the first of a new generation of methods aimed at producing accurate analyses of total analytical composition through performance-based criteria. While it handles all 26 RCRA required elements, it also provides the opportunity to extend sample preparation to most elements in the periodic table. It permits optimization for specific elements and matrices, and for the application of various detection techniques.

Method 3052 can be used to evaluate elemental concentration as a screening method for method 1311, the "TCLP" method. Section 1.2, of Method 1311, states:

> **Method 1311: Toxicity Characteristic Leaching Procedure**
>
> **1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.**

Accordingly, EPA Method 3052 could be used to determine the potential elemental contamination. If the results of the analysis using Method 3052 were below the defined elemental contamination limits, performing TCLP Method 1311 would not be required.

The original closed vessel microwave protocol that became EPA method 3052 was developed for elemental certification of Standard Reference Materials (SRMs) at the National Institute of Standard and Technology (NIST) by Dr. Kingston and his research staff (1-3). This technology was developed for the sample preparation procedure for elemental analysis by many instrumental techniques, including isotope dilution mass spectrometry (IDMS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectrometry (GF-AAS), neutron activation analysis (NAA), chelation ion chromatography (ChIC), polarography, and laser enhanced ionization (LEI). Due to the method's flexibility of using different chemistries, matrices, analytes, and analytical techniques, this method is one of the most robust performance based methods ever proposed to EPA.

Validation of this method has been underway for over eight years, starting at NIST and continuing at Duquesne University and at other collaborating sites. A description of some of the analytical aspects is presented.

EXPERIMENTAL

A 0.25 to 2.0 g sample, depending on the reactivity and the potential for the production of gaseous by-products during digestion, of the NIST SRMs were transferred into a fluoropolymer digestion vessel liner (Milestone Corporation or CEM Corporation). 9 mL of sub-boiled distilled concentrated nitric acid and various quantities of sub-boiled distilled concentrated hydrofluoric acid and sub-boiled distilled concentrated hydrochloric acid were added to each vessel. The choice of digestion reagents is dependent on

many factors including the matrix, analytes of interest, and detection technique. The vessels were capped and sealed according to manufacturer's directions. The samples were simultaneously digested by heating the samples to 180 ± 5°C within 5.5 minutes and maintaining the temperature at 180 ± 5°C for the remainder of the 15 minute heating program. This heating profile may be altered for reactive matrices or excessively slow decomposing components and shall be viewed as the general heating profile. A typical digestion temperature and pressure profile of a soil and an oil are illustrated in Figures 1 and 2. Once the vessels were cool, the vessels seal integrity was evaluated to determine whether the vessel had vented during dissolution. The sample was filtered through a 0.2 µm Teflon filter and then diluted to 100 mL with 18 MΩ-cm water (Barnstead NANOpure). All operation steps involving an uncapped microwave vessel as well as all post-digestion procedures were performed in a class 10 clean environment.

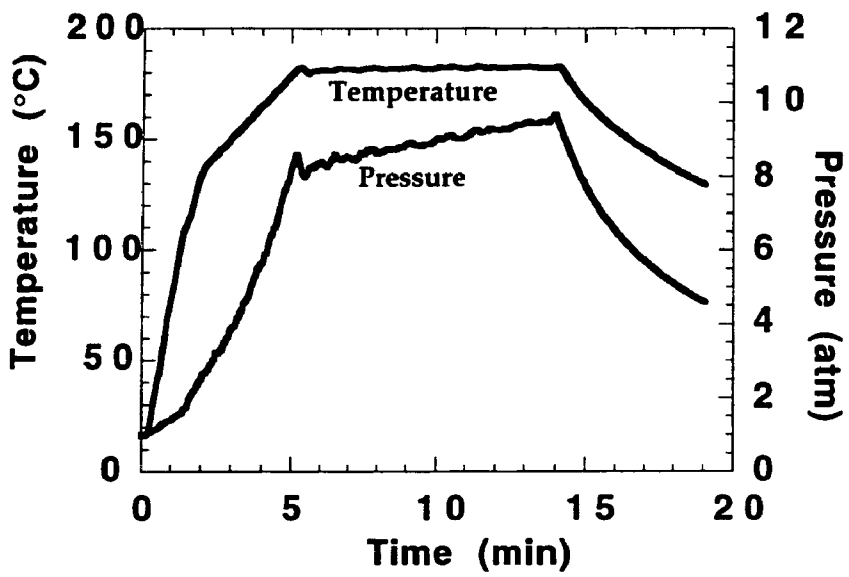

Figure 1: The typical temperature and pressure profiles for the digestion of a soil. Approximately 0.25 g soil digested with 9 mL HNO_3 and 4 mL HF.

RESULTS and DISCUSSIONS

EPA Method 3052 is a total digestion method designed to achieve total digestion of a wide variety of matrices. Data will be presented for elemental analysis of NIST SRMs including biological, botanical, geological, and metallurgical matrices.

EPA Method 3052 is a performance based method, designed to achieve or approach total decomposition of the sample through achieving specific

reaction conditions. The temperature of each sample should rise to 180 ± 5°C in approximately 5.5 minutes and remain at 180 ± 5°C for 9.5 minutes.

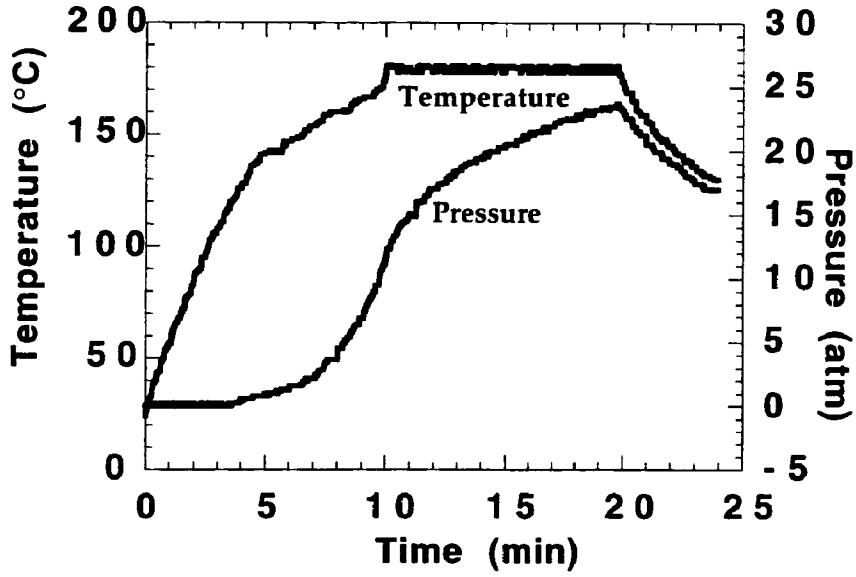

Figure 2: The temperature and pressure profiles for the digestion of an oil. 0.306 g motor oil digested with 9 mL HNO_3.

Reactive Matrices

If the matrix is composed of reactive materials, the digestion profile may be altered for safety purposes. The digestion of motor oil is an example of a matrix that will decompose rapidly and produce considerable quantities of gas. For safety reasons, the matrix should be decomposed by slowly heating the sample to 180 ± 5°C, thus allowing the easily decomposable components to react in a controllable manner. The decomposition should be maintained at a temperature of 180 ± 5°C for 9.5 minutes to complete the digestion. The safe and controlled decomposition of motor oil is illustrated in Figure 2.

Scale-up of Digestion

The method's robustness and new higher pressure microwave vessels enable the sample size to be scaled up to larger sample sizes, see section 7.3.12 of Method 3052 (4).

The scale-up of the digestion of NIST SRM 2710 (soil) is illustrated in Figure 3. The linear relationship between the analyzed concentration of cadmium to the mass of the soil digested indicated that as the sample size was increased, the digestion chemistry and reaction conditions were sufficient to completely

7.3.12 Sample size may be scaled-up from 0.1, 0.25, or 0.5 g to 1.0 g through a series of 0.2 g sample size increments. Scale-up can produce different reaction conditions and/or produce increasing gaseous reaction products. Increases in sample size may not require alteration of the acid quantity or combination, but other reagents may be added to permit a more complete decomposition and oxidation of organic and other sample constituents where necessary (such as increasing the HF for the complete destruction of silicates). Each step of the scale-up must demonstrate safe operation before continuing.

decompose the matrix. However, this does not imply that any matrix can be scaled-up to 2 g. The limits of scale-up are dependent on a number of factors including the pressure produced from the digestion of organic components, the stoichiometric limitations or the consumption of digestion reagents, and the stability of the analytes in the digest solution.

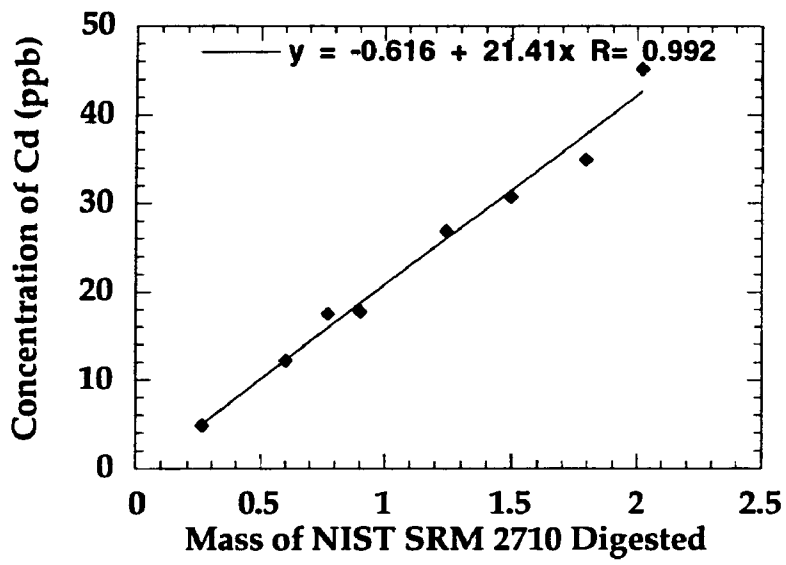

Figure 3: The linear range of cadmium analyzed from 0.25 to 2g of NIST SRM 2710. The soil was digested with 9 mL HNO_3 and 3 mL HF.

Reagent Reactions and Analyte Stability (Robustness)

Method 3052 allows the analyst to select the specific digestion reagents for specific matrices and analytes of interest. The method suggests the acid digestion solution should be 9 mL nitric acid and 3 mL hydrofluoric acid.

However, hydrochloric acid, hydrogen peroxide, water, and many other reagents could be added for several reasons including aiding the completeness of the reaction and the stabilization of a particular analyte(s). This latitude in the digestion chemistry requires that the analyst be knowledgeable of the fundamental chemistry of the digestion acids and matrix. Comprehensive reviews of acid digestion chemistry have been prepared to support this need (5-7) and will be maintained and expanded on the world wide web "SamplePrep Web" site at Duquesne University.

URL: http://nexus.chemistry.duq.edu/sampleprep/prepnet.html

A table providing guidance in selecting acid combinations has been prepared and will be included in the final draft of Method 3052.

The following two sections are brief examples that describe some of the attributes of hydrochloric and hydrofluoric acids.

Complexation and Stabilization Effects of Hydrochloric acid

Hydrochloric acid is a non-oxidizing acid which exhibits weak reducing properties during dissolution. Most metals form soluble metal chlorides with several notable exceptions: AgCl, HgCl, TiCl, and $PbCl_2$. The solubility of silver can be dramatically increased by the complexation of silver chloride with excess chloride ions.

$$Ag^+ + Cl^- \Longleftrightarrow AgCl$$

$$AgCl + Cl^- \Longleftrightarrow AgCl_2^{-1}$$

Some metals are stabilized by the combination of high temperature acid digestion and complexation with chloride ions. 70% of antimony can be lost during a typical open beaker digestion with an oxidizing acid such as nitric acid. However, using a combination of nitric and hydrochloric acids at an elevated reaction temperature, the antimony can be oxidized to the Sb(V). It then readily forms a stable complex anion with chloride ions as described below (7, 8).

$$Sb\,(V) + Cl^- \Longleftrightarrow SbCl_6^{-1}$$

The recovery and stabilization of antimony and silver are illustrated in Table 1.

Removal of Hydrofluoric acid

Hydrofluoric acid is most commonly used in inorganic analysis because it is one of the few acids that can dissolve silicates, as described in the equation below:

$$SiO_2 + 6\,HF \longrightarrow H_2SiF_6 + 2\,H_2O$$

Dissolution by hydrofluoric acid produces primarily soluble fluorides, with the exception of insoluble or sparingly soluble fluorides of the alkaline earth, lanthanide, and actinide elements.

Table 1: Stabilization and Recovery of Elements from NIST SRM 2710 with the addition of HCl.

Element	HNO_3 & HF	HNO_3, HF & HCl	Certified
Antimony	33.1 ± 2.1	39.3 ± 0.9	38.4 ± 3.0
Silver	10.6 ± 4.5	36.6 ± 0.5	35.3 ± 1.5

All analysis reported in µg/g

Once dissolved, many analyses require the removal of all hydrofluoric acid to prevent damage of the instrumental equipment, or to resolubilize insoluble fluorides. The fluorosilicic acid can be dissociated by heating the solution down to fumes in a ventilated system with other acids, such as hydrochloric acid, nitric acid, or perchloric acid. This procedure is frequently repeated a second time, for the complete removal of fluoride.

$$H_2SiF_6 \longrightarrow SiF_{4\,(g)} + 2\,HF_{(g)}$$

Care should be taken in the design of a fuming procedure to prevent the possible volatilization of numerous elements including: As, B, Se, Sb, Hg, Ge, Cr, Re, Os, and Ru.

Data are presented demonstrating the complete removal of fluoride ions by fuming off hydrofluoric acid using a microwave evaporation system (Milestone Corporation) that is beneficial in three ways. The fuming process results in statistically accurate analytical data (i.e. no loss of analytes through volatilization or precipitation), resolubilization of some metal fluoride precipitates, and removal of some ICP-MS interferences.

Another approach to the removal of hydrofluoric acid after digestion is to complex the fluoride ion with boric acid. The reaction of boric acid with hydrofluoric acid is a two step process with the slowest step being the formation of fluoroboric acid (9).

$$H_3BO_3 + 3\,HF \longleftrightarrow HBF_3(OH) + 2\,H_2O$$

$$HBF_3(OH) + HF \longleftrightarrow HBF_4 + H_2O$$

Cooling the solution after the addition of boric acid will increase the reaction rate (9). Many knowledgeable analysts suggest using 10 to 50 times stoichiometric excess boric acid.

CONCLUSIONS

The flexibility and robustness of EPA Draft Method 3052 has been demonstrated for many matrices and many analyte elements. The selection of decomposition reagents and reaction conditions has been shown to have dramatic effects on the efficiency of digestion and analysis. With the careful planning of a digestion protocol, based on the fundamental chemical reactivity of the acids and matrices, a total decomposition with a wide variety of matrices can be achieved. Method 3052 has broad applicabilities and promises to become a widely used method.

ACKNOWLEDGMENTS

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The Accurate Determination of Species by Speciated Isotope Dilution Mass Spectrometry: Exemplified by the Evaluation of Chromium(VI) in Soil

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ABSTRACT

A new generally applicable method for the accurate determination of chemical species in the environment has been developed called Speciated Isotope Dilution Mass Spectrometry (S-IDMS). The method compensates for specie transformations that can occur in many of the steps of sample processing due to unwanted side reactions. It has been specifically developed to address the problems of accurately quantifying different species in complicated matrices. It is an excellent diagnostic tool for identifying the most error prone steps in the measurement, storage, sample preparation and the sampling process. These unique capabilities will eventually make it possible to establish standard measurement methods and to develop standard sampling procedures for speciation.

Preliminary speciation study of the Cr(VI) and Cr(III) has demonstrated the unique advantages of this method. These examples demonstrate that up to 53% degradation of Cr(VI) to Cr(III) can be accurately corrected back to the original concentration in the sample. In theory it will be possible to corrected for up to 90% interconversion. These results are used as examples to demonstrate the S-IDMS concept.

The method is applicable to approximately 80% of the species that must be measured and extends to oxidation states, organometallics, and molecular forms of species. Examples of mercury, chromium, tin, selenium, and other species represent only some of the first applications. A US patent has been issued for the method of Speciated Isotope Dilution Mass Spectrometry (1). It discusses how the method can be used as a diagnostic tool for collecting data that must be legally defensible and definitive with regards to species of varying toxicity.

INTRODUCTION

Speciation measurements are made for a variety of reasons, including characterization and evaluation of systems in environmental science, medicine, biological process monitoring, nutrition, and industrial troubleshooting. Since the chemistry in these processes is specie specific, there is a great need to answer these questions at the speciated level. Until

now, no definitive diagnostic measurement capability has been available. Speciated Isotope Dilution Mass Spectrometry (S-IDMS) provides a new technological advance necessary to make these measurements that are currently beyond the capability of accurate metrology methods.

Almost every facet of scientific research involves measurement of the composition of matter. Currently, only bulk measurements of total elemental concentration and composition can be made accurately and routinely. It is known that these measurements are not adequate to resolve the complex questions that are raised for many chemical systems that undergo different reactions depending on the elemental form. Elements and molecules react differently in their speciated forms. For example, Cr(III) is a trace element essential for human health, but Cr(VI) is a poison and carcinogen to humans and most other animals. The difference in this case is only the oxidation state of the element. Each of these forms of chromium is called a species of chromium, and each has unique chemical reactions associated with it.

Two methods currently used for speciated chromium analysis are electrochemistry and chromatography. Electrochemistry can distinguish between the two different forms of chromium in a simple mixture, and chromatography can separate the mixture before presentation to a species non-specific detector such as ICP-MS. For complex sample matrices, chromatography can be used to separate Cr(III) in time from Cr(VI). Because each specie can react with its surroundings, and even with the separating agents, detection after a chromatographic separation is only a snapshot of the specie distribution at that time. Each specie may have reacted with other sample components, reagents, or been transformed during the storage and analysis steps. With time resolution, there is no way to determine how much chromium was actually in each speciated form when the sample was originally taken.

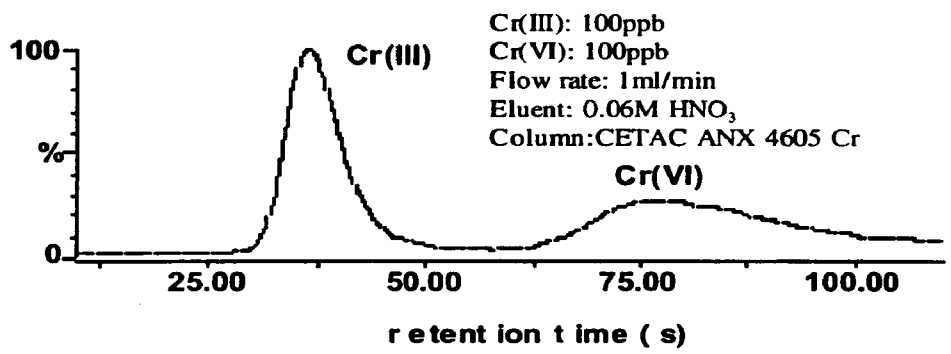
WHAT IS SPECIATED ISOTOPE DILUTION?

The speciated isotope dilution method is a procedure for the measurement of elemental species that uses isotope dilution mass spectrometry to determine the quantity of the species in the sample. The method will permit the measurement of elemental species in environmental, biological, pharmaceutical, and industrial samples. It uses the concept of spiking the sample with one or more separated isotopes that have been chemically converted into a single specie, equilibrated with the naturally occurring species, and extracted from the sample material with the naturally occurring species of interest.

Conventional methods of chromatographic separations are used to separate the species, and isotope ratios are evaluated for each specie, across the

chromatographic peak, to determine the extent of crossover between the various species prior to and during analysis. It is thus possible to correct for degradation of the species, or interchange from different species, at each step in the sampling and analysis protocol. This allows for accurate back calculation of the original sample concentration(s) of the different chemical species, something that has previously been impossible. Figure 1 shows a sample separation for this procedure using two spikes of isotopically enriched chromium species (^{50}Cr(III) and ^{53}Cr(VI)).

Figure 1 The Chromatogram of the On-line Separation of Cr(III) and Cr(VI)



An Example of Speciated Isotope Dilution

Chromium has several minor stable isotopes described in Table 1 that are suitable to be transformed into the two important oxidative species Cr(VI) and Cr(III). By spiking the original sample with separated isotopes in a speciated form as previously described, the stability and convertibility of the species can be evaluated and corrected. The isotopically enriched specie will undergo the reactions of the same "natural" specie, and this alteration will leave shifted isotopically labeled related species. The natural specie undergoes the same reactions and is chemically indistinguishable from the spiked specie. This is a very important additional application of this technology and no other measurement method can provide this information. The S-IDMS patent (1) describes a study where evaluations have been performed without using speciated isotope dilution and would provide an example where this new technology will provide vital definitive information. The patent also represents the first time a correction for transformation has been able to be made and accurate analyses made feasible.

PROCEDURE FOR CHROMIUM SPECIATION IN WATER

Step 1. Spike Preparation

Separated (enriched) isotope spikes for each of two species is prepared for Cr(III) and Cr(VI). The isotopically enriched specie spike of ^{50}Cr for Cr(III), and the isotopically enriched specie spike of ^{53}Cr for Cr(VI) were used:

Table 1. Isotopic Abundance of Chromium

Natural Isotopic Abundance Cr(III) and Cr(VI)	*Enriched Isotope ^{50}Cr* Cr(III) spike*	*Enriched Isotope ^{53}Cr** Cr(VI) spike*
50 - 4.35%	50 - 93.1%	50 - 0.03%
52 - 83.79%	52 - 6.8%	52 - 2.19%
53 - 9.50%	53 - 0.1%	53 - 97.7%
54 - 2.36%	54 - 0%	54 - 0.08%

* Isotec Inc. Lot #2691 ** Isotec Inc. Lot #2692

Step 2. Sample Collection and Spiking

Water is collected from a natural water aquifer. Using the single enriched specie spike of ^{50}Cr for Cr(III), the sample is spiked with a known quantity of the spiked (^{50}Cr, Cr(III)) species. The optimal ratio would be ^{50}Cr(III) in a concentration that approaches approximately a 1:1 ratio with the natural ^{52}Cr(III). This permits higher accuracy during the measurement. The same procedure is applied to the ^{53}Cr spike for Cr(VI)

Step 3. Sample Specie and Spike Specie Equilibration

Equilibrate the sample (natural) with the spikes. For this example we mix both the natural and enriched material in aqueous form. From this point on the total Cr(VI) has a isotopic ratio of ^{53}Cr(VI) to ^{52}Cr(VI) in the sample of approximately 1:1, depending on the amount of Cr(VI) in the original sample.

Step 4. Resolve the Species Temporally or Spatially

For this example, the species were separated using chromatography similar to that described in Figure 1. This is determined by the chemistry of the species. Separation in time on-line to an inductively coupled plasma mass spectrometer (ICP-MS) provides physical resolution of the Cr(III) and Cr(VI) fractions in different portions of the chromatogram. Cr(III) and Cr(VI) are separated from each other with the equilibrated isotopic distribution based on any conversion of the spike and the sample. (Note: Time resolution chromatography is available for these species and has been demonstrated in the literature.)

Step 5. Isotope Ratio of Each Speciated and Resolved Component

Each sample point on the chromatographic peaks contains the isotopic distribution of that species allowing replicate measurements of the isotope ratios for each injection. Isotope ratio measurements of each individual species isotope resolved component is made separately for Cr(III) and for Cr(VI). The concentration of the species is determined from isotope dilution

calculations. A total concentration for both isotopes can also be performed as a check.

Step 6. Determination of Specie Conversion

Deconvolution of each specie in the presence of the other using isotopic ratios is required at this stage. For example if Cr(VI) is converted to Cr(III), the isotope ratio $^{52}Cr/^{53}Cr$ in Cr(III) will show a decrease compared to no reduction of Cr(VI). If Cr(III) is converted to Cr(VI), then the isotopic ratio of Cr(VI) will have a lower $^{52}Cr/^{50}Cr$ ratio compared with no conversion. For more complicated scenarios where there are conversions in both directions, the previously described equations can be used to definitively calculate the concentrations of Cr(III) species and Cr(VI) species in the water, as well as the amount of interconversion between Cr(III) and Cr(VI) after spiking.

Double-spiking the solutions containing Cr(III) and Cr(VI) with different isotope enriched spikes is very unique in S-IDMS. If the spikes for different species have the same isotope enrichment, the crossover among them can not be determined. In this situation, when IDMS is applied to speciation, the crossover between the different species is not allowed and the complete separation of the species from each other must be carried out. Using the double-spiking technique described here, the crossover between different species after spiking is permitted. The incomplete separation of the species is also allowed if the initial concentrations of the species at the time of spiking, but not the amount of the crossover, are desired because the incompleteness of the separation can be treated as the interconversion between the species.

The previously described process is being applied and evaluated various samples such as natural waters and soil samples. The process may be altered depending on the matrix and each step is being evaluated and altered during the development stage to optimize the performance, precision, and accuracy of the method for both matrix types.

RESULTS

An example of some preliminary data showing the interconversion of Cr(III) and Cr(VI) is shown Table 1. Isotopically enriched speciated spikes of chromium were added to NIST SRMs 2108 and 2109 and analyzed by speciated isotope dilution mass spectrometry (S-IDMS) and isotope dilution mass spectrometry (IDMS). Even though the samples were very clean (in dilute nitric acid) some interconversion of the species was seen and identified as is shown in Table 2.

Table 2. Comparison of the Results Obtained from IDMS and Speciated-IDMS

Sample	*Dates*	*Speciated-IDMS*				*IDMS*	
		Concentration (ppb)*		Conversion (%)		Concentration (ppb)**	
		Cr(III)	Cr(VI)	(III) to (VI)	(VI) to (III)	Cr(III)	Cr(VI)
Sample 1	Jan 27, 96	69.76±0.21	68.85±0.20	4.87±0.14	3.57±0.02	72.42±0.21	72.70±0.20
100 ppb	Jan 30, 96	69.23±0.35	69.38±0.18	3.47±0.07	11.92±0.31	78.20±0.36	72.52±0.22
$KMnO_4$	Feb 8, 96	70.50±0.59	68.54±0.24	2.80±0.08	22.35±0.15	86.74±0.65	71.31±0.27
Sample 2	Jan 27, 96	69.87±0.13	68.77±0.25	17.65±0.04	2.95±0.01	72.41±0.13	82.68±0.26
200 ppb	Jan 30, 96	69.30±0.45	69.63±0.40	14.55±0.84	11.40±0.43	78.87±0.46	82.09±0.93
$KMnO_4$	Feb 8, 96	70.67±0.25	68.78±0.30	12.82±0.04	22.08±0.20	88.61±0.24	81.48±0.27
Sample 3	Jan 27, 96	69.75±0.38	68.98±0.16	23.79±0.21	2.76±0.05	72.32±0.36	87.66±0.20
400 ppb	Jan 30, 96	69.01±0.50	69.56±0.21	21.61±0.15	10.21±0.06	78.34±0.53	87.77±0.10
$KMnO_4$	Feb 8, 96	70.39±0.32	68.90±0.48	17.65±0.21	22.07±0.08	89.41±0.24	86.34±0.43
True Concentration		69.67	68.63			69.67	68.63

* Interconversion between Cr(III) and Cr(VI) was considered in the calculation
** No interconversion between Cr(III) and Cr(VI) was considered in the calculation

Other data will be presented on actual soils and spiked sand using a modified EPA proposed method 3060A procedure and microwave extraction. These additional data support this technique as a successful method for very difficult and practical speciated environmental samples.

In an attempt to show the power of the S-IDMS method, the method is being applied to the determination of Cr(VI) in extracts of contaminated soils. Proposed EPA method 3060A uses a sodium hydroxide/sodium carbonate leach to selectively extract, and stabilize, Cr(VI) from soils sediments and sludges.

Preliminary data is shown in Table 3. The extract solutions were spiked with isotopically enriched Cr(III) and Cr(VI) even though only Cr(VI) is being determined. Recoveries of chromium(VI) using both hotplate and microwave heating were statistically indistinguishable for both matrices indicating that the microwave radiation does not have any additional affect on the stability of the chromium(VI) species in solution. However, in both cases the recoveries as determined by the UV-Vis method were not 100% indicating two points. First, the low recovery of the spiked extract solution using UV-Vis, indicates interconversion of chromium(VI) to chromium(III)

by the analysis procedure (colorimetric method with diphenylcarbazide). In addition some interconversion of the chromium(VI) is induced by the sand matrix (probably due to low levels of iron). There is also incomplete recovery of the chromium(VI) by the SIDMS method for the sand extraction indicating some chromium(VI) has been lost from solution (e.g. by adsorption onto the sand particles) before the isotopic spike is added.

Table 3. Results of Chromium Analysis from Spiked Samples

Description	Heating method	Initial [Cr(VI)] in extract (ng g^{-1}) UV/Vis	SIDMS	Cr(VI) to Cr(III) percent conversion
Spiked Sand	Microwave	867 ± 6	981 ± 8	36.18% ± 0.76%
Spiked Sand	Hot plate	869 ± 6	970 ± 28	40.27% ± 0.29%
Spiked Extract	Microwave	970 ± 7	999 ± 11	14.87% ± 0.13%
Spiked Extract	Hot plate	974 ± 7	1013 ± 9	13.81% ± 0.17%

* Values listed are the averages from the analysis of three replicates of a sample ± std dev
The samples were extracted, spiked with isotopic standards, and acidified to 0.06M HNO_3.
The samples were analyzed nine days after acidification.

APPLICATIONS OF SPECIATED ISOTOPE DILUTION

The effect of species on chemical reactions point to the need to sample, separate, and measure different species and determine whether any interchange occurs during each of the various processes. Also, tracking species in reactive systems and monitoring their distribution in various forms requires specific measurement methods. With conventional measurement techniques, the origin of one specie, and its possible transformation or distribution between several species, is impossible to determine.

Another use for this technique is in the chemical processing of environmental, biological and other samples for speciated components. Species stability and the precise transformations species undergo are currently indeterminable by every other method of speciated analysis. It is imperative that a definitive method of analysis be developed for sample processing or preparation prior to all forms of analysis. Use of this speciated isotope dilution technique may fulfill this measurement need.

Currently, almost all speciated data measurements are being discredited in the legal process due to their reliability. There has not previously been a diagnostic method that was applicable to provide quality assurance for speciated measurements such as Cr(VI) and other transformable and highly reactive species. The method of speciated isotope dilution may permit the correction for species shifts that have occurred during analysis and also during other portions of sample handling if they are included in the method protocol. This could provide both a measurement technique and a diagnostic

tool to validate or calibrate other speciation measurement methods for a variety of different species.

CONCLUSIONS

The preliminary data and the theoretical background both support the potential of the S-IDMS method. A complete evaluation of this new tool is necessary to determine where it is appropriate and where it must be altered for specific applications. New and intermediate species may be found to play important roles that have not thus far been evaluated for their significance in specie transformations. Multiple forms of speciated spikes may be required for some species. However, this is the first time a diagnostic tool has been available to permit validation of other speciated methods as well as provide legally defensible data for speciated metrology.

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ON-SITE X-RAY FLUORESCENCE SPECTROSCOPY FOR THE DETERMINATION OF METALS AND PREDICTING ACID ROCK DRAINAGE

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ABSTRACT

On-site measurement (OM) techniques have been recognized as providing equal or better information compared to a fixed laboratory product. Traditionally, issues regarding the nature and extent of contamination and the effectiveness of waste removal or other remedial actions have been addressed using fixed-based laboratory analyses. However, OM techniques have a number of demonstrated advantages and their use has rapidly gained support. OM techniques provide analytical data using dedicated project personnel who are on-site and able to respond to changes as data are generated. Additional sample handling effort and expense, especially at a remote site, and delays in field activities while waiting for laboratory data are avoided.

The OM used at a copper/cobalt mine is an example of providing cost-effective dedicated analytical equipment and personnel for a remote site. Analytical support included the design and implementation of a Spectrace 9000 X-Ray Fluorescence (XRF) laboratory to evaluate waste rock acid generation or acid rock drainage (ARD) potential. XRF measurements of iron and sulfur (pyrite minerals) were used to predict waste rock ARD potential, to determine the extent of the waste rock boundaries, and to provide information for removal decisions in near real-time. Limited use of off-site analysis of acid:base accounting (ABA) using standard laboratory methods provided confirmation of decisions as construction activities were occurring.

Copper, cobalt, and arsenic residuals were measured simultaneously with the XRF ARD analyses. Through the development of site-specific reference samples, accurate and precise XRF measurements in the ppm (mg/kg) range were determined for samples throughout the site. The cost efficiencies of OM allowed for a greater density of sampling and analysis than would otherwise be feasible. This provided more data to characterize the spatial heterogeneity of the site and increased the confidence of decision-making. High-density sampling and analysis also provided additional data that were useful in the determination of acceptable decision error

OM XRF analyses were also used to evaluate potential control measures. Both field and laboratory scale extraction procedures were utilized to delineate waste rock units contributing to the generation of acid. Short-term leach tests were evaluated to provide information on soluble and non-extractable metal loads of waste rock, colluvium below waste rock, and sediment samples. In addition, XRF analyses were used to better understand the nature of copper and cobalt adsorption and release of mine loadings into receiving waters by determining metals concentration in creek bed sediments.

XRF correlation with ABA provided a useful, cost-effective, and time-saving method of identifying waste capable of generating ARD. XRF measurements were also used to determine

metals concentrations in sediments and colluvium underlying waste rock, enabling the extent of impacted areas to be determined and providing near real-time direction of construction activities.

INTRODUCTION

Standard fixed laboratory-based metals and inorganic analyses have some drawbacks that confine them to off-site fixed labs. First, they require sample dissolution before introduction into laboratory instruments, this requires additional support equipment for sample preparation. Second, routine environmental laboratories do not usually have the equipment available to perform total sulfur analyses. And finally, fixed-based laboratory instruments cannot operate without well conditioned power, stable temperature and humidity required of critical optical components and on-board computers often lacking at remediation/construction sites.

OM techniques have a number of advantages over fixed-based laboratory techniques. Chief among these advantages is in providing dedicated project personnel who are on-site and able to respond directly to the needs of the project as data is generated and evaluated. Once an action level is established for site activities, OM techniques are matched to meet these objectives and used to guide removal actions as they are occurring, enabling contractors to operate more efficiently. In addition, the cost efficiencies of OM allow for a greater density of sampling and analysis. This provides additional data to more precisely characterize the spatial heterogeneity of the site and increased the confidence in the data. High-density sampling and analysis also provided additional data that were useful in the determination of acceptable decision error. Ten percent of the field samples (approximately 800 samples) were analyzed by ICP on the hydrofluoric acid digest and regressed against the XRF results to reveal any relative bias in the data sets. The relative percent difference (RPD) between the two determinations was calculated to indicate the average disparity between the analyses.

OM using XRF at the Blackbird Mine site is an example of providing cost-effective dedicated equipment and personnel for a remote site. The site covers approximately 830 acres of private patented mining claims held by the Blackbird Mining Company, and 10,000 acres of unpatented claims previously held by Noranda Minerals Corporation within the Salmon National Forest near the town of Cobalt, Idaho. The site is located within the Northern Rocky Mountain province and the topography is characterized by deep stream cut canyons with steep and rocky slopes. Regional elevations range from 3,000 ft to approximately 9,000 ft. Mining activity has resulted in construction of approximately 14 miles of underground workings and a 12 acre open pit. Additionally, the mine site includes graded roads, numerous piles of waste rock, a tailing impoundment, sedimentation ponds, a water treatment plant, a wastewater sludge pond, and support structures. Historic mining activity has also occurred in the area since the late 1800's. The Blackbird site is drained by two streams: Bucktail Creek to the north, and Meadow Creek to the south. Both discharge to Panther Creek, a major tributary to the Salmon River.

Prediction, control, and monitoring of waste rock acid generation or acid rock drainage (ARD) potential is of major importance when considering the environmental aspects at mining sites (1). XRF measurements of iron and sulfur (pyrite minerals) were used to predict waste rock ARD potential, to determine the extent of the waste rock boundaries, and to provide information for removal decisions. Copper, cobalt, and arsenic concentrations were measured simultaneously with the XRF for iron and sulfur analyses. Residual metals were also measured under a variety of

circumstances independent of ARD evaluation, in these cases sulfur was not included in the analysis in order to reduce sample excitation time and increase analytical throughput.

MATERIALS AND METHODS

Analytical support included the use of Spectrace 9000 field portable X-Ray Fluorescence (XRF) instrument. The Spectrace 9000 uses three isotopes, ^{55}Fe, ^{109}Cd, and ^{241}Am for the production of primary x-rays for sample excitation and a high resolution mercuric iodide X-ray detector. Quantitation was based on a fundamental parameters calibration model.

The majority of excitation time (400 seconds) was due to the excitation of sulfur species using the ^{55}Fe source. The ^{109}Cd provided excitation (200 seconds) for the analysis of iron, cobalt, copper, and arsenic. Total processing time, including the 600 second excitation, was slightly more than 10 minutes. Data processing accomplished with the on-board microprocessor, results and spectral storage to a PC were accomplished while loading the next sample for analysis.

Prior to initiating and during the OM activities, Blackbird mine reference samples (BMRS) were selected to provide the appropriate range of concentrations in various matrices that were expected to be encountered during field work carried out at the site. The three major categories of sample matrices: waste rock, colluvium below waste rock, and debris flow and alluvial deposition, were evaluated. The references samples were used to validate the calibration model initially during project planning and on an on-going basis during field activities.

Element	BMRS 0920	BMRS 1950	BMRS 1960
Iron	50,100±3,478	68,300±6320	180,000±11,700
Cobalt	104±79	196±8.22	157±5.78
Copper	857±195	1,120±105	4,710±140
Arsenic	312±108	1,530±131	2,720±191
Sulfur	ND	4,570±115	32,700±115

BMRS 0920, 1950 and 1960 were selected based on the concentration of target analytes which bracket expected soil, sediment, debris, and waste material concentrations. BMRS 1950 and 1960 were prepared from bulk samples collected from test pits from the site. BMRS 0920 was prepared by compositing surface debris flow collected from an area adjacent to the toe of a waste rock dump. All BMRS's were pulverized and sieved to 75 mM (200 mesh), HF digested, and analyzed in triplicate by ICP by the off-site laboratory and confirmed using an additional off-site laboratory independent of the project. All BMRS samples were within ±16% difference from the reference values for XRF target analytes as measured throughout the duration of the project.

SCREENING VS CONFIRMATORY LEVELS OF ANALYSIS.

Two sample preparation methods were used for the XRF analysis and performed in selected areas of the site: screening-level sampling including ABA screening, and confirmatory composite sampling.

The screening-level sampling and analysis were intended to provide rapid-turnaround, qualitative, inorganic analysis. The screening-level protocol included collection of grab samples. Sample representativeness was estimated by comparing a large number of individual sample measurements, in contrast to the more rigorous composite sampling, where reduction and homogenization of a large composite was performed using splitting techniques, followed by sieve fractional analysis, pulverization, and additional mixing. The confirmatory composite sampling protocol was developed for specific site areas where action level criteria were established and the need for defining the precision and accuracy limits were warranted (2).

SAMPLE PREPARATION

The on-site lab received samples collected specifically for XRF screening analysis consisting of minus 2-inch waste rock or other solid materials/soil stored in 4 oz HDPE sample jars or other suitable polymeric containers. Separate samples were also collected as field duplicates at a frequency of 5% of the total number of field samples.

An aliquot (approximately 10-100 grams depending on particle size distribution), typically consisting of both fine and coarse material, was removed from sample jars with a disposable plastic spoon and dried to less than 2% moisture. Where sample crushing was necessary (i.e. >20% of the sample over 10 mesh), samples were manually crushed using a hand sledge, until an adequate amount of minus 10 mesh sample material was obtained for analysis. All samples requiring size reduction were crushed prior to sieving. Samples collected from boreholes (drilled using air rotary) or from sediments generally did not require the crushing step. Pulverization was not required by the XRF screening-level protocol. However, a number of samples collected for evaluation sample preparation protocol were pulverized using a Bico-Braun direct motor-driven pulverizer. The dried samples were sieved to minus 10 mesh and the over-sized fraction discarded. Differences in metals concentration between the over-size and sieved fractions were compared on a periodic basis and were found to be insignificant when analysis was performed on samples collected from waste areas. XRF sample cups were filled approximately 3/4 full, tapped to distribute fine particles to the window side of the XRF cups and compacted by tapping with the window side down prior to analysis.

PRE-OPERATIONAL CHECKS

Element X-ray response checks were performed and recorded each day. A sample of pure iron for XRF-metals and pure titanium for XRF-sulfur was used for these analyses. The ^{109}Cd source provided excitation for the XRF-metals (iron, arsenic, cobalt, and copper). To verify response of this source, the ^{109}Cd spectrum was examined after excitation of a pure iron (Fe) sample for 50

seconds. A relative response greater than 0.95 for iron was required. Iron spectral interference with cobalt and manganese values must be less than 0.006 relative to iron. Similar X-ray response checks were performed for XRF-sulfur which utilizes the ^{55}Fe source for excitation. The relative response for titanium in a pure titanium (Ti) sample measured for 50 seconds must be greater than 0.95. No spectral interference is present in the Ti spectrum and adjacent energies were not evaluated.

Energy calibration was checked by examining the ^{109}Cd spectrum. The K alpha line associated with iron was verified and recorded at 6.4 ± 0.02 keV before proceeding with sample analysis. After verifying the energy calibration, spectrum resolution was confirmed by verifying that the number of counts at the centroid of the iron K alpha line (6.4 keV) were more than twice the number of counts at ± 0.3 keV (resolution at half height). These results were recorded each day. Goals for energy calibration were met for all analyses. Energy calibration during operation was maintained automatically by examining X-ray back-scatter in between each analysis.

An analytical background check was performed at least once each day to verify both the spectrometer operation and the condition of the probe window. A Teflon® (blank) sample was placed within the sample positioning ring and contaminant-free conditions verified before proceeding with field sample analyses. Goals for contaminant free blanks were met for all analyses.

The analytical computations of the Spectrace 9000 are based on a fundamental parameter (FP) calibration algorithm. When using FP, the highest degree of accuracy is obtained when the entire sample composition is known. Since many of the elements in the site samples could not be measured with the instrumentation employed, it was necessary to make assumptions about the elemental composition of the sample. As a result, certain sample types (i.e. waste rock, overbank, colluvium,) exhibit minor amounts of bias (deviation from a known reference value) due to variations in the unmeasurable element balance in the sample. The application used at the site assumed that use of a SiO_2 (silica) balance, accounting for the majority of the unmeasurable balance in field samples, provided sufficiently accurate analyses without a need for further adjustment. The accuracy of the measurements could be fine-tuned by adjusting the slope and off-set values for a given target analyte when reference samples have been characterized for the site. Calibration adjustments were not considered trivial, but were performed based on knowledge of the site material being analyzed. Adjustments to slope and off-set were performed only when: 1) appropriate references samples were available and have been fully evaluated, and 2) the samples collected for analysis had characteristics similar to the reference material. At all times, 10% of all samples analyzed by XRF were confirmed using ICP. This was the basis for quality control of reported XRF results and provides the quality assurance that the adjustments have been applied correctly.

The method minimum detection limit was obtained by measuring the appropriate BMRS representative of the matrix and level or levels at which decision criteria had been established. Statistical analysis of XRF BMRS data were performed and a method detection limit was calculated. The method reporting limit was defined as the standard deviation (rounded up to the nearest whole number) multiplied by three and reported to two significant figures. The calculated method detection limits were determined to be: 3,000 mg/kg for iron, 1,500 mg/kg for cobalt, 300 mg/kg for copper, and 150 mg/kg for arsenic. The detection limits were applied to all

measurements reported. The method reporting limit for sulfur was evaluated and established in conjunction with the XRF instrument manufacturer and determined to be less than 2,000 mg/kg.

PRECISION AND ACCURACY

Data precision and accuracy were evaluated to determine the usability of the data. The primary concern in this evaluation was elimination or minimization of the decision error resulting from false negative results; that is, the determination that an area was non-impacted when in actuality it was. Evaluation of all target elements were considered in this evaluation. However, cobalt was not detected in any of the duplicate measurements, and sulfur was not quantitatively measured for the majority of field samples due to the extended measurement time required for this analyte. Therefore, cobalt and sulfur were not included in the determination of analytical precision.

Precision was measured by evaluating field and laboratory duplicates and BMRS data. Overall field and laboratory analytical precision were evaluated by comparing the relative percent difference (RPD) between the field or laboratory sample and the respective field sample. Field duplicate samples were collected for the majority of test pit locations in order to assess sample homogeneity within the testing location. To evaluate field sample variation at the specific field sample location, a field duplicate sample was collected from opposing location, either top and bottom or opposite sides of the test pit. Borehole samples were similarly collected using the top and bottom portion of a core sample or a first and second sample of air rotary cuttings. Combined laboratory (measurement) and field (collection) precision were measured. Duplicate recoveries for these samples demonstrated an overall average RPD $\leq$ 45%. RPDs were generally less than 35% when analytes were detected near the proposed level of concern. Repetitive analysis results of the appropriate BMRS's were evaluated for percent relative standard deviation (RSD %) to assess analytical precision. The RSD should be within ±40% for the data to be considered adequately precise. All calibration reference samples were within this limit.

Accuracy was evaluated by performing confirmation analysis on the same samples used for field XRF analysis. Random samples were selected and submitted for HF digestion and ICP analysis for iron, cobalt, copper, and arsenic at a frequency of at least 10% of the number of field samples. Sulfur was analyzed off-site using a LECO sulfur analyzer requiring no additional sample preparation. Analyte concentrations, as determined from field measurements, ranged from non-detect to one or two orders of magnitude above the MDL for most analytes. Confirmation samples were submitted throughout the field program as field data were generated and evaluated. To evaluate accuracy, the coefficient of determination (r^2), defined as the amount of variation in the dependent variable (XRF analysis) that can be attributed to the independent variable (ICP analysis), was used. Using the mining model developed for the project, the coefficient of determination was greater than 0.8 ($r^2 \geq 0.8$) for all sample results and $r^2 > 0.9$ was achieved when concentrations of target metals were near the proposed level of concern. The initial sulfur application assumed a high lead content because it was developed using the NIST SRM 2710 before a suitable site reference sample was available. The NIST standard contained the appropriate concentration of sulfur (2,400 mg/kg), but because of the elevated lead content (5,500 mg/kg), the initial application model generated assigned an X-ray region for the detection of sulfur which was too narrow. This error affected sulfur accuracy and precision, and was only useful for determining the presence or absence of sulfur. Subsequent calibration models were designed to be used in the absence of lead, as is the case at the site. This allowed for a broader

sulfur window that vastly improved XRF measurement statistics. The use of this new calibration model is currently being evaluated and the associated sulfur accuracy and precision has improved dramatically compared to the initial results.

ACID-BASE ACCOUNTING (ABA) PREDICTION

Acid-base accounting (ABA) is an accepted criterion for evaluating the potential of mine waste rock to create acid drainage and associated mobilization of metals (1). However, ABA testing cannot be efficiently conducted on-site without extensive laboratory facilities. Therefore, XRF analysis was employed for rapid-turnaround estimation of metals concentrations to provide an indication of ABA potential and the amount of copper, cobalt, and arsenic available for potential release. Detection of high levels of iron >100,000 mg/kg and total sulfur >2,000 mg/kg appeared to be indicative of acid-generation waste rock, most likely related to the presence of pyrite (FeS_2).

	OM XRF					OFF-SITE LAB	
Location	Iron (mg/Kg)	Arsenic (mg/Kg)	Cobalt (mg/Kg)	Copper (mg/Kg)	Sulfur (mg/Kg)	Pyr Sulfur (mg/Kg)	A/B Potential
TP-95-15	165,500	6,138	ND	1,650	8,600	9,600	-21.1
TP-95-57	154,400	6,422	ND	3,600	2,400	2,600	3.4
TP-95-7	147,900	4,200	ND	2,116	9,300	9,200	-18.4
TP-95-15	141,440	5,943	ND	958	7,100	15,400	-38.4
TP-95-7	136,880	4,055	ND	1,633	8,200	5,000	-4.2
TP-95-25	136,330	3,015	1920	855	2,200	43,600	-127.4
TP-95-35	127,370	1,982	ND	1,129	4,300	10,300	-26.9
TP-95-7	124,000	1,336	1560	1,778	6,400	7,000	-12.4
TP-95-43	123,220	783	ND	371	7,200	3,800	-0.2
TP-95-15 FD	119,890	3,959	ND	832	5,200	18,000	-48.4
TP-95-35	117,350	1,359	ND	287	7,700	7,600	-21.5
TP-95-13	112,360	603	ND	250	2,200	980	-12.9
TP-95-13	106,150	1,692	ND	400	4,500	3,900	2.0
TP-95-58	104,720	1,760	ND	1,624	4,300	3,500	4.6
TP-95-43	103,970	1,762	ND	565	3,600	23,400	-60.9
TP-95-4	77,800	1,318	5740	7,980	6,600	100	15.6
TP-95-57	70,980	212	ND	863	2,040	400	12.8
TP-95-43	68,250	486	ND	682	2,060		6.3
TP-95-43 FD	67,550	430	ND	608	1,190		6.3
TP-95-5	67,050	1,095	ND	513	6,200	3,900	-5.3
TP-95-50	66,350	170	ND	528	4,270		14.4
TP-95-13	63,260	404	ND	1,537	1,260		10.3
TP-95-9	61,400	645	ND	440	1,660		15.8
TP-95-6	56,760	92	ND	298	5,030		10.8

TP-95-60	53,350	137	ND	242	2,000		10.4
TP-95-11	50,530	2,533	5770	3,116	7,500	5,800	-14.4
TP-95-53	49,280	104	ND	207	3,070	100	12.8

SUMMARY

OM XRF instrumental and sample preparation techniques have proved to be a very useful tool especially in a remote site. XRF versus fixed lab techniques were not statistically different, especially considering the variation due to sample collection. The cost efficiencies of XRF allowed for implementation of high-density sampling versus low density sampling which overall achieved a higher degree of sample representativeness providing increased confidence in decision making. The strong positive correlation between XRF iron and sulfur and acid generating potential provides a predictive tool which can be used for remedial activity decisions in near real time.

ACKNOWLEDGMENT

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(2) USEPA, April 1990 "Quality Assurance Quality Control Guidance for Removal Activities" EPA 540 G-90/004, OSWER Directive 9360.4-01 U.S. Environmental Protection Agency, Office of Emergency and Remedial Response , Washington DC ,

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Extraction of Anions from Solid Phase Samples for Capillary Ion Electrophoresis

Roy-Keith Smith[1], David Roth[2], Jim Krol[3], and Joe Romano[4]

The analysis of inorganic anions in solid phase samples has been addressed in the US Environmental Protection Agency's National Sewage Sludge Survey[5] and in the context of analysis of agricultural soils[6]. The EPA testing needs were addressed as one line sample preparation modifications to already existing traditional wet chemical methods for determination of the specific anions total phosphate, chloride, sulfate, nitrite and nitrate. These for the most part these involved mixing a portion of the solid with reagent grade water, agitating for up to 24 hours, then filtering and treating the filtrate as a normal aqueous sample. A number of procedures are available in a methods manual used by agricultural soils testing laboratories. These involve extraction of the sample with either reagent grade water alone or reagent grade water with various additives such as calcium sulfate, ammonia, and/or diethylenetriaminepentaacetic acid (DTPA).

As part of an effort to develop methods for the analysis of inorganic anions using capillary electrophoresis, attention was directed toward solid phase samples. The problem was formulated as first evaluating known procedures with an eye toward capillary electrophoresis, examining possible alternative sample preparations, then generating precision and accuracy data for a suitable procedure.

Reagents, materials and apparatus

Reagent grade water was prepared using a cartridge purification system from Continental Water consisting of 2 mixed bed ion-exchange resin cartridges, a series of two activated charcoal cartridges and finally a 0.45 um filter cartridge.

Class A volumetric glassware was used for all liquid manipulations. The analytical balance calibration was checked daily with a set of Class S calibration standards.

Anion standards were prepared as follows:

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[1] Analytical Services, Inc. 110 Technology Parkway, Norcross, GA 30092.
[2] Analytical Services, Inc. 110 Technology Parkway, Norcross, GA 30092.
[3] Waters Corporation, 34 Maple Street, Milford, MA 01757.
[4] Waters Corporation, 34 Maple Street, Milford, MA 01757.

[5] Analytical Methods for the National Sewage Sludge Survey, USEPA WH-585, September 1990; POTW Sludge Sampling and Analysis Guidance Document, USEPA August, 1989.

[6] *Handbook on Reference Methods for Soil Analysis*, Soil and Plant Analysis Council, Inc., 1992; *Wisconsin Procedures for Soil Testing, Plant Analysis and Feed & Forage Analysis*, Department of Soil Science, College of Agricultural and Life Sciences, University of Wisconsin-Extensión-Madison, 1987; *Soil Sampling and Methods of Analysis*, M.R. Carter (Ed), Canadian Society of Soil Science, 1993, CRC Press, Boca Raton FL; *Methods of Soil Analysis: Part 2 - Chemical and Microbiological Poperties*, 2nd Edition, American Society of A,gronomy Soil Science Society of America, Madison WI 1982

Anion stock standard solution, 1000 mg/L: Prepare a series of anion standard solutions by weighing the indicated amount of salt (obtained from Aldrich Chemical Company), dried to a constant weight at 105°C, to 1000 mL. Store in plastic bottles (HDPE) in a refrigerator.

Anion	Salt	CAS	Amount g/L
Bromide	NaBr	7647-15-6	1.2876
Chloride	NaCl	7647-14-5	1.6485
Fluoride	NaF	7681-49-4	2.2102
Nitrate	$NaNO_3$	7631-99-4	1.3707#
Nitrite	$NaNO_2$	7632-00-0	1.4998*
Ortho-phosphate	Na_2HPO_4	7558-79-4	1.50
Sulfate	Na_2SO_4	7757-82-6	1.48

This gives a 1000 mg/L solution as nitrate, 225.8 mg/L as nitrate-N.

* Do not oven dry, but dry to a constant weight in a desiccator over phosphorus pentoxide. This gives a 1000 mg/L solution as nitrite, 304.3 mg/L as nitrite-N.

Mixed stock standard: Add 5.00 mL of the chloride, sulfate, nitrate and phosphate anion stock standard and 2.50 mL of the bromide, nitrite and fluoride anion stock solutions to a 100 mL Class A volumetric then dilute to volume to give 50 mg/L of the first 4 anions and 25 mg/L of the bromide, nitrite and fluoride anions.. Store for up to one month in a HDPE container in the refrigerator.

Mixed working standards: Prepare a series of 5 different concentration standards by diluting 1.00, 10.00, 20.00 and 50 mL of the mixed stock standard to 100 mL. The mixed stock standard is the fifth standard. This results in calibration standards with concentrations of 0.50, 5.00, 10.0, 25.0 and 50.0 mg/L for chloride, sulfate, nitrate and phosphate, and 0.25, 2.50, 5.00, 12.5 and 25.0 mg/L for the bromide, nitrite and fluoride. Prepare these standards weekly and store in the refrigerator in HDPE bottles. A fresh 5-point calibration was prepared daily and checked every 10 samples.

The 50 mg/L mixed matrix spiking solution was prepared by adding 5.00 mL of each stock anion standard to a 100 mL volumetric flask and then diluting to volume. A 1:10 dilution with extraction solution gave a 5.00 mg/L matrix spike.

Diethylenetriaminepentaacetic acid (CAS 67-43-6, Aldrich Chemical Company 28,556-0) was prepared by adding 0.500 g to a 100 mL volumetric flask containing about 50 mL water, adding 3.00 mL of 1.00 *M* NaOH solution, then diluting to volume. A 1:10 dilution of this stock solution gave the 0.050% extraction solution.

Ammonium hydroxide (CAS 1336-21-6, Fisher Scientific, 28-30%) was diluted 1:10 to give a 3% solution, then diluted 1:10 again to give a 0.3% extraction solution.

Chromate electrolyte solution[7]. 4 *mM* chromate and 3.0 *mM* TTAOH; dilute 20 mL of chromate concentrate and 15 mL TTAOH concentrate with 400 mL water. Add 5 mL CHES buffer which gives a pH of 9.0. Dilute to 500 mL. Filter and vacuum de-gas daily. Prepare fresh weekly and store capped at room temperature. *Chromate concentrate* (100 *mM*): Dissolve 23.41 g sodium chromate tetrahydrate[8] (CAS 10034-82-9) Mwt 234.04 in 500 mL water, then dilute to 1 L. This concentrate is stable for 1 year when stored in a capped plastic or glass container at room temperature. *Electroosmotic flow modifier concentrate:* Dissolve 3.364 g tetradecyltrimethyl ammonium bromide[9] (CAS 1119-97-7) Mwt 336.4 (TTAB) in 50 mL reagent water, dilute to 100 mL, giving a 100 *mM* solution. Immediately prior to use pass the required volume through an ion-exchange cartridge[10] directly into the 500 mL volumetric flask used to prepare the working electrolyte, to exhange bromide for hydroxide ion and generate TTAOH. *CHES Buffer* (100 *mM*) Dissolve 20.73 g 2-(N-cyclohexylamino)-ethanesulfonic acid[11] (CAS 103-47-9), Mwt 207.3 (CHES) in 500 mL water, then dilute to 1L. This concentrate is stable for up to 1 year when stored in a capped glass or plastic container

The following solid samples were dried at 104°C, then ground and sieved through a 1.0 mm double aluminum screen to prepare a homogeneous sample for testing:

Type	Source
Sandy silt	Douglasville, Georgia, 1.0 meter subsurface ("Georgia Red Clay")
Silty sand	Atlanta, Georgia
Sediment	Red water pond sediment, Sandusky Ohio
Clay	San Joaquin NIST Standard Reference Material 2709
Clay	Montana Soil NIST Standard Reference Material 2711

Wastewater sludge samples were obtained from Greensboro, Georgia (1.4% solids) and Manchester, Georgia (5.6% solids).

Syringe filters of 0.45 um pore size (Acrodisk Ion Chromatography, Gelman catalog # P/N 4585) and a 10 mL gas tight syringe with Teflon® tipped plunger (Hamilton catalog # 1010) were used to filter samples prior to analysis. Syringe and filter were rinsed with 5 mL water and 1 mL sample prior to collecting the solution for testing in a 0.6 mL polypropylene capped centrifuge tube.

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[7] Available pre-prepared from Waters, Com

[8] Catalog #21,662-3, Aldrich Chemical Company, 1001 West Saint Paul Ave, Milwaukee WI 53233, 1-800-558-9160.

[9] Catalog #T4762, Sigma Chemical Company, P.O. Box 14508, St. Loius MO 63178-9916, 1-800-325-3010. This solution is available pre-prepared from Waters Corporation as a 100 *mM* solution of TTAOH.

[10] Available from Alltech Corporation part number 30254.

[11] Available from Sigma Chemical Company, catalog number C2885.

Cavitator ™ Ultrasonic Cleaner obtained from Mettler Electronics, Inc., Model ME 4.6, 115 v, 2 amp, 85 watt bath.

Capillary ion electrophoresis was performed on a Waters Capillar Ion Analyzer with Mellinium software. A 60 cm, 75 um id fused silica capillary column was used with 30 second hydrostatic sample introduction and 15 kV potential with UV detection. Electrolyte was replaced between each sample.

Methods and Results

An Instrument Dection Limit and a Method Detection Limit study following EPA protocols (40 CFR 136, Appendix B) on reagent water were conducted. The results are presented in Table 1.

Reagent blanks and matrix spiked reagent blanks were prepared for each extraction solution and treated as samples to test for process contamination. Other than substantial amounts of carbonate in the ammonia reagents and some formate, no laboratory contamination was found. The results for these blanks and blank matrix spikes are presented in Table 2.

Samples were weighed (1.00 ± 0.02 g) into 20 mL polyethylene scintillation vials with polyethylene cone-shaped cap liner (Kimble catalog number 58515), then 10.00 mL extraction solution with or without matrix spike was added. The treatments used were reagent water, reagent water plus matrix spike, 0.3% ammonia, 0.3% ammonia plus matrix spike, 0.050% DTPA, 0.050% DTPA plus matrix spike and 0.3% ammonia plus 0.050% DTPA. The samples were capped and irradiated in the ultrasonic bath containing about 1 cm water for 1 hour. After filtration the sample extracts were analyzed by CE.

Table 1. Instrument Detection Limit (IDL) and Method Detection Limit (MDL) for anions.

Anion	IDL (mg/L)	MDL (mg/L)	MDL spike level (mg/L)
Chloride	0.023	0.046	0.100
Bromide	0.039	0.046	0.100
Nitrite	0.025	0.072	0.200
Sulfate	0.036	0.032	0.100
Nitrate	0.084	0.084	0.200
Fluoride	0.011	0.020	0.100
Phosphate	0.042	0.041	0.100

Table 2. Anion blank and blank MS recoveries for a 5.0 mg/L spike into empty sample vials

	Reagent water		NH_3		DTPA		NH_3-DTPA
Anion	Blank	MS	Blank	MS	Blank	MS	Blank
Chloride	nd	97	nd	87	nd	97	nd
Bromide	nd	102	nd	105	nd	103	nd
Nitrite	nd	101	nd	97	nd	101	nd
Sulfate	nd	101	nd	94	nd	98	nd
Nitrate	nd	99	nd	103	nd	102	nd
Fluoride	nd	115	nd	109	nd	111	nd
Phosphate	nd	102	nd	102	nd	110	nd

Results for the extraction and analysis of the dried soil samples are presented in Tables 3 through 9 for the calibrated anions. The values are corrected for the amount of sample weighed into the vial. Matrix spike results are expressed in terms of percent recovery, corrected for background target analyte in the sample. An 'nd' is used to indicate that the target analyte was not detected in the sample.

Table 3. Chloride results in mg/kg and percent recoveries of 50 mg/kg matrix spike

	Reagent water		NH_3		DTPA		NH_3-DTPA
Soil	Sample	MS	Sample	MS	Sample	MS	Sample
Sandy silt	1.7	97	nd	74	nd	98	nd
Silty sand	1.2	97	nd	89	nd	102	nd
Clay SJ	72	94	70	98	71	116	74
Clay Mon	24	98	20	109	21	105	17
Sediment	2.9	93	1.4	85	23	53	2.1

Table 4. Bromide results in mg/kg and percent recoveries of 50 mg/kg matrix spike.

	Reagent water		NH_3		DTPA		NH_3-DTPA
Soil	Sample	MS	Sample	MS	Sample	MS	Sample
Sandy silt	nd	98	nd	82	nd	102	nd
Silty sand	nd	102	nd	101	nd	101	nd
Clay SJ	nd	103	nd	101	nd	104	nd
Clay Mon	nd	98	nd	105	nd	91	nd
Sediment	nd	88	nd	87	nd	100	nd

Table 5. Nitrite results in mg/kg and percent recoveries of 50 mg/kg matrix spike.

	Reagent water		NH_3		DTPA		NH_3-DTPA
Soil	Sample	MS	Sample	MS	Sample	MS	Sample
Sandy silt	nd	98	nd	81	nd	95	nd
Silty sand	nd	98	nd	95	nd	98	nd
Clay SJ	55	120	nd	99	57	93	nd
Clay Mon	11	105	nd	95	7.7	99	nd
Sediment	nd	89	nd	92	nd	97	nd

Table 6. Sulfate results in mg/kg and percent recoveries of 50 mg/kg matrix spike.

	Reagent water		NH_3		DTPA		NH_3-DTPA
Soil	Sample	MS	Sample	MS	Sample	MS	Sample
Sandy silt	58.6	165	481	0	258	36	493
Silty sand	62	196	564	62	366	84	548
Clay SJ	240	42	190	71	229	88	202
Clay Mon	58	81	56	99	66	74	51
Sediment	809	111	864	10	775	232	825

Table 7. Nitrate results in mg/kg and percent recoveries of 50 mg/kg matrix spike

	Reagent water		NH_3		DTPA		NH_3-DTPA
Soil	Sample	MS	Sample	MS	Sample	MS	Sample
Sandy silt	nd	98	10.2	50	nd	99	9.3
Silty sand	nd	99	nd	88	nd	98	nd
Clay SJ	212	28	288	70	208	121	311
Clay Mon	14	62	30	94	14	62	27
Sediment	187	108	210	67	202	70	208

Table 8. Fluoride results in mg/kg and percent recoveries of 50 mg/kg matrix spike

	Reagent water		NH_3		DTPA		NH_3-DTPA
Soil	Sample	MS	Sample	MS	Sample	MS	Sample
Sandy silt	nd	20	15.7	76	0.3	40	14.3
Silty sand	nd	5	30	83	nd	26	26
Clay SJ	4.4	55	6.0	63	1.1	52	7.1
Clay Mon	3.2	67	6.7	86	2.6	58	6.5
Sediment	nd	102	nd	101	nd	97	nd

Table 9. Phosphate results in mg/kg and percent recoveries of 50 mg/kg matrix spike

	Reagent water		NH_3		DTPA		NH_3-DTPA
Soil	Sample	MS	Sample	MS	Sample	MS	Sample
Sandy silt	nd	1	nd	22	nd	13	nd
Silty sand	nd	5	nd	43	nd	5	nd
Clay SJ	nd	25	nd	41	nd	42	nd
Clay Mon	3.8	67	nd	50	15.2	49	1.4
Sediment	nd	54	nd	143	nd	109	38

The San Joaquin SRM and a matrix spike were analyzed 7 times with the 0.05% DTPA extraction solution to determine repeatability of the extraction/analysis procedure. The results are presented in Table 10.

Table 10. Analysis of 7 replicates of the San Joaquin SRM and 50 mg/kg matrix spike.

Anion	Sample Mean	%RSD	MS Mean %R	%RSD
Chloride	67	2.0	93	2.5
Bromide	nd	-	97	1.7
Nitrite	nd	-	90	3.2
Sulfate	187	5.7	94	3.7
Nitrate	282	2.4	90	3.0
Fluoride	1.8	18	56	6.5
Phosphate	nd	-	37	28

Duplicate samples of approximately 5 g of the wastewater sludges were weighed into the 20 mL scintillation vials. One of the duplicates was mixed with 10.00 mL of 0.050% DTPA solution, while the other was mixed with 10.00 mL of 0.050% DTPA containing 5.00 mg/L matrix spike. The samples were irradiated in the ultrasonic bath for 60 min, then filtered and analyzed by CE. High levels of organic acids and carbonate in the sludges interferred with the fluoride and phosphorus responses. The results are presented in Table 11.

Table 11. Anion results for sludge samples in mg/kg wet weight and percent recoveries of matrix spiked sludges

	1.4 % sludge		5.6% sludge	
anion	Sample mg/kg	MS %	Sample mg/kg	MS %
Chloride	271	254#	14.4	63
Bromide	0.69	93	nd	106
Nitrite	nd	0	nd	74
Sulfate	7.2	109	33	0
Nitrate	0.94	50	nd	32
Fluoride	int	int	int	int
Phosphate	int	int	int	int

Sample background about 20 times matrix spike amount.

Discussion

A number of recipes which have been used in the past for extraction of anions from soils have relied upon additives such as calcium sulfate, ammonium fluoride, hydrochloric acid, silver sulfate and phosphate buffers to assist the solubilization of the analytes. None of

these were considered as acceptable procedures for an anion screening method due to addition of one or more target analytes to the sample.

A preliminary set of 4 samples was extracted with reagent water, 0.050% EDTA and 0.050% DTPA with 15 minute ultrasonic extraction and 90 minute heating in a water bath (60-80°C). Some nitrite was detected in one sample which was extracted using ultrasound, while the nitrite was missing from the heated sample. Otherwise no substantial differences in the heating and ultrasonic treatments were noted. Heating the samples was not considered further.

EDTA was found to migrate close to the carbonate peak and contributed to electropherogram distortion, while the migration of DTPA was considerably retarded and analyte anion migration times were more stable. As no differences were obvious in the extraction efficiencies of the two chelating agents, use of EDTA was abandoned and further experiments concentrated on DTPA.

In another preliminary evaluation, total phosphorus analysis using the persulfate digestion procedure was attempted using CE. The amount of sulfate in the digestate completely masked the electropherogram and further attempts along these directions were abandoned.

Ammonia was evaluated as an aid in digesting the samples. The ammonia used contained substantial carbonate which presented interference problems due to migration time changes in the fluoride and phosphate signals.

The results obtained from comparative analysis of the five soil samples indicated that the different extraction solutions exhibited different strengths and weaknesses for the individual anions.

Chloride

The four extraction solutions exhibited similar results for four of the five test soils, with acceptable recoveries of the matrix spikes (74-116%). The redwater pond sediment was the lone outlier, as the DTPA extraction pulled about 10 times more chloride out of the sample than did the water, ammonia or ammonia-DTPA solutions. Because of this single sample, DTPA would be a preferred extraction solution for general use.

Bromide

None of the test soils exhibited any background bromide, and overall marix spike recoveries were excellent for all four test solutions.

Nitrite

Similar sample results and good to excellent matrix spike recoveries were obtained for the water and DTPA extractions. The DTPA extractions exhibited a tighter range of recoveries (93-99%) than did the water (89-120%). Even though good to excellent (81-99%) matrix spike recoveries were obtained from all samples with the ammonia solution, no background nitrite was recovered from the two samples which exhibited nitrite by the water or DTPA extractions.

Sulfate

Ammonia and DTPA pulled substantially more sulfate out of the silt containing samples than did the water. Ammonia and the ammonia-DTPA combination are noted to performed as well or better than DTPA by itself for these samples. The high levels of sulfate in these samples (greater than five times the matrix spike) make the interpretation of the spike recoveries difficult. However, the greater than 100% spike recovery of the water extracted samples suggests that even the modest amounts of anions in the spike solution can serve to displace sulfate from the silt matrix. Water by itself is shown be be a poor choice for sulfate isolation.

Nitrate

The ammonia and ammonia-DTPA extractions are noted to isolate more nitrate than the DTPA or water extractions. Comparison of the nitrite results in Table 5 with the nitrate results in Table 7 suggests that this may be due to a conversion of nitrite in the sample to nitrate by the ammonia. This is particularly noticeable with the two clay soils where the nitrite extracted by the water or DTPA is approximately equal to the increased amount of nitrate found in the ammonia extractions. The sediment sample which exhibited no nitrite, gives similar results for nitrate in all four extracts.

Fluoride

The ammonia and ammonia-DTPA solutions extracted substantially more fluoride from the silt and clay containing samples, as compared to the water and DTPA extracts. Further the low MS recoveries suggest that fluoride is being actively absorbed by the matrix from the solution, *i.e.*. the matrix is not saturated with respect to fluoride. The improved performance of the ammonia solution over that of the DTPA suggests that heavy metals are responsible for the fluoride absorption rather than alkaline earth metals. The sediment sample exhibited no difference between the different treatments and further the matrix spike recoveries were excellent.

Phosphate

Substantial interference with the phosphate signal in the electropherogram was noted in most of the samples due to carbonate and organic anion, particularly formate, presence. The poor to fair matrix spike recoveries obtained from all the four extraction treatments on the silt and clay samples further indicates the samples were unsaturated with respect to phosphate and the extraction treatments were unable to overcome the absorption of phosphate by the matrix. These results suggest that a simple extraction and CE analysis is not suitable for phosphate determination in solid samples. This is unfortunate, however the traditional acidic oxidative digestion followed by molybdate colorimetric determination used for total phosphorus is one of the few good procedures for analysis of anions in solids.

Sludge samples

The two sludge samples were run as solids without drying. The heterogeneous nature of the samples makes the interpretation of the matrix spike results difficult. Further the electropherograms exhibited large amounts of interference with the fluoride and phosphate anions. A good picture of the chloride, bromide, nitrite, sulfate and nitrate contents of the sludges were obtained in a short period of time.

Conclusion

Overall what is seen is that the tradition recipes for anion isolation from soil matrices may work very well for indivdual anions tested one at a time using conventional wet chemical procedures. However for the multi-analyte techniques which are the technology of the future, more generally applicable processes need to be developed. This short survey has indicated that there are procedures other than the use of plain water which are substantially more efficient for analyte isolation. Future promising directions of development include looking at ethanol amines as extraction additives.

"Choosing Between Closed Vessel and Atmospheric Pressure Microwave Sample Preparation for Environmental Analysis"

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Closed vessel microwave technology has been well documented showing fast and precise sample preparation for many types of environmental samples. The microwave transparent, pressurized vessels used in this study quickly reached the target temperature of 175°C. The digestion period was only 10 minutes, compared to the traditional 90-100 minute hot plate procedure. Control of the method was possible through remote PC access. Windows-based software allowed real-time monitoring, data storage, and more. The study will demonstrate the improvements in time and precision for closed vessel microwave sample preparation compared to the standard hot plate sample preparation methods, for animal tissue, plant tissue, and sediment standard references.

Atmospheric pressure microwave technology is more appropriate for larger sample types and samples with high organic content. Atmospheric pressure microwave sample preparation was performed in quartz vessels with air reflux columns to eliminate the possible loss of volatile analytes. Programmed methods allow for sequential reagent addition. The focused microwave instrument can prepare four samples at a time for Kjeldahl nitrogen and phosphorus analysis. Catalyst-free digestions were obtained in 20-25 minutes, much less than the traditional 1-2 hour procedures that often require a metal catalyst. Speed and precision gains when performing atmospheric pressure microwave sample preparation for Kjeldahl nitrogen and phosphorus analysis will also be demonstrated.

THE EXTENSION OF EPA MICROWAVE LEACH METHODS 3015 AND 3051

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ABSTRACT

Microwave leach methods have been developed as an alternative to traditional leach methods that use hot-plate technology. These include EPA microwave acid leach methods 3015 "Microwave assisted acid digestion of aqueous samples and extracts" and 3051 "Microwave assisted acid digestion of sediments, sludges, soils, and oils". Method 3051 was designed as an alternative to hot plate method 3050, but due to differences in the reagents specified for use in each method, it does not reproduce the chemistry of method 3050. This results in chemical biases between methods. Using hydrochloric acid along with nitric acid in method 3051 provides better comparability of the chemistries, and leads to better recoveries for those elements which typically are biased low when using method 3051. As method 3015 currently uses only nitric acid, similar results in recoveries are expected upon adding hydrochloric acid to the leach.

INTRODUCTION

Microwave leach methods have been developed as an alternative to traditional leach methods that use hot-plate technology. These include EPA microwave acid leach methods 3015 "Microwave assisted acid digestion of aqueous samples and extracts" and 3051 "Microwave assisted acid digestion of sediments, sludges, soils, and oils". Each of these methods uses nitric acid and microwave heating to perform leaches of environmental matrices. These methods have shown low recoveries for several elements because of the stipulation that only nitric acid be used.

EPA Method 3051 was designed as a microwave alternative to hot-plate EPA method 3050. Method 3050 allows for the use of nitric acid, hydrogen peroxide, and hydrochloric acid, while method 3051 specifies that only nitric acid be used as the leaching acid. The EPA specified that method 3051 use only nitric acid in an attempt to avoid potential interferences by high chloride concentrations on several instrumental methods, including electrothermal

vaporization atomic absorption spectrometry and inductively coupled plasma mass spectrometry. If hydrochloric acid is not included in the microwave leach procedure, chemical biases can be introduced between the methods. Microwave method 3051 does not reproduce the chemistry that is taking place in hot-plate method 3050, resulting in differences in leach recoveries for some elements. For example, it has been shown that recoveries for the elements iron and aluminum are 12% and 50% lower, respectively, when using method 3051 than when using method 3050 for the leaching of a standard sediment sample (NIST SRM 2704) (1). In order to improve the comparability of the microwave methods, the chemistry of the microwave methods has been modified to more accurately reproduce the chemistry of the standard hot-plate methods. Hydrochloric acid is added to enable the complexation and stabilization of elements such as aluminum, antimony, iron, and silver. By including hydrochloric acid in the microwave method, the chemical biases between microwave and hot-plate leach methods are minimized. A recent study has shown that for the leaching of standard soils and sediments, the optimum acid ratio for EPA method 3051 is 9 mL nitric acid to 3 mL hydrochloric acid (2). By using this ratio to leach standard reference materials using method 3051, recoveries of elements that were traditionally low, like antimony, iron, and silver, were increased and are comparable to recoveries using method 3050. Further studies will demonstrate the range of applicability of method 3051 using the new 9 mL nitric to 3 mL hydrochloric acid combination. The altered method will be used to leach a variety of different standard reference materials of various matrix types for which the current method 3051 is applicable, including soil, sediment, oil, and oil-contaminated soil.

EPA method 3015 is an acid leach of aqueous samples, such as wastewater, for determination of 23 RCRA regulated elements. This method only uses nitric acid in the leaching of the aqueous matrices. It is expected that recoveries for elements which were low using method 3051, namely antimony, iron, and silver, will also be low using 3015. The chemistry of this method does not take advantage of the complexation power of hydrochloric acid. It will also be shown that by including hydrochloric acid in method 3015, recoveries for traditionally less soluble elements, such as iron, antimony, and silver, will be improved by complexation and stabilization by hydrochloric acid.

SUMMARY

Current EPA methods 3051 and 3015 only use nitric acid to leach RCRA regulated elements out of environmental matrices. Exclusive use of nitric acid results in low recoveries of some elements. In current studies, hydrochloric acid has been added to the nitric acid, and each leach method

was performed on a variety of matrices for which they are applicable. Improvements in recoveries for elements such as antimony, silver, and iron are demonstrated.

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Application of Automated Microwave Digestion for Envrionmental Sample Analysis

By: S. Leikin, B. Moshiri & M. Moses
Presented by: Michael Moses

Microwave Digestion has tremendously reduced the time required for preparation of samples prior to analysis by AA and ICP. However, Microwave digestion still remains a labor intensive technique. Several manufacturers have attempted to automate this process with continuous flow systems. A new technology has been developed by Questron under a grant from the Ontario Ministry of Energy and the Environment. This technology involves the technique of Discreet Flow for Microwave Digestion. This technology permits complete isolation of each sample without dilution and contamination. It also permits the application to solids and larger particles.

In this paper we will discuss the application of automated discrete flow automated microwave digestion including: dispensing, reagent mixing, predigestion, heating cooling and dilution sample. Applications and results will be presented for soils, vegetation, geologicals and EPA protocols.

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Heterogeneous Reduction of Nitrate Nitrogen in Water and Wastewater for Compliance Monitoring

Abstract Submitted for 12th Annual Waste Testing & Quality Assurance Symposium July 23-26, 1996 Washington, DC

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The objective of this paper is to present the data and conclusions of the nitrate determination performed on water samples using heterogeneous and homogenous reduction of nitrate to nitrite method.

Several methods have been used for nitrate determination in water and wastewaters. Most of these methods have limited sensitivity or suffer from serious interference by other constituents present in the water samples. For example, nitrate determination by nitration of 2,6-xylenol (1) is interfered by large chloride concentrations. A polorographic method of catalytic reduction of nitrate in the presence of uranyle ions(2) is not suitable in today's strict OSHA and EPA regulations due to the use of elemental mercury. Ion Selective Electrode(ISE) methods for nitrate determination have been used for fresh water samples. Application of ISE method in wastewater and seawater sample is limited due to the interference from most common anions.

One of the most sensitive method for nitrate determination is reduction of nitrate to nitrite followed by formation of azo dye. Mullin and Riley(3) proposed the homogeneous reduction of nitrate by hydrazine in the presence of copper ions as catalyst. However, the hydrazine reduction method is not quantitative, highly dependent on external conditions and lengthy(4). The reduction of nitrate in a heterogeneous system using metallic cadmium granules have been reported by several authors(6,7,8). This paper will discuss the method performance, reaction of nitrate reduction and applicability of method for different types of samples for nitrate analysis.

The information provided in this presentation would be helpful to water treatment professionals, wastewater analysts, and water treatment plant engineers.

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QUALITY ASSURANCE

THE DEVELOPMENT OF NIST STANDARD REFERENCE MATERIALS (SRMs) FOR METHYLMERCURY CONTENT IN COMPLEX MATRIX ENVIRONMENTAL SAMPLES

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BACKGROUND

Many mercury-containing compounds are currently used or were previously used by industry and agriculture for applications such as wood preservatives, seed treatments, thermometers, marine paint additives, batteries, pesticides, fabric softeners, and furniture polish[1]. The initial forms and amounts of mercury introduced into the environment are a poor indication of actual pollution levels and dangers to marine organisms, however. This is caused by the natural interconversion of mercuric compounds and ions in the marine environment. Therefore, quantification of the most toxic mercury compounds formed in this cycle is especially important to correctly assess environmental damage. For this reason, scientists have focused their efforts on the formation and quantification of methylmercury and other alkylmercury compounds in the marine environment.

The speciation of toxic metals is vital to the accurate assessment of pollution levels due to the variability in toxicities of different metallic compounds. Few speciated certified reference materials (CRMs) are currently available for complex matrix materials similar to those routinely monitored for environmental contamination. CRMs are necessary to ensure method validation and data quality assurance.

In response to the growing trend toward speciation and the need for method and data validation, an analytical method based on solid-liquid extraction, gel permeation chromatography (GPC) cleanup, and gas chromatography with microwave-induced plasma atomic emission detection (GC-AED) was developed at the National Institute of Standards and Technology (NIST) to quantify methylmercury in biological tissues and sediments. Ten NIST standard reference materials (SRMs)(SRMs are CRMs from NIST) were screened for methylmercury content using the GC-AED method to determine which materials would be appropriate for eventual certification[2]. The two materials with the highest methylmercury content were SRM 1974a Organics in Mussel Tissue and SRM 2974 Organics in Freeze-dried Mussel Tissue. A third mussel tissue reference material, RM 8044, also was chosen for further investigation due to the similarity in matrix types.

In addition to the three mussel tissue materials being analyzed for total mercury and methylmercury content at NIST, the materials also were analyzed by the International Atomic Energy Agency (IAEA), Marine Environment Laboratory (Monaco) and the Institute for Applied Physical Chemistry, Research Centre Jülich (Germany) for the same two analytes. The analytical methods used by all three laboratories are independent from each other, thus providing three sets of independent data for the determination of certified methylmercury and total mercury values in the three mussel tissue materials. The methods used by each laboratory are described briefly in the experimental section of this manuscript. More detailed descriptions of these methods can be found in the references indicated.

EXPERIMENTAL

Determination of Methylmercury by NIST using GC-AED: Samples were mixed with 1 mL 1 M copper sulfate, 8 mL water (only added for standard solutions and RM 8044), 4 mL acidic potassium bromide solution, and 2 mL toluene in individual 50 mL centrifuge tubes for 1 h. The toluene layers were then separated, and the extraction was repeated with a second 2 mL aliquot of toluene. The combined toluene extracts for each sample were concentrated to 0.5 mL, and high molecular weight pigments and lipids were removed using preparative GPC. The cleaned extracts were analyzed using gas chromatography (OV-1701 column, 0.53 mm x 15 m, 3.0 µm film thickness, Quadrex, New Haven, CT) with mercury-specific microwave-induced plasma atomic emission detection[3].

Determination of Methylmercury by IAEA using cold vapor atomic fluorescence spectrometry (CV-AFS): Samples were saponified in closed Teflon vial overnight at 70 °C with 10 mL 25% potassium hydroxide in methanol and diluted to 25.8 mL with methanol. Methylmercury in the saponified samples was derivatized with sodium tetraethyl borate at pH 4.9 and collected on a Tenax trap. Separation of the individual organomercury species was achieved by isothermal gas chromatography (glass capillary SPB-5 column, 0.75 mm x30 m, 1.0 µm film thickness) followed by pyrolysis and CV-AFS detection. All analysis were done during the same day[4].

Determination of Methylmercury by Research Centre Jülich using cold vapor atomic absorption spectrometry (CV-AAS): Samples were extracted three times with 6 M hydrochloric acid and the extracts combined. Methylmercury in the acid extract was decomposed to inorganic mercury with nitric acid or ultraviolet light followed by CV-AAS detection[5-6].

Determination of Total Mercury by NIST using flow injection cold vapor atomic absorption spectrometry (FI-CV-AAS): Samples were mixed with 5 mL concentrated nitric acid and microwave digested for 10-20 min at a maximum temperature of 228 °C and a maximum pressure of 1242 kPa. After digestion was complete, the contents of the vessels were transferred to 100-mL volumetric flasks containing 0.75 mL 1% potassium dichromate solution and diluted to volume with 1% (v/v) sulfuric acid. Samples were then analyzed by cold-vapor generation using the FIAS-200 flow injection system and a Perkin-Elmer 5000 atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT). Peak height measurement was used for quantification[7].

Determination of Total Mercury by NIST using instrumental neutron activation analysis (INAA): Samples were weighed into individual quartz vials and flash frozen in liquid nitrogen prior to sealing the vials. The vials were encapsulated in polyethylene film followed by packaging in sets of eight in polyethylene irradiation vessels. Each vessel was irradiated for 3 h at a reactor power of 20 MW. The samples were removed from the vessel approximately 1-2 months after irradiation, the polyethylene films removed, and the outer vial surface cleaned. Each vial then was encapsulated in clean polyethylene films and gamma radiations were collected for ≥ 8 h using a germanium detector and associated electronics. Quantification of mercury was based on comparison with standards using the 279 keV line from ^{203}Hg, corrected for the interference from ^{75}Se.

Determination of Total Mercury by IAEA using cold vapor atomic fluorescence spectrometry (CV-AFS): Samples were digested in closed Teflon vials with 4 mL nitric acid and 2 mL sulfuric acid for 3 h at 70 °C and diluted to 25.8 mL with milliQ water and 500 µL of a preservative. The digested samples were analyzed by double gold trap amalgamation using CV-AFS detection. Each sample was analyzed twice and all analyses were done during the same day[8].

Determination of Total Mercury by Research Centre Jülich using gold amalgamation cold vapor atomic absorption spectrometry (GA-CV-AAS): Samples were mixed with 10 mL nitric acid and digested at 150 °C for 10 hours. The digested samples were diluted to 20 mL with distilled water prior to analysis by cold-vapor atomic absorption spectrometry. A portion of each samples solution was mixed with tin chloride to reduce any Hg(II) to Hg(0), and the resulting mercury vapor was collected by amalgamation on a gold wire. The collected mercury was thermally desorbed from the wire by heating the wire to 600 °C, and transported to the glass cuvette for absorption measurement at 253.5 nm (slit width 2.0 nm, cuvette temperature 50 °C)[9].

RESULTS AND DISCUSSION

Table 1 contains the mean methylmercury and total mercury concentrations for each mussel tissue material as determined by each laboratory. IAEA has not reported a total mercury value for SRM 1974a or an uncertainty for methylmercury in RM 8044 as indicated in the table. Methylmercury results are presented as ng methylmercury expressed as mercury per g of dry material, and total mercury results are presented as ng total mercury per g of dry material. The mean of the method means is reported for each material as an indication of the certified value, although the exact certified concentrations have yet to be finalized. The uncertainties for these overall mean values are expressed as 95% confidence intervals.

The total mercury and methylmercury results for SRM 2974 and SRM 1974a agree within the uncertainties of the values. These two materials were prepared from the same tissue homogenate, so this agreement indicates freeze-drying has had little or no effect on the materials' mercury contents. The data for these two materials are currently being evaluated by NIST statisticians for eventual certification.

The methylmercury value determined by NIST for RM 8044 was lower than the results from IAEA and Research Centre Jülich. The NIST extraction procedure may not be quantitatively extracting methylmercury from this material. Research Centre Jülich observed an unusual sample size dependence to the measured methylmercury concentrations in this material, but believe this dependence did not affect their final reported results. IAEA indicated that a problem with their extraction procedure may have initially caused an elevation in their measured methylmercury concentrations in RM 8044 which they corrected before reporting results. These problems encountered by IAEA and Research Centre Jülich during the analyses of RM 8044 and the disagreement among the three laboratory results indicates that further investigations of this material are needed. The total mercury results for RM 8044 agree quite well, however, as compared to the methylmercury values.

ACKNOWLEDGMENTS

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Table 1 Summary of methylmercury and total mercury results for mussel tissue materials

		Institute	SRM 1974a	SRM 2974	RM 8044
MeHg	GC-AED:	NIST	74.3 ± 15	80.6 ± 10	20 ± 2
(ng/g as Hg)	CV-AAS:	Jülich	81.1 ± 3	71.7 ± 3	28.1 ± 1.5
	GC-AFS:	IAEA	78.1 ± 5	80.6 ± 5	28
Mean values:			77.3 ± 12	77.8 ± 8.4	~ 28
Total Hg	FI-CV-AAS:	NIST	184 ± 17	186 ± 2	61 ± 2
(ng/g)	INAA:	NIST	203 ± 18	155 ± 16	59 ± 8
	GA-CV-AAS:	Jülich	170 ± 10	182 ± 4	62 ± 2
	CV-AFS:	IAEA	-	174 ± 8	64 ± 6
Mean values:			186 ± 41	174 ± 22	62 ± 3

VARIABILITY AMONG TOXAPHENE REFERENCE STANDARDS

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ABSTRACT

Toxaphene is a chlorinated camphene insecticide which yields a complex, multi-component gas chromatogram. The accurate identification and measurement of toxaphene in the environment depend on the availability of a suitable reference standard. Toxaphene standards were purchased from nine suppliers. The comparison of these standards by electron capture gas chromatography resulted in the discovery of a wide range in the relative proportions of the gas chromatography peaks among the materials studied. Such variations will have serious implications on the qualitative and quantitative determination of toxaphene in environmental samples. Chromatograms to illustrate the differences will be presented.

INTRODUCTION

Toxaphene has been a widely used pesticide in the United States. Over the past several years, Hercules has collected environmental samples as part of monitoring activities and has submitted those samples to contract laboratories for the determination of toxaphene. Recommended methods[1] specify that quantitation is done by using peaks in the latter half of the toxaphene chromatogram. Because Hercules observed differences among results of analyses between laboratories, a search for the cause of the variations was undertaken.

When no obvious differences (which could cause the observed variations in the results of analysis) in the practice of the methods were discovered, the question of the uniformity of toxaphene calibration standards was investigated. In the summer and fall of 1995, a survey revealed that there were more than twenty providers of toxaphene reference standards, but the number of primary suppliers was reduced to nine upon further investigation.

RESULTS

Samples from the various suppliers were purchased as neat standards. The reference sample for this comparison study was a retained portion of a toxaphene lot designated as X16189-49, which was produced in the Hercules Brunswick, Georgia, plant in 1968. Each standard purchased was compared with technical toxaphene X16189-49 after injection on 30-meter X 0.53-mm J&W Megabore columns: DB-5 and DB-1701. Hexane solutions of all standards were injected into a Hewlett-Packard 5890 gas chromatograph equipped with an electron capture detector, and the detector response was monitored by HP ChemStation software (client/server version).

Figures 1 through 3 illustrate the differences in the distribution of the component peaks of the various standards purchased. The chromatograms shown are from the DB-1701 column, and technical toxaphene X16189-49 is the uppermost sample in each set. It is obvious that the qualitative differences among the standards vary greatly. Some standards have larger peaks in the first half of the chromatograms, and some have larger peaks in the latter half. In addition to the obvious differences in the distribution of the GC peaks among the samples, the physical appearance of the toxaphene is different, particularly in the case of Supplier #9, where the normally waxy toxaphene is a viscous liquid at refrigeration temperature.

Two standards (Figure 4; DB-5 GC column) give an excellent match for technical toxaphene X16189-49 -- a neat standard from Supplier #8 and a solution in hexane purchased from Supplier #10.

How standards are prepared may result in differences in analytical results. The chromatograms in Figure 5 show the difference between two standards purchased from Supplier #8. The top chromatogram is technical toxaphene X16189-49, the middle chromatogram is a neat toxaphene standard, and the bottom chromatogram is a solution of a toxaphene standard supplied as a solution in methanol. The differences in the GC profiles are significant and illustrate the problem of obtaining consistent standards -- even from the same supplier.

In addition to the qualitative comparisons reported here, work is in progress at the Hercules Research Center to demonstrate the effects of the variations among commercially available toxaphene reference standards on calibration curves and on the quantitative determination of levels of toxaphene in environmental samples.

CONCLUSIONS

This comparison of toxaphene reference standards from commercial suppliers has demonstrated significant variations among the materials currently available. These variations have serious implications for the accurate identification and quantitation of toxaphene in environmental samples.

Action should be taken by suppliers of reference standards to establish a true toxaphene reference standard for use by all laboratories involved in the analysis of environmental samples for toxaphene.

SUMMARY

Hercules personnel have conducted a survey of the suppliers of toxaphene calibration standards. The results of that survey demonstrate significant differences among the qualitative GC profiles of the "standards" purchased from different suppliers. Also demonstrated is the significant difference between two toxaphene standards purchased from the same supplier.

These differences have serious implications for the accurate qualitative identification and quantitative determination of toxaphene in environmental samples.

Work is in progress at the Hercules Research Center to determine the potential analytical problems caused by such variations in the toxaphene "reference standards" which are currently available to analytical laboratories.

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FIGURE 1 - COMPARISON OF HERCULES TOXAPHENE AND STANDARDS FROM COMMERICAL SUPPLIERS.

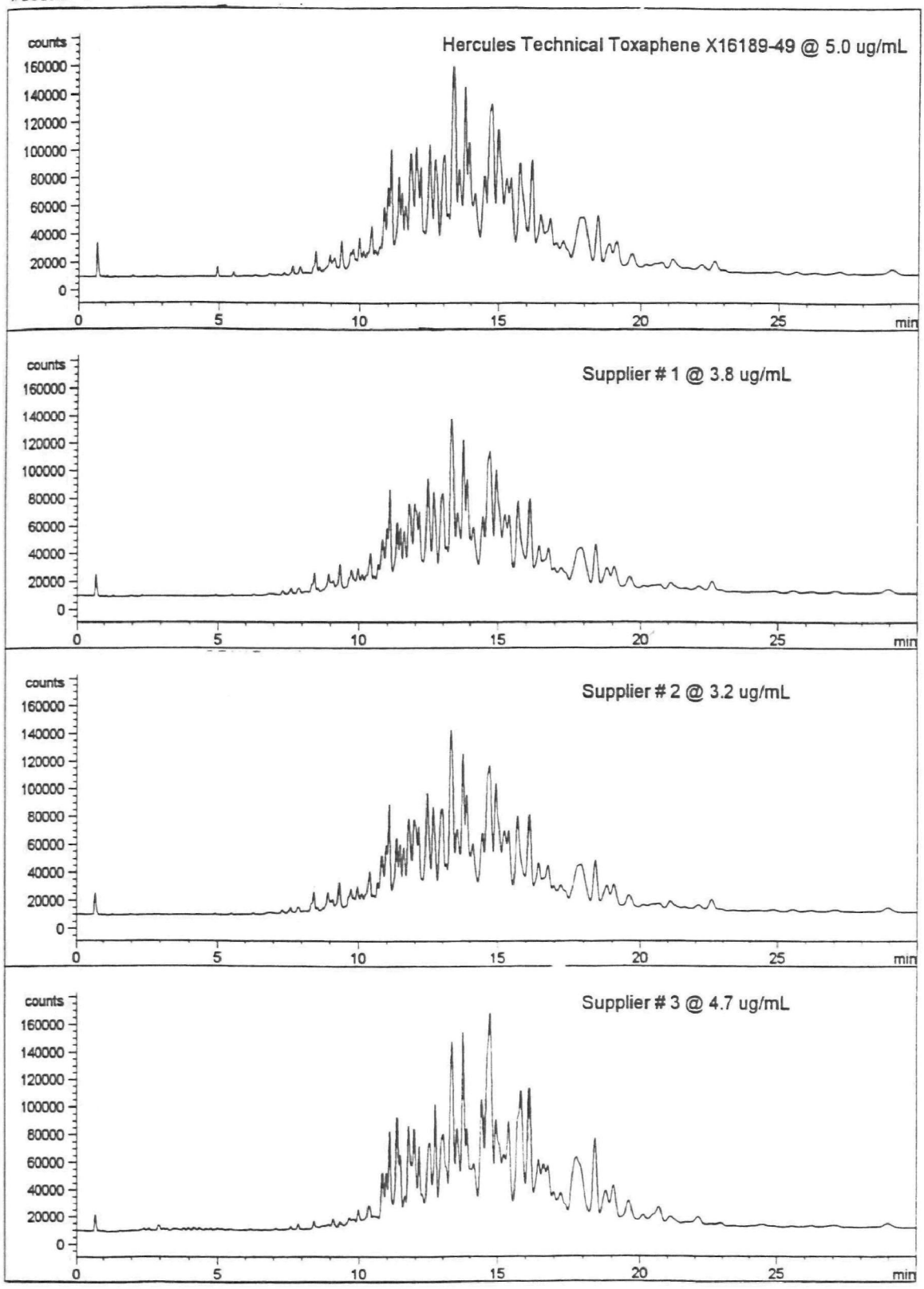


FIGURE 2 - COMPARISON OF HERCULES TOXAPHENE AND STANDARDS FROM COMMERCIAL SUPPLIERS.

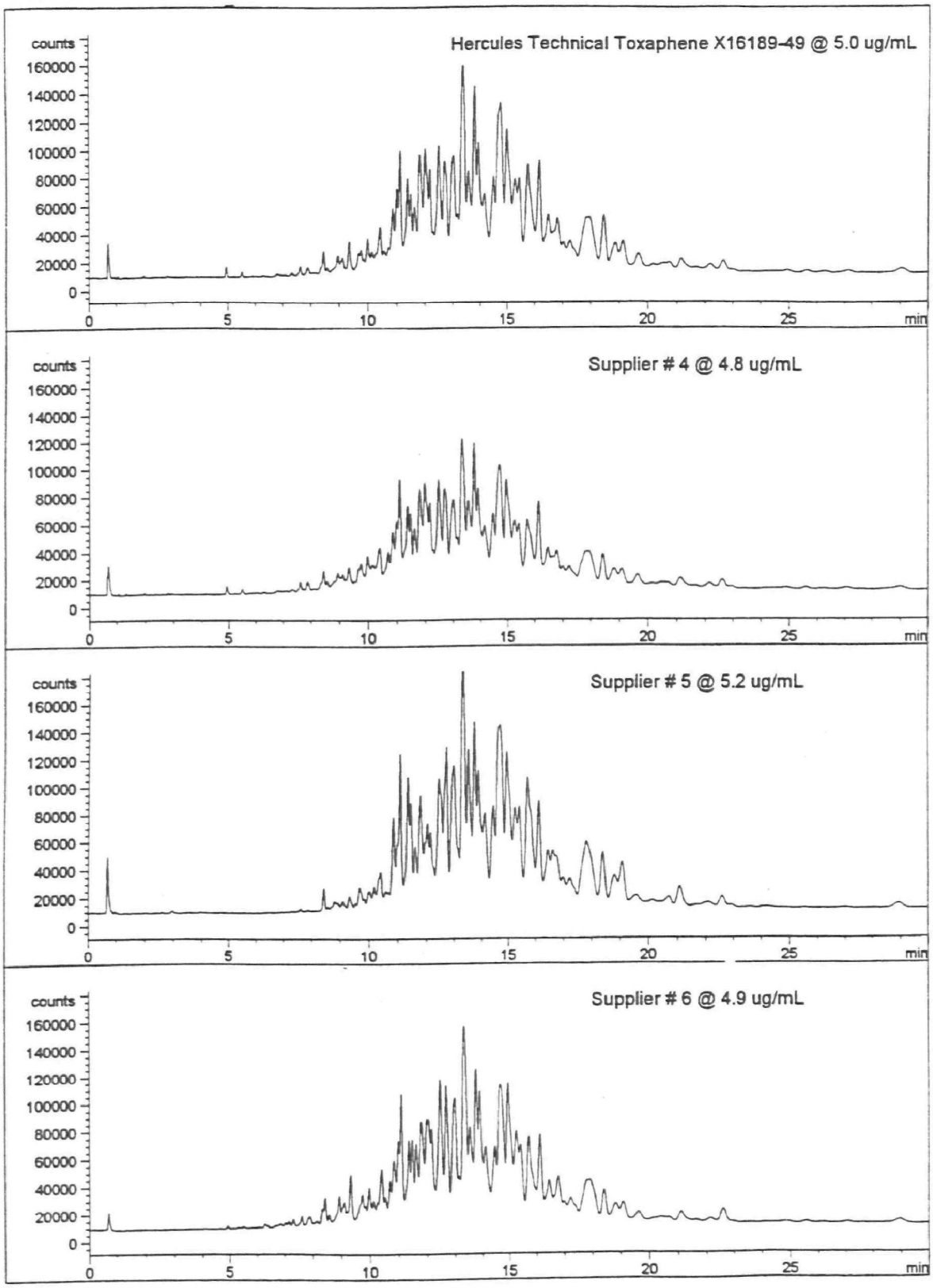


FIGURE 3 - COMPARISON OF HERCULES TOXAPHENE AND STANDARDS FROM COMMERCIAL SUPPLIERS.

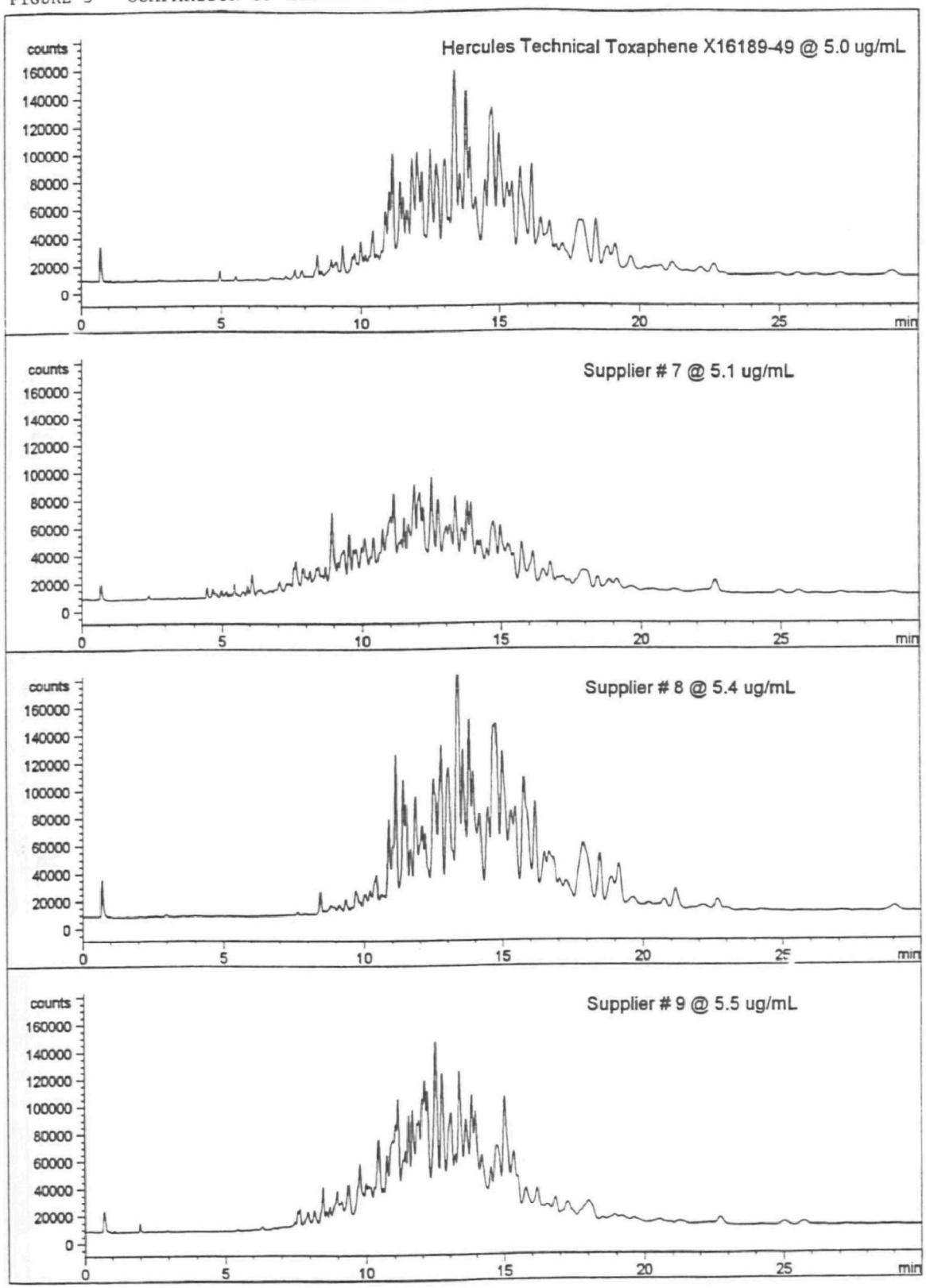


FIGURE 4 - COMMERICAL STANDARDS WHICH MATCH HERCULES TOXAPHENE.

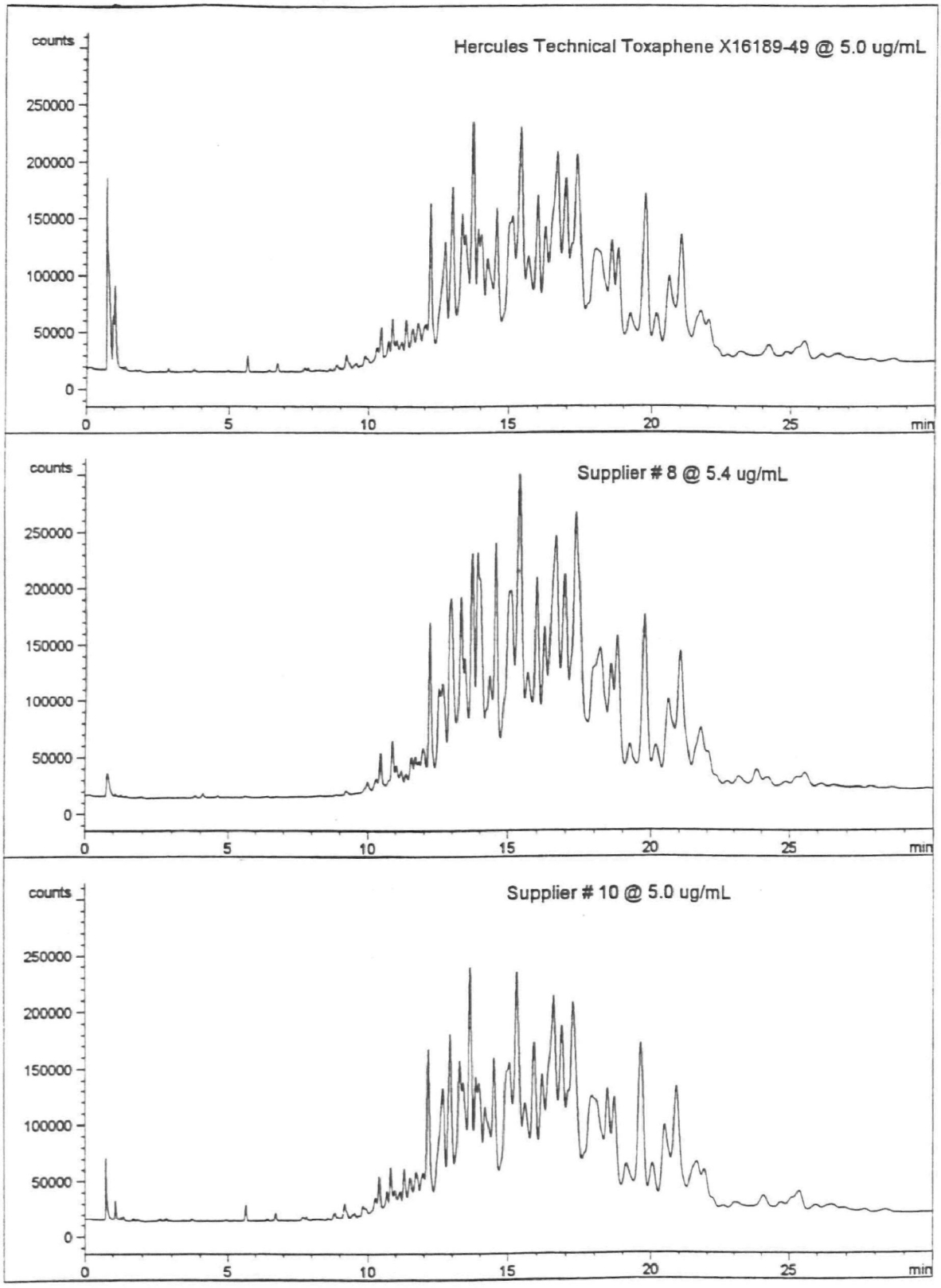
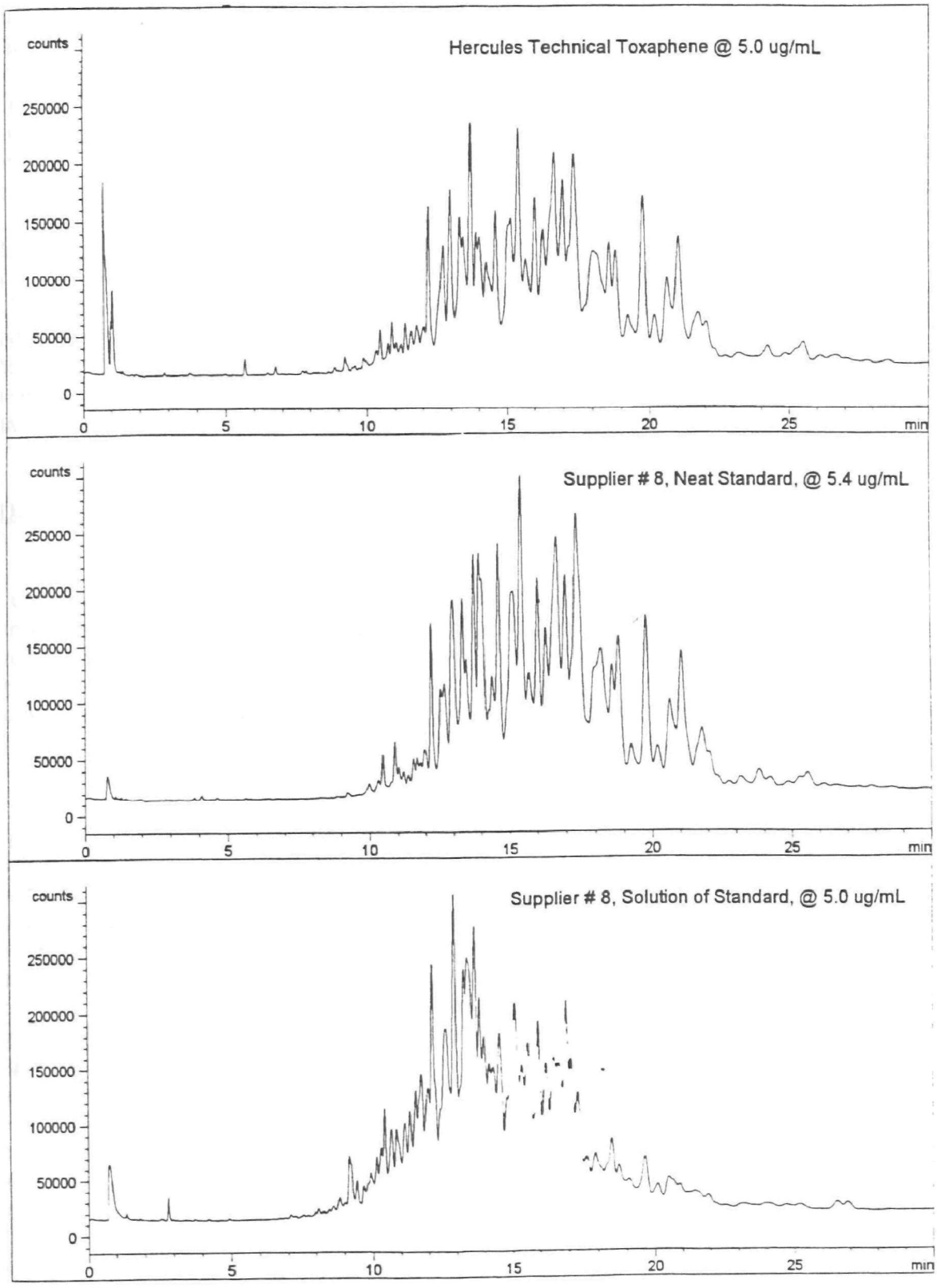


FIGURE 5 - DIFFERENCES BETWEEN TOXAPHENE STANDARDS FROM A SINGLE SUPPLIER.



GC/MS AUTOMATION TECHNIQUES FOR THE ENVIRONMENTAL CHEMIST

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ABSTRACT

Both semivolatile and volatile gas chromatograph/mass spectrometry (GC/MS) methods are automated with minimal financial and manpower investment through the use of automated intelligent sequencing procedures and spreadsheets. The amount of time required for sample analysis and data processing is greatly reduced thereby increasing operator efficiency and productivity. This increase in productivity translates into a reduction in per analysis cost.

INTRODUCTION

The environmental laboratory market has evolved from a large number of independent laboratories relying mostly on the quality of analytical data to attract and retain clients to a highly competitive arena with key players concerned about continuing pressure on cost and profitability. The quality of the data and sample turnaround are still of paramount importance, however, due to the larger proportion of corporate monies earmarked for environmental services, cost is and remains a deciding factor when choosing an environmental laboratory. To compete profitably, laboratory managers need to implement methods to increase productivity and thus reduce per analysis cost. The gas chromatograph/mass spectrometry (GC/MS) instrumentation is an integral part of the modern environmental laboratory and the GC/MS automation techniques discussed in this paper provide a method to improve the cost-effectiveness of the method and thus enhance the profitability of the laboratory.

PURPOSE

The daily activities of a GC/MS analyst in an environmental laboratory includes analyzing an endless backlog of samples and reviewing acquired data. In addition, many laboratories request their GC/MS departments to perform special analyses or to

adhere to specific customer demands, i.e., quick sample turnaround, creating an additional burden on an already overworked laboratory. To respond to these requests, the analyst must develop a working routine integrating efficient and maximum use of the GC/MS instrument with quick but thorough data review, qualification, and reporting. Automation procedures can significantly reduce analysis time, calculation and transcription errors, and project turnaround time. Toward this end, several automation procedures were developed using standard analytical laboratory GC/MS instrumentation and third party spreadsheet software.

Following sample extraction, GC/MS analysis of aqueous environmental samples falls into three major categories: 1) instrument analysis of sample extract, 2) data review and 3) data qualification / reporting. Automation of all these tasks is easily accomplished as described below using a method of semivolatile analysis to demonstrate and discuss intelligent sequencing and a volatile method to discuss data review and data qualification / reporting. The flexibility of these automation techniques is also portrayed.

PROCEDURE

The order of sample injection is automated by using intelligent sequencing, a fully automated procedure allowing the program to make logical decisions concerning instrument analysis of extracts. By employing supplied keywords in a sequence log table coupled with system macros, decisions can be made by the software concerning various aspects of instrument analysis of extracts, i.e., sample injection. The following are examples of the unique capabilities of the sequencing procedure.

Entry number one in the sequence log table (Example 1A) is the keyword SeedName, an automated sequential numbering system used either to prevent overwriting of data files upon reinjection or to allow a jump in the sequence. A brief format report of the sequence log is printed before analysis begins and a final sequence sample log is printed after analysis is completed to verify sample analysis. The second and third keywords in Example 1A are Reinject and On_Flag. These keywords are set to either a pass or fail flag by a system macro. The macro first analyzes the sample data and makes decisions based on sample type, i.e., standard, method blank or sample. The sample type is set to a numerical value that is recognized by the macro. After deciding the sample type, the macro checks the sample data based on criteria set by the user. If for example the macro decides that a sample does not meet the specified criteria, the macro sends a fail message to the sequence log table which then carries out the appropriate action defined by the keyword. On_Flag causes a jump in the sequence to the keyword Label which initiates a wash blank while Reinject directs the autosampler to reanalyze the sample.

This decision making process by the system macros is very useful when determining whether or not tuning compounds meet the specified criteria, an essential analytical consideration prior to sample analysis. When a decafluorotriphenylphosphine (DFTPP) tune sample is analyzed (number 4 on Example 1A), the instrument determines whether or not the collected data of DFTPP passes or fails the prescribed tuning criteria. If a pass condition exists, the analytical sequence continues. If a fail condition exists, the software determines whether or not the DFTPP sample is reanalyzed or a target tune procedure is performed . The target tune procedure retunes the GC/MS instrument, reanalyzes the calibration sample DFTPP and checks the response against the criteria.

After the DFTPP tune sample passes, a daily calibration check standard is injected. Again the system macros are employed to check if the daily calibration standard meets acceptance criteria. If a fail flag is passed to the sequence log table, the computer directs the autosampler to reinject the continuing calibration standard. If the daily calibration standard meets acceptance criteria, the response factors, compound retention times, and reference spectra is updated, printed and saved for sample quantitation and/or qualification. It should be noted that if the DFTPP or continuing calibration standard fails after reinjection, the sequence may either be halted, continued for use in sample screening or instructed to analyze an initial calibration curve.

Before the analysis of the method blank, the keyword DB_Start is used to inform the computer to start logging sample data to a spreadsheet (the keyword DB_End is self explanatory). The spreadsheet is used as a database to automatically plot control charts and is linked to other spreadsheets for data qualification. The analysis of a method blank is checked using the system macros for contamination of target compounds above the allowable limits, internal standard response, and surrogate recovery. If any of the acceptance criteria is not met, the method blank is either reinjected or a jump in the sequence occurs to the sample labeled wash blank. The wash blank is injected and analyzed for contamination above the allowable limits and is used to help clean up the system from a previous sample run and/or determine if any carryover exists from a previous injection.

Sample analysis is initiated after all the quality control samples have been injected, analyzed and checked for criteria acceptance. Samples are analyzed and scrutinized using the same criteria as the method blank discussed previously. If the acceptance criteria, i.e., surrogate recovery or internal standard response, is not passed, the sample may be reinjected or a wash blank analyzed before the next sample injection. LastRun in the sequence log table informs the macro that this is the last sample analyzed in this sequence and to log the data to the database and to send the control charts to the printer.

The intelligent sequence in this example was instructed to perform decisions concerning DFTPP, daily calibration, internal standard recovery, surrogate recovery, and saturation of the linear range of the initial calibration curve. The intelligent sequence routine is a powerful tool that can be used for more elaborate procedures as part of the sample analysis protocol of GC/MS laboratory automation process. For example, the intelligent sequence can be programmed to retune the instrument or reinject DFTPP every twelve hours for continuous operation.

The second and third part of the analysis of environmental samples deals with data review and qualification / reporting. The procedures that follow were developed using spreadsheets in combination with a personal computer based environmental software package. The procedures are tailored for environmental sample analysis however are adaptable to any laboratory procedure.

The first procedure performed using the spreadsheet generated from the analysis of the quality control and environmental samples is the QC Summary Report (Example 1B). The report is automatically printed at the conclusion of an analysis sequence. The QC summary report provides a quick review of important quality control criteria. For this example, surrogate recovery, internal standard area, internal standard retention time and injection time are checked for acceptable performance. The spreadsheet may be modified to criteria limits to meet unique laboratory specifications. Any data that fails to meet the analyst's specified limits is flagged indicating a problem with that particular run. Printouts of the QC summary report, tuning report, and continuing check standard report enable the analyst to determine instantly the status of the analysis. The QC Summary Sheet can also be used as documented proof of meeting acceptable QA/QC standards. Along with the QC Summary Report, control charts for surrogate recovery are also created and printed. Control charts (Example 1D) are essential for monitoring trends in instrument performance. QC summary sheets save the analyst considerable time and effort in sifting through data searching for retention times/injection times or performing menial calculations.

After user defined edits, i.e., false positive, the final automation procedure is used for the qualification and reporting of the sample data. As part of data qualification, the reporting limits are automatically corrected for sample dilutions. In the example spreadsheet 1C, the final report is qualified for sample concentrations detected lower than corrected reporting limits (J, QM) and non-detects (U). Procedures can also be designed to qualify data for variances in internal standard recovery, surrogate recovery, initial calibration %RSD, and continuing calibration percent difference (%D) acceptance criteria. The capability exists in the software for the batching of the data files for sequential data processing and generation of the final report. The report format and the qualification parameters may also be tailored to meet client specifications.

SUMMARY

Although the examples presented are simplistic, the limitations to automation are confined only by the extent of user knowledge of macro programming or the system commands available. More elaborate procedures are easily developed to perform complicated sequences with minimal operator interaction thus allowing the analyst to perform other functions in the laboratory or conduct the analysis unattended during nonworking hours. In addition, these procedures are adaptable to the determination of organic compounds in other matrices, e.g., soil/sediment.

The Hewlett-Packard 5972 GC/MS with EnviroQuant software (version C.01.00) and Microsoft Excel (version 5.0) was used in this study. Trade and company names are used for identification purposes only and do not imply endorsement by Lockheed Engineering Systems and Technologies or the U.S. EPA.

DISCLAIMER

This work has been funded in part by the United States Environmental Protection Agency contract 68D-10158 to Lockheed Environmental Systems and Technologies Company. The work does not necessarily reflect the views of the agency and no official endorsement should be inferred.

REFERENCES

Hewlett-Packard MS ChemStation User's Guide, Copyright 1993
Microsoft Excel User's Guide 1, Copyright 1992

EXAMPLE SEQUENCE LOG 1A

Sequence Name: C:\CHEM\1\SEQUENCE\SEQ1.S
Comments:
Operator:
Data Path: C:\CHEM\1\DATA
Pre-Seq Cmd:
Post-Seq Cmd:

Method Sections To Run	On A Bartcode Mismatch
(X) Full Method	(X) Inject Anyway
( ) Reprocessing Only	( ) Don't Inject

Line Type	Vial	DataFile	Method	Sample Name
1 SeedName	A00005			
2 Reinject	1 time			
3 On_Flag	Run_Blank			
4 DFTPP	1	--------	625	DFTPP Tune
Sample				
5 DailyCal	2	--------	625	Con Cal
Standard				
6 DB_Start	qcsummdb.xls			
7 Blank	3	--------	625	Method Blank
8 Sample	4	--------	625	Client Sample
9 Sample	5	--------	625	Client Sample
10 Sample	6	--------	625	Client Sample
11 LastRun	7	--------	625	Client Sample
12 DB_End	qcsummdb.xls			
13 End				
14 Label	Run_Blank			
15 Wash Blank	8	--------	625	Wash Blank
16 Return				

EXAMPLE 1B

QC SUMMARY SHEET

DATA FILE	SAMPLE NAME	1 st IS AREA	Q	2nd IS AREA	Q	3rd IS AREA	Q	1st IS RT	Q	2nd IS RT	3rd IS RT	1st SURR	Q	2nd SURR	Q	3rd SURR	Q	12HR CLOCK	Q
C00407.D	P-BFB																	4/19/96 9:24	
C00408.D	VSTD050	358302		1901181		1511658		9.17		10.90	16.19	98		99		98		4/19/96 9:44	
C00411.D	VBLK474	328282		1711740		1354532		9.20		10.93	16.21	108		106		103		4/19/96 11:18	
C00412.D	#096777	333139		1730779		1373301		9.22		10.96	16.24	107		106		104		4/19/96 11:49	
C00413.D	#096778	327207		1689684		1332769		9.21		10.95	16.24	107		107		104		4/19/96 12:21	
C00414.D	#096779	326421		1717440		1350506		9.19		10.93	16.23	107		107		103		4/19/96 12:52	
C00415.D	#096780	145556	#	1666246		1324785		9.70	#	10.96	16.25	135	#	106		105		4/19/96 23:24	#

1st IS = BROMOCHLOROMETHANE
2nd IS = 1,4-DICHLOROBENZENE
3rd IS = CHLOROBENZENE-D5

AREA UPPER LIMIT = +100% OF INTERNAL AREA
AREA LOWER LIMIT = - 50% OF INTERNAL AREA

1st SURR = 1,2-DICHLOROETHANE-D4 LIMITS= 76-114
2nd SURR = TOLUENE-D8 LIMITS= 88-110
3rd SURR = BROMOFLUOROBENZENE LIMITS= 86-115

INCORPORATION OF POLLUTION PREVENTION PRINCIPLES IN ENVIRONMENTAL METHODS

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ABSTRACT

The principles of pollution prevention (P^2) have not been sufficiently incorporated into analytical methods. In this paper, we focus on the needs for, the potential of, and the benefits of incorporating the principles of P^2 into environmental analytical methods. Although the amount of reagent used per experiment is often only a few milliliters, these small amounts can quickly add up, especially when they are aggregated across the entire research community. Effective P^2 requires operational or even fundamental changes in the techniques and methods employed. "End-of-pipe" recycling is not practical with small streams. The high potential for P^2 in the laboratory will be specifically illustrated with improvements in routine analytical techniques. Routine analytical methods for environmental and waste samples are quite prescriptive and often do not include the principles of waste minimization and P^2. Many methods require preparation of 100-fold or more excess sample for an instrumental determination. Many methods also use reagents that are not now considered "green."

We have adapted P^2 principles, along with other modern analytical approaches, to develop routine analytical methods that significantly reduce waste generation while they maintain acceptable analytical figures of merit and achieve cost savings through reduced reagent consumption *and* reduced labor costs. Results will be reported, and the significance of and need for incorporating P^2 into environmental methods will be discussed.

INTRODUCTION

The chemical industry has embraced and implemented P^2 practices over the past decade. Conversely, adoption by routine environmental laboratories has been slow because "regulatory standard methods must be followed." Adoption of P^2 practices is increasingly necessary for the environmental analytical community as regulations tighten, waste disposal costs escalate, and public scrutiny increases. It is incumbent on the analytical chemist to become less introverted and "to take a lead towards the preserving of our environment rather than to [merely] measure its deterioration" (de la Guardia and Ruzicka, 1995).

Regulatory approved analytical methods are quite prescriptive and often do not include principles of waste minimization and P^2. A classic example is the procedure currently approved and in use for the Toxicity Characteristic Leaching Procedure published in the *U.S. Code of Federal Regulations* (40 CFR Part 261, Appendix II, Method 1311 [SW-846]). This procedure tests materials for the leachability of toxic components. The approved procedure requires that a 100-g sample of the unknown be leached with a solvent 20 times its weight. This procedure generates 2 L of liquid waste, which becomes hazardous waste if any one of 40 inorganic or organic contaminants exceeds the established regulatory level. Add to this level any secondary waste associated with instrument calibration and quality control for the analysis, and the waste stream has multiplied over 20-fold. Only a small percentage of the sample generated in the previous scenario is actually used for the analysis. This example is by no means unique.

We are developing and demonstrating techniques for routine environmental analysis that incorporate P^2 principles. Here we report on the adaptation of commonly used routine methods published by the U.S. Environmental Protection Agency (EPA) for polychlorinated biphenyls (PCBs) in water, solids, and oils and for metals analyzed by inductively coupled plasma spectroscopy (ICP). Necessary practical techniques and methods for implementation in the routine environmental laboratory community have been considered.

RESULTS

Polychlorinated Biphenyls

Solvent substitution for PCB analysis can achieve comparable results and eliminate environmentally less-desirable solvents, as illustrated in Table 1. A wide variety of solvents are used as extractants (Erickson, 1986), generally without significant comparative evaluations among potential solvent systems. Technically acceptable solvents are those that yield quantitative extraction of the analyte (as measured by a spiked sample); solubility of the PCBs and wetting of the soil matrix are contributing factors to the efficacy of a solvent. Our results indicate that many common solvents or solvent mixtures can yield quantitative extractions.

Microscale extractions can cut the scale of the analysis by at least a factor of 10, as illustrated in Tables 2 and 3.

Matching sample to determination size requirements. We can better match the amount of sample used with the amount needed for the gas chromatographic (GC) determination step, as illustrated in Table 4.

Waste volume reduction. The volume of waste generated can be cut by at least a factor of 10, as shown in Tables 2 and 3. This reduction is increasingly important as we move toward full cost accounting, including waste disposal costs, in the analytical chemistry laboratory.

Table 1 — Solvent Recoveries Using Soxhlet Extraction in Soil

Extraction Solvent	Aroclor 1254
Hexane	101
Acetone	101
1:1 Hexane/Acetone	105
3:1 Hexane/Acetone	109
3:1 Acetone/Hexane	94
Methylene Chloride	89
1:1 Methylene Chloride/Acetone	104
9:1 Hexane/Methylene Chloride	99
10:1 Toluene/Methanol	101

Cost considerations. Costs are reduced significantly in apparatus, reagent consumption, and labor. The apparatus and reagent cost reductions are illustrated in Tables 2 and 3. The labor costs were not quantified but can be inferred directly from several rows of both tables. A cost impact will occur during the transition: new glassware will be purchased, method validation will require some overhead time (see next section), training will require some downtime, and some efficiencies will be seen only after a break-in period. Laboratories are advised to plan transitions such that they do not occur during a crisis period and to phase in changes in methods over a period of time.

Quality assurance. Any adaptation of a method requires some sort of internal validation. The changes discussed here are no different. Any laboratory adapting their routine methods to green/microscale techniques needs to validate the changes with the appropriate quality control samples to demonstrate that the laboratory is providing data of known and consistent quality. In addition, quality control measures need to be modified as necessary to clearly monitor the performance of the analyses.

Resource Conservation and Recovery Act Metals

The sensitivity and versatility of analytical instrumentation has improved dramatically over the last two decades. The mismatch between the size of the sample prepared in the laboratory (as required by regulatory accepted procedures) and that needed for the instrumental characterization is often different by a factor of 1,000 or greater. With this fact in mind, we attempted to adapt currently approved methods for analysis of Resource Conservation and Recovery Act (RCRA) metals in soils to microscale techniques. We used two different methods of acid digestion, three different methods for sample introduction, and two different analytical instruments to investigate whether smaller samples can be used for environmental characterization of soils without a loss of precision or accuracy.

Table 2 — Comparisons of Soxhlet, Micro Soxhlet, and Shakeout Procedures

Parameters	Soxhlet	Micro Soxhlet	Shakeout
Sample Size (g)	10	1	0.5
Sodium Sulfate Used (g)	10	1	0.5
Extraction Solvent Volume (mL)	300	15	15[a]
Extraction Time	16-24 hr	5 hr	15 min
Concentration Technique	Kuderna-Danish	Nitrogen Blowdown	Nitrogen Blowdown
Concentration Time (min)	10-20	10 - 20	10 - 20
Florisil Used for Cleanup (g)	20	1	1
Solvent Used for Cleanup	Methylene Chloride	Hexane	Hexane
Final Concentration Volume (mL)	10	1	1
Waste Volume (mL)[b]	610	25	24
Apparatus Cost ($)[c]	2.50	1.40	0.19
Reagent Cost ($)[d]	12.76	2.76	2.76

[a]The 15 mL consisted of three 5-mL extractions, each lasting 5 min.

[b]Assumes no recycling at this point; does not include gloves and other ancillary waste.

[c]Based on manufacturer's catalog prices or actual purchase requisitions. Soxhlet and micro Soxhlet amortized over 100 uses (i.e., Soxhlet investment = $250).

[d]Based on manufacturer's catalog prices or actual purchase requisitions; assumes complete consumption of amount purchased for sodium sulfate, Florisil, and solvent.

Table 3 — Florisil Extraction of PCBs from Motor Oil: Macroscale and Microscale Solid Phase Extraction (SPE)

Reagent	Macroscale	Microscale
Florisil (g)	20	1
Hexane (mL)	280	25
Oil Sample (g)	1.5	0.2
TOTAL WASTE (mL)[a]	~ 300	~ 26
Time (min)		
Dilution/Cleanup	120	20
Eluate Concentration[b]	50	50
GC Analysis Time	45	45
TOTAL	215	115
Cost ($)		
Florisil	2.61	2.37 (SPE syringe)
Hexane	3.28	.29
Apparatus[c]	0.52	-
TOTAL[d]	6.41	2.66
Yield		
% Yield	100	100

[a]Assumes no recycling; does not include gloves and other ancillary waste.

[b]Nitrogen blowdown technique used for concentration of eluate. Time required is based on volume of solvent evaporated.

[c]Glass chromatography column with reservoir amortized over 100 uses (i.e., column investment = $52) for the macroscale procedure. Microscale requires no comparable apparatus.

[d]Based on manufacturer's catalog prices or actual purchase requisitions; assumes complete consumption of amount purchased.

Table 4 — Scaling Chemistries to What Is Needed for the Determination Step (PCB Example)

Problem	Solution	Result
1 µL/injection	Use of an internal recovery standard	Smaller initial sample
Currently 10^3 to 10^4 of sample injected	Final (small) inexact volume compensated	Fewer reagents

To better match sample size with the instrumental requirements, we evaluated the use of microscale techniques to adapt currently approved methods for analysis of RCRA metals in soils. We used two different analytical instruments that are currently approved for environmental characterization of the metal content of soils: (1) the inductively coupled plasma atomic emission spectrometer (ICP/AES) and (2) the inductively coupled plasma mass spectrometer (ICP/MS). We chose these instruments because they are capable of multielement analysis on the same sample. We modeled our analysis after regulatory approved analytical methods that exist for both of these instruments (*method 6010A and method 6020* in *Test Methods for Evaluating Solid Waste,* EPA document SW-846 [EPA, 1994]). We also used two different acid digestion methods that are approved for use with these instrumental methods: (1) method 3050A (hot-plate digestion using nitric and hydrochloric acid and hydrogen peroxide); and (2) method 3051 (microwave-assisted digestion using nitric acid alone). Finally, we used pneumatic nebulization (PN), ultrasonic nebulization (USN), and direct-injection nebulization (DIN) as techniques for sample introduction to investigate efficiency for the combinations of instrument, digestion method, and technique of sample introduction.

We digested progressively smaller soil aliquots in the range of 2.0 to 0.1 g by using both acid digestion methods and analyzed these solutions for the RCRA elements that are approved for each individual method. The precision and accuracy of the analysis, the cost, the volume of secondary waste produced, a term for instrumental versatility (ratio of analytes analyzed to analytes needed for analysis), and the initial sample weight required were used to estimate and qualify the various methods tested.

The elemental recovery obtained from 2.0 g samples by using hot-plate digestion and ICP/AES were 85% to 99% for elements such as Pb, As, Cd, Cr, and Ag. Samples under 2.0 g were not analyzed by this procedure due to the concentrations of many of the elements studied. With the exception of Pb and Ba, concentrations for other elements were closed to instrumental detection limits.

By using ICP/MS, samples of 0.1 g, 0.25 g, and 0.5 g were digested by hot-plate and microwave digestion procedures. For most elements, the results showed statistically equal recoveries when both digestion procedures were used. Percent recoveries of mercury were highly variable. Barium showed low percent recoveries with both digestion techniques, and the percent recovery of silver was better when the hot-plate digestion procedure was used. In general, microwave digestion procedures should yield higher percent recoveries for most elements compared with the hot-plate digestions.

In addition to sample digestion procedures, PN, DIN, and USN were studied as sample introduction techniques. Each sample introduction technique was evaluated in terms of sample uptake, method detection limits, and time required per analysis. These parameters were considered as part of the overall qualifications of the method.

The general trend observed was that the effectiveness of the method increases as the sample size decreases. Smaller samples produce less secondary waste, reduce the quantity of hazardous chemicals used, and lower the overall cost of the analysis. The conclusions presented here are based upon analysis by ICP/AES and ICP/MS using PN, DIN, and USN; however, sample introduction by electrothermal vaporization was not addressed during this study. The cost savings are directly proportional to the reduction in waste volume generated.

General Results

Regulatory considerations. Analyses for PCBs are most often conducted to comply with regulatory guidance under several statutes, notably the Toxic Substances Control Act (TSCA). Except in specific instances, TSCA rules do not specify the analytical methods to be used. Because of this fact, dozens of standard methods have been issued (Erickson, 1986). Among the more broadly applied is the EPA's manual, *Test Methods for Evaluating Solid Waste* (EPA, 1986; and any newer updates, editions, or revisions), which has document number SW-846 and is commonly referenced by that alphanumeric shorthand. This multivolume document contains methods to be applied under the RCRA but is widely applied beyond the regulatory requirements. For most applications, SW-846 is a guidance document, and **analyses using reasonable adaptations of the published procedures are permitted.** Except for four specific federal applications and any imposed by states or other authorities, the manual is a "guidance document setting forth acceptable, though not required, methods to be implemented by the user, as appropriate, in responding to RCRA-related sampling and analysis requirements" (58 FR 46041, August 31, 1993), and "any reliable analytical method may be used to meet other requirements under Subtitle C of RCRA" (abstract of SW-846, Revision 1, July 1992). Lesnik (1992) clearly amplifies this by stating that "the manual is intended to be a collection of flexible methods, suitable for adaptation to cover the wide range of analytical applications and matrices required by the RCRA regulations. ... Examples of this flexibility include adjusting sample sizes to fit the optimum analytical range of methods, or using alternate glassware or equipment provided that method performance is not compromised." The disclaimer in the manual states that "SW-846 methods are designed to be used with equipment from any manufacturer that results in suitable method performance (as assessed by accuracy, precision, detection limits, and matrix compatibility)" (disclaimer of SW-846, Revision 0, July 1992). Similar text is found in Chapter 2 (Section 2.1.2, Rev. 2, November 1992): "... glassware and supplies ... specified in these methods *may be replaced by any similar types* as long as this substitution does not affect the overall quality of the analyses" [emphasis added]. Thus, contrary to the beliefs of many of those requesting or conducting analyses, PCB analysis according to verbatim SW-846 procedures is not required for many applications, and reasonable adaptations are permitted.

CONCLUSIONS

We have demonstrated that P^2 can pay off in the laboratory through the adaptation of commonly used routine EPA methods for soils and oils. We have developed miniature extractions and cleanups feeding into standard GC analysis for PCBs and demonstrated that smaller sample sizes are preferable for RCRA metals. The "green chemistries" applied include:

- Smaller sample sizes that match the instrumental consumption needs,
- Substitute solvents,
- Minimization of reagent consumption,
- Reduction of apparatus costs with microscale glassware, and
- Reduction of energy consumption.

The methods developed here have direct applicability to the routine PCB and RCRA metal analysis laboratory. The applications presented here can be applied now without awaiting regulatory approval.

The results reported here are but a few steps along the path toward implementing P^2 in the routine analytical chemistry. Much more remains to be done.

ACKNOWLEDGMENTS

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CONTRACT LABORATORY PROGRAM (CLP) 2000 - A MODEL FOR PROVIDING SUPERFUND ANALYTICAL SERVICES INTO THE NEXT MILLENNIA

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Abstract

With the impending reauthorization of Superfund, two themes have been prevalent throughout public debate. These are: 1) the acceleration of the site cleanup process and 2) providing a better link between the site cleanup activities and the risk to the public. By increasing the focus on these two areas of concern, the EPA not only protects the public health and but can speed up the economic recovery of the areas surrounding these sites including the "brownfield" sites located in urban areas. These concepts can also be applied outside the context of Superfund to the Department of Defense's base realignment and closure (BRAC) program and to initiatives at the cleanup of the Department of Energy's laboratory complexes. However, in order to accomplish these goals, access to a reliable source for obtaining the levels and types of contamination at these sites in a cost effective and timely manner must be first be identified. While many new improvements to existing field methods are being implemented, these procedures are still not as reliable as those that can be provided by fixed off-site laboratories.

The Contract Laboratory Program (CLP) has been providing EPA users data of known and documented quality to support Superfund site inspection, remedial, removal and enforcement activities since 1980. During this time, approximately two million environmental samples have been analyzed through this program. The CLP provides a community of commercial environmental laboratories that perform a variety of chemical analyses to identify the levels and types of contamination at these Superfund sites. The CLP is also supported by an infrastructure consisting of technical EPA staff, procurement officials and support contractors for quality assurance and tracking support.

This paper discusses why the centralized functions provided by the CLP is the most appropriate mechanism for ensuring that reliable analytical data can continually be obtained to support Superfund into the next century. It discusses the overall structure of the CLP, the services it currently provides and the benefits the CLP can provide data users in the areas of cost-effective analytical services, data management and quality assurance. It discusses several modifications to the program which can be quickly implemented to enhance the effectiveness of these services in terms of the delivery of analytical services, the electronic delivery of data, data review, and communication. This paper also discusses the potential advantages to EPA by providing CLP services to other government agencies. Data supporting this paper are obtained from the results of various internal program reports and reports generated by outside organizations (i.e., GAO, OIG, etc.).

HANDLING NONLINEAR CALIBRATION PLOTS

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ABSTRACT

There are well known analyte, matrix and instrumental deviations from Beer's Law for absorbance vs concentration calibration plots. If a nonlinear calibration plot is obtained during method development or method validation, then the validity of the plot must be verified. It must be established that the plot is 1) reproducible, 2) is not an anomaly of standard preparation, and 3) accurately represents the behavior of the analyte within the matrix of interest. Once these criteria have been met, then nonlinear functional forms can be used to analyze the absorbance vs concentration relationship. Common functional dependencies include quadratic and exponential fits. Alternative functional forms are presented including the tools necessary to obtain an R_2 fit in order to meet Quality Assurance criteria. If there are more than two adjustable parameters in the functional form of the calibration plot, then this must be accompanied by an increase in the number of standards used in the calibration.

INTRODUCTION

It is accepted practice to use a curve and not restrict analysis to the linear range as long as standards bracket all sample concentrations and there are enough standards such that the curve is well characterized. R^2 fits are then based on the fit to the curve rather than a line. Increasingly, instruments are computerized and have built in regression capabilities for calibration curves. What happens if a reproducible relationship between absorbance and concentration for standards is not consistent with the instrument's curve fitting software?

First, troubleshooting must be done to explore the possible sources of the atypical calibration curve. Aspects of standard preparation which may contribute to the atypical calibration curve must be investigated. This may result in a typical calibration curve.

Second, if these investigations do not produce a typical calibration curve, then other mathematical models may be more appropriate. Many instruments use a quadratic function to fit absorbance calibration curves. Alternative equations will be provided which include an "S-curve" fit.

TROUBLESHOOTING NONLINEAR CALIBRATION CURVES

When performing an analysis which is new to the analyst, there is much to learn about the method of analysis, the analyte, and the matrix of the analyte. Clearly, analytical methods are developed which take into account the nature of each analyte. If adapting a method to an analyte, the method must be validated even if the analyte is chemically very similar to species for which the method was developed. An entire method validation is beyond the scope of this paper. This discussion will be limited to calibration plots.

Figure 1 provides an example of an atypical calibration curve. This figure illustrates a flame atomic absorption calibration plot for cadmium in water. The relationship between absorbance and concentration is not well represented by either a linear or a quadratic function. The absorbance readings of the low concentration standards fall well below those expected in a typical calibration plot. If it is determined that such a profile is reproducible, then an investigation of possible causes of such an atypical calibration curve would be necessary.

The first possible cause to consider is the volumetric glassware and dilution scheme used in the preparation of the low concentration standards. These same concentrations can be prepared by using an intermediate stock in order to verify that the standards are of the reported concentration. If the results are consistent with the atypical curve then other considerations must be investigated.

A calibration curve must accurately represent the response of the instrument to the analyte within the matrix of interest in order to provide quantitative results. The Standard Addition Method can be used to test the concentration dependence of the analyte absorbance within the sample matrix. Figure 2 clearly demonstrates that the atypical calibration curve in Figure 1 must be an anomaly of standard preparation. The absorbance vs concentration plot for cadmium within the sample matrix is a straight line.

Figure 3 is also a calibration plot for cadmium in water. The only difference in the preparation of this set of standards and those in Figure 1 is that the standards were diluted to the mark with 3% nitric acid rather than with water. Since the cadmium was dissolved in acid in order to prepare the stock solution, the low concentration standards demonstrate the effect of not only the dilution of the analyte, but also the dilution of the acid concentration. Diluting with nitric

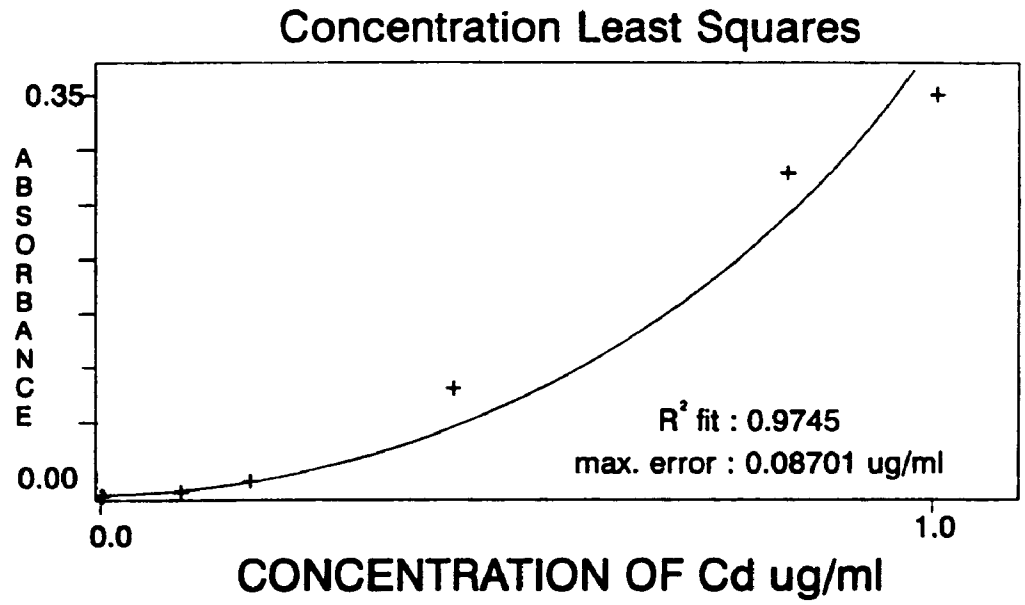

FIGURE 1: Flame Atomic Absorption calibration curve for cadmium. The standards were prepared by dilution with reagent grade water.

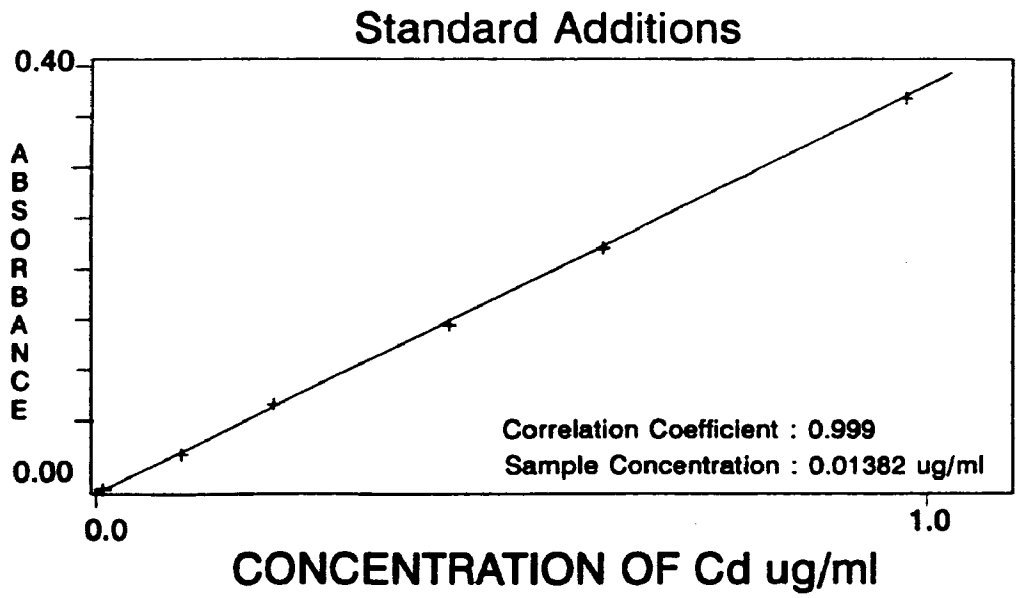

FIGURE 2: Flame Atomic Absorption calibration plot for cadmium using the standard additions method.

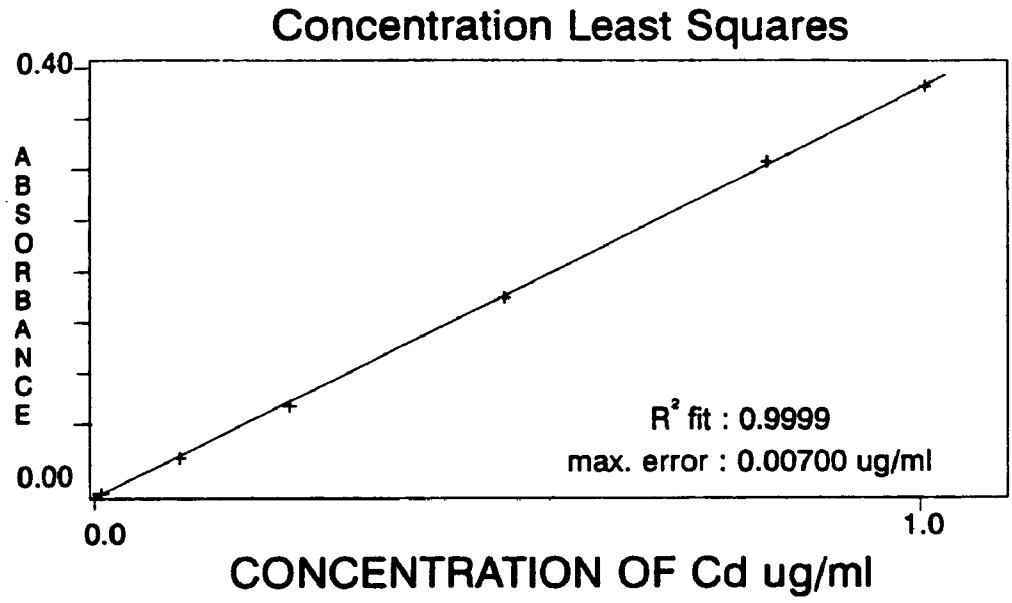

FIGURE 3: Flame Atomic Absorption calibration plot for cadmium. Standards were prepared by dilution with 3% nitric acid.

acid maintains a near constant acid concentration for all of the standards and also matches the concentration of acid in the samples resulting from the digestion procedure.

The comparison of Figures 1 and 3 provides a vivid reminder that standards must be identical in every respect except concentration of analyte. The effect of acid dilution is not as pronounced with other metals as it is with cadmium. This is a reminder of the unique interactions of each analyte.

MATHEMATICAL MODELS FOR NONLINEAR CALIBRATION CURVES

Some calibration plots which can be validated are not linear. Many computerized instruments now come with data fitting and regression analysis capability. Typically, a quadratic function is used for the data fit, in which case, a linear relationship simply determines a coefficient of zero for x^2.

Use of a quadratic model requires a greater number of standards to adequately characterize the calibration curve. Standard Methods[1] states that for atomic absorption analysis of metals a calibration curve should be "composed of a blank and three or more standards (depending on instrumentation)..." Three standards and a blank, or four points, is the minimum needed to determine a <u>linear</u> relationship. Since a line can

be placed through any two points, four points would provide only two additional points for the regression analysis.

A quadratic curve can be placed through any three points. Therefore, a calibration plot with only four points would not adequately determine the regression curve. Five standards plus a blank, or six points, are needed to obtain a good calibration curve using a quadratic model, or any model with three adjustable parameters.

The most common regression analysis, or determination of an R^2 fit, is based on a linear model. The least squares fit to data is the most familiar approach. A regression analysis of a quadratic curve can also be done by least squares when the equation is transformed to a linear form[2]. The quadratic equation

$$Y = a_0 + b_1(X - \bar{X}) + b_2(X - \bar{X})^2 \qquad \text{Eq. 1}$$

can be transformed with the relationships $X_1 = X - \bar{X}$, and $X_2 = (X - \bar{X})^2$, into the linear equation

$$Y = a_0 + b_1X_1 + b_2X_2 \,. \qquad \text{Eq. 2}$$

Equation 2 is now in the form of a multiple regression equation, and an R^2 fit can be obtained for the transformed equation.

A variety of other mathematical models can also be treated in the standard linear form using multiple regression by a suitable transformation of the variables[3]. For example, an exponential model of the form

$$Y = e^{b_0 + b_1 X_1 + b_2 X_2} \qquad \text{Eq. 3}$$

can be transformed to a linear model by taking the natural logarithms of both sides. This results in

$$\ln Y = b_0 + b_1X_1 + b_2X_2 \qquad \text{Eq. 4}$$

The residuals which result from a regression analysis such as this are for the transformed responses, not the original instrument responses.

As was seen in Figure 1, a curve may not be adequately fitted by the curve fitting software which comes with the instrument. Figure 1 represents an anomalous calibration plot which has distinctive "s-shaped" character.

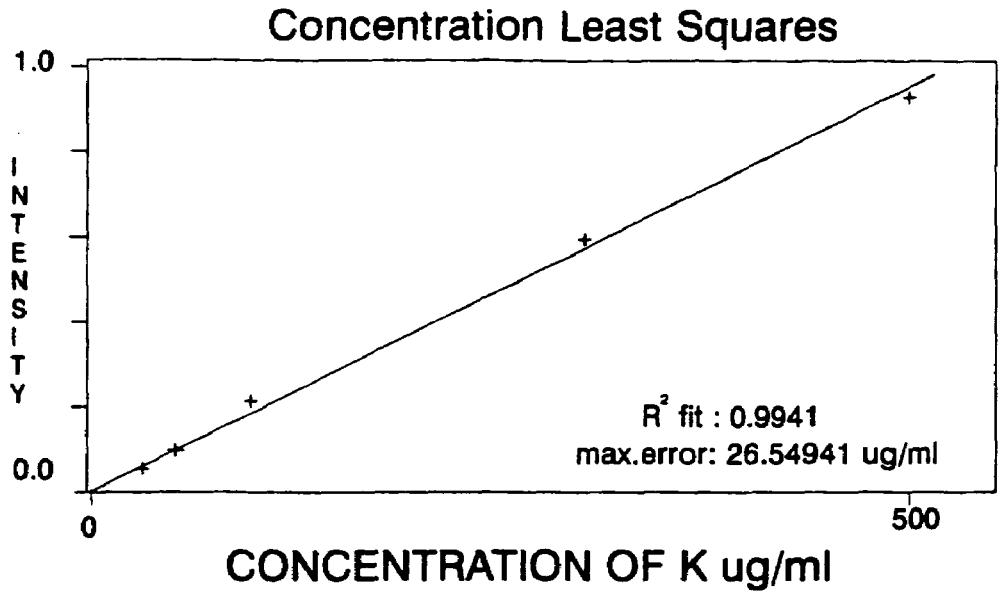

FIGURE 4: Flame Atomic Emission Calibration plot for high concentrations of potassium.

Figure 4 illustrates an actual calibration plot which has some s-type shape to the curve. It is not nearly as pronounced as that in Figure 1. The shape of the K calibration plot is attributed to effects of ionization and self-absorption[4]. This particular calibration plot has the best fit using a quadratic model. However, s-type curves can also be fit using a model which can be transformed to a linear equation.

The mathematical model which exhibits an s-type shape is given by the equation

$$Y = aX^2/(X^2 + b) \qquad \text{Eq. 5}$$

This equation involves only two adjustable parameters. A third parameter can be introduced for the coefficient of X^2 in the denominator, however, when the equation is transformed to a linear model, only two parameters can be solved for independently. The transformation requires taking the reciprocal of both sides of Eq. 5. This transformation requires a positive value for the blank as it is undefined when Y=0. The transformation of Eq. 5 to linear form requires first taking the reciprocal of both sides.

$$1/Y = (X^2 + b)/(aX^2) = 1/a + b/(aX^2) \qquad \text{Eq. 6}$$

Setting $X^1 = X^2$, the transformed linear equation is

$$1/Y = 1/a + b/(aX_1) \qquad \text{Eq. 7}$$

Since this transformed linear equation has only two adjustable parameters, a and b, it has the same requirements for the number of standards as a linear fit.

SUMMARY

In conclusion, nonlinear calibration plots can be justified, however, it must be validated that they accurately represent the response of the instrument to the analyte within the matrix of interest. If a nonlinear calibration is used, then it may require a greater number of standards to provide a good calibration. Five standards plus a blank are needed for functional forms with three adjustable parameters. Instruments typically use a quadratic fit when the data is not linear. This is adequate for most applications, however, additional mathematical models, an exponential and an s-type curve, have been presented. These mathematical models can be transformed to a linear equation which fits the form of a standard multiple regression.

ACKNOWLEDGEMENTS

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Comparability of Commercial Environmental Reference Standards

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Abstract:

It is widely recognized that commercial environmental reference standards vary considerably from manufacturer to manufacturer. Because of this, laboratories are forced to purchase multiple versions of a similar products from different vendors and prove that they are equivalent, yet independent, standards. This added laboratory cost is perceived as a necessary burden practiced to meet the quality assurance requirements of SW-846 and other regulatory methods. While costs differ considerably from laboratory to laboratory, eliminating the costs of useless standards inventory and non-revenue generating testing is beneficial to any laboratory operating in today's soft economic climate.

One approach which will minimize the need to repeatedly purchase similar products from multiple vendors, thus reducing the level of non-revenue generating testing, involves intervendor comparison of standards by commercial producers before sale. However, it has historically proved difficult to bring competing manufacturers together to accomplish this goal. Subsequently, existing sources of commercial reference standards are different enough to drive the need for additional testing on the part of the laboratory.

This paper reviews comparability between two commercial environmental standards vendors. Presented are the results of a several month project designed to establish and perpetuate comparability between two commercial environmental standards sources. Comparability of two commercial sources of standards by compound class and the variability across product lines will be discussed. Data are to be presented illustrating the degree to which environmental standards from independent commercial different vendors match and do not match. The presentation will present a recommendation on how commercial vendors may cooperate to minimize the cost to commercial laboratories consuming environmental standards through incorporation of Reciprocal Data Review in to product quality assurance programs.

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IMPROPER USE OF SIGNIFICANT FIGURES AND NUMBER ROUNDING BY LIMS JEOPARDIZES CHEMICAL DATA USABILITY

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ABSTRACT

Chemical data usability is inherently based on the proper usage of significant figures and the application of the principles of number rounding. When a Laboratory Information Management System (LIMS) is commissioned or modified, particular attention must be paid that all calculations that generate data take into account the cardinal rules of significant number usage in mathematical operations. Figures reported in the Quality Control Data section of a Sample Delivery Group (SDG) must allow for the verification of the calculated percent recovery and relative percent difference (RPD) values, without triggering an on-site raw data audit. The paper compares the way several different analytical laboratories report identical data for chemical analyses; it discusses recent occurrences of jeopardized data during the calculation of spike and surrogate percent recoveries. Since modification of the LIMS system is onerous once the system is in place and processing data, it is suggested that laboratory management can avoid the expense and embarrassment of hand entering the correct data and issuing replacement SDG pages by exercising strict up-front quality control on the first sample SDG generated by the new or modified LIMS system. The laboratory's credibility is jeopardized when no action is taken even after the client alerts the proper quality assurance personnel. It is proposed that continuous trend analysis of SDGs being produced for various clients and programs be used as a means of ensuring that the LIMS system and its programmers do not deviate in their proper usage of significant figures.

INTRODUCTION

All laboratories use a form of Laboratory Information Management System (LIMS) to collect and manage data. There is a proliferation of operating system and application softwares, database management systems, automated data collection and processing instrumentation. A LIMS system makes use of all of these in a plethora of available configurations based on the specific needs of the laboratory. The U.S. Environmental Protection Agency (EPA) defines the LIMS as an automated laboratory system where the user has *"the ability to effect changes to original observations or measurements."*[1] Historically LIMS systems were created for the manufacturing industry, not to collect and process data from environmental laboratories. Most laboratories purchasing a LIMS, had to custom program it to handle a number of very important processes such as calculations, number rounding, proper use of significant figures, *etc.* These functions do not come in prepackaged versions. For a laboratory using an older system, the programming becomes a major undertaking since the system may have "maxed out" and may not be able to accept so many new codes. Besides managing data the LIMS is also used to generate data reports, a.k.a. Sample Delivery Groups (SDG). Koller and Liesegang recognized as early as 1993 that the LIMS was limited in its ability to handle significant figures; the data management systems did not have the calculation capabilities that laboratory instrumentation had.[2] Industry sources claim that as recently as two years ago LIMS systems addressed decimal figures only and were not programmed to tackle significant figures [3]

SIGNIFICANT FIGURES AND ROUNDING OFF NUMBERS

Since every measurement involves an estimate, numbers resulting from measurement are qualified as *not exact*, while numbers that can be counted are considered to be *exact* numbers, *e.g.*, the number of pages in a book, the number of people in a room.

When a competent person makes a measurement, the last digit of the measured number is considered to be a *best estimate*. If further experiments or measurements were conducted this digit is the one that might change. All the other digits of the measured number will not change. Such a number contains only *significant figures*, including the last estimated digit. An *exact* number is one with unlimited significant figures.[4,5,6,7]

The number of significant figures that one uses for a chemical measurement is detemined by the uncertainty inherent in the equipment and instrumentation used to obtain the measurement. Although modern electronic instrumentation and computers may use a bewildering array of digits in their automated calculations, it is an axiom of analytical chemistry that analytical results can be only as accurate as the information that leads to them. The use of digits beyond the acceptable number of significant figures is unnecessary. Hence the need for the proper rounding of significant figures.

Accuracy of a measurement indicates how close the latter is to the correct value, while *precision* indicates how close are the measurements to each other. Highly accurate measurements can not be imprecise, although highly precise measurements can be inaccurate. In both instances the role of proper rounding of significant figures can not be underemphasized. *Accuracy* and *precision* are numerically dependent on the number of significant figures used in the calculations and the manner in which they are rounded off.

RULES OF USAGE

The following are the simple and well-known rules of usage of significant figures and for rounding off of measurements:[4,6,7]

1. Zeroes used to position the decimal point are not significant figures, *e.g.*, 0.000123 contains only three significant figures; it could also be written as 1.23×10^{-4}.
2. Zeroes to the right of digits are considered significant figures when a decimal point is placed after the number, *e.g.*, 120. contains three significant figures, while 120.00 contains five significant figures.
3. The answers of multiplication and division operations can contain no more significant figures than the least number of significant figures used in the operation. For example, a 20 ug/L spike contains one significant figure, its recovery of 24 ug/L contains two significant figures. The percent recovery can not be expressed as $\frac{24}{20} x100 = 120\,\%$, since 120 contains *two* significant figures. Unless 20 is expressed as 20. or 20.0 the answer should be rounded off to 100% with a significant loss of information.

4. In addition and subtraction the number of significant figures in the answer is determined by the *least* number of figures to either the right or left of the decimal point.[6]
5. During complex calculations involving multiplication or division and addition or subtraction, the operations are performed serially, and the final result is rounded off to the least number of significant figures involved.[6]
6. During rounding off when 6, 7, 8, or 9 is dropped, the preceding digit is increased by one unit; if the digit 0, 1, 2, 3, or 4 is dropped the preceding digit is not altered. If the digit 5 is dropped, the preceding digit is rounded off to the nearest even number. While 4.45 becomes 4.4, 4.55 is rounded to 4.6.[7]
7. When a group of two or more figures is to the right of the last significant figure, the number is considered as a group, such as in 3.4(503) the 503 is considered >5, while in 3.4(498) the 498 is considered to be <5. This is a very important consideration to remember while programming your new LIMS.

DISCUSSION

The EPA clearly mandates that "*computer programs used for data reduction should be validated before use and verified on a regular basis*", and that "*analytical results (be) reported with an appropriate number of significant figures*".[8] Acceptance criteria for the upper control limits for surrogate and spike recoveries in Laboratory Control Samples (LCS) and Matrix Spike and Matrix Spike Duplicates (MS/MSD) are expressed in three significant figures; therefore all calculations that result in numbers that are compared to these limits should always have at least three significant figures.

The EPA started the trend of disregarding the usage rules of significant figures by lackadaisically suggesting "spike with 20 ug/L," or proposing control limits with a mixed number of significant figures, *e.g.* 80-120%, or ±30% (1). Unfortunately this approach still continues to plague the analytical community, the most recent example being the brand new February 1996 version of the Air Force Center for Environmental Excellence (AFCEE) Quality Assurance Project Plan.[9]

An SDG should contain enough information to allow the user to calculate the reported values, such as percent recovery and relative percent differences (RPD), from the data provided. This includes reporting the actual spiking concentrations and the recovered concentrations. Anything less invalidates the data, is not legally defensible, and, of course, triggers a raw data audit. Even greater confusion and consternation will result in a few years' time when the archived raw data are not available anymore.

Most laboratories conscientiously use an adequate number of significant figures in their calculations of surrogate and spike recoveries. However a nationally known midwestern laboratory(KP) submitted voluminous data similar to the ones reported in Tables I and II, as recently as December 1995. The SDGs carried the following misleading disclaimer: "*The Quality Control Sample Final Results listed above have been rounded to reflect an appropriate number of significant figures. Consistent with EPA guidelines unrounded concentrations have been used to calculate % Rec and RPD values*". Upon closer scrutiny it was discovered that similar inconsistencies in the reported results affected the LCS and MS/MSD results of almost all the analytical methods under consideration, *i.e.*, total petroleum hydrocarbons (diesel/gasoline),

pesticides and polychlorinated biphenyls (8080), volatile organics (601 and 8260-modified list), semivolatile organics (8270), metals, *etc*. The laboratory's LIMS used up to six digits (not all of them significant figures) to calculate the *percent* spike and surrogate recoveries, which were then consistent with the raw data. However the same LIMS reported the spike and surrogate values and their recovered values after rounding them off to two significant figures, resulting in the discrepancies noted. in Tables I and II. For example, the diesel MS/MSD spike recoveries in Table II are both reported as 12 mg/kg but the RPD is reported as 6%, because the LIMS calculates the RPD based on the percent recoveries - otherwise the RPD will be 0%. When the laboratory

Table I
Quality Control Data for Laboratory Control Sample (Method 8260/Water)
KP Laboratory (Midwest US)

Parameter	Spike Conc. ug/L	LCS Result ug/L	Lab Reported Spike % Recovery	Client Calculated Spike % Recovery
Chloromethane	20	19	96	95
Bromomethane	20	17	84	85
Vinyl Chloride	20	17	87	85
Chloroethane	20	17	86	85
Methylene Chloride	20	19	97	95
Acetone	20	17	87	85
1,1-Dichloroethene	20	17	86	85
1,1-Dichloroethane	20	18	88	90
trans-1,2-Dichloroethene	20	17	84	85
Chloroform	20	17	84	85
1,2-Dichloroethane	20	15	77	75
2-Butanone	20	24	119	120
1,1,1-Trichloroethane	20	17	87	85
Carbon Tetrachloride	20	16	82	80
Bromodichloromethane	20	18	92	90
1,2-Dichloropropane	20	19	94	95
trans-1,3-Dichloropropene	20	17	85	
Trichloroethene	20	18	92	90
Dibromochloromethane	20	18	88	90
1,1,2-Trichloroethane	20	19	93	95
Benzene	20	20	100	
cis-1,3-Dichloropropene	20	17	87	85
Bromoform	20	18	89	90
4-Methyl-2-Pentanone	20	23	117	115
Tetrachloroethene	20	17	87	85
1,1,2,2-Tetrachloroethane	20	21	103	105
Toluene	20	20	98	100
Chlorobenzene	20	18	88	90
Ethyl Benzene	20	17	86	85
Styrene	20	18	88	90
Xylenes (total)	60	52	87	
1,2-Dichlorethane-d4 (S)	No datum	No datum	87	
Toluene-d8 (S)	No datum	No datum	106	
4-Bromofluorobenzene (S)	No datum	No datum	102	

programmed its LIMS to take into account three significant figures, the MS and MSD percent recoveries became consistent with the reported values. It also became obvious that the RPD must be calculated from the *actual recovery values* rather than using already rounded percent recoveries.

Table II
Matrix Spike/Matrix Spike Duplicate Recoveries and RPD for Diesel Fuel (Method OA2/soil)
Using Two and **Three** Significant Figures

Spike Conc. mg/kg	MS result X_1 mg/kg	MS Spike % Rec.	MSD result X_2 mg/kg	MSD Spike % Recovery	Lab RPD from % Rec.	Calculated RPD from X_1 and X_2
17	12	70	12	74	6	0
16.5	**11.6**	**70**	**12.2**	**74**	**6**	**5**

The laboratory had failed to exercise adequate quality control on its products because it considered this practice acceptable. This was compared to SDGs from seven nationally known laboratories as shown in Table III. The majority used an adequate number of significant figures in their reports and calculations. The DC laboratory even reported all *acceptance limits* with six significant figures. CTI on the Pacific Coast used only two significant figures and yet the reported percent recovery and RPD were consistently justified.

Table III
Number of Significant Figures Used in LCS and MS/MSD Percent Recovery Reports
by Various US Laboratories

Laboratory	No.of Significant Figures Used	Actual Spike and Recovery Values Reported	Reported Data and % Recovery Are Consistent
QP (US East Coast)	4	Yes	Yes
DC (US West)	4-5	Yes	Yes
PHB (Pacific Coast)	1-4	**No**	**No**
CTI (Pacific Coast)	2	Yes	Yes
CTB (Pacific Coast)	4	Yes	Yes
LA (US West)	4	Yes	Yes
SL (Midwest US)	4	Yes	Yes
KP (Midwest US)	2	Yes	**No**

The KP laboratory acknowledged that its ChemWare Horizons™ LIMS had been modified from a commercial application using an Oracle™ database. It did not address QC adequately. The LIMS had been programmed to round off to two significant figures, which meant that, in a worst case scenario, 95 could be rounded to 100. If three significant figures had been used then 99.5 will be rounded to 100 - a major reduction in uncertainty. Although the laboratory was equipped with

Hewlett Packard™ instrumentation capable of reporting up to four decimal places and transmitting the raw data measurements directly into the LIMS, a special code had to be added to report surrogate recoveries with three significant figures. In fact, each analytical method had to be coded separately into a QC reference file.. A new code was not used in the production database until it had been successfully tested on the laboratory's development data base. The laboratory was asked to replace the pages with the correct information; this request was only partially fulfilled by hand entering the most glaringly erroneous calculations, leaving a pile of invalid data pages still to be accounted for.

The PHB laboratory reported recoveries using from one to four significant figures, depending on the method. It did not report the actual recovered concentrations. The percent recoveries contained minor discrepancies of up to 1%, that only an on-site raw data audit could clarify.

In another instance the LIMS of the CTB laboratory had been programmed to round off intermediate results for percent moisture calculations. This resulted in up to 5% discrepancies from the results that were obtained when rounding took place only at the conclusion of the mathematical operations.

SUMMARY

It is obvious that all automated calculations should be carried through with the maximum permissible number of significant figures, without intermediate rounding off of the results of mathematical operations. The principles of usage for significant figures and rounding off numbers must be scrupulously adhered to. When results are close to the outer limits of acceptance criteria even a few percent deviation may affect the acceptance or rejection of data.

All LIMS users should implement the principles and guidance enunciated in EPA's 1995 Edition of Good Automated Laboratory Practices (GALP). [1]

When a new LIMS is installed, or an old one upgraded or modified the laboratory quality assurance unit (QAU) should conduct an in-depth audit of the LIMS for each analytical method and the SDGs that are produced using the LIMS data. The LIMS programmer must address the fact that uncertainties inherent in instrumentation and methodology, including preparation and extraction, are accurately reflected in the proper use of significant figures and the rounding off of the *final* data.

To minimize erroneous RPDs the latter must be calculated from actual recovery values, *i.e.*, concentrations, not from already rounded off percent recoveries.

Laboratories must use trend analysis of their final product - the SDGs, to quality control the LIMS performance for accuracy and consistency. Reports from clients regarding inconsistent SDG data , should be immediately investigated, as they may be indicative of LIMS problems that may have escaped the QAU audits.

ENDNOTES

1. In 1980-1981 the EPA was involved in a historic imbroglio involving significant figures. A highly placed EPA official(RL) responded favorably and in writing to the request from two petroleum refining corporations to increase the concentration of tetraethyl lead (TEL) in gasoline to the maximum concentration which (for monthly reporting purposes) could still be rounded down to the EPA mandated two significant figure limit. The actual amount of TEL emissions and the accompanying profits increased significantly while the refiners stayed within the letter of the law. The ensuing congressional hearing ended up with the dismissal of the official from her position and the imposition of a jail sentence.

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How to Use U.S. Environmental Protection Agency World Wide Web and Listserv Internet Resources to Increase Environmental Compliance and Reduce Environmental Compliance Costs

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The U.S. Environmental Protection Agency (EPA) World Wide Web (WWW) site has been recognized as one of the best sites on the WWW. For example, McKinley's Magellan Internet Directory gives the EPA WWW site a four star rating, which is its highest rating. The EPA WWW site allows individuals to search EPA data bases, review regulations, and focus explorations of EPA on: Key Word Searches, Offices, Programs, Regions, Initiatives, News, Grants, Contracts, Publications, etc. The EPA WWW site is remarkable because it allows individuals myriad search preferences.

In addition to the WWW, EPA operates approximately 80 Internet Listservs. These Listservs are not widely used because most environmental professionals are not aware they exist. Listervs are sometimes called Listervers, Internet Mailing Lists, and Electronic Mailing Lists, but this paper will only use the term "Listserv". Individuals who subscribes to an EPA Listserv receive e-mail from EPA on one topic, such as federal register notices of new and proposed hazardous waste regulations. Although non-government Listservs allow subscribers to post notes to all other subscribers, EPA Listervs do not allow subscribers to transmit comments to other subscribers. EPA Listervs only distribute e-mail generated by EPA.

Why are Listservs so helpful? Listservs are narrowly focused because people only receive e-mail on topics they select. In addition, listservs do not require anyone to spend time "surfing" the net. All Listserv information is delivered via e-mail. The following are examples of EPA Listervs, which anyone with outside e-mail service can subscribe to. Subscribing to EPA Listservs is extremely easy, and it is free.

mercury@unixmail.rtpnc.epa.gov (U.S. EPA MERCURY mailing list)

epa-press@unixmail.rtpnc.epa.gov (U.S. EPA Press Releases)

epa-meetings@unixmail.rtpnc.epa.gov (U.S. EPA FEDERAL REGISTER documents for MEETINGS)

epafr-contents@unixmail.rtpnc.epa.gov
(U.S. EPA FEDERAL REGISTER CONTENTS documents)

epa-sab@unixmail.rtpnc.epa.gov
(U.S. EPA FEDERAL REGISTER SCIENTIFIC ADVISORY BOARD)

Comparison of the Region 2 QA Program to the Air Force Center for Environmental Excellence: CERCLA Outreach in Region 2

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Increased flexibility in designing and implementing a practical environmental program has become an absolute necessity in this era of shifting and tightening resources. At the same time, the OIG has identified the need for improved QA oversight by EPA of Superfund Federal Facilities, that is, smarter application of QA principles, in their September 1995 audit report. Region 2 has consistently maintained an open relationship with the QA personnel from the Army Corps of Engineers as well as with the Army Environmental Center, both of whom are responsible for many federal facilities in this region. This has aided Region 2's ability to determine the reliability of each entity's Quality Assurance Programs in addition to ensuring the quality of the environmental data produced.

An effort will now be undertaken to enhance this Region's oversight responsibility to include the Air Force Center for Environmental Excellence, the Quality Assurance "nerve center" for AF projects. This initiative is intended to facilitate communication with the federal facility, their consultants, and the analytical lab, thus solidifying the QA partnership. In addition, relevant QA/QC issues and concerns will be addressed thus achieving appropriate and cost effective environmental monitoring.

Region 2 QA staff have also developed a Home Page on the information superhighway of the World Wide Web. This valuable on-line resource will provide the ability to contact the appropriate technical QA experts in Region 2 directly on-line. Thus, the cross training of its nationwide audience to the EPA Region 2 QA and the various Federal Facility QA Programs will be easily accomplished.

"QA in Cyberspace": The Region 2 Quality Assurance Outreach Program For The '90s

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In an effort to keep Regional personnel informed of current U.S. EPA Region 2 quality assurance policies, the quality assurance (QA) office of the Environmental Services Division has developed an outreach program suitable for the '90s, "QA in Cyberspace". To promote the CERCLA and RCRA outreach efforts, the QA office has uploaded numerous guidance documents electronically through CLU-IN (formerly the OSWER Bulletin Board System (BBS)) and the information superhighway of the World Wide Web (WWW). A recent initiative of the Region 2 QA Office is the quarterly QA newsletter via the Region 2 Home Page, which may be of particular interest to WWW site users. The QA newsletter is intended to: (a) facilitate communication with the regulated community, environmental consultants, testing laboratories, and state and federal regulators, (b) forum relevant Quality Assurance/Quality Control (QA/QC) issues and concerns, and (c) promote appropriate and cost effective environmental monitoring.
The USEPA Region 2 QA newsletter contains: (a) one or more feature articles, (b) three ongoing task specific columns (Field QA/QC Support, Laboratory QA/QC Support, & RCRA QA/QC support notes), (c) a QA fact or definition, (d) a summary of our outreach efforts and upcoming training events, and (e) a listing of active Contract Laboratory Program (CLP) Routine Analytical Services (RAS) contracts. In addition, a brief biography of each author is provided to supplement each article and establish points of contact for the user.

The USEPA Region 2 QA newsletter will provide first hand QA/QC information to anyone undertaking an environmental monitoring project. This will enable one to access QA/QC support from USEPA's many technical experts directly on-line. Working in partnership with the regulated community, testing laboratories, and consultants will ensure environmental compliance is undertaken in a correct and cost effective manner. Increased flexibility in designing and implementing a practical environmental program is a current goal of the Agency. The USEPA Region 2 QA newsletter is one of the Agency's many innovative on-line information resources which can positively impact the way we do business.

NON-TRADITIONAL USE OF ENVIRONMENTAL SITE ASSESSMENTS: A TOOL FOR DETERMINING POTENTIAL ENVIRONMENTAL IMPAIRMENT/COMPLIANCE

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ABSTRACT

Phase I environmental site assessments (ESAs) traditionally have been the tool used by buyers and sellers to identify potential environmental liabilities associated with property transfers. However, ESAs also can be used by property owners to assess their present and past site activities that may have resulted in environmental impairments. The U.S. Environmental Protection Agency (USEPA) recently has promulgated policy that encourages the voluntary discovery, disclosure, correction, and prevention of regulatory deficiencies (60 FR 66706, December 22, 1995). The use of an ESA to compliment an environmental compliance audit comprehensively addresses past, as well as present use in evaluating a facility's regulatory compliance.

As part of a voluntary compliance audit program for the Owner, we performed ESAs at twelve large Connecticut facilities involved in industrial activities. Current and past practices were identified and evaluated for their possible impact on the environmental quality of the sites. The ESA process was modified to meet the criteria of both American Society of Testing and Materials (ASTM) Standard E 1527-94 and Connecticut Transfer Act Site Assessment (TASA) guidance.

This case study presents the modified ESA process, as well as findings which included: asbestos pipe insulation, lead paint, abandoned leach fields that received chemical wastes, leaking underground storage tanks, and potential contamination of soil and groundwater. It also presents a discussion of recommended corrective actions and management practices to prevent future deficiencies in the areas identified. The Owner is committed to correct the problems that were identified.

INTRODUCTION

Environmental compliance is a key part of any industry's goals. Obeying the law is understood, but managing industrial environmental issues in a proactive mode moves those enlightened firms into the "Good Corporate Citizen" category. To that end, the Owner of twelve facilities which perform industrial activities in Connecticut is in the process of having URS Consultants, Inc. (URS) render comprehensive environmental compliance audits. In addition, the Owner wanted a review of potential environmental impacts from past property uses and practices so that these potential impacts could be addressed proactively, using a program like USEPA's Voluntary Site Cleanup Program.

Most environmental compliance audits (ECAs) are a snapshot of compliance at a facility when the audit is performed and historic uses/practices usually are not addressed. URS' approach to meet the Owner's expectations was to perform Phase I ESAs to evaluate the Owner's more immediate need for identifying potential environmental impairments for the sites, followed by the comprehensive ECAs.

The ESAs were performed to ASTM Standard E 1527-94, which establishes minimum criteria for parties seeking a definition of environmental due-diligence for Phase I ESAs. In addition, the Owner wanted to comply with Connecticut Department of Environmental Protection (CTDEP) TASA guidance to follow that agency's recommendations. The ASTM E 1527-94 standard allows for flexibility and professional judgement in performing Phase I ESAs. Also, the ASTM standard is consistent with the TASA guidance, provides more detail and guidance in performing proper Phase I ESAs, and has been nationally adopted by the financial, commercial, and industrial sectors. The major departure of TASA from typical ASTM Phase I ESAs was to require an in-depth review the federal, state and local enforcement history of each site.

Newer facilities ranged in age from 2 to 5 years old; the older facilities dated back to use during the Civil War. Sites varied in size from a large city block to several hundred acres. Typical current industrial operations at these site included machine shops, metal fabrication, motor pool, farming, and woodworking. The potential environmental impacts also varied with historic use; that is, older sites used different fuel sources over the years for heating such as wood, coal, oil, and natural gas.

THE ENVIRONMENTAL SITE ASSESSMENT PROCESS

Prior to conducting the ESAs at the twelve facilities, URS personnel met with the Owner and outlined the extent (and limitations) of the ESAs. URS prepared due-diligence site walkover forms that addressed the requirements of both the TASA guidance and the ASTM standard, and submitted the walkover forms to the client for review and comment prior to finalizing the forms.

Approximately two weeks prior to the scheduled site walkover inspections, the Owner provided URS with their comments on the site walkover forms along with accurate site location maps and a contact person at each facility. Since access to the facilities was restricted, URS personnel involved with the site walkover inspections were required to obtain photo identification security passes.

Upon receipt of the site location maps, URS contacted the ERIIS database service[1] to perform a federal and state database search to identify and locate reported known environmental problems within the radii recommended in the ASTM standard. ERIIS provided URS with information on sites listed on: the federal National Priorities List (NPL) Site List; the federal Comprehensive Environmental Risk, the Compensation and Liabilities Information System (CERCLIS) List; the federal Resource Conservation and Recovery Act (RCRA) Treatment, Storage and Disposal (TSD) Facilities List; the federal RCRA Generator List; the federal Emergency Reporting and Notification System (ERNS) List; the Connecticut Hazardous Waste Site List; the Connecticut Landfills List; the Connecticut Leaking Underground Storage Tank (UST) List; and the Connecticut Registered UST List.

URS verified the ERIIS database information by submitting Freedom of Information Law (FOIL) inquiries to the appropriate federal agencies and conducting a manual file search of the CTDEP files. Additional information was obtained by reviewing State of Connecticut Department of Public Works (CTDPW) records for asbestos abatement information and local government files. The information compiled helped identify areas of potential environmental concern, disclosed historic environmental compliance enforcement actions, and provided information on investigations involving spills of

hazardous materials and hazardous wastes. Copies of appropriate documents were obtained for inclusion in the final ESA reports.

In addition to environmental information, URS also developed historic information and property ownership information. Historic information was developed by reviewing aerial photographs (when available), Sanborn fire insurance maps, and cross-reference telephone directories. Property ownership information, in general, was established to the early 1900s. However in one instance the ownership of one of the properties was tracked to the early 1800s. Interviews also were conducted to help verify and provide additional detail to the significant/relevant historic and property information. URS used U.S. Geological Survey (USGS) 7.5 minute topographic maps to describe the physical setting of each property. Soil survey reports, geological maps, and water resource maps also were utilized to assess the environmental setting at each property.

URS personnel experienced in conducting ESAs completed the site walkover inspections. Prior to conducting the site walkover inspection, facility personnel knowledgeable in the operation of the facility were identified and due-diligence interviews were conducted. Information obtained during the records search was provided to facility personnel who then addressed questions concerning historic hazardous materials and hazardous waste handling and disposal practices. Site maps indicating the locations of USTs, aboveground storage tanks (ASTs), historic waste disposal areas, and active hazardous material storage areas were prepared prior to conducting the site walkover inspection. URS also reviewed available engineering drawings to note the possible presence of historic subsurface structures, such as past leach fields or landfills, that may be of concern.

The site walkover inspections included an inspection of both the interior of any onsite structures and the surrounding exterior of each property. The URS team made note of adjoining property uses and general land use of the surrounding area. In addition, any land uses that had the potential for impact on/near the subject properties were identified.

Following the completion of each site walkover inspection, copies of the due-diligence assessment form were made for facility personnel. Upon the return of the URS team to their office, individual ESA reports were prepared that were consistent with the TASA guidance document and ASTM standard. Since the ESA was conducted to identify potential historic problems at the facilities, any areas where the potential for historic environmental impairment or current environmental compliance were identified and an aggressive Phase II ESA sampling program was recommended to determine the presence, nature and extent, and impact of a potential environmental hazard.

FINDINGS AND DISCUSSION

The findings and deficiencies identified at each of the facilities, as well as recommendations to correct any deficiencies, were presented in individual ESA reports prepared for each facility. Following a review of the individual ESAs by the Owner, a formal presentation was made to the Owner that summarized the ESAs findings and recommendations.

Hazardous Material Issues: The types and quantities of hazardous materials varied by facility. In general, limited quantities of hazardous materials for building maintenance (such as paint and cleaning

compounds) were present in each building. Buildings housing industrial activities contained the greatest variety of hazardous materials including oil-based paints, degreasing solvents, inks, chlorinated solvents, flammable liquids, corrosive liquids, and oils. Heat at the majority of the facilities was provided by oil-fired boilers.

Areas where hazardous materials were stored and used were inspected to determine if spills would be contained or controlled. The majority of the non-industrial storage areas inside the buildings did not have floor drains and there were no indications of spills. Also, floor drains were not present or had been sealed in the majority of the storage buildings associated with industrial activities. Buildings that had floor drains discharged into the sanitary sewer line. One of the storage buildings was found not to be properly ventilated which resulted in a buildup of flammable vapors; the building also was found not to meet the building code for electrical wiring.

Except for three facilities, USTs were used for the storage of fuel oil for the boilers and emergency electrical generators. Records disclosed that a few of the USTs had been taken out of service after leaks were discovered. While monitoring wells were installed near a few of the USTs, the facilities generally depended on inventory controls to determine if a UST has a possible leak. URS recommended that the soils adjacent to the leaking USTs be tested to determine if residual petroleum products were present. URS also recommended that a facility-wide UST leak detection program be developed, or the USTs be removed and replaced by ASTs. Since a significant number of the USTs had not been registered with the CTDEP, URS recommended that all USTs be registered. At facilities with ASTs, no significant oil spills were noted inside the secondary containment structures. Since it was discovered that spill prevention control and countermeasure (SPCC) plans were not prepared for these facilities, URS recommended that SPCC plans be prepared in accordance with 40 CFR 112.

Hazardous Wastes: Industrial wastes generated at the majority of the facilities consisted of waste oil, paint wastes, and air compressor blowdown fluids. These industrial wastes, in most instances, were shipped offsite for recycling. Designated hazardous waste storage areas met the RCRA criteria for small quantity generators as outlined in 40 CFR 262. Even though recycled industrial wastes are not considered hazardous wastes, copies of non-hazardous waste manifests were kept on file at most of the facilities.

One of the older facilities recently replaced ten old electrical transformers which had been placed temporarily outside the designated RCRA storage areas. While dielectric fluid samples were collected from each transformer and tested for polychlorinated biphenyls (PCBs), none of the transformers had been marked as required in 40 CFR 761. URS recommended that the transformers be marked as "NON-PCB" and disposed of as non-hazardous waste. Other hazardous wastes stored at this facility included 5-gallon drums of a chlorinated solvent (perchloroethylene) and lead-acid batteries. URS recommended that arrangements be made to dispose of the perchloroethylene at a RCRA TSD facility as soon as possible. URS also recommended that procedures be developed to ensure that all hazardous wastes brought to the RCRA storage area be characterized, stored, marked, and labeled in accordance with 40 CFR 261-262, and that wastes be removed from the facility within 90 days.

Discharges to the Environment: Spills of gasoline and fuel oil from USTs represented the greatest percentage of discharges to the environment. However, historic waste disposal practices represent the

most significant potential environmental impacts. Sanitary sewer lines at two of the facilities discharged into leach fields before being connected to regional sewer systems. Historic disposal of hazardous materials and wastes into the sanitary sewer system may have resulted in hazardous materials percolating into the groundwater. Results of historic groundwater sampling down-gradient of the former leach fields contained chlorinated solvents and other organic and inorganic materials. URS recommended that soil and groundwater samples be collected in the vicinity of the abandoned leach fields to determine the types and concentrations of organic and inorganic materials. The analytical results will be compared against the CTDEP and federal water quality standards.

Historic solid waste disposal areas, some of which covered 3 acres, also represent a potential source of groundwater and surface water contamination. Surface water, groundwater, and sediment samples collected in and around the former solid waste disposal areas were found to contain high levels of heavy metals. URS recommended that additional soil and groundwater samples be collected from the former solid waste disposal areas and that hydrogeologic information be obtained to better define the potential for offsite migration of contaminants. The analytical results will be compared against the CTDEP and federal water quality standards.

At one of the facilities, boiler cooling water that had been treated with biocides was being discharged to the storm sewer which emptied into a nearby pond. URS recommended that the boiler cooling water be tested and that arrangements be made to discharge the boiler water into the sanitary sewer lines. Other uncontrolled or unpermitted discharges included a paint spray booth discharge and an air compressor blowdown onto the ground.

Health Issues: The ESAs disclosed that some of the facilities still had asbestos-containing materials (ACM) as insulation on hot water and steam pipes; possible lead-based paint on walls, ceilings, and fixtures; and possible PCB-containing electrical ballasts. URS recommended that the insulation on the pipes be tested to determine if it posed an airborne hazard and that any ACM be removed. URS further recommended that paint samples be collected and tested for lead and that information on the electrical ballasts be obtained to determine if the ballasts contained PCBs.

Permits and Registrations: The types of permits required varied greatly for each facility. The records of facilities with oil-fired boilers were checked to determine if air discharge permits had been obtained and were current. Other point sources of air discharges in manufacturing areas also were identified and the records checked to determine the monitoring requirements for these discharges. At one of the older facilities, it was discovered that a paint booth was not permitted; it was recommended that a permit be obtained prior to using the paint booth.

A review of the facility records disclosed that a number of the older USTs had been taken out of service and either replaced with new USTs or ASTs. The majority of the facilities had registered their USTs when Connecticut initially required registration. However, a significant number of the facilities had not informed the state when USTs had been taken out of service. URS recommended that a organization-wide UST management program be instituted to correct the discrepancies, maintain current registrations, and verify UST compliance.

CONCLUSIONS AND SUMMARY

As seen in the process and findings sections, ESAs compliment ECAs with some overlap. ESAs and ECAs both deal with the site's current use, storage, handling and disposal of hazardous materials. However, ESAs also focus much more on historic uses and practices and less on recordkeeping than ECAs.

The Owner's need for an assessment of potential environmental impacts from past and present uses and activities was met efficiently and effectively by performing Phase I ESAs on the twelve industrial activity sites. This proactive approach by the Owner will result in several Phase II ESA studies to determine the presence, nature, extent, and impact of potential contamination. The Owner is committed to voluntarily cleaning up areas that exceed regulatory thresholds under programs like the USEPA's Voluntary Site Cleanup Program.

FOOTNOTE

1. ERIIS stands for Environmental Risk Information & Imaging Services, Herndon, VA 22070. Phone: (800) 834-0600.

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2. "Transfer Act Site Assessment Guidance Document," Connecticut Department of Environmental Protection, 1991 revision.
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A Report on Sample Precisions in Hanford Tank Waste Samples

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High-level radioactive mixed wastes generated at the Hanford site during nuclear defense production were stored in underground tanks. Tank wastes are characterized for safety, health, and tank stability concerns. Data quality requirements for the tank characterization program are established by the Data Quality Objective process for confirmation of historical information, waste tank safety, expected future processing for immobilization, and regulatory requirements. Data quality control parameters and acceptance criteria are specified in Tank Sampling and Analysis Plans for each tank. However, there is no appropriate basis to establish data quality requirements on sample precision for the tank waste samples. A reasonable amount of precision information from different tank samples have been accumulated in the 222-S Laboratory data management system, but have not been evaluated. The objectives of the present report are to compare sample precision between liquid and solid matrix samples obtained from various tank wastes, to provide performance based precision information, and to compare against the current regulatory basis.

Core tank wastes were sampled by the Tank Waste Characterization System (TWRS) and submitted to the 222-S Laboratory for analyses. Tank samples were extruded from the core sampling apparatus in the Hot Cell and were subsequently subsampled. Subsamples were either subjected to water leaching (for anion analysis), fusion digestion (for total alpha and total beta analysis, plutonium 239/240), or subject to direct analyses e.g., cyanide and/or total organic carbon analyses. The data analyzed for the present study were generated by the analysts at the 222-S Laboratory in 1995. These data were entered into the data management system (MULTI-LIMS) and were verified by the responsible chemists. Precision in the tank waste samples is calculated as the relative percent difference (RPD) between laboratory sample duplicates. Laboratory sample duplicates were generated for each sample after sample extrusion in the Hot Cell, but prior to sample digestion. Sample precision data were retrieved from the MULTI-LIMS system and subjected to Histogram analysis. Sample precisions were evaluated for chloride, fluoride, nitrite, nitrate, phosphate, sulfate, bromide, total organic carbon, total alpha, and plutonium 239/240.

For all the analytes that were evaluated in this study, the following trends have been observed. Majority of RPD for the liquid samples falls into the category of less than 20% RPD, except for plutonium. Approximately 50% to 75% of the RPD of solid samples falls into the category of less than 20%. Approximately 70 to 90% of the RPD of solid samples falls into the category of less than 35%. The larger RPD in the solid samples than in the liquid samples indicates that issues e.g., inhomogeneity, subsampling, dissolution are present in the solid samples. For Hanford tank waste samples, quality control acceptance criteria for evaluating data quality should be established based on performance in the samples. A larger precision acceptance criteria is recommended for solid tank waste samples as long as the analytical system performance on standards is maintained at the tighter limits. (Sponsored by the Department of Energy/Richland operations office, Analytical Services Program, WPD99L10).

Jerry L. Parr, Quanterra Environmental Services; John J. Austin Jr., U.S. Environmental Protection Agency's Office of Solid Waste; Charles W. Carter, Lockheed Analytical Services; Roger Claff, American Petroleum Institute

COMPARISON OF EPA AND API LABORATORY RESULTS AS PART OF THE 1992-1996 PETROLEUM REFINERY LISTING STUDY

In 1992, as part of a consent agreement, EPA's Office of Solid Waste (OSW) initiated a program to characterize 29 residuals from petroleum refineries. As part of this effort, EPA performed sampling and analyses of a variety of refining residuals at 25 petroleum refineries across the United States. Because EPA's activities could result in a regulation that could significantly impact the petroleum industry, the American Petroleum Institute (API) decided to provide independent analyses of split samples.

EPA had prepared a draft Quality Assurance Project Plan (QAPP) and selected a contractor for the laboratory services (Lockheed Analytical Services). API provided constructive input into EPA's QAPP, especially relative to the sampling and analysis protocols, and selected a laboratory to provide the split sample analyses (Quanterra Environmental Services).

With the EPA QAPP as the framework, each laboratory independently performed analyses on a variety of complex petroleum refining residuals, including tank bottoms, spent catalysts, off spec solutions, and process sludges. These samples are probably some of the more challenging and complex samples analyzed in environmental laboratories.

The EPA and API laboratories were both expected to utilize considerable judgment in how to optimize the laboratory procedures to achieve the best possible data suitable for regulatory decisions.

This presentation will illustrate the differences in analytical procedures used by the two laboratories to address these complex matrices. The presentation will also provide a comparison of the EPA and API data sets, focusing on differences in qualitative and quantitative accuracy between the two data sets.

COMPARABILITY OF MEASUREMENTS OF SELECTED PCB CONGENERS, PAHS, AND CHLORINATED PESTICIDES IN THE MARINE ENVIRONMENT — RESULTS OF A PERFORMANCE-BASED QUALITY ASSURANCE PROGRAM

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ABSTRACT: NIST efforts in providing mechanisms for assessing data quality and comparability for laboratories monitoring selected organic contaminants in the marine environment include method development, production of certified reference and other control materials, conduct of intercomparison exercises, and the coordination of quality assurance workshops for laboratories. Results from the intercomparison exercises can be used to assess current levels of PAH, PCB congener, and chlorinated pesticide measurement comparability among participating laboratories.

INTRODUCTION

Tools and mechanisms for the assessment of data produced by laboratories providing environmental analyses are critical because decision-making based on inaccurate results or data of unknown quality can have significant economic and health consequences. NIST provides a variety of activities in support of environmental monitoring programs for organic contaminants. The largest of these programs has been in cooperation for the past ten years with the U. S. National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Marine Monitoring Program and the U. S. Environmental Protection Agency (EPA) Environmental Monitoring and Assessment Program[1-3]. For this program, NIST efforts focus on providing mechanisms for assessing the interlaboratory and temporal comparability of data, and on improving measurements for the monitoring of over 60 organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl congeners (PCBs), and chlorinated pesticides in marine bivalve, sediment and fish samples. Table 1 lists the analytes targeted in these exercises. This program includes the development of improved analytical methods, production of needed NIST Standard Reference Materials (SRMs) and other control materials, conduct of yearly interlaboratory comparison exercises, and the coordination of workshops to discuss the results of these exercises. Since 1993, private sector and other laboratories that are not associated with these NOAA or EPA programs and that reimburse NIST for the participation costs of these exercises and workshops have subscribed to the "NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment." Current participants represent a number of multi-laboratory monitoring programs and include over forty federal, state/municipal, university/college, private sector and international laboratories. In this performance-based program, participants use methods currently in use in their laboratories for these analyses.

Natural matrix SRMs, NIST SRM 1941 and the renewal SRM 1941a, Organics in Marine Sediment, and SRM 1974 and the renewal SRM 1974a, Organics in Mussel Tissue; PAH, PCB, and chlorinated pesticide calibration solution SRMs at two concentration levels; and sediment and tissue control materials for routine use were developed in response to the needs of this program.

INTERCOMPARISON EXERCISES: MATERIALS AND CONDUCT

To facilitate the isolation of sources of analytical variability and bias, the materials chosen for the intercomparison exercises have progressed from simple hexane solutions of target analytes to enriched extracts of natural materials to unenriched extracts of natural materials to natural-matrix-based materials. Since 1991, samples of two natural-matrix-based homogeneous materials derived from the marine environment that have not been fortified with any of the target analytes have been used for the annual intercomparison exercises. Exercise materials are chosen and prepared to be as similar as possible to the samples. Table 2 shows typical concentration ranges in exercise materials. The homogeneity of each material is assessed by NIST. One of the most difficult tasks of the exercise coordinators is the choice of the "assigned value," the concentration of each analyte in a particular material to which comparisons will be made. Candidate SRMs, true unknowns during the time frame of the exercise, are used as exercise materials whenever possible. This enables eventual comparisons of the exercise assigned values and the results of the individual laboratories with certified concentrations for these reference materials.

Z-scores and p-scores[4] are used to assess and track performance (for accuracy and precision, respectively) of federal, state/municipal, university/college, private sector and international laboratories participating in these exercises.

RESULTS AND DISCUSSION

Results from 1994 Mussel Tissue VI, 1993 Mussel Tissue V, and 1992 Marine Sediment III intercomparison exercises in which candidate reference materials were analyzed can be compared with concentrations of target analytes certified in these materials. These results and those from the 1994 and 1995 exercises can be used to illustrate current levels of measurement comparability among the participating laboratories for these selected analytes present at tracé level concentrations in natural-matrix materials.

As discussed previously, when candidate SRMs are used as exercise materials, the assigned values for the exercise can be compared with the certified values when issued. Figure 1 shows this comparison for PAHs in the Mussel Tissue V exercise material which were relabeled bottles of SRM 1974a. In general, there is good agreement between the exercise assigned values and the certified concentrations.

Typically, the performance of laboratories that have participated in this program for a number of years was better than that of the laboratories in their first or second year of participation. As expected, laboratories reporting concurrent reference material analyses results (perhaps an indicator of regular reference material use) typically showed better performance than those who did not analyze the reference materials. The percentage of PAH results from laboratories participating more than two years in the program that were within 50% of the accepted concentrations (i.e., z-scores (25%) in the -2 to +2 range) was 90% for the Sediment IV and 75% for the Mussel Tissue VI. The percentage of acceptable results for those laboratories participating in the intercomparison exercise program for one to two years was 58% and 53% for the Sediment IV and Mussel Tissue VI, respectively.

The use of the z-scores for assessing performance in a number of exercise materials is illustrated in Figure 2 which shows phenanthrene z-scores (25%) for four laboratories for the NOAA NS&T Program on two sediment and three mussel exercise materials analyzed over a three-year period. One can see by the results of Lab 4 for the Mussel VI in comparison with results for the previous four materials which were well within the Program's acceptability criteria that the demonstration

of acceptable performance should be an ongoing process of which participation in intercomparison exercises is but one part. Charts of z-scores as illustrated in Figure 3 are useful for assessing intra- and interlaboratory bias trends and relative performance.

For the 1994 Marine Sediment IV exercise, 97.4% of the p-scores (precision indicators) of reported PAH results were acceptable. In these exercises, interlaboratory variability is a greater contributor to PAH measurement incomparability than is the intralaboratory variability.

CONCLUSIONS

Intercomparison exercises provide an important mechanism for assessing the comparability of data being produced by the participating laboratories. Exercise materials similar in matrix, form and analyte concentration to typical samples being analyzed by the laboratories are most useful for demonstrating the level of comparability and for revealing potential problem areas. The use of candidate CRMs as exercise materials is very useful in evaluating the procedures used to determine the assigned values for an exercise material.

For the determination of the target analytes in these complex marine matrices with relatively low levels of these analytes, the levels of bias and reproducibility of many of the participating laboratories meet their current acceptability requirements; however, there is certainly room for improvement. Minimizing the between-laboratory bias such that the analytical variability is significantly less than the sampling variability should be an achievable goal.

At the beginning of this activity, the NOAA NS&T and EPA EMAP program managers had no tools to assess the comparability and quality of the measurements made by the various laboratories providing data for their monitoring programs nor could they effectively document changes in the quality of the data produced. With continuous participation in these annual intercomparison exercises, laboratories can now demonstrate the quality and comparability of their results. Two natural matrix SRMs (i.e., sediment and mussel tissue) and six calibration solution SRMs have been developed at NIST in response to the needs of this program. The availability of these SRMs provides the opportunity for laboratories to evaluate their performance on a continuous basis.

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Table 1. Analytes[a] of Interest in NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment

Chlorinated Pesticides

hexachlorobenzene	2,4'-DDE
alpha-HCH (alpha-BHC)	4,4'-DDE
gamma-HCH (gamma-BHC, Lindane)	2,4'-DDD
heptachlor	4,4'-DDD
heptachlor epoxide	2,4'-DDT
cis-chlordane (alpha-chlordane)	4,4'-DDT
trans-chlordane (gamma-chlordane)	aldrin
oxychlordane	dieldrin
cis-nonachlor	endrin
trans-nonachlor	endosulfan I
mirex	endosulfan II

Polychlorinated Biphenyl Congeners

PCB No.	*Compound Name*	*PCB No.*	*Compound Name*
8	2,4'-dichlorobiphenyl	128	2,2',3,3',4,4'-hexachlorobiphenyl
18	2,2',5-trichlorobiphenyl	138	2,2',3,4,4',5'-hexachlorobiphenyl
28	2,4,4'-trichlorobiphenyl	153	2,2',4,4',5,5'-hexachlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl	170	2,2',3,3',4,4',5-heptachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl	180	2,2',3,4,4',5,5'-heptachlorobiphenyl
66	2,3',4,4'-tetrachlorobiphenyl	187	2,2',3,4',5,5',6-heptachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl	195	2,2',3,3',4,4',5,6-octachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl	209	decachlorobiphenyl

Polycyclic aromatic hydrocarbons (PAH)

naphthalene	fluoranthene
2-methylnaphthalene	pyrene
1-methylnaphthalene	benz[*a*]anthracene
biphenyl	chrysene
2,6-dimethylnaphthalene	benzo[fluoranthenes [*b*+*j*+*k*]
acenaphthylene	benzo[*e*]pyrene
acenaphthene	benzo[*a*]pyrene
1,6,7-trimethylnaphthalene	perylene
fluorene	indeno[1,2,3-*cd*]pyrene
phenanthrene	dibenz[*a,h*]anthracene
anthracene	benzo[*ghi*]perylene
1-methylphenanthrene	

[a] The following are typically reported by participants and evaluated as sums of the indicated components:

PAH	chrysene + triphenylene
	benzo[b]- + benzo[j]- + benzo[k]fluoranthene
	dibenz[a,h]anthracene + dibenz[a,c]anthracene
PCB congeners	PCB 66 + PCB 95
	PCB 101 + PCB 90
	PCB 138 + PCB 163 + PCB 164
	PCB 187 + PCB 182 + PCB 159
	PCB 170 + PCB 190

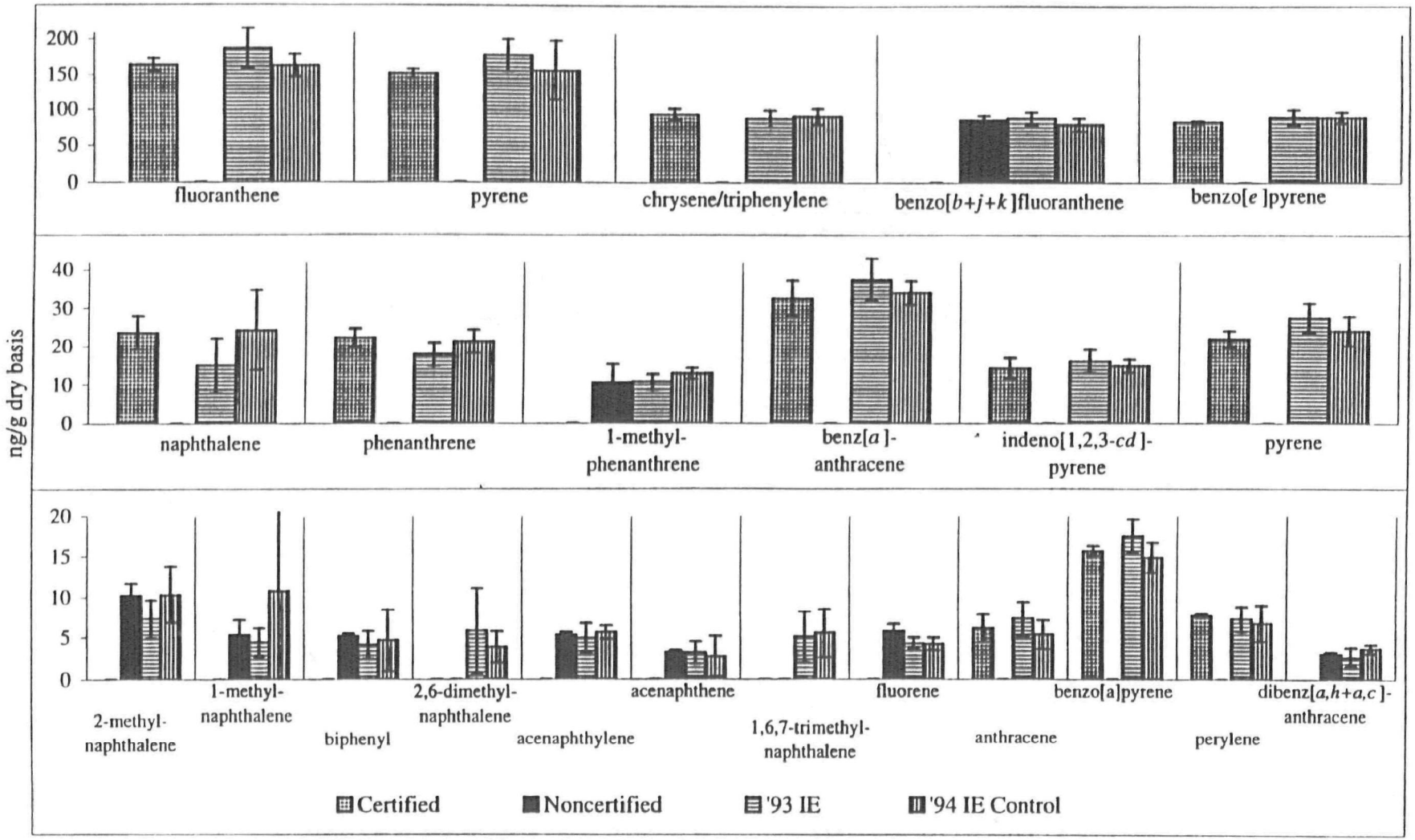

FIGURE 1 Comparison of certified and noncertified concentrations for SRM 1974a, Organics in Mussel Tissue (issued November, 1995) with assigned values from a 1993 intercomparison exercise and from 1994 when used as an exercise control material. The error bars represent 95% confidence limits.

Table 2. Typical Concentration Ranges of Determined Compounds

	Great Lakes Fish Homogenate ng/g wet wt.	Marine Sediment ng/g dry wt.	Mussels ng/g dry wt.
PAHs	not determined	40 to 10 000	1 to 300
PCB Congeners	1 to 150	1 to 90	1 to 150
Chlorinated Pesticides	1 to 150	1 to 150	1 to 100

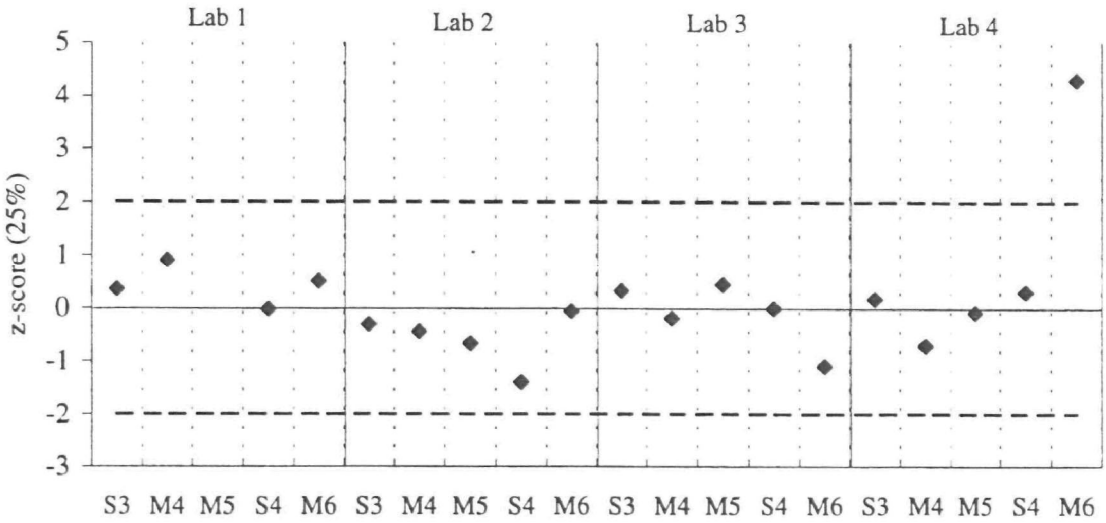

FIGURE 2 Phenanthrene z-scores of four NS&T laboratories for three mussel tissue (M4, M5, M6) and two sediment (S3, S4) intercomparison exercises conducted during a three year period.

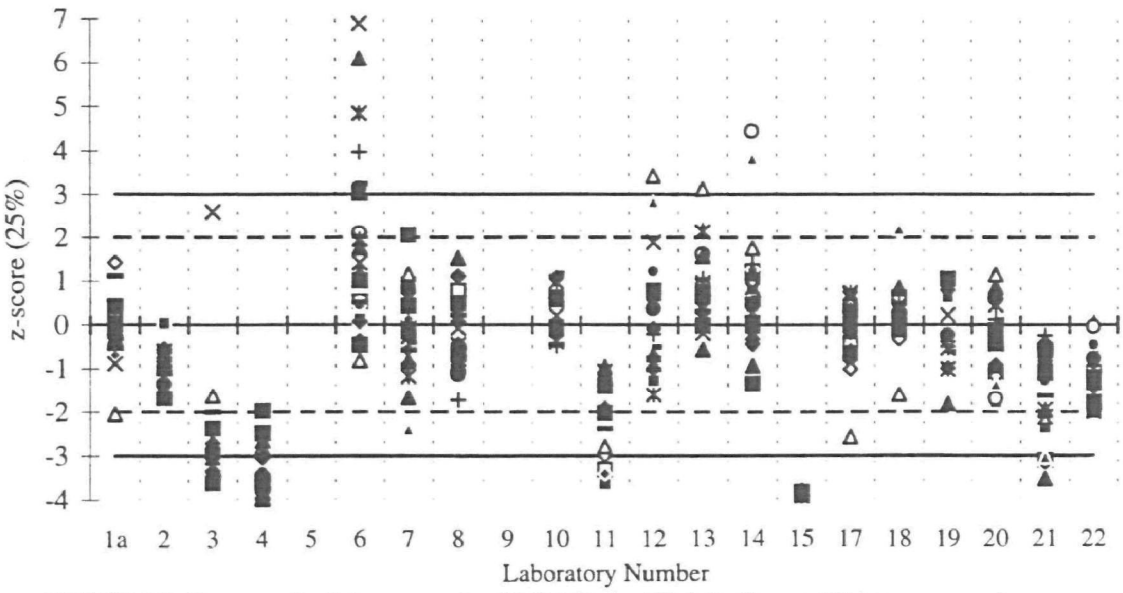

FIGURE 3 Z-scores by laboratory for 23 PAHs in 1994 Sediment IV intercomparison

ABSTRACT

The Effectiveness of the Procedure for Estimating Instrument Detection Limits for Inorganic Analyses in the Contract Laboratory Program

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The U.S. EPA, National Exposure Research Laboratory, Characterization Research Division (Las Vegas, NV) conducts studies of the quality assurance and quality control (QA/QC) measures required in EPA methods. These studies determine whether specific QA/QC measures add value to the data and whether these QA/QC measures are the most effective way of controlling a given parameter. The QA/QC of the Contract Laboratory Program (CLP) inorganic analyses are currently being tested. This presentation covers the evaluation of the requirement for determining the instrument detection limit (IDL). The CLP inorganic contracts require that laboratories determine and report IDLs quarterly. These determinations are made by analyzing a standard at three to five times the estimated IDL seven times on each of three consecutive days and averaging the standard deviation of the results for each day. This investigation evaluated whether the procedure measures a realistic IDL, whether the frequency of measuring the IDL is appropriate, and whether alternative procedures could provide the same or better information at lower cost. Data from the CLP analytical results database (CARD) were used to perform the evaluation. Study results showed that the current procedure provides an optimistic IDL, that the IDL varies significantly from day to day, and that similar IDL information can be obtained from QA/QC analyses that are already performed on a daily basis. Alternatives to the current IDL procedure are suggested.

AUTOMATED DATA VALIDATION: WHAT ARE THE LIMITATIONS?

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INTRODUCTION

In the past, the validation of environmental samples has been performed manually. The reports may have been generated using a computer, but the data evaluations were done using a trusty pen and a hand-held calculator. However, now that computers are so much a part of analytical processes, why not computerize data validation? Since most of the validation tasks involve comparison of numbers, it makes sense to automate these sometimes mundane reviews. But what about the tasks that involve more than simply comparing control limit windows to sample results? Those validation processes that may involve making judgment calls are beyond the capabilities of current computer programs. The USEPA has successfully used one computer program to automate certain parts of validation but other aspects of data validation may not be easily performed by a computer.

VALIDATION PROCESS

Data validation has typically been performed by an experienced chemist who diligently inspects page after page of a data package which is generated by a laboratory during the analysis of environmental samples. The process of validating laboratory data involves evaluating the sample data by recreating the analysis process. Each chain of a custody form, sample preparation log, instrument injection log, sample quantitation form, chromatogram, mass spectrum, quality control form, and sample result form is examined to determine whether the requirements of the analysis have been met. The validator then determines whether the accuracy, precision, comparison, reproducibility, and completeness of the analysis meets requirements set by the project Sample and Analysis Plan (SAP), or the Quality Assurance Project Plan (QAPP), and finally a report listing the excursions and conclusions is generated.

COMPLICATIONS

The validation process can be straightforward if the sample matrix has little affect on the instrument's ability to generate data, and if analyses follow the required methods without deviations which affect the sample results. However, with complicated sample matrices, and deviations from the methods, data validation can become more complicated. For example, if a sludge sample has been analyzed for polychlorinated biphenols (PCBs), it may contain any of several mixtures of Aroclors, one of the most common of which were trade named Aroclors; it may be difficult to identify the Aroclor peak pattern in the chromatograms produced by the instrument because the Aroclor may be masked by interfering peaks. Many Aroclor patterns that samples exhibit will not match the standard pattern exactly since the Aroclors in the samples have been weathered. If a weathered Aroclor pattern is present, the identification of the Aroclor will require experience and judgment since the Aroclor pattern will appear altered.

If that same sample is analyzed for semivolatile organics by gas chromatograph/mass spectroscopy (GC/MS), the mass spectra may contain fragments from other interfering compounds that disguise the spectra of the target compound. Even after using the best techniques to clean the samples up before running them on the instruments, matrix interferences may be present in the samples and can cause interpretation to be difficult.

In the case of samples that are analyzed for volatile organics, if a sample is purged in the same instrument vessel that was previously used to analyze a sample that contained a high concentration of volatile organic, such as trichloroethene, the trichloroethene result for that second sample may be high because carryover has occurred. A review of the injection log (which is typically hand written) can determine whether the trichloroethene concentration is erroneously high; if applicable, a qualifier can be applied to warn of this analysis error.

Due to the pressure of schedules associated with getting sample results to the data user on time, analysts occasionally make decisions during the analysis process that affect the final sample results. Samples are analyzed outside of holding times (since the client requested the analysis after the holding times have been exceeded), samples are analyzed on instruments with poor calibration response factors (because the method listed in the QAPP is not current), and sample results associated with low laboratory control sample recoveries are reported (because the recovery criteria listed in the QAPP and the laboratory control limits differ). While these decisions may seem reasonable at the time, the overall affect of these decisions are evaluated during validation.

Though laboratories continue to improve data processing and reporting processes, many still use manual entry of data results into computer systems to generate final data packages. While quality control measures are in place to check for data entry errors in the laboratory, occasionally data which contain transcription errors are reported. These errors can involve using the wrong initial calibration factor when several initial calibrations are involved, adjusting the compound areas if manual integrations are used, forgetting to include dilutions used, and the lack of adjustment to account for percent solids in reporting detection limits. These mistakes are easily corrected by the laboratory, but the data user may not realize that a mistake has been made.

COMPUTER VALIDATION

The ability of computer systems to validate environmental sample data depends on the extent of the tasks that the computer would be expected to perform. If number comparisons are involved such as evaluation of quality control sample recoveries, blank contamination, calibration relative standard deviations, response factors, and percent differences, holding times, and retention time windows, the computer program can be used to perform the validation. As long as data is available for the computer to review, and hand written logs are provided in electronic form, the program can evaluate the analysis process.

However, if complications are detected in the sample analysis process, it would be difficult for a computer system to thoroughly and properly evaluate the resultant sample data. While the criteria that the computer are capable of reviewing are important to the evaluation process, other factors are as important to reporting accurate data to the data user. These may include providing a second opinion of identified Aroclors with patterns that appear to be weathered or mass spectra with erroneous fragment patterns, judging whether carryover affects a particular compound result, or determining whether detection limits seem reasonable considering the type of sample matrix involved in the analysis. It would be difficult for current computer programs to make these important judgment calls.

THE USEPA CADRE SYSTEM

The USEPA Computer Aided Data Review and Evaluation (CADRE) system is an automated system that compares analytical results to quality control criteria established for the Quick Turnaround Methods (QTMs) [1]. The QTMs are methods that involve single column gas chromatography (GC) analysis, therefore situations that involve evaluating second column confirmations or the interpretation of GC/MS spectra are not involved in the review of this sample data. After the CADRE program evaluates the data, it applies data qualifiers to indicate usefulness of the data.

Table 4 - *Qualifiers added to QTM data by the CADRE program*

Qualifier	Quality control problem detected by the program
U	Sample is affected by method blank contamination
B	Sample is affected by instrument blank contamination
L	Compound is outside LCS recovery criterion
P	Compound is outside PVS recovery criterion but inside expanded criterion
T	Absolute retention time is used to the identify compound
S	SMC in the sample is outside recovery criterion
E	Compound concentration is above initial calibration range
M	Retention time shift is detected during sample analysis

The CADRE performs the evaluations of quality control sample results, calibrations, laboratory control samples, performance verification standards, method and instrument blanks, and system monitoring compounds. This system compares holding times to analysis and extraction dates, determines whether retention time window criteria were met for compound identification, and evaluates peak resolution. These evaluations all involve comparing numbers and performing calculations, which a computer is fully capable of doing.

SUMMARY

While computers can automate the process of determining whether sample results are within control limits and meet method criteria, situations may arise during the validation process that would prove to be challenging to current computer programs. In many cases judgments must be made during the validation process that involve much more than number comparisons. These judgments often involve investigations that utilize a validator's knowledge of anlaytical chemistry, past experience and the application of laboratory common sense. Whether the judgment involves deciding not to reject sample results because the data user acknowledges that the concentration reported may be inaccurate due to exceeded holding times, or determining if a weathered Aroclor pattern can be reported as Aroclor 1248 or Aroclor 1254, limitations in the validation process exist. While data users may trust the computers to perform part of the validation, as long as these limitations exist, data validators will need to manually review at least some analytical data.

REFERENCES

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Automation of ICP Data Validation for Environmental Analysis.

M.Tatro

WITHDRAWN

12th Waste Testing and Quality Assurance Symposium

New Quality Systems at the U.S. Environmental Protection Agency

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Abstract

The U.S. Environmental Protection Agency (USEPA) established the first mandatory quality assurance (QA) program in 1979. Guidance on the preparation of QA program plans and QA project plans was issued in 1980. While these documents laid the foundation for today's quality systems, they focused on analytical quality control with only limited recognition of the contribution of network design, field operations, and data assessment to the quality of environmental data used in decision making.

In the late 1980s, there was wide recognition that the 1980 QA program description was not serving the environmental community well. Environmental restoration programs were expanding in both the public and private sectors. More holistic approaches to environmental testing and monitoring programs were needed to meet the competing interests of limited resources and growing expectations for performance of monitoring systems.

The USEPA Quality Assurance Division (QAD) was instrumental in the development of the American National Standard Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs (ANSI/ASQC E4-1994). This standard provides the basis for revisions to the USEPA quality system.

The USEPA quality system has a number of components that will be outlined in this presentation. Included will be discussion on the content and status of proposed revisions to the EPA Order that provides the basis for the internal USEPA quality program, the Quality Manual that contains the requirements for the internal Agency programs, and the regulatory changes that will affect contractor/cooperator/grantee operations. Training in the details of these documents will also be discussed.

12th Waste Testing and Quality Assurance Symposium

Achieving Flexibility Through Effective QA Practices

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It is an axiom of good science that effective alternatives, or flexibility, can only be achieved if it is anticipated or planned for at the very early stages of development; the same axiom applies equally well to environmental monitoring activities. The U.S. Environmental Protection Agency (USEPA) recognizes this need for flexibility in its data collection activities by insisting on a planned approach to data acquisition, for example, use of the data quality objectives (DQO) process.

This paper outlines the DQO process as it applies to the overall goal of flexibility and integrates this planning aspect with the latest quality assurance tool from the Agency, "Data Quality Assessment" (DQA). Attention will be given to the analytical features of DQA, and also to the way in which DQA can be used to efficiently reformulate DQOs to achieve the desired flexibility. Copies of Guidance for the Data Quality Objectives Process (EPA QA/G-4) and Guidance for Data Quality Assessment (EPA QA/G-9) will be available for participants.

DATA QUALITY MANAGEMENT FOR EMERGENCY RESPONSE CLEANUP SERVICES

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ABSTRACT

Data Quality Management (DQM) is a particular challenge for U.S. EPA Superfund Emergency Response Cleanup Services (ERCS). The ERCS mechanism of the Office of Superfund provides cleanup services for active and abandoned industrial sites classified as an imminent threat to human health and the environment. Upon initial notification, rapid onsite mobilization (typical response within 3 to 6 hours) can be required at a site over 500 miles away. The emergency nature of these projects preclude opportunities for traditional data quality management such as preparation, review, and implementation of a site-specific sampling and analysis plan. Analytical laboratory support for these efforts must typically be chosen based on the location for sample delivery and availability to meet rush turnaround times. The laboratories providing analytical support for this service are often required to provide appropriate quality, defensible data within the minimum possible time. All analytical results must be generated and reviewed and even validated without delay to the project, so that work at the site may continue without interruption.

In the face of these challenging circumstances, typical laboratory performance and usability of data have yielded marginal results. As a corrective action, DQM program improvements were implemented for the U.S. EPA Region V ERCS Contract. These program improvements help ensure that data collected in support of cleanup efforts are defensible, of appropriate quality, and meet the rapid turnaround time requirements.

The elements of this improved emergency response DQM program include:

- Enhanced Comprehensive Program-wide Quality Assurance Plan (QAPP)
- Emergency Response Laboratory Approval Program (ERLAP)
- Site Control Samples
- Program-Specific Analytical Method Standard Operating Procedures (SOPs)
- Quality Assurance oversight performed by the Analytical Services Coordinator
- Standard Reporting Procedures

During the development and implementation of the DQM program improvements over a 6-quarter period, performance was measured in terms of the percentage of samples rejected or qualified as estimated due to quality control criteria not being met. Sample data were simplified to conduct a trend analysis. One sample may have been analyzed for several different parameters, however, if any one of the parameters was rejected then the entire sample was counted as rejected. Additionally, data qualified as estimated due to sample matrix effects were not included in this measurement. The percentage of samples with rejected data decreased from 25% to 0% over the period, and percentage of samples with data qualified as estimated decreased from 75% to 2%.

INTRODUCTION

The ERCS Contract mechanism provides for rapid response service for removal and remediation of oil, petroleum, and hazardous substances releases that pose an imminent threat to human health or the environment. Projects are conducted under Section 311 of the Clean Water Act and Section 104 of the Comprehensive Environmental Response, Compensation and Liability Act of 1980 as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA), and Subtitle I of the Resource Conservation and Recovery Act as amended by SARA of 1986.

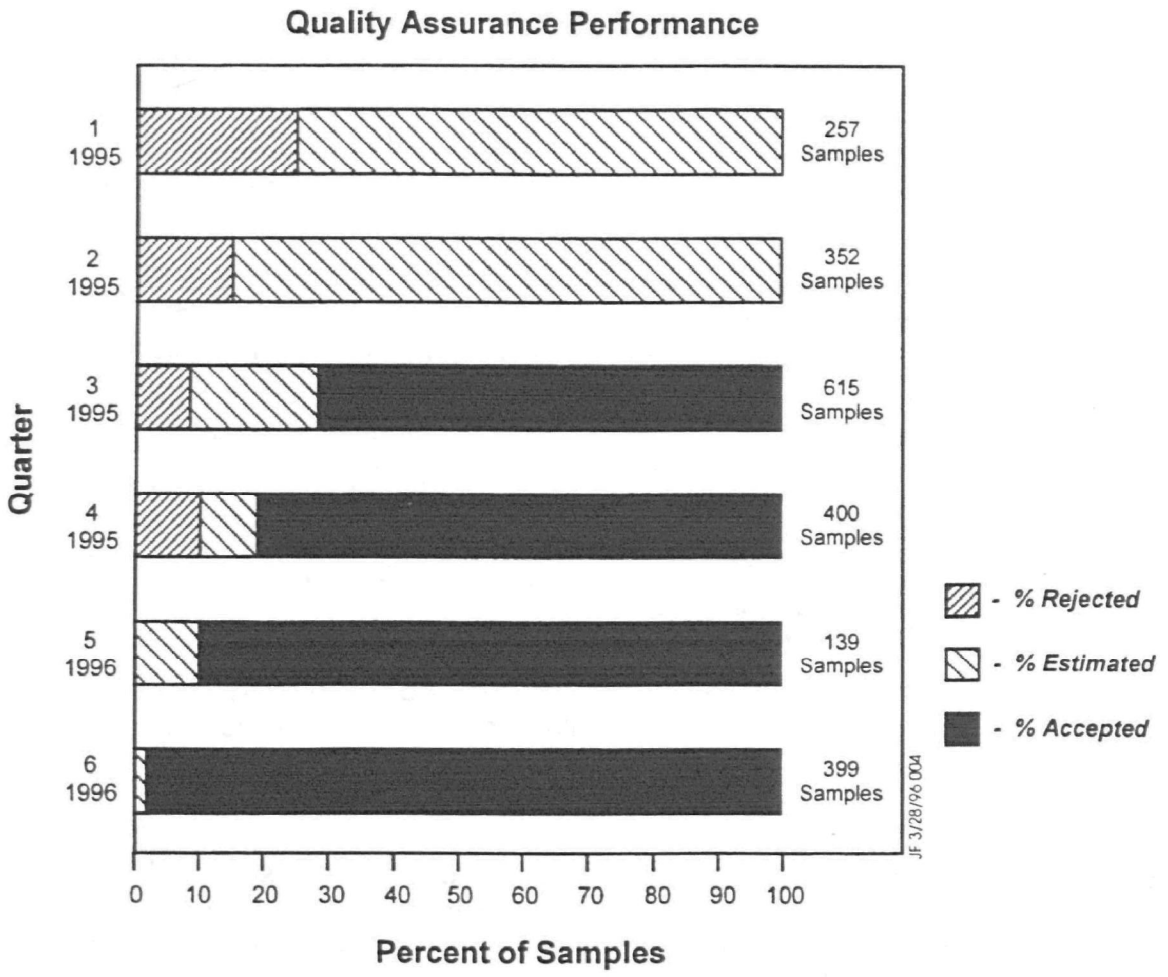
The ERCS mechanism requires rapid onsite mobilization, typically within 3 to 6 hours upon initial notification, at a site that can be over 500 miles away. The emergency nature of the project precludes opportunities for traditional data quality assurance planning such as preparation, review, and implementation of a site-specific sampling plan. Analytical laboratory support is chosen based on laboratory location and the ability to meet rush turnaround times. The laboratories providing analytical support are often required to provide appropriate quality, defensible data within the minimum possible time. All analytical data must be generated, reviewed, and even validated without delay to the project, so that work at the site can proceed without interruption.

DQM Program improvements were implemented for the U.S. EPA Region V ERCS. These improvements ensure that data collected in support of cleanup efforts are defensible, of appropriate quality, and meet the rapid turnaround time requirements.

The DQM program is driven by litigation for cleanup cost recovery and is specified by the Office of Solid Waste, Emergency Response, Quality Assurance/Quality Control Guidance for Removal Activities, Sampling Plan and Data Validation Procedures, EPA/540/G-90/004 (OSWER Directive).

IMPLEMENTATION OF DQM IMPROVEMENTS

Working with a prepared, standard QAPP in support of the ERCS program resulted in marginal laboratory performance and data usability concerns. As a result, the ERCS QA staff determined that a more proactive approach was needed in order to bridge all site-related activities and achieve QA objectives. To that end, program elements were added to improve quality performance. Through continuous improvement, the program quality performance measurement improved dramatically over a 6-quarter period. Prior to implementation of improved program elements, virtually all samples had at least one analytical result that was qualified as estimated or rejected because quality control criteria established by the OSWER Directive were not being met.



The implementation of the Emergency Response Laboratory Approval Program (ERLAP) provided a dramatic improvement in data quality for results provided to ERCS. Over a 2-quarter period, rejected data decreased 15% and data qualified as estimated dropped by 70%. With the implementation of an upgraded program-wide QAPP, standard reporting procedures, and increased QA responsibility by the analytical coordinator, QA performance again improved as rejected data decreased an additional 5% and data qualified as estimated decreased by an additional 10% over the next 2-quarter period. With the implementation of program-specific analytical method SOPs, QA performance again improved as rejected data decreased an additional 10% and data qualified as estimated also decreased by an additional 10%.

ELEMENTS OF DQM IMPROVEMENTS

COMPREHENSIVE PROGRAM-WIDE QUALITY ASSURANCE PLAN (QAPP)

A generic program-wide QAPP is applied to all sites where environmental measurements are conducted. This QAPP must consider all potential program activities including site characterization and extent of contamination assessment, waste compatibility testing, waste characterization, efficiency of applicable treatment procedures and systems, and air monitoring for health and safety.

This program-wide QAPP is a tool for ensuring that the data quality objectives (DQO) of all data collected under the ERCS program are known and documented. To that end, the QAPP presents the organization, objectives, functional activities, and specific QA/QC procedures associated with the program. The QAPP also describes specific protocols to be followed for sampling, sample handling and storage, chain of custody, and laboratory and field analysis. Additional information in the QAPP includes laboratory evaluation and selection criteria and QA program performance measurements. All sampling and analytical method SOPs and data review and validation checklists are provided in the appendices of the QAPP.

A copy of the program-wide QAPP is provided to each ERCS program site, approved laboratories, and analytical coordinators. The QAPP is updated annually to include new requirements and upgraded procedures developed through continuous improvement.

EMERGENCY RESPONSE LABORATORY APPROVAL PROGRAM (ERLAP)

ERLAP was developed and implemented as a corrective action for addressing marginal laboratory performance. The laboratory approval program consists of a preliminary capability review to determine qualifications and a formal technical

systems audit to review procedures and documentation. Those laboratories successfully completing the audit, which includes resolution of all audit exceptions and re-audit, as appropriate, are approved in ERLAP for the ERCS program.

Prior to the selection of a laboratory for providing service to ERCS, a preliminary review is conducted that consists of an evaluation of the following: state and federal certifications including audit sample results; run logs or bench sheets for analytes of interest; a laboratory prepared analyst experience table; and the laboratory's Quality Assurance Management Plan (LQMP).

The LQMP can provide evidence of the existence of an acceptable quality management program. The LQMP should, at minimum, contain descriptions of the following: organization and policy, facilities and equipment, document control, analytical methodology and acceptance criteria, data and report generation, QA and QC procedures. The following factors are evaluated in the LQMP: visibility of the QA Organization, QA policy, facilities and equipment capabilities, documentation control, definition of QA objectives for every analyte and method, data and report preparation procedures, QC sample procedures, internal systems audits, and performance evaluation samples.

A formal systems audit is performed of those laboratories successfully meeting the requirements of the preliminary review. This audit includes both form and facility evaluations, review of laboratory procedures and documentation against the requirements of SW-846, and the ability and willingness to meet OSWER Directive requirements, regional requirements, the program-wide QAPP and the laboratory's own internal SOPs. An audit checklist, standardized to address all specific requirements, is utilized to maintain consistency and objectivity across all laboratories that are evaluated.

Laboratories are provided a 1-week advance notification of the audit, when possible. An inbriefing meeting is held to introduce audit participants, discuss the goal of the audit, identify specific areas for review, and to introduce laboratory personnel to the ERCS program. Facility evaluations and form auditing are conducted, along with laboratory staff interviews. At the conclusion of the audit, an outbriefing is held to discuss findings and observations.

In general, the areas for review include sample receipt and storage, chain of custody, sample container and glassware cleaning requirements, sample preparation and analysis, preparation and analysis documentation, detection limit studies, instrument calibration, instrument maintenance, data management, document control, Laboratory QA and QC procedures, organizational structure, and personnel experience.

Following the audit visit, a written report is provided to the laboratory detailing audit exceptions. A forum is established with the laboratory and the ERCS program QA staff to address and resolve all exceptions. Upon successful resolution of audit exceptions, the laboratory is revisited to review all corrective action that was taken and to ensure that all compliance issues have been met. The laboratory is classified as ERLAP approved for the ERCS program only after successful resolution of all audit exceptions.

SITE CONTROL SAMPLES

Site control samples were implemented to address QA for data validation purposes on smaller sites when an approved laboratory is not available and auditing is not cost-effective and for other laboratory performance evaluation requirements. Three different types of control samples have been designed to meet ERCS program requirements.

The site media control sample, which is least expensive, is prepared by the ERCS QA staff by spiking a QC standard into sample media from the site in a controlled environment. This control is then shipped to the laboratory with other site samples for analysis. Although statistical data is not available to evaluate absolute laboratory performance, certain qualitative information can be derived. In the event of poor recovery or other QC issues concerning this control sample, a reference laboratory may also be asked to evaluate the sample. This approach is utilized for a site where samples submitted to the laboratory are comprised of an extremely complicated matrix. The site media control sample used in conjunction with matrix spike and duplicate sample data can be used to extrapolate the laboratory's qualitative performance in recovering the analytes of interest.

Another type of site control sample is the standardized performance evaluation (PE) sample. This sample is provided by a supplier and is prepared with standard media and established acceptance ranges. The supplier ships the samples directly to the laboratory. Purchased PE samples generated by an external source provide statistical data for comparability studies with multiple laboratories. This approach is more expensive, however, and the laboratory will know the true nature of the sample and may treat it differently than the site samples. This approach is appropriate for a relatively easy sample matrix, such as drinking water, for performing a preliminary evaluation of a laboratory, or when the samples are used in an on-going study with multiple participants.

A third option is the "double blind " PE sample in which the site sends a supplier a bottle identical to those used in the field. The supplier prepares a PE sample and sends it to the site to be labeled and delivered to the laboratory with other samples for analysis. The control is designed to appear similar to other site

samples and permits a relatively absolute evaluation of laboratory performance. Although this option is the most expensive, it is appropriate for certain confirmational analyses.

The decision to use a specific option is site specific based on many factors, including the data quality objectives for the site. Ultimately, the choice of a particular type of control sample may result in obtaining qualitative information concerning data usability, rather than a strict determination of laboratory performance. The needs of the site and cost-effectiveness may warrant no additional requirements for laboratory performance data.

PROGRAM-SPECIFIC ANALYTICAL METHOD SOPs

A program interpretation for ERCS sample testing, based on requirements recommended by the OSWER Directive, regional requirements,.and the guidance of the SW-846 protocols, is detailed in parameter specific preparation and analysis method SOPs. These SOPs specify requirements for sample preservation, preparation and cleanup, initial and continuing calibration, method performance (check and/or laboratory control samples), precision and accuracy, method blanks, and quantitation. The SOPs define acceptance criteria for each parameter as well as required laboratory corrective action when the criteria are not met.

The SOPs were generated by using the SW-846 protocol as the basis for sample preparation and analysis and modifying where appropriate with OSWER Directive specifications, regional requirements, and program-wide standard method interpretation of the protocol. Additionally, the SOPs specify a notification requirement for the laboratory to report any modifications prior to performing the sample analysis.

The SOPs are provided to potential laboratories during the bidding process, along with the request for pricing and procurement terms and conditions documentation. This provides each potential laboratory with the knowledge of the exact preparation, analytical, deliverable, and reporting requirements so that the service may be appropriately priced. The SOPs are also included in the program-wide QAPP available to all site personnel, ERLAP Laboratories, and analytical coordinators.

ANALYTICAL SERVICES AND QA/QC COORDINATION

The analytical coordinator plays a critical role in DQM for ERCS. The coordinator is the point of contact for both the site and the laboratory, and as such provides technical support for sampling and analytical activities. The coordinator

continuously monitors the laboratory to ensure that all data meets the data quality objectives. The coordinator also works with site personnel to interpret data quality objectives and provide guidance during sampling activities to ensure that sample handling will not compromise data quality. The coordinator also performs the function of data review and validation, and determines corrective action as necessary.

STANDARD REPORTING PROCEDURES

Documentation is an essential part of the QMP. As such, standard reporting forms have been created with a convenient, user-friendly checklist format. These checklists are used for the initial notification QA/QC requirements, and the daily laboratory coordination and QA/QC status form, analytical testing requirements, and data review and data validation. These checklists are a tool by which all information can be easily recorded, reviewed, and audited as necessary. All checklists are included in the program-wide QAPP provided to each site, ERLAP approved laboratory, and the analytical coordinator.

SUMMARY

The implementation of the DQM program corrective action elements for marginal laboratory performance and usability of data concerns has resulted in significant performance improvement. The development of ERLAP and improved laboratory auditing procedures, as well as implementation of analytical method SOPs are elements that are particularly significant in the program's success.

The modified procedures with the additional form and checklist requirements not only provide an appropriate level of documentation but facilitate effective communication between the site, program management, and the laboratory. The program requirements necessitate a team approach to working the project, and when accomplished properly, the DQM program performs at an optimum level.

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DOCUMENTATION AND RECORD KEEPING GUIDELINES

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ABSTRACT

In order for analytical data to be considered legally defensible, the general rule is that the sampling and analysis activities must be performed according to published analytical methods and that adequate documentation is available to support the sample results. A previous publication addressed guidelines for generating defensible data.[1] Although documentation and record keeping are major components in the generation of analytical data used for environmental assessment and monitoring, the emphasis has historically been placed on the adherence to technical methods for performing the field sampling and analysis activities. While technical requirements are usually documented in published analytical methods and procedures, the criteria for proper documentation and record keeping is typically not clearly defined or readily available. Analytical data may be technically acceptable but not defensible due to poor documentation and record keeping practices. Without adequate and accurate records, data that is subpoenaed for litigation purposes may be disqualified and any subsequent decisions that were to be made based on the data may be dismissed.

This paper provides guidance on the proper documentation procedures and record keeping practices that should be used for environmental field sampling and analysis activities. General do's and don'ts for documentation as well as ways to streamline the process using electronic notebooks, bar coded sample labels, and electronic chain of custody records are also addressed. Specific information that should be recorded are provided for the following: document control logs, signature lists, field logs, sample bottle labels, chain of custody records, sample receipt logs, sample receipt checklists, sample preparation logs, sample analysis logs, instrument run logs, instrument maintenance logs, chemical/standard receipt logs, standards/reagent preparation logs and standard/reagent labels.

INTRODUCTION

This paper provides general guidelines for documenting information and a list of minimum information that should be included when recording data for the following categories: (1) Document Control, (2) Sampling and Sample Handling, (3) Sample Preparation and Analysis, and (4) Chemical Handling.

GENERAL GUIDELINES

All information related to environmental sampling and analysis activities should be accurately and adequately documented in order to allow reconstruction and verification by

a third party at a future time. General guidelines on how to document information are listed below.

- Record all data in permanently bound logbooks that have consecutively numbered pages. Computerized log sheets may be used in place of a bound logbook if the sheets are numbered and kept in a bound format.

- Record all entries promptly and legibly using indelible ink. Pencil or non-permanent ink pens should not be used.

- Record information accurately and completely, identifying the who, what, where, when and how of each activity.

- Do not erase, obliterate or overwrite information. Correction fluid should not be used.

- Make corrections to errors by drawing a single line through the error and dating and initialing the correction.

- Cross out blank pages or sections of pages in logbooks with an "X" or "Z" to prevent the addition of data at a later date.

- Review logs on a regular basis by supervisory personnel to verify adherence to required analytical and documentation procedures.

DOCUMENT CONTROL

All records and documentation related to environmental sampling and analysis should be included in a document control system.

Document Control Logs

Document control logs are used to maintain a record of all documents (i.e., logs, forms, QA Manuals, SOPs, etc.) that should be controlled. Record the following minimum information in a document control log:

- Title of document
- Assigned document control number
- Location or distribution of document
- Date issued
- Inclusive dates of use
- Date archived

Signature Lists

Signature lists are used to keep a record of the signatures and initials of all personnel that record data. Record the following minimum information in a signature list:

- Employee's typed or printed name and initials
- Employee's handwritten signature and initials
- Employment start date
- Employment termination date

SAMPLING AND SAMPLE HANDLING

Information on the collection and handling of samples should be completely documented to allow the details of sample collection and handling to be recreated and used with the sample results.

Field Logs

Field logs are used to document events that occurred during field sampling and to identify information on individual field samples. For projects involving drilling operations, boring logs should be used. Record the following minimum information in a field log:

- Project name/ID and location
- Sampling Personnel
- Geological observations
- Atmospheric conditions
- Field measurements
- Sample dates, times, and locations
- Sample identifications
- Sample matrix
- Sample descriptions (e.g., odors and colors)
- Number of samples taken per location
- Description of any QC samples
- Any deviations from the sampling plan
- Any difficulties in obtaining sample or any unusual circumstances

Sample Bottle Labels

Sample bottle labels are used to identify sample bottles and to link each sample with the information documented in the field log and Chain of Custody Record. The sample bottle label should contain enough information to avoid misidentification. The use of a bar code system is recommended for electronically creating the sample bottle labels. Record the following minimum information on a sample bottle label:

- Sample ID (or bar code with ID number)
- Date and time of collection
- Sampler's signature
- Parameter(s)
- Preservative (if applicable)

Chain Of Custody Records

Chain of Custody Records are used to document the custody and exchange of sample(s) as they are transported from the point of collection to receipt by the laboratory. In some situations, chain of custody may begin when clean containers are provided by the laboratory. The use of a bar code system is recommended for completing the Chain of Custody Record. Record the following minimum information on a Chain of Custody Record:

- Project name/ID and location
- Sample specific information: sample ID, date/time collected, sample matrix, container type, preservatives, parameter and method(s) of analysis, etc.
- Sampler's signature
- Signatures of all personnel who had custody of the samples
- Date and time of each transfer
- Air bill or carrier ID number

Sample Receipt Logs

Sample receipt logs are used to document the receipt of the samples by the laboratory. The documentation must be chronological and permanent. Record the following minimum information in a sample receipt log:

- Date and time of receipt
- Sample collection date
- Client sample ID
- Laboratory sample ID
- Number of samples
- Sample matrices
- Requested analysis, including method number(s)
- Signature or initials of the sample custodian or designee
- Sampling kit code (if applicable)

Sample Receipt Checklists

Sample receipt checklists are used to document the condition of the samples as received by the laboratory. Any unacceptable conditions or nonconformances with the samples should be documented and the client notified immediately. Record the following

minimum information on a sample receipt checklist:

- Client sample ID
- Laboratory sample ID
- Presence or absence of Chain of Custody Record with samples
- Presence or absence of custody seals
- Condition of custody seals (if applicable)
- Temperature of cooler
- Sample condition at time of receipt
- Acceptability of sample container, volume, and preservation
- Presence of headspace in samples for volatile organics analysis
- Agreement between Chain of Custody Record and sample labels
- Radioactivity screen (if applicable)

SAMPLE PREPARATION AND ANALYSIS

Information on the preparation and analysis of samples should be completely documented to allow the details of sample preparation and analysis to be recreated and reviewed. Data generated on laboratory instruments should correspond with the sample information entered in the preparation and analysis logs. Electronic logs generated through the laboratory information management system are recommended.

Sample Preparation Logs

Sample preparation logs are used to document the preparation of samples by a specific method or procedure (e.g., metals digestions or organic extractions). Record the following minimum information in a sample preparation log:

- Parameter/analyte
- Method number
- Date and time of preparation
- Analyst's initials or signature
- Laboratory sample ID
- Type/matrix of samples
- Initial sample volume or weight
- Final sample volume
- Concentration and amount of spiking solutions used
- Quality control samples included with the sample batch
- ID for reagents, standards and spiking solutions used
- Comments

Sample Analysis Logs

Sample analysis logs are used for documenting information related to the analysis and

calculation of the final analytical results. The sample analysis log may either be parameter specific or may contain several related parameters. Data should be recorded in the order in which it was generated. Record the following minimum information in a sample analysis log:

- Parameter/analyte
- Method number
- Date and time of analysis
- Analyst's initials or signature
- Laboratory sample ID
- Sample aliquot
- Dilution factors and final sample volumes (if applicable)
- Absorbance values, peak heights, or initial concentration reading
- Final analyte concentration
- Calibration data (if applicable)
- Correlation coefficient, slope, and y-intercept (if linear regression is used)
- Calculations
- Comments on interferences or unusual observations noted during the analysis
- Quality control information, including percent recovery for laboratory control standards and matrix spikes and RPD for sample duplicates.

Instrument Run Logs

Instrument run logs are used to record the analysis of all calibration standards, field samples and quality control samples processed during an analytical run. An instrument run log is generally used for recording the analyses performed on all major instrumentation, such as an ICP, GFAA, FLAA, GC and GC/MS. The data should be recorded on the instrument run log in chronological order based on the actual analytical run sequence. Record the following minimum information in an instrument run log:

- Instrument ID
- Parameter/analyte
- Method number
- Date/time analyzed
- Analyst's initials or signature
- Laboratory IDs for standards, field samples, and quality control samples
- Comments

Instrument Maintenance Logs

Instrument maintenance logs are used to document the maintenance and repair activities performed on major instrumentation. The instrument maintenance log should be kept near the instrument to facilitate the documentation of all repairs and maintenance activities.

Record the following minimum information in an instrument maintenance log:

- Name/type of instrument
- Instrument manufacturer and model number
- Serial number
- Date received and date placed in service
- Instrument ID assigned by the laboratory (if used)
- Service contract information, including the phone number and name of the service representative
- Description of each maintenance or repair activity performed
- Date and time when each maintenance or repair activity was performed
- Initials of person who performed the maintenance or repair activity

If an instrument must be removed from service due to a non-routine maintenance procedure or repair, then the date and reason for removing the instrument from service should be recorded. Document in the log the repair or non-routine maintenance which was performed, including the date, service representative's name and company, and the date the instrument was returned back to service.

CHEMICAL HANDLING

Information on chemical handling should be completely documented to allow the details of standards preparation to be recreated and traceable from the analysis back to the source materials. The accuracy and validity of chemicals used for preparing reagents and standards used for calculating analytical results must be verifiable.

Chemical/Standard Receipt Logs

Chemical/standard receipt logs document the receipt of analytical standards and chemicals used for the preparation of standards and reagents used in the laboratory. Record the following minimum information in a chemical/standard receipt log:

- Laboratory control number
- Date of receipt
- Initials or signature of person receiving chemical
- Chemical name and catalog number
- Vendor name and lot number
- Concentration or purity of standard
- Expiration date

All standards and chemicals received by the laboratory should have a chemical receipt label affixed to the bottle or container. Record the laboratory control number, date of receipt, and expiration date on the chemical receipt label.

Standards/Reagent Preparation Logs

Standards/reagent preparation logs are used for documenting the preparation of standards, reagents, spiking solutions, surrogate solutions, and reference materials. Record the following minimum information in a standard/reagent preparation log:

- Date of preparation
- Initials of the analyst preparing the standard solution or reagent
- Concentration and identification of stock solution or neat materials
- Volume or weight of the stock solution or neat materials
- Final volume of the solution being prepared
- Final concentration of the solution being prepared
- Laboratory ID/control number assigned to the new solution
- Standardization of reagents, titrants, etc. (if applicable)
- Expiration date

Standard/Reagent Labels

Standard/reagent labels are used to label standards and reagents. Labels should be affixed to the container for each standard or reagent prepared by the laboratory. Record the following minimum information on standard/reagent labels:

- Laboratory ID/control number
- Name of standard or reagent
- Concentration or purity of standard or reagent
- Preparation date
- Initials of preparer
- Expiration date

SUMMARY

As environmental enforcement actions increase, the importance of documentation of sampling and analysis activities has escalated. By ensuring that technically sound practices are employed and that information is adequately documented, environmental data can be verifiable and withstand the intense scrutiny during legal review or litigation. Good documentation and record keeping procedures not only ensure that environmental measurement results are accurate and traceable and but also allow appropriate decisions to be made based on the correct sample results.

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NIST SRMs FOR ORGANIC ENVIRONMENTAL ANALYSES - CURRENT AVAILABILITY AND APPROACH TO CERTIFICATION

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ABSTRACT: NIST has many Standard Reference Materials (SRMs) for use by the organic environmental community ranging from simple solutions containing a number of analytes to natural matrix materials. SRMs are certified reference materials (CRMs) issued by NIST. NIST SRMs for use in this field are listed. Certified values for NIST SRMs are generally based on agreement of results obtained from two or more independent and reliable analytical procedures. For NIST certification measurements of organic components in complex natural matrix materials, the extraction and cleanup/isolation steps as well as the final analytical measurements are generally based on different separation characteristics to minimize the possibility of similar biases in both measurements. The use of this approach is shown in the certification design of a number of recently issued NIST SRMs.

Currently Available NIST SRMs

In the past 15 years, the National Institute of Standards and Technology (NIST) has developed a number of SRMs to assist the environmental community in validating measurements of organic environmental contaminants such as aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl congeners (PCBs), and chlorinated pesticides.[1,2] Table 1 lists NIST SRMs for this field that are simple solutions, each containing a number of these analytes of interest for uses such as calibration of chromatographic instrumentation for retention times and detector response factors or in analyte recovery studies. Sixteen natural matrix NIST SRMs that are representative of different environmental samples are described in Table 2. These natural matrix SRMs can be used in the development and validation of analytical methods and can also be analyzed on a regular basis in conjunction with unknown samples with similar matrices to continually monitor the accuracy and precision of the analytical measurements.

Certification Measurements of Recently Issued SRMs for Organic Contaminants

Introduction: Certified values for NIST SRMs are generally based on agreement of results obtained from two or more independent and reliable analytical procedures. For the determination of organic components in complex natural matrix materials, the extraction and cleanup/isolation steps as well as the final analytical measurements are based on different separation characteristics to minimize the possibility of similar biases in both measurements[2]. The use of this approach can be shown in the certification design of a number of recently issued NIST SRMs. For example, the certification of polychlorinated biphenyl (PCB) congeners and chlorinated pesticides in the recently issued SRM 1945, Organics in Whale Blubber, included using different extraction/sample preparation procedures and analytical techniques based on two gas chromatographic (GC) capillary columns with different selectivity and two different detectors, electron-capture (ECD) and mass spectrometric (MSD).

Determination of PCBs and Pesticides in SRM 1945: An example of the use of this approach is shown in the certification of the recently issued NIST SRM 1945, Organics in Whale Blubber[3], for PCB congener and chlorinated pesticide concentrations that is described in detail in Reference 4. Two groups of this frozen blubber tissue homogenate samples, were selected from the SRM sample pool according to a stratified random scheme. Analytical techniques used for these two groups of samples utilized two different detectors, ECD and MSD. Schantz *et al.*[5], have reported and compared the results of the validation of these analytical procedures for the analysis of five existing natural-matrix CRMs (a marine sediment, a marine tissue, and three fish [cod and mackerel] oils). The ECD measurements included using two GC capillary columns with different selectivity (a 5% phenyl-substituted methylpolysiloxane stationary phase and a dimethylpolysiloxane phase containing 50% methyl C-18). For the ECD analyses, samples were Soxhlet-extracted with dichloromethane, the majority of the lipid and biogenic material was removed using size exclusion chromatography, and normal-phase liquid chromatography was used to isolate two fractions containing (1) the PCB congeners and lower polarity chlorinated pesticides and (2) the more polar chlorinated pesticides. For the GC/MS analyses, the second group of samples were Soxhlet-extracted with 1:1 hexane/acetone (v/v), sulfuric acid was used to remove lipid interferences, and a silica solid-phase extraction column was then used to remove the polar interferences in the extracts. Aliquots of a solution of five internal standards were added to the blubber prior to extraction for quantification purposes. Calibration response factors for the analytes relative to the internal standards were determined by analyzing aliquots of the following: SRM 2261 (Concentrated Chlorinated Pesticides in Hexane), SRM 2262 (Concentrated PCB Congeners in Iso-octane), gravimetrically prepared solutions of additional analytes not contained in SRMs 2261 and 2262, and the internal standards. (The purities of the components in the solution of "additional analytes" were assessed and the concentrations verified chromatographically.) Samples of SRM 1588, Organics in Cod Liver Oil, were analyzed similarly and concurrently with the whale blubber samples. Experiments for each technique were designed so that sources of possible random error in the measurements would be replicated to reduce the bias they could cause. The results from these three analytical procedures were in good agreement and were combined to provide certified concentrations for 27 PCB congeners and 15 chlorinated pesticides[4]. A summary of the analytical results by method and the resulting certified concentrations and uncertainties for 36 of the 42 certified constituents is shown in Table 2.

Determination of PAHs in SRM 1974a: Similarly, the certification of PAHs in SRM 1974a, Organics in Mussel Tissue[6], is based on results obtained using different extraction/sample preparation procedures with four different analytical techniques: (1) reversed-phase liquid chromatography with fluorescence detection (LC-FL) of the total PAH fraction; (2) reversed-phase LC-FL of isomeric PAH fractions isolated by normal-phase LC (i.e., multidimensional LC); (3) GC/MS of the PAH fraction on a 5% phenyl-substituted methylpolysiloxane stationary phase; and (4) GC/MS of the PAH fraction on a smectic liquid crystalline stationary phase that provides excellent shape selectivity for the separation of PAH isomers. Details of the use of these techniques have been reported previously for the certification of PAHs in SRM 1941a, Organics in Marine Sediment[7,8].

Certification in progress – SRM 1944: Independent and validated procedures are being used for the determination of selected PAHs, PCB congeners, and chlorinated pesticides in a new NIST reference material, SRM 1944, a highly contaminated sediment. In addition, the candidate SRM

1944 sediment is being analyzed by a large number of national and international laboratories in intercomparison exercises for both selected organic and elemental analytes. These data, from laboratories using a number of different extraction, cleanup, and analytical techniques, will be evaluated for use in the certification.

CONCLUSIONS

In the past 15 years, NIST has produced many SRMs for trace organic contaminants, especially in support of measurement activities for the marine environment. Through the use of validated procedures designed to differentiate among potential sources of measurement bias by exploiting differences in separation and selectivity characteristics in the extraction, isolation, and measurement steps, the possibility of having similar biases in these certification measurements is minimized. Even though these analytical procedures have some similarities (e.g., nonpolar solvent extraction and GC separations for PCB congeners and chlorinated pesticides) and are therefore not totally independent, this approach is appropriate for NIST SRM certification given the current state of the art for these measurements.

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Table 1. NIST Calibration Solution SRMs for the Determination of Organic Environmental Contaminants

SRM No.	Title	Date Issued	Certified Constituents	Noncertified Constituents
1491	Aromatic Hydrocarbons in Hexane/Toluene	1989	PAHs (23)	PAHs (1)
1492	Chlorinated Pesticides in Hexane	1992	Pesticides (15)	
1493	Chlorinated Biphenyl Congeners in 2,2,4-Trimethylpentane	1995	PCBs (18)	PCBs (2)
1494	Aliphatic Hydrocarbons in 2,2,4-Trimethylpentane	[a]	Hydrocarbons (20)	
1583	Chlorinated Pesticides in 2,2,4-Trimethylpentane	1985	Pesticides (5)	Pesticides (1)
1584	Priority Pollutant Phenols in Methanol	1984	Phenols (10)	Phenols (1)
1585	Chlorinated Biphenyls in 2,2,4-Trimethylpentane	1986	PCBs (8)	
1586	Isotopically Labeled and Unlabeled Priority Pollutants in Methanol	1984	Priority pollutants (10)	
1587	Nitrated PAHs in Methanol	1985	Nitro-PAHs (6)	Nitro-PAHs (1)
1596	Dinitropyrene Isomers and 1-Nitropyrene in Methylene Chloride	1987	Nitro-PAHs (4)	
1614	Dioxin (2,3,7,8-TCDD) in Iso-octane	1985	Dioxins (2)	Dioxins (2)
1639	Halocarbons (in Methanol) for Water Analysis	1983	Halocarbons (7)	
1647c	Priority Pollutant PAHs (in Acetonitrile)	1992[b]	PAHs (16)	
2260	Aromatic Hydrocarbons in Toluene (Nominal Concentration 60 µg/mL)	1991	PAHs (23)	PAHs (1)
2261	Chlorinated Pesticides in Hexane (Nominal Concentration 2 µg/mL)	1992	Pesticides (15)	
2262	Chlorinated Biphenyl Congeners in 2,2,4-Trimethylpentane (Nominal Concentration 2 µg/mL)	1995	PCBs (25)	PCBs (4)
2269	Perdeuterated PAH-I	[a]	Perdeuterated PAHs (5)	
2270	Perdeuterated PAH-II	[a]	Perdeuterated PAHs (6)	
2273	DDTs and Metabolites in Solution	[a]	DDTs and Metabolites (7)	
2274	PCB Congener Solution-II	[a]	PCBs (11)	
2275	Chlorinated Pesticide Solution-II	[a]	Pesticides (9)	
2276	Three Planar PCBs in Solution	[a]	PCBs (3)	

[a] Certification in progress.

[b] SRM 1647 was first issued in 1981.

Table 2. NIST Natural Matrix SRMs for the Determination of Organic Contaminants in Environmental Samples

SRM No.	Title	Date Issued	Certified Constituents	Noncertified Constituents
1580	Organics in Shale Oil	1980	PAHs (5); Phenols (3) PANH (1)	Phenols (6); PANH (1)
1581	Polychlorinated Biphenyls in Oils	1982	Aroclor 1242/1260	
1582	Petroleum Crude Oil	1984	PAHs (5); PASH (1)	PAHs (5); Phenols (2); PANH (1)
1588	Organics in Cod Liver Oil	1989*	PCBs (5); Pesticides (10)	PCDDs/PCDFs (7)
1589	PCBs (as Aroclor 1260) in Human Serum	1985	Aroclor 1260	Dioxins (2)
1597	Complex Mixture of PAHs from Coal Tar	1987	PAHs (12)	PAHs/PASH/PANH (18)
1648	Urban Particulate Matter	1978	Trace elements (9)	Trace elements (25); PAH (13)
1649	Urban Dust/Organics	1982*	PAHs (5)	PAHs (9)
1650	Diesel Particulate Material	1985*	PAHs (5) Nitro-PAHs (1)	PAHs (6); Nitro-PAHs (3); PAQ (1)
1939	PCBs (Congeners) in River Sediment	1990	PCBs (3)	PCBs (14); Pesticides (5); PAHs (5)
1941a	Organics in Marine Sediment	1994	PAHs (23); PCBs (21) Pesticides (6)	PAHs (14); PCBs (7); Pesticides (3) Aliphatics (17); Trace Elements (27)
1944	Highly Contaminated Marine Sediment	**	PAHs; PCBs; Pesticides Trace Elements	Aliphatics, PCDDs/PCDFs
1945	Organics in Whale Blubber (Frozen)	1993	PCBs (27); Pesticides (15)	PCBs (2); Pesticides (2)
1974a	Organics in Mussel Tissue (*Mytilus edulis*) (Frozen)		1995 Trace Elements (28) Pesticides (7)	PAHs (15); PCBs (20)Aliphatics (16); PAHs (18); PCBs (4); Pesticides (4) Methylmercury
1975	Diesel Particulate Extract	**	PAHs; Nitro-PAHs	
2974	Organics in Mussel Tissue (*Mytilus edulis*) (Freeze Dried)	**	PAHs; PCBs; Pesticides Methylmercury	Aliphatics, Trace Elements

PANH = Polycyclic aromatic nitrogen heterocycles
PAQ = Polycyclic aromatic quinones
PASH = Polycyclic aromatic sulfur heterocycles
PCDD = Polychlorinated dibenzodioxins
PCDF = Polychlorinated dibenzofurans
* = Certification of additional analytes in progress.
** = Certification in progress

Table 3. Certified Concentrations and Summary of Analytical Results for 36 of the 27 PCB Congeners[a] and 15 Chlorinated Pesticides Certified in SRM 1945, Organics in Whale Blubber[3)]

	Concentration (µg/kg wet basis)			
Constituent	Certified[b] Concentration	GC-ECD[c] (CP Sil 5 C18 CB)[d]	GC-ECD[c] (DB-5)[d]	GC-MSD[c] (DB-5)[d]
PCB 18	4.48 ± 0.88	4.91 (0.32)	3.78 (0.30)	4.76 (0.33)
PCB 44	12.2 ± 1.4	12.25 (0.64)	13.17 (0.74)	11.25 (0.94)
PCB 49	20.8 ± 2.8	18.54 (0.84)	22.64 (0.74)	21.28 (0.95)
PCB 52	43.6 ± 2.5	45.1 (2.5)	42.8 (2.9)	42.4 (2.1)
PCB 66	23.6 ± 1.6	23.2 (1.8)		23.7 (1.9)
PCB 95	33.8 ± 1.7	34.1 (1.7)		33.6 (1.6)
PCB 66/95			[59.7][e] (2.8)	
PCB 87	16.7 ± 1.4	16.25 (0.68)	17.71 (0.91)	16.66 (0.47)
PCB 99	45.4 ± 5.4	41.5 (2.9)	47.3 (2.8)	47.3 (2.3)
PCB 101/90	[65.2 ± 5.6]	61.6 (3.3)	[66.3] (4.3)	[68.3] (2.3)
PCB 105	30.1 ± 2.3	31.6 (2.4)	30.0 (2.4)	29.8 (1.3)
PCB 118	74.6 ± 5.1	74.9 (4.7)	75.6 (4.8)	71.7 (3.7)
PCB 128	23.7 ± 1.7	23.2 (2.2)	24.6 (2.1)	22.9 (1.5)
PCB 138/163/164	131.5 ± 7.4	131.7 (8.0)	127.7 (9.0)	134.2 (5.7)
PCB 149	106.6 ± 8.4	101.6 (6.6)	106.6 (7.5)	110.6 (4.7)
PCB 156	10.3 ± 1.1	9.76 (0.69)	10.93 (0.66)	10.07 (0.72)
PCB 170/190	[40.6] ± 2.6	39.3 (2.6)[h]	[40.2] (2.6)	[42.4] (1.9)
PCB 180	106.7 ± 5.3	105.5 (6.2)	108.8 (6.7)	109.5 (4.9)
PCB 183	36.6 ± 4.1	39.5 (2.9)	36.0 (2.8)	34.4 (1.8)
PCB 187	105.1 ± 9.1	111.7 (7.0)	103.1 (6.7)	100.9 (5.1)
PCB 194	39.6 ± 2.5	39.2 (2.4)	41.3 (2.6)	39.4 (1.8)
PCB 206	31.1 ± 2.7	32.9 (1.9)	30.7 (1.9)	29.7 (1.6)
PCB 209	10.6 ± 1.1	10.75 (0.87)	11.16 (0.94)	9.95 (0.85)
2,4'-DDE	12.28 ± 0.87	12.46 (0.57)	11.69 (0.70)	12.27 (0.54)
4,4'-DDE	445 ± 37	421 (31)	453 (25)	440 (34)
2,4'-DDD	18.1 ± 2.8	20.0 (1.3)	16.2 (1.4)	17.96 (0.93)
4,4'-DDD	133 ± 10	128 (10)	132.4 (9.1)	138.3 (6.2)
2,4'-DDT	106 ± 14	113.0 (7.0)	98 (10)	101.6 (6.3)
4,4'-DDT	245 ± 15	238 (46)		246 (12)
HCB	32.9 ± 1.7	32.2 (2.1)	33.1 (2.2)	33.8 (1.8)
γ-HCH	3.30 ± 0.81	3.90 (0.37)	2.63 (0.37)	3.37 (0.24)
α-HCH	16.2 ± 3.4	18.6 (1.2)	14.4 (1.3)	15.3 (1.0)
heptachlor epoxide	10.8 ± 1.3	10.74 (0.87)	10.1 (1.2)	11.2 (1.0)
oxychlordane	19.8 ± 1.9	20.6 (1.5)	20.7 (1.0)	18.61 (0.83)
cis-chlordane	46.9 ± 2.8	47.2 (3.2)	46.0 (3.4)	47.2 (2.5)
trans-nonachlor	231 ± 11	229 (16)	233 (16)	232 (10)
Mirex	28.9 ± 2.8	30.1 (2.3)	29.6 (2.3)	26.8 (2.2)

[a] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell[9]. When two or more congeners are known to coelute, the PCB congener listed first is the major component and the additional congeners may be present as minor components. Quantitative results are based on the response of the congener listed first.

[b] The certified values are weighted means of results from three analytical techniques. The uncertainty is based on a 95% confidence interval for the true concentration and includes an allowance for differences between the analytical methods used.

[c] Numbers in parentheses are one standard deviation of a single measurement.

[d] Capillary column stationary phase

[e] Numbers in [ ] indicate known coelution of two or more congeners. PCB 66 and 95 coelute under the GC-ECD (DB-5 column) conditions used; PCB 164 is separated from PCB 138 and PCB 163 when using the CP Sil 5 C18 column; PCB 190 is separated from PCB 170 when using the CP Sil 5 C18 column.

ABSTRACT

DATA USABILITY: THE NEXT STEP TO DATA VALIDATION FOR SITE REMEDIATION

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In order to properly evaluate analytical data and determine its usability for site remediation, the data reviewer must not only understand the analytical methods and how to apply USEPA validation qualifiers to the data, but must be familiar with the project-specific documents (e.g., investigative reports and sampling and analysis plans) and fully understand the objectives of the project. The objectives to consider include: the type of investigation taking place (e.g., site characterization, remedial investigation/feasibility study, human/ecological risk assessments, engineering design, etc.); the principal contaminants of concern; the regulatory agencies reviewing the data; and the comparison of reported values/detection limits to regulated cleanup limits and/or health-based criteria. These items must be considered before making a complete assessment of the analytical results. Based on our experience, we will present how these factors affect the validation process and the ultimate usability of the data.

Oftentimes, data usability is determined solely on the basis of the data validation process. Published data validation guidelines, such as USEPA CLP National Functional Guidelines for Data Review, depict methods to alert the data user of potential problems by applying qualifiers to the data. An overview of the input of flags on data and their interpretation and impact on usability will be discussed.

Rejection of data would be the worst case scenario involving data usability. This could lead to resampling/reanalysis, thus driving up the cost of investigations. However, data which are rejected based upon USEPA data validation criteria may be deemed conditionally usable when applying professional judgement in conjunction with project-specific information. Rejecting data solely on data validation guidelines may be premature. The data reviewer must understand the project data quality objectives and the intended use of the data before deciding to qualify the data. Properly evaluated data potentially reduces the need for resampling/reanalysis, thereby minimizing unnecessary project costs. We will describe the validation process with a focus on specific case studies from a user's perspective.

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ABSTRACT NOT AVAILABLE
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THE SHELL REQUIREMENTS FOR CHEMISTRY DATA GENERATED FOR USACE PROJECTS

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ABSTRACT

The purpose of the 'Shell' is to establish the basic approach to be used when performance-based methods, especially the SW-846 methods, are employed by the U.S. Army Corps of Engineers (USACE) for the analytical testing of environmental samples. These methods are flexible and can be readily adapted to individual project-specific requirements. The chemistry data generated for USACE projects must be produced by a process or system of known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The 'Shell' outlines such a process. A related document, the 'Method's Compendium,' is available that applies the concepts as presented in the 'Shell' to specific SW-846 methods for relatively critical data uses. The USACE has also developed laboratory specific standard operating procedures (SOPs) consistent with the 'Shell' for many SW-846 methods and general laboratory operations.

Project-specific data quality objectives (DQOs) must be established for both the field and laboratory operations. Each laboratory would normally define their own set of laboratory-specific objectives for general day-to-day use for their implementation of any given method. Any differences between project DQOs and lab operational criteria must be reconciled before project execution. For each project, data quality must be demonstrated for the analytes of concern at the levels of concern.

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

The 'Shell' describes the requirements for instrument calibration. Initial calibration curves are verified with standards from an independent source. Continuing calibration verification is performed for all method target analytes at the beginning and end of each analytical sequence. Each preparation batch is to contain a method blank and a laboratory control sample containing all of the project-specific analytes of concern spiked at the levels of concern to monitor laboratory performance. Each preparation batch would typically contain additional QC samples to monitor the effect of the matrix on the method. Corrective actions are carefully detailed and involve interaction with project managers to avoid the generation of a significant amount of flagged data.

The intent of the 'Shell' is to ensure the generation of chemistry data of known quality. Laboratories should not be treated as black boxes where samples go in and only numbers come out. Laboratories employ chemists and others who are experts in the interpretation of analytical data. Much is to be gained by enhancing the interaction between the laboratory and project personnel. The 'Shell' encourages this.

INTRODUCTION

The U.S. Army Corps of Engineers (USACE) currently executes remedial and compliance activities under several environmental regulatory programs. The analytical testing of various environmental samples is often a significant part of these activities. The data must be produced by a process or system of known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. All USACE projects require a comprehensive and multifaceted approach to quality assurance and quality control (QA/QC) to achieve and document attainment of appropriate quality for the intended data usage. The project technical team must establish project-specific quality standards for chemical data early in the planning process. These standards are documented as project-specific data quality objectives (DQOs).

The purpose of this document (the 'Shell') is to establish the basic approach to be used when performance-based methods, especially the SW-846 methods, are employed by the USACE during the execution of its projects. The strategies presented in the 'Shell' shall be used by laboratories in conjunction with the project-specific DQOs when providing chemistry analytical services to the USACE. A related document, the 'Method's Compendium', is available that applies the concepts as presented in the 'Shell' to specific implementations of the SW-846 methods. Default target analyte lists are presented along with default acceptance criteria for relatively critical data uses. The USACE also has available laboratory specific standard operating procedures (SOPs) for many SW-846 methods and general laboratory operations. These SOPs implement the concepts as presented in the 'Shell' and are now being carried out by the USACE Division Laboratories.

As stated in the Final Rule that incorporated the Third Edition of SW-846 (and its updates) into the RCRA regulations, this document is required to be used for certain activities in the RCRA program. In other situations, this EPA publication functions as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, in satisfying RCRA-related sampling and analysis requirements.

SW-846 covers many separate test methods addressing hundreds of analytes. For any given analyte, multiple methods, with varying detection limits, are potentially available. SW-846 is a dynamic document that is constantly changing as new information and data are developed. Any of these promulgated or draft SW-846 methods or any other methods may be used by the USACE to support the project-specific requirements.

The 'Shell' is not a stand alone document. The 'Shell' does not reference the use of specific analytical methods, does not cite specific target analyte lists for individual methods, and does not provide default QA/QC criteria for individual methods. The 'Shell' does outline the strategy for implementation for any given method and must be used in conjunction with the project-specific DQOs. The use of the 'Shell' provides for a uniform implementation of the various analytical testing methods by the laboratory community and clarifies the ambiguities that are present when laboratories implement the SW-846 and other performance-based methods. The 'Shell' and 'Method's Compendium' shall be incorporated into EM200-1-3 (Requirements for the Preparation of Sampling and Analysis Plans dated 1 September 1994) referenced by ER1110-1-263 (Chemical Data Quality Management for Hazardous, Toxic, Radioactive Waste Remedial Activities dated 1 April 1996). ER1110-1-263 is the umbrella regulation that defines the chemical data quality management and integrates all of the other USACE guidance on the topic.

QUALITY ASSURANCE OBJECTIVES FOR DATA MEASUREMENT

Project-specific DQOs must be established for both the field and laboratory operations. The DQO process will assist in determining the appropriate reporting limits, extraction/digestion methods, clean-up methods, analytical methods, target analytes, method quality control samples, quality control acceptance ranges, and corrective actions. Chemical data is typically procured by separate contracts between the architect/engineering (A/E) firm and the laboratory. The contract laboratories are bound by the DQOs as approved in the final documents for each project. Project-specific DQOs should not be confused with laboratory-specific objectives. Each laboratory would define their own set of laboratory-specific objectives for general day-to-day use for its implementation of any given performance-based method, including the SW-846 methods. Any differences shall be reconciled prior to project execution. If differences are noted, then either a different method must be chosen that does meet the project-specific DQOs or the current laboratory method must be modified.

The determination of data quality includes the evaluation of the PARCC parameters (i.e., precision, accuracy, representativeness, comparability, and completeness) and sensitivity. The PARCC parameters, including sensitivity, are quantitative or qualitative limits that, when exceeded, generate data that is questionable for the intended use. It is important that data quality be demonstrated for the analytes of concern at the levels of concern. Of these parameters, sensitivity is the one that has caused the greatest confusion. The 'Shell' interrelates the concepts of the method detection limit (MDL), method quantitative limit (MQL), and method reporting limit (MRL). Under the 'Shell' strategy, the laboratory shall perform MDL studies annually, as a minimum, and whenever the basic chemistry of the procedures are changed using the procedures presented in 40 CFR, Part 136, Appendix B. The MDLs shall be extraction/digestion method specific and shall include all method target analytes. The MDLs shall be demonstrated on individual instruments when multiple instruments are used for any given method. To ensure that reasonable MDL values are determined, the laboratory should analyze an MDL check sample quarterly by spiking an interference free matrix with all method target analytes at about two times the determined MDL. If any of the method target analytes are not recovered, then the MDL study shall be repeated. The determination of method detection limits in site-specific matrices may be required for certain projects. The method quantitation limit (MQL) is defined as the lowest calibration standard used during the initial calibration. The lowest calibration standard would normally be set at between three and ten times the MDL for each method target analyte. The method reporting limit (MRL) can be set no lower than the value of the low standard used during initial calibration. The low standard would typically be below the project-specific action levels or regulatory levels. This item is critical since it will directly affect the use and interpretation of laboratory-specific quality control samples. A laboratory shall not claim to reliably quantitate values below the low standard. Analyte values can be reported below the low standard but shall be reported as estimated (flagged) values.

A laboratory shall prepare a written Quality Assurance Plan (QAP) (or Laboratory Quality Management Manual (LQMM)) which describes the general and specific procedures used within the laboratory to achieve scientifically sound and legally defensible data.

ANALYSIS REQUIREMENTS

The laboratory shall have, in-house, the appropriate standards for all method target analytes.

Laboratories shall be required to maintain written, approved laboratory-specific standard operating procedures (SOPs) for all methods and general operations. Laboratory-specific SOPs are mandatory that fully detail the actual procedures and documentation used to implement performance-based methods that are often presented as guidance. Simply referencing a given method or method number is not sufficient.

For each method performed, the laboratory shall maintain documentation that demonstrates the laboratory's ability to perform the method within the sensitivity and precision/bias limits as stated in the method, if applicable. For each method performed, the laboratory shall maintain documentation that demonstrates each employee's ability to perform the method within the precision/bias limits as determined by the laboratory or as stated in the method, if applicable.

Under certain conditions, due to the introduction of new technology or when an unusually difficult matrix is encountered, modifications to the methods may be necessary. The MDL and the precision/bias noted for a modified method shall be no worse than the performance criteria as given in the original method unless the project-specific DQOs can still be achieved. The demonstration of equivalency shall be required whenever the basic chemistry of the original method has been altered and may need to be repeated when samples from different matrices are received. This decision will be based on project-specific DQOs and will be made on a case by case basis.

The data produced by a laboratory typically provide the primary basis for environmental cleanup decisions and enforcement actions. The data may also end up in court. To be legally defensible, the data must be produced according to the project-specific requirements as specified in the final approved project documents. The laboratory must be aware of these requirements and be able to show that these requirements were followed. Documentation that would clearly show how all analytical values were obtained must be maintained. There is a significant difference between scientifically valid and legally defensible data. Intentional falsification of process results or quality control parameters, or failure to document actual conditions for the purpose of misrepresentation, constitutes fraud. Inappropriate use of manual integrations, for example, to meet calibration or method QC criteria would be considered fraud. Mistakes happen, but mistakes must be documented and corrected.

CALIBRATION PROCEDURES AND FREQUENCIES

Calibration of instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity. All reported method target analytes shall be within the high and low initial calibration standards. All samples analyzed shall be sequentially bracketed by calibration verification standards that typically would include all method target analytes.

Linearity is best determined using linear regression analysis for each method target analyte by calculating the 'Coefficient of Determination' (r^2, the squared correlation coefficient). The use of the 'Coefficient of Determination' should be used in preference to the use of average calibration or response factors. A visual inspection of the calibration curve should be performed. If the visual inspection indicated problems or if the acceptance criterion was not met, then the laboratory shall evaluate each of the following items in the listed sequence: (1) The first option would be to check the instrument operating conditions or the standards used and make adjustments to achieve a linear calibration curve; (2) The second option would be to narrow the calibration range using the same

number of standards as required by the individual method; (3) The third option would be to use a nonlinear calibration curve. The statistical considerations in developing a nonlinear calibration model require more data than the more traditional linear approaches.

The initial calibration curve shall be checked with a standard purchased or prepared from an independent source. This initial calibration verification (ICV) involves the analysis of a standard containing all of the method target analytes each time the initial calibration is performed.

Continuing calibration verification (CCV) involves the analysis of a single standard at the beginning and end of each analytical sequence. For methods that contain multi-component target analytes, typically only a subset of these analytes would be used in the CCV. Calibration 'verification' differs in concept and practice from 'continuing calibration'. Calibration verification shall be used for all analytical methods.

As an alternative for ICP initial multipoint calibration, a single high standard and a calibration blank may be used for initial calibration if calibration is verified using both mid and low level standards.

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

Laboratory internal quality control checks shall be designed to determine if laboratory operations are in control and to determine the effect of the sample matrix on the data being generated. Laboratory performance QC shall be based on the analysis of a laboratory control sample to generate precision and accuracy data that are compared to control limits and on the analysis of a method blank. Matrix specific QC shall be based on the use of an actual environmental sample for precision and accuracy determinations and commonly relies on the analysis of matrix spikes, matrix spike duplicates, matrix duplicates, and surrogate spikes, if appropriate.

The basic unit for laboratory quality control is the batch. Samples shall be prepared and analyzed in batches and be traceable to these individual batches. Batch sizes are normally limited to twenty field samples of a similar matrix. Samples prepared together would normally be analyzed together on a single instrument. Samples taken from the same site would normally be grouped together. If samples from multiple clients are grouped into a single batch, additional batch QC samples may be needed that evaluate the effect of the matrix from each site on method performance.

The preparation batch shall be defined as samples that are prepared together by the same person, or group of people, using the same equipment/glassware with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in limited continuous sequential time periods, usually not to exceed one analytical shift. The analytical, or instrumental, batch shall be defined as samples that are analyzed together within the same time period or in sequential continuous time periods. Within this period of time, each batch may be subdivided into individual run sequences. Run sequences would be bracketed by the appropriate continuing calibration verification standards and other QC samples (i.e., tunes, instrument blanks, etc.) as defined by each method.

A summary of the minimum required QC samples for each preparation batch follows. (1) Method blanks (MB) are analyzed to assess background interference or contamination that exists in the analytical system. The method blank is defined as an interference-free blank matrix similar to the

field sample matrix to which all reagents are added in the same volumes or proportions as used in sample preparation and carried through the complete sample preparation, cleanup, and analytical procedures. At least one method blank shall be analyzed with each preparation batch of samples. (2) The laboratory control sample (LCS) is analyzed to assess the ability of the laboratory's method to successfully recovery the method target analytes from a control sample of known composition. The LCS is similar in composition to the method blank and is spiked with all of the single component method target analytes, and a subset of the multi component method target analytes, before it is carried through the complete sample preparation, cleanup, and analytical procedures. The spiking levels would normally be set at the project specific action limits. At least one LCS shall be analyzed with each preparation batch of samples. Control charts, or tables, shall be maintained for these samples to establish the accuracy and precision of the method. (3) Matrix spike samples are analyzed to assess the ability of the method to successfully recover the method target analytes from an actual matrix. A MS is an environmental sample to which known concentrations of the method target analytes, or a subset of representative method target analytes, have been added before it is carried through the complete sample preparation, cleanup, and analytical procedures. The levels would normally be set at the project specific action limits. If method target analytes were known to be present in samples from a given site, then the spiking level should be adjusted to a concentration that would approximately double the concentrations of the original method target analytes. The sample to be used for the MS would normally be specified in the field. The requirements for the frequency and quantity of MSs would be specified in the project specific DQOs. For batches consisting of samples from the same site for the same matrix, the frequency of analysis of the MS would normally be one per preparation batch. A MS from one site could not be used to evaluate the matrix effects on samples from other sites. (4) The matrix duplicate (MD) and/or matrix spike duplicate (MSD) is analyzed to assess the precision of the method in an actual matrix. The requirements for the frequency of MDs or MSDs would normally be specified in the project-specific DQOs. A MD would normally be included with each preparation batch of samples processed where method target analytes were expected to be present. An MSD would normally be included with each preparation batch of samples processed where method target analytes were not expected to be present. (5) Certain methods may require additional QC procedures or samples besides those already identified.

The laboratory is encouraged to analyze additional standard reference materials (SRMs) and participate in external performance evaluation (PE) programs.

CORRECTIVE ACTIONS

When errors, deficiencies, or out-of-control situations exist, the laboratory's QA program shall provide systematic procedures, called corrective actions, to resolve problems and restore proper functioning to the analytical system(s). Problems noted during sample receipt shall be documented. The project manager, or their designee, shall be contacted immediately for problem resolution. If samples cannot be prepared and/or analyzed within the method required holding times, the project manager, or their designee, shall be immediately notified, such that an appropriate corrective action plan can be generated. Sample analysis shall not be allowed until all initial calibrations and initial calibration verifications meet the appropriate requirements. All continuing calibration verifications that do not meet method requirements shall result in a review of the calibration. Continued failure of the CCV shall result in the construction of a new initial calibration curve followed by the reanalysis of all samples affected. All method QC shall meet the appropriate project-specific requirements and

associated corrective actions. Failure of method QC shall result in the review of all affected data. If no errors can be noted, the affected sample(s) may need to be reanalyzed or reprepped then reanalyzed within method holding times, if possible. The project manager, or their designee, shall be notified as soon as possible to discuss possible corrective actions should unusually difficult sample matrices be encountered.

For method blanks, the concentration of all method target analytes shall be below the MDL for each method target analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent of the sample result for the same analyte, whichever is greater. The first step of corrective action is to assess the effect on the samples Typically, the contaminated samples of the batch would be reprepped and reanalyzed with a new method blank and batch specific QC samples.

The LCS is evaluated by comparing the recovery for all of the method target analytes to the recovery windows as determined by the laboratory or as specified in the project-specific DQOs. A batch of samples shall be considered acceptable only for those analytes that had acceptable recoveries in the LCS. The first step of corrective action is to assess the effect on the samples. Typically, the LCS, method blank, and all associated samples of the batch would be reprepped and reanalyzed for the failed analytes.

The MS is evaluated by comparing the recovery for all method target analytes to the recovery windows as determined by the laboratory for the LCS or as specified in the project-specific DQOs. MS data evaluation is more complex than method blank or LCS data evaluation. In general, laboratories will not base batch control on the results of the MS unless a general method failure is indicated. MSs that fail to meet the appropriate acceptance criteria would indicate that a potential matrix effect is present. The associated sample(s) would typically be reprepped then reanalyzed to verify the effect. Corrective action shall include the immediate notification of the project manager, or their designee, to discuss the implementation of additional cleanup procedures, method modifications, etc. to compensate for the matrix effects noted.

The MSD is evaluated using the same accuracy criteria as described for the MS. The MD or MSD is evaluated by comparing the precision for all method target analytes to the windows as determined by the laboratory for the LCS or as specified in the project-specific DQOs. Corrective actions shall be performed as described for the MS.

DATA REDUCTION, VALIDATION, AND REPORTING

All analytical data generated by the laboratory shall be extensively reviewed prior to report release to assure the validity of the reported data. This internal data evaluation process shall include a minimum three levels of documented review.

Level 1 review shall be performed by the analyst based on an established set of guidelines. Level 1 analyst review shall be documented by using a check list and by the signature and date of the reviewer.

Level 2 review shall be performed by a supervisor or data review specialist whose function is to provide an independent, peer review of the data package. Level 2 review shall be structured so that all calibration data and QC sample results are reviewed and all of the analytical results from at least

25% of the samples are checked back to the raw data and/or bench sheets. If no problems are found with the data package, the review is complete. If any problems are found with the data package, then all sample results shall be checked. Level 2 peer review shall also be documented on a check list with the signature and date of the reviewer.

Level 3 review shall be performed by the program administrator at the laboratory. This review shall provide a total overview of the data package to ensure its consistency and compliance with project-specific requirements. Level 3 administrative review shall also be documented on a check list with the signature and date of the reviewer.

QA review shall be performed by the QA Officer or QA Branch. This review is not part of the normal production data review process. The QA Officer would typically review at least 10 percent of the data produced by the laboratory using the procedures as outlined in the Level 3 data review. Additional technical details could be reviewed based upon the results of this QA review.

Data qualifiers shall be added by the laboratory during the data generation/review process. These qualifiers would be applied when acceptance criteria were not met and corrective action was not successful or when corrective action was not performed. All flags used by the laboratory shall be defined. These flags should also identify any suspected bias in the data. The project manager, or their designee, shall be notified as soon as possible to discuss possible corrective actions should data be qualified. Additional data flagging may be performed by the USACE based upon overall project-specific requirements, by using external data review or validation.

The USACE does require a minimum level of data reporting that includes the reporting of all sample data along with the supporting QC information. This format allows for the review and validation of the data by an independent organization. This format does not allow for the complete independent reconstruction of the analytical data. An electronic deliverable would also be highly recommended. The format of this electronic deliverable shall be specified in the project-specific documents.

SUMMARY

The intent of the 'Shell' is to ensure the generation of chemistry data of known quality. The strategy as presented in the 'Shell' is applicable to the SW-846 methods and to any performance-based method. This strategy should reduce the ambiguities that presently exist between the implementation of methods between different laboratories. The interaction of project and laboratory staff is critical at the beginning and during project execution to ensure that project-specific DQOs can be and are being achieved. This interaction should reduce the amount of flagged data being generated for any given project.

INTEGRATION OF THE DQO PLANNING PROCESS IN THE CLOSURE OF MIXED WASTE STORAGE UNITS

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ABSTRACT

The Data Quality Objectives (DQO) Planning Process was used to facilitate the completion of a Resource Conservation Recovery Act (RCRA) Closure Plan for the 324 Radiochemical Engineering Complex (REC) and High Level Vault (HLV) tanks.

INTRODUCTION

The Data Quality Objectives (DQO) planning process was used to define requirements in the development of a RCRA Closure Plan for unpermitted mixed-waste storage units at the Hanford Site. The DQO process is a facilitated decision-making method; it develops in logical step-wise fashion a solution to which all key decision makers and involved parties agree. Developing a Closure Plan for an unpermitted mixed waste storage unit carries with it many issues that do not lend themselves to resolution by industry convention or standards. In the development of the Closure Plan, the DQO process proved to be a valuable tool in resolving all the key issues in a timely and mutually acceptable manner.

Background

The Pacific Northwest National Laboratory (PNNL) in support of the U.S. Department of Energy - Richland Operations (DOE-RL) is preparing a RCRA Closure Plan for unpermitted waste storage units in the 324 Building, 300 Area, Hanford Site. The waste is stored in the Radiochemical Engineering Complex (REC) in the 324 Building. The REC consists of four hot-cells with a common airlock, two underground vaults that contain stainless-steel liquid-storage tanks , and ancillary support components. The wastes are highly radioactive and are stored in the REC because no facility now in

operation can accept high activity mixed waste for interim storage or final disposition. The facility is being closed under a consent order manifested as a Tri-Party Agreement (TPA) Milestone. The TPA is a Hanford Facility Clean-up agreement between the U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (EPA), and Washington State Department of Ecology (Ecology).

In the REC the mixed wastes are stored in B Cell, tanks in the High Level Vault (HLV), and tanks in the Low Level Vault (LLV) (See Figure 1.0). B Cell is 7.6 m long x 6.7 m wide x 9.3 m high and is the largest of the four hot cells in the complex. The floor and walls, up to 8.2 m high, are lined with stainless steel plate that is fully welded at the seams. The HLV is located under the floor of the cask handling area and contains four stainless steel tanks, three of which contain stored mixed waste solutions. The LLV is also a sub-basement vault housing four stainless steel tanks, one of which contains a residue of a mixed waste solution.

The B-cell waste is consists primarily of dispersible debris that accumulated in the cell during many years of operation and during clean-up activity initiated in 1988. The debris is made up of dust that has settled from intake air, process fines, decomposition materials, small tools, and pieces of equipment. The debris was designated as hazardous from heavy metals through process knowledge. Additional waste materials

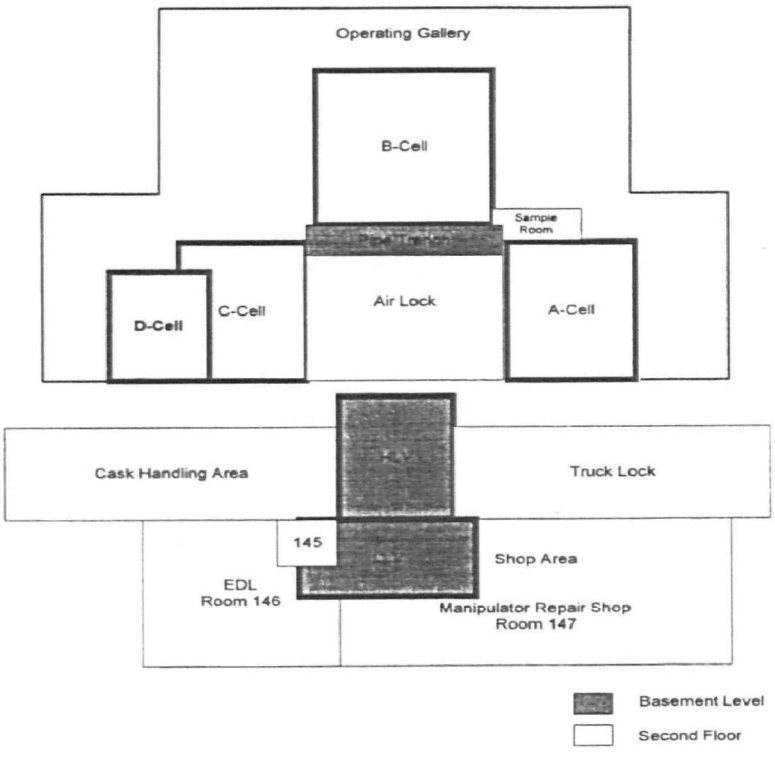

Figure 1 - Plan View of the 324 Building REC

being stored in B-cell include dried melter feed material, elemental lead, and liquid metal seal.

The HLV tanks contain approximately 4,000 liters of highly radioactive solutions. Two tanks house 3,400 liters of a solution containing $^{137}CsNO_3$ and $^{90}Sr(NO_3)_2$. The remaining 600 liters is a process feed-stock solution that contains higher levels of ^{137}Cs and ^{90}Sr. These solutions are considered hazardous due to both a corrosive characteristic and the presence of heavy metals.

One of the LLV tanks at one time contained a radioactive-only waste solution. That solution has evaporated, and the concentrations of hazardous constituents rose above designation levels. At this time the solution has evaporated completely, and a mixed waste residue remains.

Closure Plan Development Strategy

The primary objective of the Closure Plan is to describe the closure of the unpermitted storage units in the 324 Building. A secondary objective is to meet the milestone agreements in the TPA, which act as consent orders. To meet the objectives, we used a simple strategy that integrated the schedule required by the TPA and the regulatory requirements that drive the development of the closure plan.

Our first Closure Plan milestone was to deliver a draft to Ecology by December 29, 1995. To meet this objective a subcontractor was hired to assemble the information and develop a draft closure plan. A draft was delivered on December 22, 1995.

The draft Closure Plan acted as a basis for negotiation and discussion with decision makers. In cases where no documentation has been gathered, it is essential to compile and summarize data, facility information, process history and any other information that may be pertinent to decision making and sampling design. Participants received an information package that included the draft Closure Plan, regulatory documents applicable to the situation, and other documents pertinent to various clean-up work underway in the facility. To facilitate, document, and streamline these discussions and negotiations, we initiated a DQO Planning Process, which will help guide the revision of the draft closure plan. On completion of the DQO process, the Closure Plan will be revised, and the

first revision will be finalized through workshop reviews with Ecology.

Central to our strategy is the DQO Planning Process. By facilitating and documenting discussion among decision makers, we can obtain closure of the more difficult issues related to the Closure Plan before open forum/workshop discussions are initiated. A timely, mutually agreeable framework for closure will save precious time and money in the completion of the 324 REC Closure Plan.

THE DQO PLANNING PROCESS

Our DQO process started with the hiring of an experienced facilitator, Ms. Mitzi Miller, President of EQM. The facilitator was a critical factor in bringing credibility and independence to the process. An experienced facilitator guided each meeting and prevented distraction by agendas or tangents from participants. The facilitator also helped to focus discussion on issues and persistently induced feedback from the group until issues were resolved or a clear path for resolution was defined. In the hands of an able facilitator our DQO process proceeded as planned with few surprises.

Ground rules

Our DQO Process followed the following Ground rules as established by our facilitator:

1. All decision makers must be at the scheduled meeting, or the meeting will not proceed.

2. All attendees will have a specific purpose at the meeting or will be asked to leave.

3. All scheduled speakers and presenters must be prepared for each meeting.

4. Decisions must be based on logic and regulatory requirements.

5. Attendees may make multiple agreements regarding listening behavior and discussion to avoid conflict.

Roles and Responsibilities

Every attendees at our DQO meeting had one of three primary roles. The most critical participants are the decision makers. Usually they represent the regulatory agency and the facility/unit/site being discussed. For our DQO, representatives from Ecology and the DOE acted as the decision makers.

The second category of attendees are support staff. They support the decision makers, and for the most part gather and present the information at the DQO meetings.

The third category of attendees for our DQO were observers. They are interested in learning about the DQO process and are invited to the meetings to gain first hand DQO experience.

In addition the these three primary categories, subject matter experts, were asked to attend specific meetings to provide detailed information related to a complex issue or to provide information that which could not be supplied by other participants. A court reporter attended to document the discussion at each meeting.

Meeting Format

Meetings are the heart of the DQO process. Through presentation and dialog, critical issues can be addressed and resolved. The DQO process helps to streamline discussions and addresses the issues in a logical format. The meetings are not open discussion forums. Instead the DQO meeting is a series of presentations and focused discussions used to isolate issues and resolve them before moving forward. Preparation is therefore the key to any DQO meeting. Presenters must understand their subject and objectives and should format their information to be readily assimilated; data should be tabulated, key points highlighted, and lengthy text summarized.

To support several of our DQO meetings, dry runs were held, and presentations critiqued. These dry runs are important if clear communications is to occur at the DQO meeting.

In any decision-making meeting, issues may be skirted and decision

postponed. The facilitator controls this problem, forcing the decision makers to engage each issue and either resolve it or clear a path to resolution. This policing by the facilitator prevents unnecessary posturing by the participants so that the issues are addressed and resolved.

Documentation of Decision

Two forms of documentation were used to support our DQO process. The primary form is meeting minutes. Documentation provided by the court reporter is the basis for a meeting summary that identifies each major decision made and any assigned action items. The minutes are accepted by the decision makers at the following meeting. Some decision makers prefer to sign the agreements from each meeting; others prefer to sign the final DQO Summary Document, which includes a list of agreements. In this case, no formal signatures are applied to the minutes.

The second form of documentation is the DQO Document. This document, which is prepared by the facilitator with assistance from subject matter experts, outlines each decision made as a result of the DQO Process. This document is reviewed and signed by each decision maker and is the official documentation of a formal agreement by each party.

Results of the DQO Process

The DQO process helped to resolve many of the big issues related to the closure of the 324 REC. The standardized DQO format provided ready resolution of such issues as the boundary of an unpermitted unit, closure standards for highly radioactive storage units, and applicable sampling and analysis to determine if closure standards were met. Most importantly, with each of these discussions thoroughly documented, and the Closure Plan poised for revision, any moves to revisit or reopen these closed issues can be met with a signed DQO agreement.

SUMMARY

To achieve those remarkable results from the DQO process required a remarkable amount of work from all participants. Preparation is the key for each DQO meeting, information must be formatted appropriately for easy

assimilation, and all participants must review material assigned to them (including previous meeting minutes). In addition to a highly participative group, the presence of a skilled facilitator is critical to completing the process successfully. A facilitator will make sure that the logical format of the DQO is followed, will detect hidden agendas, and will abort low-value discussions. With proper preparation, participants who understand their roles and responsibilities, and a capable facilitator, the DQO process can add significant value in addressing even the most intractable environmental problem.

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PROPER SELECTION OF PERFORMANCE EVALUATION SAMPLES FOR CHEMICAL DATA ACQUISITION BASED ON VENDOR ACCEPTANCE LIMIT CRITERIA

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ABSTRACT

Performance Evaluation (PE) samples are widely used by laboratories and their clients to verify the accuracy and precision of the analytical methods employed by the laboratory. Although the U.S. Environmental Protection Agency (EPA) supplies some PE samples for its programs, the bulk of PE samples is usually purchased from commercial vendors as either off-the-shelf or customized samples. Interpretation of the results of the PE sample analyses is based on the acceptance limits provided by the vendor. Different vendors offer significantly varying acceptance limits for the same analytes to be analyzed by the same analytical methods. When, for a specific analyte, the vendor acceptance limits exceed the suggested method recovery limits the usability of the analytical result, *i.e.*, the PE sample, is usually jeopardized. The paper discusses the advantages and disadvantages of using single-blind *versus* double-blind samples, and the pitfalls in receiving, repackaging and shipping of PE samples to the laboratory. It also discusses and compares the acceptance limits of various vendors to analytical method limits. A method is proposed for the proper selection of PE samples to satisfy the requirements of the data quality objectives of a program and maximize the analytical information that can be derived from the interpretation of the PE analytical result.

INTRODUCTION

The environmental laboratories are going through a period of economic and professional turmoil. The ubiquitous requirement in government contracts for the mandatory use of small and disadvantaged business spawned the proliferation of new laboratories that operated with poorly trained personnel using antiquated or inadequately maintained equipment. As the focus of the Federal and State environmental efforts changed from Remedial Investigations/Feasibility Studies (RI/FS) to actual remediation, the number of environmental field samples drastically diminished. This resulted in a price cutting scramble for the dwindling supply of analytical dollars. Mergers and acquisitions removed respected and renowned laboratory names from the analytical stage, replacing them with regional or international players, some lacking experience in US laboratory management.

The surviving environmental laboratories are undergoing wrenching reductions in personnel, up to and including total closure and liquidation of assets. The seasoned analytical technicians and chemists who, due to their intimate knowledge of the quirks of their instruments, were able to coax excellent results from them, are increasingly being replaced by temporary professionals. The latter come into a project unfamiliar with the specific analytical instrument at hand, with arguably ambiguous corporate loyalty and commitment to quality control (QC). Their lack of knowledge of company memory makes their use in the middle of large and long term projects a most risky proposition.

Meanwhile the rostrum of debarred laboratories or ones currently under Federal or State investigation keeps mounting. Data integrity has become an area of major QA concern, so much so that the EPA recently issued guidelines for Good Automated Laboratory Practices (GALP).[1] Unrealistic regulatory or client expectations of laboratory conformance and method compliance are increasing the potential for fraudulent manipulation of data. The U.S. Air Force Center for Environmental Excellence (AFCEE) recently issued its generic Quality Assurance Project Plan (QAPP) for use in its upcoming programs.[2] The QAPP requires the laboratory to perform data validation on its deliverables, with the implicit understanding that rejected data will not be paid for, and the laboratory may be required to pay for resampling and reanalysis. It also requires the spiking of laboratory control samples (LCS), matrix spike/matrix spike duplicates (MS/MSD) with *all the analytes* of the method. When the recoveries of the LCS spiked analytes are outside the AFCEE specified acceptance limits, the QAPP requires the repreparation and reanalysis of *all* the samples in the corresponding analytical batch. In the case of a method, such as SW 8270B (Semivolatile organics) with 237 analytes (of which only 64 have method specified limits) the chances of non-compliance are a statistical certainty. Such radical increases in the analytical effort may lead to sharply higher prices or lower quality, or both. Laboratories are already switching to cheaper "non-traceable" reference materials and standards rather than using fully documented certified and "traceable" ones.

Thus, the evaluation and selection of analytical laboratories have become a hybrid of quality assurance(QA) and risk management. Not only are we concerned whether the selected laboratory can analyze the samples correctly, providing legally defensible data, but we also have to investigate and evaluate its financial stability, as well as its viability to stay in business for the mandatory or contractual five year period for archiving records.

EVALUATING AND MONITORING LABORATORY PERFORMANCE

Traditionally laboratory performance is evaluated and monitored through:

1. On-site evaluations.
2. Raw data and magnetic tape audits.
3. Proficiency in analyzing PE samples.
4. The potential client's past experience with the laboratory.

All four provide a past status report of the laboratory's performance. All have to be extrapolated into predicting future performance.

As contracting officers of Federal and State programs keep insisting that expenses for laboratory selection can not be charged to the respective program/project costs, more and more environmental engineering/remediation firms are eliminating or greatly abridging the in-depth on-site laboratory evaluation. It is being replaced by preaward visits and reviews of greatly expanded statements of qualifications. The latter now include, but are not limited to, the following:

1. The PE results of the past two years' EPA administered Water Pollution (WP) and Water Supply (WS) studies.
2. On-site evaluation reports by third parties and the laboratory's responses to them.

3. Method Detection Limit (MDL) studies and their backup documentation.
4. Interlaboratory PE study results, such as those administered by Analytical Standards, Inc. (ASI), Environmental Resource Associates (ERA) and others.

A cost effective way of evaluating and monitoring laboratory performance is through the use of: two types of PE samples, namely,

1. Preaward samples- usually off-the-shelf single-blind commercial samples.
2. Post-award monitoring samples, preferably double-blind commercial samples, or program specific ones, supplied and evaluated by the EPA, US Army Corps of Engineers (USACE), *etc*.

The pros and cons of using PE samples for laboratory monitoring have been extensively discussed in recent literature.[3, 4, 5, 6, 7]

SINGLE-BLIND *versus* DOUBLE-BLIND PE SAMPLES

Guidelines for administering and scoring PE samples are, as a rule, not found in project specific QAPPs. The recent U.S. Navy "...*Laboratory Quality Assurance Guide*" discusses the administration of single-blind samples only, while the AFCEE QAPP completely bypasses the issue.[2, 8] Single-blind samples are those recognized by the laboratory as PE samples with unknown content. Usually they are delivered in ampules to be diluted to a volume of one liter. Double-blind PE samples are delivered already diluted and in identical sample containers as those from the field. They are shipped in field coolers together with routine samples. Customized double-blind PE samples contain only those analytes that have been identified at the site and their concentrations have been adjusted to mimic field hits.

Each signed contract with an environmental laboratory should contain stipulation on the use and scoring of PE samples, both for single and double-blind samples. Depending on the data quality objectives (DQO), the contract should define what constitutes "non-acceptance" and the corrective actions that both parties will undertake in such a case. For example, when an off-the-shelf single blind sample is analyzed, it is assumed that the laboratory knows it is being tested and is on its "best behavior".[7] Therefore misidentification or misquantification of *analytes of concern* should be considered more detrimental than similar inaccuracies relating to other analytes which are routinely spiked into the "off-the-shelf" commercial samples.

David Kennedy, a 25 year veteran of the environmental laboratory industry, asserts that "*laboratories have been known to "cheat" on single blind PE samples by analyzing the contents of an ampule directly rather than preparing a dilute aqueous sample and going through the entire analytical process*".[7]

Use of customized double-blind PE samples resolves the above issues, since they are indistinguishable from routine field samples, and are already diluted to 1 liter volume, or whatever is the appropriate volume. The containers should be identical to those of the field samples.

When the laboratory misidentifies or misquantifies the contents of the PE samples, the supplier and the field technicians will be the ones to answer for the integrity of the sample preparation and shipping process. The following precautions should be taken in the preparation of the double-blind PE samples:

1. The labeling and shipping of the *empty* sample bottles to the PE supplier should be witnessed by at least one other person, preferably from the QA/QC organization of the shipper.
2. Photograph or videotape the process of opening the cooler (shipped by the PE sample supplier) and relabeling of the PE sample containers (if necessary). Frozen samples, broken containers, and mislabeled samples are infrequent but real-life occurrences.
3. Photograph or videotape the process of placing the PE samples in the cooler that contains the regular field samples.
4. All documentation relating to the PE samples, including the "key" to the sample concentrations should be kept by the project QA/QC officer under strict security until the results are reported by the laboratory.
5. Customized double-blind PE samples should contain only those analytes of concern that the laboratory may have already encountered in previous samples from the same site. The concentrations should also be in the range of interest, but should *never* be below the practical quantitation limit of the method.

SCHEDULING OF DOUBLE-BLIND PE SAMPLES

It is important to schedule the double-blind PE samples correctly. In cases when the laboratory has been unable to demonstrate proficiency in the requested analytical method, one PE sample per field batch is the norm. This is an expensive effort used only as a last resort.

It is more common to schedule an off-the-shelf commercial PE sample at the beginning of the field effort. The drawback is that off-the-shelf samples contain more analytes than would be expected from a field sample. When a "picket fence" chromatogram starts plotting, it is immediately obvious to the laboratory that a PE sample has arrived. In the case of metals, it will be the one with major hits across the whole ICP list. It is still not possible to manufacture homogenous PE samples using site soils. The commercially available solid matrix samples use Ottawa-sand type free flowing media, which are immediately recognizable by the laboratory. Shipping one aqueous PE sample in a batch of soil samples also tips off the laboratory.

For short term projects scheduling *customized* double-blind PE samples at the beginning and at 75% completion of the field effort will be adequate. Since the results will not be known for 10 to 21 business days, this schedule will provide only *ex-post facto* information - confirmation that the "bracketed" field samples were analyzed properly. On longer term projects it would be advisable to use a quarterly PE sample, or one at the beginning , 30%, 60% and 90% completion of the project.

When the laboratory fails to analyze accurately a customized or an off-the-shelf PE sample, this should be followed by a customized PE verification sample. Shipping a single-blind verification sample for purposes of claiming adequate laboratory performance and "saving the data" verges on

the manipulative and even the unethical. A raw data audit will yield far more legally defensible information than the laboratory's "acceptable" analysis of the single-blind sample.

VENDOR ACCEPTANCE CRITERIA

When selecting a PE sample vendor, the vendor's acceptance criteria must be compared to the method limits. ERA, ASI and Analytical Products Group Inc. (APG) supply PE samples with varied acceptance limits. Since some vendors determine their acceptance and warning limits based on the performance of the laboratories that have participated in the analysis, some criteria may be much wider than recommended by the method. While this practice of using wider limits may be statistically justified, and definitely laboratory friendly, it may not satisfy the DQO of the project. Hence, staying within the method limits is a more credible alternative, and legally easier to defend.

Table I presents acceptance criteria for selected semivolatile organic parameters for off-the-shelf PE samples from two commercial vendors, as compared to method QC acceptance criteria.[9]

Table I
Vendor Acceptance Criteria for Selected Semivolatile Organic Analytes
in Percent Recoveries Compared to Method SW 8270

Parameter	Vendor A	Vendor B	Method
Acenaphthene	60.1-139		47-145
Butylbenzyl phthalate	12.2-188	38.1-117	D-139.9
2-Chlorophenol	43.9-156	43.1-112	23-134
Di-n-butyl phthalate	31.2-169		1-118
1,4-Dichlorobenzene	58.0-142		20-124
Diethyl phthalate	29.7-170		D-114
Hexachlorobenzene	27.7-172		D-152
Pentachlorophenol	11.2-189	31.1-126	14-176
Phenol	7.73-192	10.2-121	5-112
Acenaphthylene		46.3-114	33-145
Pyrene		44-126.6	52-115
Fluorene		49.2-122.9	59-121

It is obvious that Vendor B has acceptance criteria closer to the method ones.

If a PE sample is used with vendor specified acceptance criteria significantly wider than the method QC acceptance criteria then it is strongly recommended that *two identical* PE samples be purchased. The second one should be analyzed by a referee laboratory.

SUMMARY

Customized double-blind PE samples are a cost-effective alternative for evaluating and monitoring the performance of laboratories engaged in long-term projects. When selecting PE sample vendors, the vendor acceptance criteria should be compared to the method recommended QC acceptance criteria. The vendor's acceptance criteria should be very close or tighter than the method ones. In

cases where PE samples with wider limits have to be administered, it is recommended that an identical PE sample be analyzed by a referee laboratory.

Labeling, packaging and shipping of PE samples require strict QC documentation, since any "non-acceptance" may lead to costly resampling and reanalysis.

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PERFORMANCE-BASED METHODOLOGY FOR THE TRANSURANIC WASTE CHARACTERIZATION PROGRAM

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ABSTRACT

The Transuranic Waste Characterization Program (TWCP) is charged with the disposal of mixed waste at the Waste Isolation Pilot Plant (WIPP) in New Mexico. Requirements for characterization of this waste have been developed based on regulatory requirements, knowledge of the processes used to generate the waste, and performance criteria of the disposal site. Based on these considerations, a sampling and analysis program has been evolving. A Quality Assurance Program Plan has been developed which sets forth the data quality objectives of the program, and the criteria to be used to assure that analytical data generated by the program is useful. Performance criteria exist for all analytes in these matrices, and guidance is taken from SW-846 in choosing methodology. This paper will describe the development of analytical methodology which meets the QAPP objectives and assures occupational safety as well.

Transuranic wastes contain primarily alpha emitters, and the work on these samples is performed mainly in glove boxes. Analytes to be determined include purgeable organics, a limited number of semivolatile organics, non-purgeable volatiles, and metals. Using Method 8260 as guidance, an automated purge and trap device has been installed in a glove box and used to perform the analysis of purgeables. A modification of Method 3550 using a closed system with ultrasonic and thermal energy input has been used for the extraction of semivolatiles, with the determination by Method 8270. The non-purgeable organics are extracted with water and analyzed using a gas chromatograph located in a radiochemical hood. Metals are digested using a microwave system in a glove box, and can be analyzed using AA or ICP. The development of these methods was constrained primarily by the performance-based criteria found in the QAPP, as well as by the need to limit exposure to radioactivity.

Because these samples provide unique analytical challenges, they represent a strong example of the advantages of performance-based analysis. Modifications to proscriptive methods are possible as long as the QAPP objectives are satisfied. These objectives

include for example: control sample recovery criteria, blank criteria, calibration criteria, surrogate and matrix spike recovery criteria, holding time criteria, and others. In fact, all aspects of the analytical methods are controlled. Still, there is no proscription for the use of methods. As a result, high quality analytical data are generated using relatively flexible methodology. While the advantages of this performance-based approach are clear, the downside is in the degree to which documentation must be established. The actual data package takes more time to produce than do the results.

INTRODUCTION

Beginning in the early 1970's, the promulgation of environmental protection legislation led to a proliferation of new analytical methods. Because of the fact that these legislative acts tended to be directed at specific environmental matrices (e.g. Clean Air Act, Clean Water Act), the methods which gradually became associated with each piece of legislation were developed with that particular matrix in mind. While methods for the Clean Water Act, the Safe Drinking Water Act, and the Resource Conservation and Recovery Act (groundwater) differed little in terms of analytical technology, they did differ in the various quality assurance measures required. With the advent of the Superfund program, the analytical methods became imbedded in contracts (the Contract Laboratory Program) and became, at least for this program, completely proscriptive. As more and more states took control of their own environmental programs, the methods suggested for the other legislative acts became equally proscriptive, because the states lacked the expertise to evaluate analytical data generated using non-standard methods. This placed burdens on the analytical laboratory community, which was forced to comply with a variety of slightly different requirements depending on the legislation under which samples were collected. These burdens became oppressive in a business which is highly competitive, and has led to the reevaluation of the methods policies.

Recently, the realization that analytical costs were becoming a major issue in environmental compliance has led to an active effort to reduce the proscriptive nature of the various methods and to substitute instead performance-based criteria which are developed in advance and driven by the needs of the program. Data quality objectives are elucidated early in the program development phase, and these objectives are supplemented with criteria for the analyses which will allow the data generated to support the objectives. Methods which were formerly proscriptive are used more as guidance, and the usefulness of the resulting data is judged based on its conformance with the performance criteria rather than on to-the-letter compliance with the written methods. The net result is expected to be the generation of data of known quality at reduced cost and increased efficiency.

The Transuranic Waste Characterization Program (TWCP) is charged with the disposal of

transuranic mixed waste at the Waste Isolation Pilot Plant (WIPP) in New Mexico. Large volumes of waste will be stored at WIPP, and there are, of course, waste acceptance criteria. In order to assure that waste destined for WIPP meets these criteria, the program has chosen a performance based system for the generation of the associated analytical data. This sytem has been implemented in the form of a Quality Assurance Program Plan (QAPP)[1], which was developed using prior knowledge of the wastes, performance criteria at the disposal site, and with the active participation of the relevant regulatory authorities. Analytical methods, while tied loosely to SW-846[2], are expected to meet the Data Quality Objectives (DQOs) of the QAPP rather than the precise language of their promulgated counterparts. DQOs include analyte lists, method detection limits, program required quantitation limits, precision, accuracy, and holding times. The central issue in this program is that these wastes contain radioactivity in the form of alpha-emitters, which requires that analytical operations be performed under containment (glove boxes or radiochemical hoods). Thus, a proscriptive approach to the methods would have a high probability of failure. This paper reports on the implementation of the QAPP requirements, from method development to validation, to ensure that the data generated support the waste acceptance criteria.

METHOD DEVELOPMENT

An examination of the analyte lists (see Tables 1-4) indicates that three organic methods are required. Many of the analytes are the traditional volatile organic class, which suggest the use of methods 5030 (purge and trap) and 8260 (capillary GC/MS). A second group includes water-miscible solvents, suggesting the adaptation of method 8015. Finally, a limited number of semivolatile organics are listed. The analysis of these compounds requires a sample preparation step, followed by method 8270 (capillary GC/MS).

Metals Analysis

The primary methods used for the TWCP include 6010A (Inductively Coupled Plasma-Atomic Emission Spectrometry, or ICP-AES), 6020 (ICP-Mass Spectrometry,or ICP-MS), 7471A (Hg-Cold Vapor Atomic Absorption, or CVAA), and the 7000 series for Graphite Furnace Atomic Absorption (GFAA). All of the analytical techniques required the containment of instruments in radiochemical hoods to ensure contamination control and worker safety. Many of the analytical problems observed with the TWCP work are typical of samples with high dissolved solids which can result in poor precision for both ICP-AES and ICP-MS. Frequently the TWCP sludges contain high levels of uranium which causes severe spectral interference with other metals by ICP-AES. At higher levels the uranium must be separated from the matrix prior to analysis to ensure satisfactory data. High levels of nitrate salts can quickly cause deteroriation of graphite furnaces used for GFAA measurements which limits the number of samples that can be analyzed in a

batch. All of these "real world" problems tend to broaden the QC acceptance criteria and degrade overall performance. Most of these matrix effects can be characterized to determine the attainable data quality and performance checks can be developed to ensure consistent data. If acceptance criteria can not be designed to handle complex matrix problems, the analytical costs can get out-of-control trying to meet unreasonable QC limits.

Volatile (purgeable) Organics

The main issue in the application of methods 5030 and 8260 for these samples was the containment of the radioactivity. With the assistance of the manufacturer, a purge and trap autosampler was constructed which allowed the physical separation of the carousel and purge head from the trap and desorption system. The carousel was installed in a glove box, with the transfer of the purge gas occurring via a heated line through the wall of the box. Samples collected in VOA vials can be placed in the autosampler without sample manipulation, and can be analyzed without ever being opened. The performance of this methodology was confirmed, although it was clear that potential existed for contamination of the purging head. Such contamination would make routine maintenance difficult. However, an examination of the performance requirements indicated that the method detection limits could be met using a methanol extraction, followed by purge and trap GC/MS analysis of the methanol. This approach reduces the total radioactivity in the glove box and in addition allows for reanalysis of the sample as needed. Thus, the method chosen involves an extraction of a sample, preweighed (ca. 2 g) and shipped in a VOA vial, with 2 mL of methanol. The methanol is removed from the sample in a glove box, and a 50uL aliquot is added to water in the purge and trap device. Using this method, the performance data in Table 2 were generated. Recoveries did not always meet the established criteria, though the data could then be used to establish acceptable limits. Performance of the method with respect to the established criteria was acceptable with the exception of a consistently low response factor for bromoform. However, because of the fact that all other performance criteria were met, this became insignificant. The QAPP can be revised to reflect the lack of significance of this parameter. Furthermore, in selecting a method for the dichlorobenzenes, it was shown that this method was capable of meeting all performance criteria, and was superior to the semivolatile analysis. The analysis of these compounds as purgeables rather than semivolatiles simplified the sample preparation steps for the semivolatiles. These are examples of the advantage of performance based criteria for data generation.

Non-pugeable Volatile Organics

As noted earlier, the method developed for these compounds was based on method 8015. Again, preweighed samples shipped in VOA vials were extracted, in this case with 10 mL

of water, the water was separated from the waste in a glove box, and placed in a GC autosampler vial. The method of direct injection was used. A gas chromatograph equipped with dual injectors, columns and dual flame ionization detectors was installed in a radiochemical hood. Samples were then analyzed in a conventional manner. Table 3 shows the results of the performance data generated using this method. As this method was developed and sample analysis began, it became apparent that some of the performance criteria could not be met. One of the analytes which was originally targeted was ethyl acetate. However, the high pH of the samples caused hydrolysis of the ethyl acetate spikes, resulting in the formation of ethanol (not a target compound) and acetic acid, which interfered with the chromatography. The ethyl acetate was subsequently deleted from the target analyte list. Ethyl ether, also a target analyte, showed consistently poor performance. It was determined that the poor performance was due in part to instability of the aqueous standards and in part to the low water solubility (low extraction efficiency) of the compound. As a result, ethyl ether was deleted from this analysis and added to the purgeable analyte list. Finally, pyridine, listed as a semivolatile analyte, was found to meet all of the performance criteria when analyzed using this method. Again, these three examples illustrate the improvement in data quality when using performance based criteria rather than proscriptive methods.

Semivolatile Organics

The advantages offered by the use of performance based criteria for data generation are most striking with respect to the semivolatile organics. First, by limiting the list of target compounds to those with a probability of occurrence, the associated QC becomes manageable. Second, by establishing method detection limits in advance, the required sample size can be kept to a minimum - a necessity when dealing with radioactive samples in containment. Finally, by establishing precision and accuracy requirements the sample preparation techniques can be evaluated on performance rather than proscription. This last issue becomes more important when considering the standard preparation techniques for wastes. In this case the use of a Soxhlet extractor (method 3540 would incur operational difficulties, including the generation of large amounts of waste from apparatus cleaning, the generation of heat in the contained area, and the general diffculty in assembling and disassembling the apparatus in a glove box. The use of a sonicator (method 3550), while minimizing operational difficulties, would result in the spread of contamination throughout the glove box, and would likely result in cross contamination of the samples. Even the use of an automated soxhlet extractor (method 3541) had operational problems. The availability of the performance criteria established in the QAPP led to the development of the following preparation technique. Using the program required detection limits, it was determined that 10 g of sample was required. The sample was weighed into a standard soxhlet thimble, and mixed with sodium sulfate. The thimble was placed in a wide mouth bottle of slightly larger dimension and 100 mL of methylene

chloride was added. The bottle was tightly capped, and placed in an ultrasonic bath for 60 min at 23° C. The thimble was removed from the solvent and the solvent concentrated using evaporative concentration. This technique minimizes sample handling, waste generation, and cross-contamination. More importantly, all of the performance criteria can be met. The resulting extract concentrate is then analyzed by method 8270. Performance data are given in Table 4.

SUMMARY

Using method performance criteria based on established data quality objectives, methods have been developed for the characterization of transuranic wastes. There has been an evolving relationship between the performance based requirements of the TWCP Quality Assurance Program Plan and the capabilities of the analytical technology. Where unexpected analytes have been detected, new DQOs have been established. Where the limitations of the analytical techniques have precluded meeting the DQOs, adjustments have been made to the performance criteria. This type of evolution allows for the incorporation of technological improvements in near real time, rather than waiting for new methods to be approved. Extremely positive impacts on data quality are observed in such a system, as compared to the use of proscriptive methods. Continuous review of the DQOs in conjunction with improvements in analytical methods offers the best hope of creating high quality data in an efficient manner.

One difficulty noted here is in the degree to which data need to be documented. Because of the nonproscriptive methods, extra documentation may be required. However, as the use of performance based criteria increases, it is likely that simplified methods will evolve for demonstrating compliance with the DQOs.

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2. Test Methods for Evaluating Solid Waste. Physical/Chemical Methods. EPA 600-SW/846. Third Edition.

Table 1.
Performance data for metals analysis

Analyte	PRQL[a] (QAPP) (mg/Kg)	IDL (Exp) (mg/Kg) n=7	Acc. (QAPP) (%)	Acc. (Exp) (%) n=7
Antimony	100	5.0	80 -120	82-87
Arsenic	100	5.0	80 -120	93-108
Barium	2000	2.4	80 -120	86-107
Beryllium	100	2.6	80 -120	82 -102
Cadmium	20	20	80 -120	78-104
Chromium	100	5.5	80 -120	75-102
Lead	100	5.0	80 -120	90-116
Mercury	4	1.0	80 -120	100-111
Nickel	100	38	80 -120	81-106
Selenium	20	5.0	80 -120	94-103
Silver	100	22	80 -120	84-101
Thallium	100	5.0	80 -120	95-108
Vanadium	100	6.9	80 -120	84-106
Zinc	100	49	80 -120	81-104

[a] PRQL assumes a 100X dilution of the sludge sample.

Table 2
Performance data for purgeable organics analysis

Compound	MDL (QAPP) ug/g	MDL (EXP)[1] ug/g	Acc. (QAPP) %	Acc. (Exp)[2] %
Vinyl Chloride	1.0	0.5	D-251	34-79
Trichlorofluoro-methane	1.0	0.80	17-181	47-103
Ethyl Ether	1.0	0.3	80-120	54-92
112-Trichloro-122-trifluoroethane	1.0	0.2	60-150	43-95
Methylene Chloride	1.0	0.3	D-221	67-108
Carbon Disulfide	1.0	0.3	60-150	36-85
Chloroform	1.0	0.3	51-138	72-111
1,2-Dichloroethane	1.0	0.3	49-155	76-112
1,1,1-Trichloroethane	1.0	0.3	52-162	71-110
Carbon Tetrachloride	1.0	0.1	70-140	54-115
Benzene	1.0	0.3	37-151	70-109
Trichloroethene	1.0	0.2	71-157	80-120
1,1,2-Trichloroethane	1.0	0.5	80-120	78-110
Bromoform	1.0	0.7	45-169	61-115
Toluene	1.0	0.2	47-150	78-109
Tetrachloroethene	1.0	0.3	64-148	79-109
Chlorobenzene	1.0	0.2	37-160	82-109
Ethyl Benzene	1.0	0.1	37-162	79-110
m+p-xylene	2.0	0.5	60-150	82-108
o-xylene	1.0	0.2	60-150	80-108
1,1,2,2-Tetrachloroethane	1.0	0.3	46-157	67-117
1,4-Dichlorobenzene	1.0	0.3	18-190	81-114
1,2-Dichlorobenzene	1.0	0.1	18-190	77-106

[1] Calculated according to (1), n=4
[2] Calculated according to (1), n=5

Table 3
Performance data for non-purgeable volatiles analysis

Compound	MDL (QAPP) ug/g	MDL (EXP)[1] ug/g	Acc. (QAPP) %	Acc. (Exp)[2] %
Methanol	10.0	6.5	50-150	49-145
Acetone	10.0	4.4	50-150	61-136
Methyl Ethyl Ketone	10.0	2.4	50-150	62-134
i-Butanol	10.0	3.5	50-150	52-126
n-Butanol	10.0	3.8	50-150	50-110
Pyridine	50.0	6.6	50-150	64-122

[1] Calculated according to (1), n=4
[2] Calculated according to (1), n=5

Table 4.
Performance data for semivolatile organics analysis

Compound	MDL (QAPP) ug/g	MDL (EXP)[1] ug/g	Acc. (QAPP) %	Acc. (Exp)[2] %
2-Methyl Phenol	5.0	0.26	60-150	46-104
Hexachloroethane	5.0	0.23	40-113	38-93
4-Methyl Phenol	5.0	.023	60-150	46-114
Nitrobenzene	5.0	0.37	35-180	49-98
2,4-Dinitrotoluene	0.3	0.23	39-139	54-146

[1] Calculated according to (1), n=4
[2] Calculated according to (1), n=5

Streamlining the Data Quality Process Without Compromising Defensibility

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ABSTRACT

The purpose of this presentation is to challenge the prescriptive approach to selection of quality control samples and the level of data quality evaluation. The methods program with performance based methods recognizes the need for streamlining the data quality process. More cost effective sampling and analysis programs can be developed without compromising legal defensibility through a critical review of each component of the data quality process. Knowledge of site history, chemicals of potential interest, potential matrix interferences, and other information and data obtained during initial stages of investigations at large facilities can be used to focus the data collection efforts while continuing to provide usable data of known quality. For, example, the number and frequency of use of trip and field blanks should be adjusted in large projects. Similarly, the level of QC samples may be adjusted to correlate with the levels of uncertainty that may be acceptable in the decisions to be made. This results in greater documentation in sensitive areas/samples (e.g. perimeter wells as compared to interior wells). The EPA's Contract Laboratory Program criteria for selection of data quality evaluators at facilities that are not under Superfund and have a more narrow range of issues results in unnecessary data collection that to not improve our ability to make defensible risk management decisions.

Similarly, the requirement for 100 percent data validation for data to be used in risk assessments also needs serious review. These procedures focus on analytical uncertainties, which are frequently much lower than other factors that are impacting the decisions. A tiered data evaluation/validation process that focuses on the decision process may include review of selected subsets of the data. Improved computer based evaluation tools (COMPARE by A. Sauter) are available to address the mechanics of process. Proposed streamlined tiered evaluation process is more cost effective than complete validation and does not compromise defensibility.

ORGANIC

COMPARISON OF INERTNESS PROPERTIES OF TUBING IN GAS CHROMATOGRAPHY

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ABSTRACT

Advancing technologies are lowering detection limits for various methods. Even with the introduction of new detectors that are sensitive down to parts per trillion, sample integrity can be compromised before it reaches the detector. Sample introduction and transportation can have adverse effects on detection of low level analytes. This paper investigates the interaction of parts per billion (by volume) levels of volatile organic gas standards with the inner pathways of various tubing used in gas chromatography. AT-Steel™, stainless steel tubing with a fused silicalike lining, demonstrated the least interaction with the gas-phase molecules studied.

INTRODUCTION

A trend in environmental analysis is to achieve lower detection limits. Advances in detector design make it possible to achieve these lower limits. However, sample integrity can be compromised before reaching the detector, therefore sample introduction and transportation pathways benefit from treatment to minimize analyte losses.

This paper investigates the interaction of low level volatile organic gas standards with tubing commonly used in gas chromatography. A switching valve and a flame ionization detector (FID) were connected by the tubing being analyzed. The tubing was purged with nitrogen, and switched in line with a low level volatile organic gas standard for a set period of time. The response recorded from the FID for various low level volatile organic gas standards indicated the amount of interaction between the tubing and the gas-phase molecules. Volatile organic gas standards, in the parts-per-billion (ppb) concentration range, were used in this investigation.

EXPERIMENTAL

The volatile organic gas standards were made using a static dilution bulb. A volume was transferred from the static dilution bulb to a SUMMA® canister. The SUMMA® canister was pressurized with nitrogen to 29.4 psig to give a final concentration in the parts per billion (by volume) range. The analytes chosen for the volatile organic gas standards were benzene, hexachlorobutadiene, methyl *tert*-butyl ether, and 1,2-dichloropropane.

The types of tubing tested were AT-Steel, nickel, stainless steel, aluminum, and copper. All of the tubing was 1/8" OD by 0.085" ID and had a length of 12'. The tubing was initially rinsed with pentane, methylene chloride, and methanol. They were purged with dry nitrogen overnight.

The apparatus used to test the tubing was constructed from a switching valve and a flame ionization detector (FID). A variation of this apparatus has been described elsewhere (1). A piece of tubing was connected between the valve and the FID. The valve was plumbed with a supply of pure nitrogen and the SUMMA® canister containing the low level volatile organic gas standard.

The run was initiated with pure nitrogen and after one minute the valve was switched to the volatile organic gas standard. The valve was left in this position for one minute allowing the gas

standard to flow through the tubing. Two minutes after beginning the run, the valve was switched back to the original position. The responses from the FID were recorded and plotted.

RESULTS AND DISCUSSION

The first analyte studied was benzene. A standard of 125ppb of benzene was made. Figure 1 shows the plot of the FID response for this analyte on each types of tubing (i.e. AT-Steel, nickel, stainless steel, aluminum, and copper). By comparing peak shape, you can clearly see that the stainless steel, nickel, and aluminum tubing each exhibit interaction with benzene. Surprisingly, copper tubing exhibited very little interaction. Upon closer scrutiny, it was evident that AT-Steel did perform better than copper. The plot for the copper tubing shows a small amount of rounding on the top front of the peak and more tailing than AT-Steel.

The next analyte studied was methyl *tert*-butyl ether (MTBE). A gas standard of 200ppb was made for this analyte. Figure 2 shows the plot of the FID response for MTBE using AT-Steel, nickel, stainless steel, aluminum, and copper tubing. Comparison of these peak shapes show the adsorbance of MTBE on nickel, stainless steel, and aluminum tubing. Once again, copper and AT-Steel show inertness to this analyte. Comparing peak shapes between AT-Steel and copper is further evidence that AT-Steel tubing is more inert.

Another analyte chosen to investigate the activity of the inner surfaces of various tubing was 200ppb 1,2-dichloropropane. Figure 3 shows the response from the FID for AT-Steel, nickel, stainless steel, and copper tubing. Again adsorbance of this analyte occurred on the nickel and stainless steel tubing. AT-Steel showed the least interaction with 1,2-dichloropropane, with copper the next least active.

Finally, Figure 4 shows the FID response for 200ppb hexachlorobutadiene on AT-Steel, nickel, and copper. As expected, AT-Steel showed the most inertness of the tubing tested.

Various levels of benzene standards (125, 50, 15, and 5ppb) were subjected to the same analysis. Figure 5 shows the FID responses for these analytes. AT-Steel tubing provides the same general peak shape for all analyte concentrations. Since, for the other volatile organic gas standards studied, copper showed similar inertness, a 5ppb standard was ran on the copper tubing. The peak shape for this low level analyte shows the superiority of AT-Steel over copper.

SUMMARY

By comparing peak shapes for various analytes using different types of tubing, we conclude that AT-Steel provides the most inertness of the tubing studied (nickel, stainless steel, aluminum, and copper). For a completely inert pathway, the ideal peak shape would be rectangular. It would have sides orthogonal to the baseline and a top parallel to it. The only peaks that resemble this shape were the peaks generated using the AT-Steel.

Surprisingly, copper exhibited remarkable inertness. Copper is not usually considered for transfer lines, but may be acceptable as a low cost alternative when working with high levels of analytes.

As seen by the results for nickel, it does not make the best tubing when it comes to inertness. Analysts considering nickel as a transfer line should perhaps consider AT-Steel in its place.

REFERENCES

[1] McAndrew, J.J.F.; Znamensky, D.; DeBord, D.; Inman, R. *Anal. Chem.* **1995**, *67*, 3075-3078.

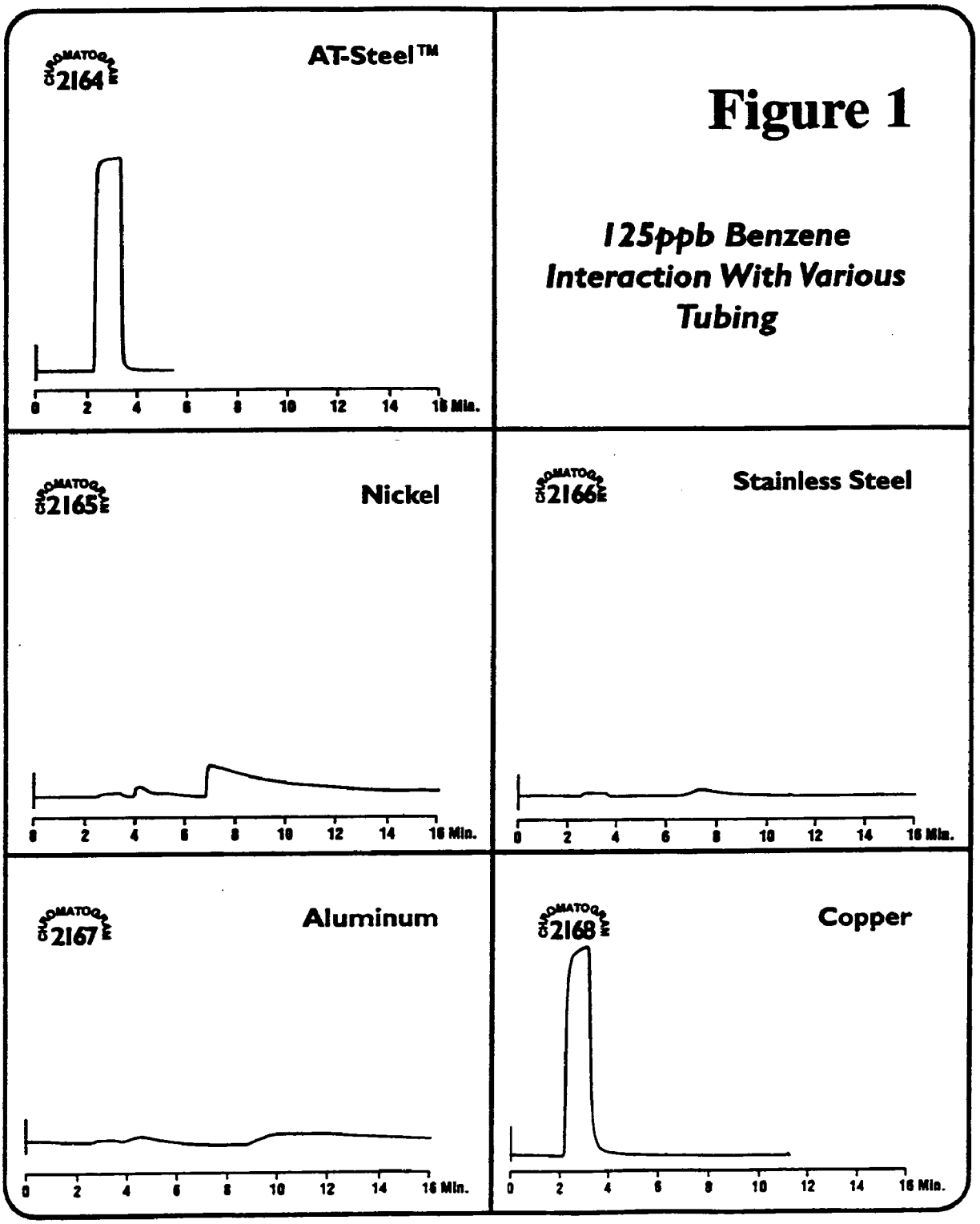

Figure 1

125ppb Benzene Interaction With Various Tubing

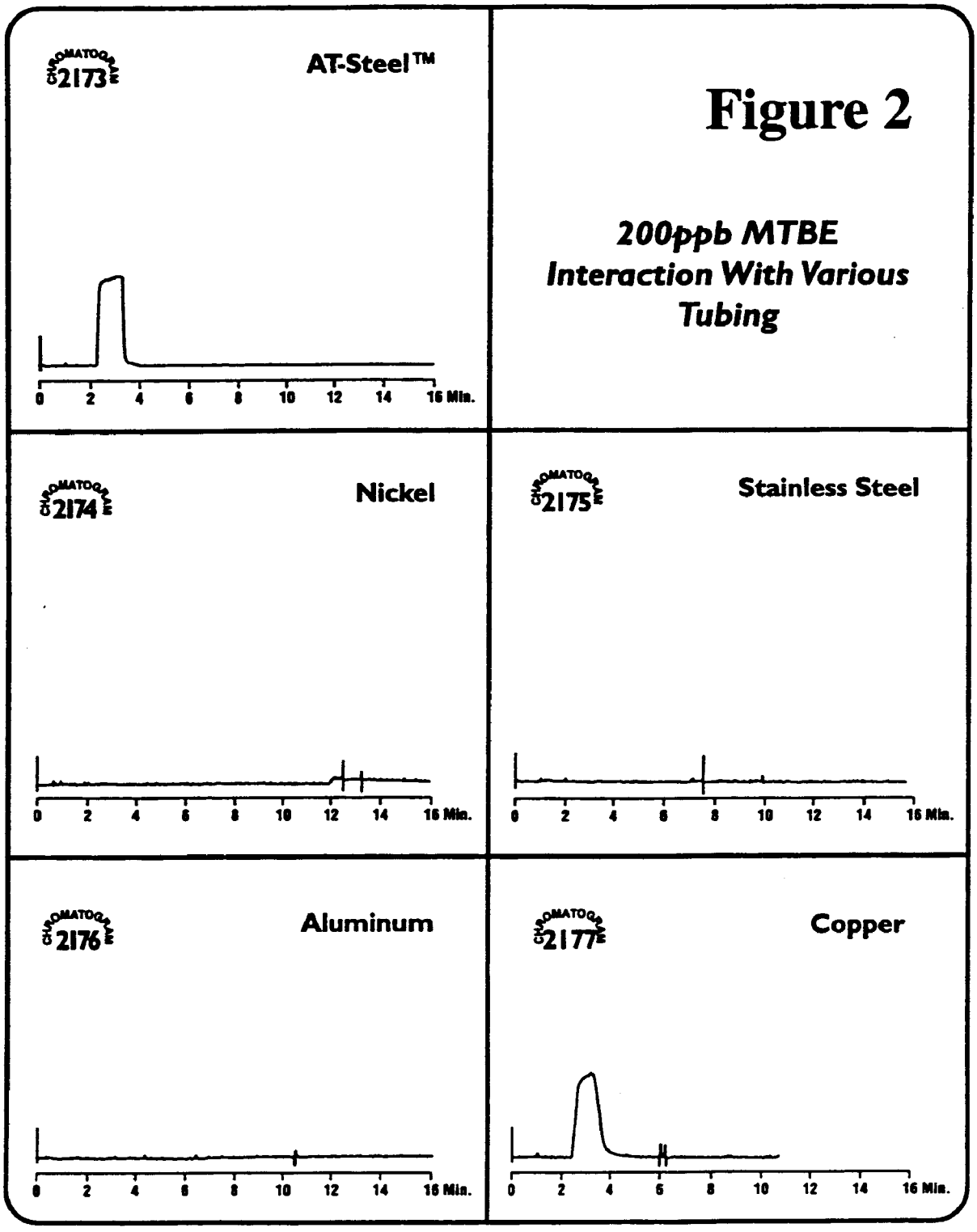

Figure 2

200ppb MTBE Interaction With Various Tubing

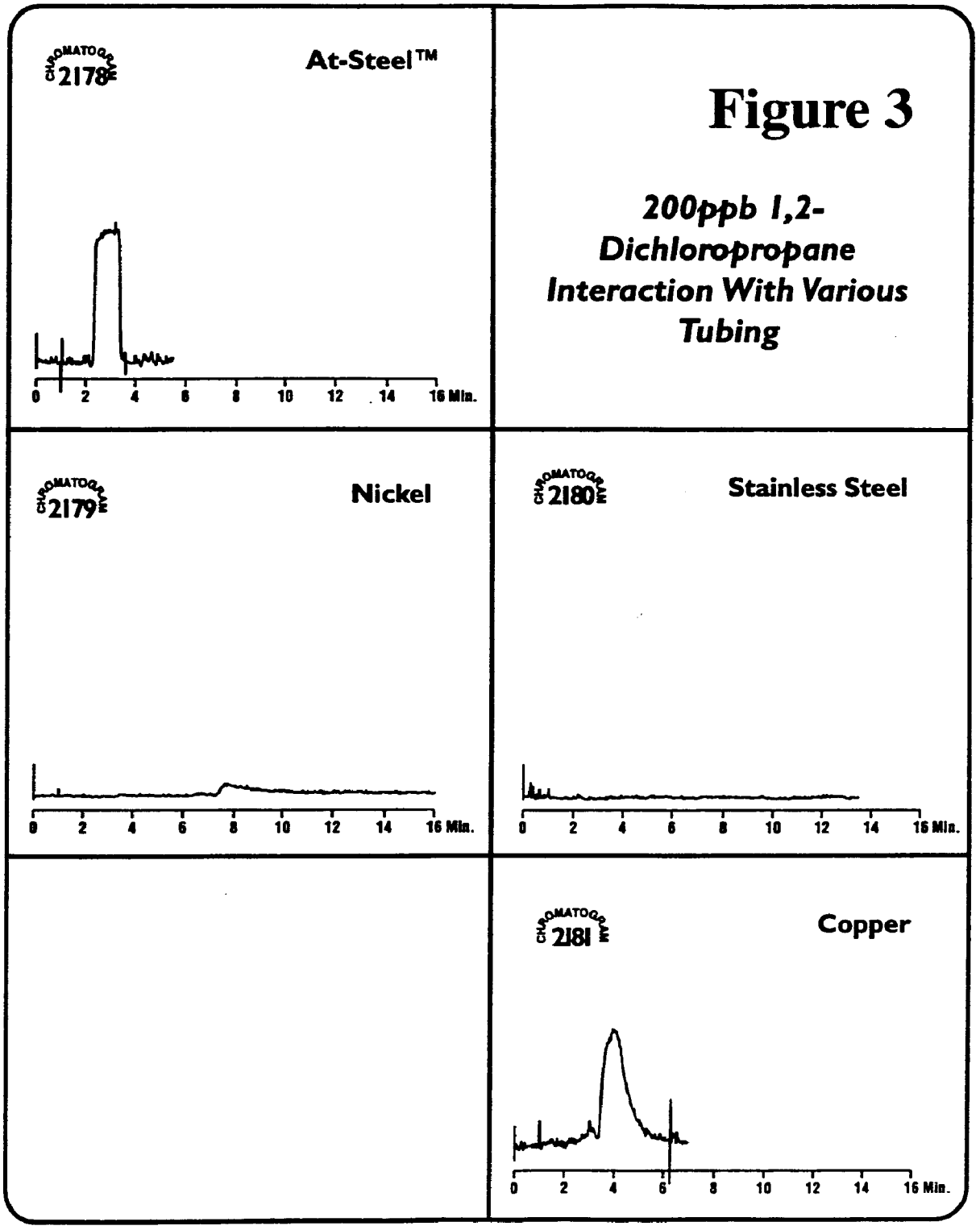

Figure 3

200ppb 1,2-Dichloropropane Interaction With Various Tubing

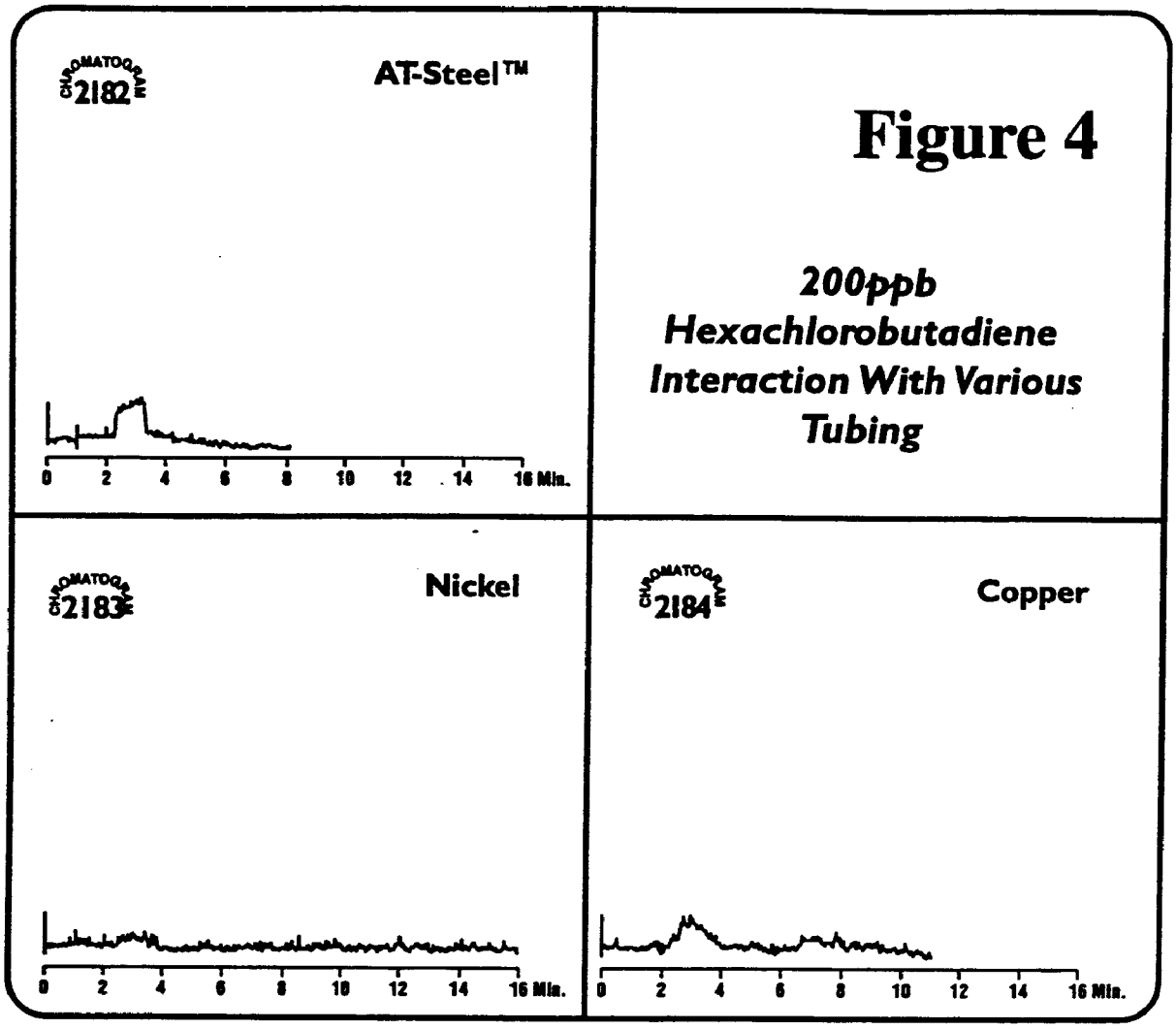

Figure 4

200ppb Hexachlorobutadiene Interaction With Various Tubing

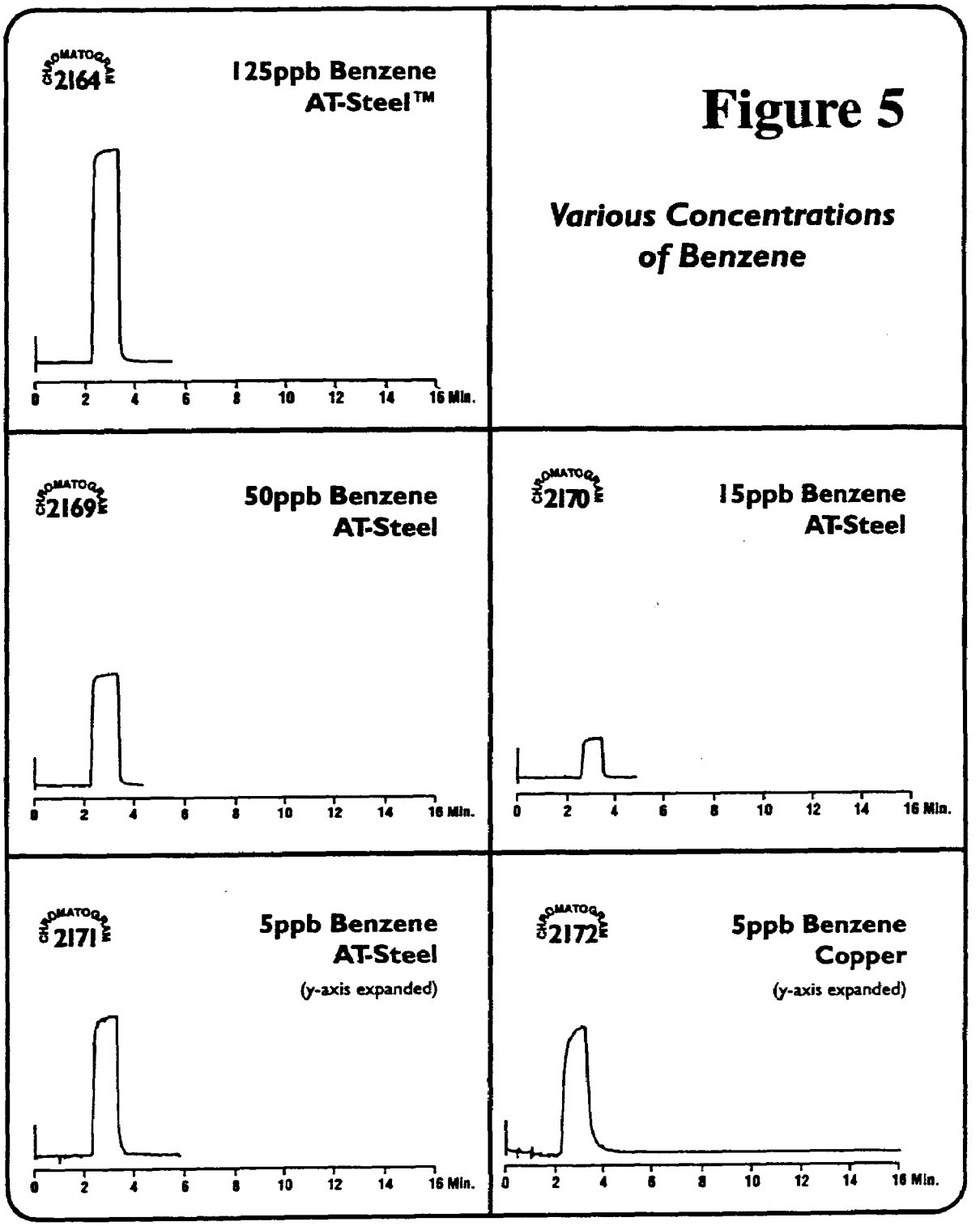

Figure 5

Various Concentrations of Benzene

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Title: **EASIER AND FASTER GC/ECD ANALYSES OF PESTICIDES AND PCB'S**

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Abstract: The generation of environmental data for pesticides and PCB's in various matrices can be very a time-consuming and expensive process for laboratories and engineering firms.
In order to keep a GC/ECD system operating within control limits, analytical time will most likely be spent on tasks, such as: recalibrations, reinjection of samples, cleaning detectors, reintegration of chromatography peaks, as well as analyzing billable samples. In addition, the reporting software may not be sufficiently optimized to generate reports in a timely manner.
We have been using an improved ECD on the Hewlett-Packard 6890 GC. This detector has been modified to provide several new features: the linear dynamic range covers several orders of magnitude, it stays cleaner longer, and it is more robust. All of this results in calibrations lasting for quite a long period of time. Also, fewer samples need to be diluted and reinjected because they were originally out of the linear range. The use of new Chemstation software results in better data reduction and easier report generation. Improved injection techniques provide greater method sensitivity and lower MDL's. Finally, the use of "fast GC" techniques results in a shorter analytical run-time. Data will be presented to demonstrate these features

COST AND QUALITY IMPROVEMENTS USING A MASS SPECTROMETER AS THE DETECTOR FOR METHODS 8010, 8020, AND 8021

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ABSTRACT

The analytes listed in SW-846 methods 8010, 8020, and 8021 can also be determined by GC/MS, method 8260. GC/MS offers much better confidence in correct identification of analytes than the GC methods and reduces the possibility of false positives. Customers of environmental laboratories often prefer and specify the GC methods because of perceived benefits in price, sensitivity, and quantitation accuracy. Problems with the GC methods include: false positives due to the limited selectivity of the PID, false positives due to the crowded chromatogram that results when extensive lists of target analytes are of concern, poor stability of the ELCD, and quantitation difficulty due to co-elution.

We show that the quantitation limits and calibration criteria for methods 8010, 8020, and 8021 can be met using MS detection. General performance characteristics such as accuracy and precision, linearity, analyte specificity, and sensitivity to water are improved. The impact of improved chromatographic performance on productivity measures such as turn-around-time, overall cost, and capacity is demonstrated.

INTRODUCTION

Volatile aromatic and halogenated compounds are of considerable environmental significance, and several methods for their determination appear in SW-846. Two approaches have been used for measurement of volatile organics in SW-846: the GC/selective detector approach (methods 8010, 8020, and 8021) and the GC/MS approach (methods 8240 and 8260). The GC/MS methods provide better confidence in identification due to the combination of retention time and mass spectral data. The GC methods rely on retention time alone and confirmation, normally on a second column, is necessary for confidence in identification. Even with the second column, complex matrices may lead to false positives. This is particularly true for the PID, which has limited selectivity.

The number of analytes listed as within the scope of methods 8010, 8020, and 8021 has typically increased with each revision of SW-846. The currently proposed method 8021B lists 57 RCRA and 13 additional non-RCRA analytes (Table 1). Separation of this number of analytes (plus the required surrogate and internal standards) presents severe

difficulties. Even when resolution is obtained for a standard, matrix effects may lead to retention time shifts in the sample, possibly leading to false positives or false negatives.

Data users have often preferred the GC methods over the GC/MS methods because of a belief that lower detection limits are possible and because of more stringent calibration criteria (Tables 2 and 3).

TABLE 1

Number of Analytes Listed in SW-846			
	8010	**8020**	**8021**
Third Edition	39	7	-
Update I (July 1992)	34	7	60
Update II (September 1994)	49	8	60
Update III (Proposed)	-	-	70

TABLE 2

Calibration Criteria		
	8021	**8260**
Initial calibration	< 20% RSD all analytes	< 30% RSD, subset of 6 analytes
Calibration verification	+/- 15%, all analytes	+/- 20%, subset of 6 analytes
Bracketing standard	Generally required	Generally not required

TABLE 3

SW-846 MDLs and PQLs		
	MDL (µg/L)	**PQL (µg/L)**
8010	0.001 - 0.34 [1]	0.01 - 3.4 [1]
8020	0.2-0.4	2-4
8021	0.01 -3	0.1 - 30
8260	0.02 - 0.5	0.2 - 5

[1] It is generally recognized that these levels cannot be met in routine operation.

EXPERIMENTAL

All work was performed on a Hewlett-Packard 6890 gas chromatograph with a single split/splitless electronic pneumatic controlled (EPC) injector coupled to an HP 5972 mass spectrometer. A Tekmar 3000 purge and trap and Tekmar 2016 autosampler were interfaced to the GC by cutting the carrier gas line to the split/splitless injector approximately 1-2 inches from the injector. The carrier supply line was then routed to the desorb flow input on the back of the purge and trap. The heated transfer line from the purge and trap was then connected to the previously cut line on the injector using a 1/16" Swagelock union. This configuration allowed complete electronic control of the desorb flows and pressures.

Needle spargers were used on the Tekmar 2016 autosampler with a purge flow of 40 mL/min. The purge time was set to 11 min. The water management system on the purge and trap was bypassed. Desorb time was set to 2 min. and the desorb flow was controlled by setting the split flow on the GC.

The split/splitless injector was operated in the split mode with a split ration of 10:1. A capillary column was installed the normal way in the injector and coupled directly to the mass spectrometer with no jet separator or splitter. The column used was a newly available 60m X 0.32mm X 1.8 μm film HP-VOC-MS (HP part #19091R-316). Column flow was set at a constant 1.5 mL/min using EPC. No cryogens were used for this work.

The mass spectrometer was tuned using the maximum sensitivity autotune and operated in the full scan mode with a scan range of 35-300 amu. The complete purge and trap GC/MS system was controlled by a Hewlett-Packard Chemstation computer networked to an HP Chemserver. Teklink software was used to communicate with the purge and trap.

RESULTS AND DISCUSSION

Method Detection Limits and Calibration Stability

A method detection limit study was performed for the mass spectrometer at a spiking level of 0.1 μg/L. These results are presented in Table 4. Reasonable spectra were obtained at this level.

TABLE 4

Compound	Spiking Level µg/L	Average of 7 Determinations µg/L	MDL µg/L
Dichlorodifluoromethane	0.1	0.09	0.02
Chloromethane	0.1	0.12	0.04
Vinyl chloride	0.1	0.08	0.03
Bromomethane	0.1	0.13	0.03
Chloroethane	0.1	0.08	0.02
Trichlorofluoromethane	0.1	0.10	0.03
Freon 113	0.1	0.10	0.02
1,1-Dichloroethene	0.1	0.10	0.02
Methylene chloride	0.1	0.36	0.06
trans-1,2-Dichloroethene	0.1	0.10	0.03
1,1-Dichloroethane	0.1	0.11	0.02
cis-1,2-Dichloroethene	0.1	0.10	0.03
Chloroform	0.1	0.11	0.02
1,1,1-Trichloroethane	0.1	0.10	0.04
1,2-Dichloroethane	0.1	0.13	0.12
Carbon tetrachloride	0.1	0.09	0.02
Trichloroethene	0.1	0.09	0.02
1,2-Dichloropropane	0.1	0.10	0.01
Bromodichloromethane	0.1	0.10	0.03
2-Chloroethyl vinyl ether	0.1	0.28	0.55
cis-1,3-Dichloropropene	0.1	0.09	0.01
trans-1,3-Dichloropropene	0.1	0.08	0.02
1,1,2-Trichloroethane	0.1	0.09	0.04
Tetrachoroethene	0.1	0.08	0.02
Dibromochloromethane	0.1	0.07	0.02
1,2-Dibromoethane	0.1	0.09	0.02
Chlorobenzene	0.1	0.09	0.01
Bromoform	0.1	0.05	0.04
1,1,2,2-Tetrachloroethane	0.1	0.09	0.03
1,3-Dichlorobenzene	0.1	0.09	0.02
1,4-Dichlorobenzene	0.1	0.09	0.02
1,2-Dichlorobenzene	0.1	0.08	0.02

Calibration Stability

Calibration stability on the GC/MS system was excellent. In all cases, the method 8000 criteria for a maximum of 15% drift from the initial calibration for all components was met. In addition, all samples were bracketed by a closing calibration that also met this criteria.

Field Samples

Thirty-six field samples were analyzed by both GC/ELCD and GC/MS. Twenty-six analytes were included on the target list, and the reporting limit was 0.5 ppb. Dual column confirmation was used in the case of electrolytic conductivity detection in order to improve the reliability of compound identification. Thirty-one analytes had positive results, ranging from 0.41 ppb to 62,000 ppb. These detected analytes are listed in Table 5. Generally, results are quite comparable. In two cases, low levels of a target analyte were identified by MS and not by ELCD. This is because the MS provided reasonable spectra at a level that appeared to be baseline noise on the ELCD.

TABLE 5

	1,1-Dichloroethene		Chloroform		Trichloroethene		1,1,2-Trichloroethane		1,2-Dichloroethane	
	ELCD	**MS**	**ELCD**	**MS**	**ELCD**	**MS**	**ELCD**	**MS**	**ELCD**	**MS**
47894-01	26	28			37	56	1100	1300		
47894-02							1.4	1.5		
47894-06			1.4	2.5						
47894-07	0.4	0.2					14	21		
47894-08	98	113					3600	4100		
47894-09					140	192	18	22		
47904-01									110	119
47904-02									600	520
47904-05									54000	62000
47904-06									34000	39000
47904-07			ND	14					62000	71000
47904-08									13000	15000
48032-01			630	750					27000	31000
48032-02			360	420					18000	20000
48032-04			1200	1370			750	690	25000	25000
48032-05			530	620					17000	17000
48032-17					ND	33	1300	1800	22000	36000

CONCLUSIONS

Modern benchtop GC/MS systems can provide the sensitivity of the ELCD in the detection of halogenated volatiles. Use of the MS instead of the ELCD carries a number of benefits for the laboratory and the data user, including:

- More confidence in compound identification and lower risk of false positives and false negatives.
- Less difficulty in meeting stringent calibration criteria.
- Easier data review and validation.
- Faster analysis time.
- No co-elution problems.

It could be claimed that disadvantages of MS include greater initial cost of the instrumentation and higher skill level needed by the operator. However, the greater initial cost is compensated by the much greater potential sample throughput of the MS system; and it is the authors' belief that production of *high quality* data with selective detectors requires a higher skill level than for GC/MS due to the more difficult data interpretation.

COMPARISON OF EXTRACTION METHODS FOR HEAVY PETROLEUM HYDROCARBON MEASUREMENT IN SOILS

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ABSTRACT

This poster provides a summary of method development to optimize recovery from soxhlet, supercritical fluid (SFE), accelerated solvent (ASE) and microwave extraction systems for petroleum hydrocarbon measurements in refinery soil. A comparison of the three methods is included along with extract molecular analyses by high pressure liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS).

The results show that under optimum conditions, both the SFE and ASE have equivalent Total Petroleum Hydrocarbon (TPH) recoveries and reproducibility of results relative to the soxhlet after a silica gel clean-up step. The SFE and ASE were shown to have a number of advantages over the soxhlet including lower solvent requirements, easy set-up, automated operations and compact designs. The ASE was found to be mechanically more reliable than the SFE in the TPH application as well as better suited to accommodating larger sample sizes.

The conclusions of the above study indicate that the ASE is a practical alternative to the soxhlet for research applications requiring the monitoring of TPH. The ASE was also shown to be flexible in its capability to use various solvents (including mixtures) and has the potential for extraction applications in a wide range of environmental analyses.

INTRODUCTION

The use of soxhlet extraction methods for the quantitative removal of organic contaminants from soils are effective and reproducible when matrix interferences from moisture content and particle size distribution are controlled. There are incentives to finding alternative methods due to inefficiencies associated with soxhlet use which include the manipulation of glassware, the monitoring of solvent cycle rates and long extraction times (4-24 hours). Other draw backs of the soxhlet include the requirements of large areas of vented hood space, handling large volumes of solvent and solvent boiling point/azeotrope limitations.

There are a number of compact commercial alternatives designed to shorten the extraction time and automate portions of the procedure based on SFE, ASE and microwave technologies. These technologies were evaluated by extracting refinery soils containing heavy aged petroleum contaminants. Hydrocarbon recoveries were compared to modified soxhlet methods (based on EPA 3540 and 418.1) designed to minimize matrix interferences.

SUMMARY

The evaluation of SFE and ASE showed nearly equivalent TPH recoveries relative to the soxhlet (see Table 1) when extracting conditions were optimized. The SFE recovery was optimized using a high density (0.99g/cc @ 25 C) initial extraction step followed by a higher temperature (0.80g/cc @ 83 C) second step. The critical limiting variable found with the SFE was the capacity of the solid analyte trap which could be exceeded when the sample size was increased above 1 gram. The ASE provided the most flexibility in this application allowing a larger sample size (10 grams soil) with TPH recovery equivalent to the soxhlet over a range of 1.0 - 4.5 wt % TPH on dry weight of soil (see Figure 1).

The ASE also provided equivalent gravimetric recoveries to the soxhlet in a comparison of a methylene chloride extraction based on EPA 3540 (see Table 2). This solvent provides a higher recovery of 4+ ring aromatics and is used for quantitative GC/MS analyses for polynuclear aromatic hydrocarbons (PAH's) and semi-quantitative characterization of molecular classes by HPLC. The evaluation of a microwave system for this application showed somewhat higher variability and required more solvent handling steps.

The methylene chloride extracts from soxhlet and ASE extractions were compared using HPLC and the results showed comparable compositions of saturates and 1-4 ring aromatics with a somewhat higher polars content in the ASE extract (see Figure 2). These extracts were also analyzed by GC/MS after EPA 3611 alumina clean-up with initial results indicating comparable recoveries of semivolatile PAH's (see Table 3).

CONCLUSIONS

The ASE provides equivalent recoveries relative to the soxhlet in a TPH application and provides the following advantages: short extraction times, low solvent use, compact design, large sample size and automated operations.

The ASE permits the substitution of Freon 113 with the less volatile tretrachloroethylene (PCE) in the TPH application. The incentives for this change in solvent include regulatory phase out of Freon and the much lower cost of PCE.

Evaluation of the ASE in a methylene chloride extraction for quantitative recovery of PAH's shows high recoveries and low variability. These results were achieved using a 20 minute ASE extraction compared to a standard 16 hour soxhlet extraction.

The SFE provides equivalent TPH recovery relative to the soxhlet under optimum conditions but required more method development than the ASE. The SFE was also limited by its smaller sample size capacity and mechanical servicing requirements.

The microwave results had higher variability than the soxhlet, SFE and ASE.

Soxhlet and ASE Sample Preparation and Extraction for TPH

- Thoroughly mix the soil sample and sieve through a Tyler 4 mesh sieve.
- Weigh the soil into a solvent rinsed beaker and mix with a 3/1 ratio of sodium sulfate to soil. Mix well and allow to dry for 1 hour.
- Break up agglomerates in sample with a pestle and quantitatively transfer into the extraction thimble. Clean beaker and pestle with glass wool and place on top of sample.
- Soxhlet extract with Freon 113 for 4 hours at a minimum 20 cycles/hour. ASE extract with PCE for two 10 minute cycles at 150 C and 2000 psi.
- Filter the extract through solvent rinsed sodium sulfate into a volumetric flask and mix well.
- Prepare standards from a reference oil containing 15 ml n-hexadecane, 15 ml isooctane and 10 ml chlorobenzene per EPA method 418.1 diluted in the extracting solvent (soxhlet Freon 113, ASE tetrachloroethylene).
- Calibrate an infrared spectrometer with the standards using the absorbance at 2930 wave numbers after subtracting the solvent background. Use a minimum 5 point calibration to plot absorbance vs. mg TPH per 100 ml.
- Remove 10 ml of extract and treat with 0.5 g of 60-200 mesh silica gel. Read the IR absorbance after 30 minutes and determine TPH.

References:Washington State WTPH-418.1, EPA Methods 418.1, 9073, and 3540

Alternative Extraction Methods for TPH

Method--> Solvent-->	Soxhlet (4 hr.) Freon 113	SFE (45 min.) Carbon Dioxide	ASE (20 min.) Tetrachloroethylene
Replicate Extractions	mg/kg	mg/kg	mg/kg
1	9800	10300	10000
2	10800	11100	10200
3	11000	10400	10200
4	9900	10600	10500
	---	---	---
Mean	10400	10600	10200
RSD*	5.91 %	3.36 %	2.02 %

* relative standard deviation

Table 1

Alternative Extraction Methods for Molecular Characterization

Method--> Solvent-->	Soxhlet (24 hr.) Methylene Chloride	ASE (20 min.) Methylene Chloride	Microwave (15 min.) Hexane/Acetone
Replicates	mg/kg	mg/kg	mg/kg
1	17500	18000	15600
2	18000	18500	18700
3	16500	17900	18400
4	17500	18500	18500
	---	---	---
Mean	17400	18200	17800
RSD *	4.85 %	1.76 %	8.27 %

Table 2

GC/MS Quantitation of PAH's from Soxhlet and ASE Extracts

		Benzo(a)pyrene (ppb)	Dibenz(a,h)anthracene (ppb)
Soxhlet	Replicates		
	1	8064	1917
	2	6635	1353
	3	7312	1466
	---	---	---
	Mean	7337	1579
	RSD	9.74 %	18.90 %
ASE	Replicates		
	1	8797	1692
	2	8232	1579
	3	8458	1466
	---	---	---
	Mean	8496	1579
	RSD	3.35 %	7.16 %

Table 3

TPH Comparison of Soxhlet and ASE Extractions

Solvents - Freon 113 and Tetrachloroethylene (PCE)

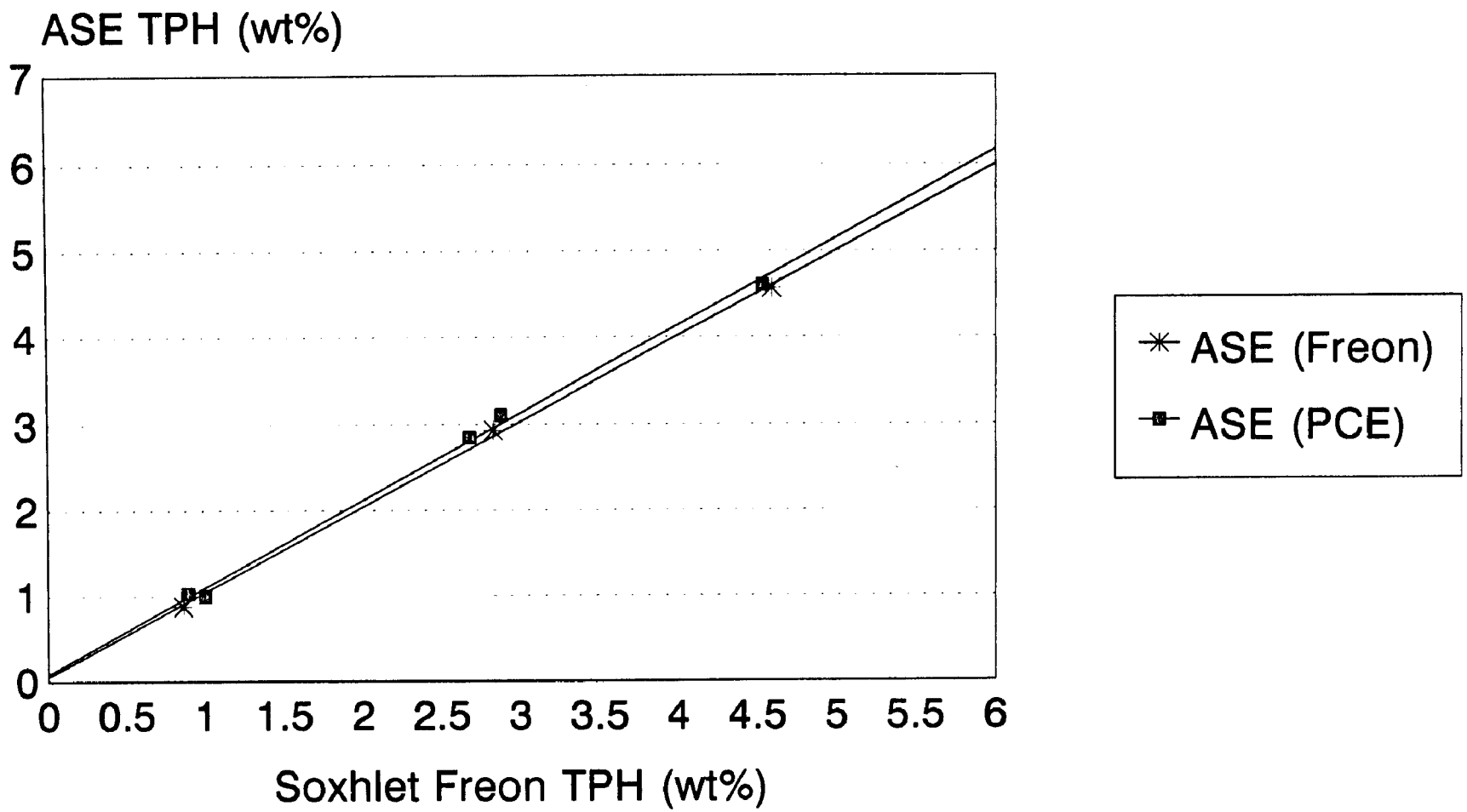

Figure 1

HPLC Molecular Classes from Soxhlet and ASE Extracts

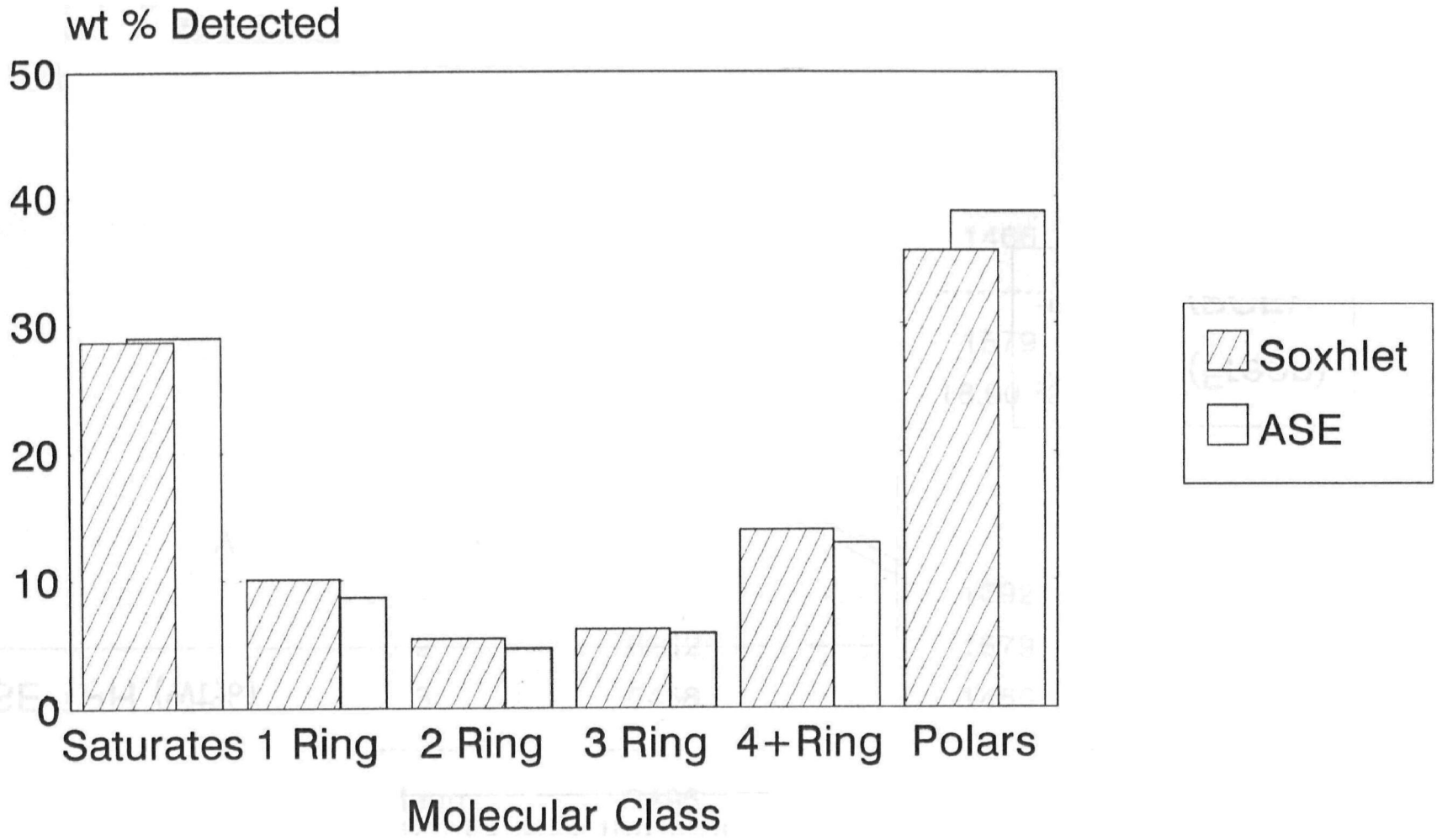

Figure 2

OPEN-VESSEL MICROWAVE EXTRACTION OF SOIL AND SEDIMENT SAMPLES

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ABSTRACT

The application of microwave technology can make organic trace-level extractions and digestions much more rapid and reproducible. Heating of and chemical reactions within mixtures can proceed more rapidly because energy is input directly to the sample and reagents using radiation rather than transferred through vessel walls and into the reagents by convection heating. Additionally, rapid localized heating can cause temperatures to be reached that are above the normal boiling points of reagents or solvents.

Higher temperatures are also reached when the microwave operation is conducted in a closed vessel, due to increases above atmospheric pressure in the system. This also contributes to faster kinetics for extraction and digestion. Higher pressures produced during closed-vessel microwave operations can introduce procedural complications.

Open-vessel microwave assisted extraction (MAE) is explored here as an alternative to closed-vessel procedures. In this work extraction vessels at atmospheric pressure were positioned in a microwave system and samples were impinged by a focused microwave beam conducted through a wave guide. Recovery and precision data are presented for soil samples containing various target analytes to demonstrate applicability of the open-vessel extraction process to trace environmental analyses.

INTRODUCTION

Removing target analytes by extraction from solid matrices is generally a matter of *kinetic* rather than *thermodynamic* limitations. In nearly all extractions there is more than enough solvent present to dissolve all trace level contaminants or even percent level impurities (e.g. fats). The speed of reaction is limited, however, by how quickly target compounds can be dislodged from active sites on or sequestered areas within the matrix material. Microwave processing inputs energy directly to the target analytes (if they are polar) and the matrix, as well as the solvent. Therefore it greatly accelerates kinetics of extraction. Microwave heating has been applied to organic extractions primarily through the use of closed-vessel systems in cavity ovens with radiation reflected about the compartment. Pressures above atmospheric are achieved in closed vessels, so that the digestion or extraction is very rapid, but a drawback is that sample size must be very limited or a very expensive high pressure vessel is required.

An alternative is microwave processing in vessels that are open to atmospheric pressure. In this type of system solvent does not reach the temperatures produced in a closed-vessel operation, yet extraction is still very rapid and requires only enough solvent to adequately contact the sample. For example, crushed rock core from a petroleum drilling operation was processed with automated Soxhlet extraction using 120 mL of methylene chloride for a period of six hours (the same sample processed by traditional Soxhlet extraction requires 24 hours or longer for extraction). Evaporating and weighing the resulting residue produced an extractables content measurement of 0.273%. Another aliquot of the same sample was processed with open-vessel MAE for 45 minutes (at a 30% power setting in a 300 Watt system) using only 60 mL of methylene chloride. Measurement of extractables content produced a result of 0.287%, demonstrating that the open-vessel extraction yields results equivalent to exhaustive Soxhlet extraction.

DISCUSSION

Some forms of extraction can produce conditions which breakdown targets analytes during the extraction process. Matrix materials may contribute to such side effects, by acting as acidic or basic catalysts, for example. Higher temperatures accelerate extraction, but also can accelerate such side effects. This may be the reason compounds such as benzidine, α,α-dimethylphenethylamine, 2-picoline, dibenzo[a,j]acridine, and the organophosphorus pesticides exhibited some low or poor recoveries during closed-vessel MAE in 1:1 acetone/hexane mixture[1]. Also, MAE of moistened soils showed decreasing recoveries of some compounds when the soil samples were aged (seven or fourteen days).

Another example of differences between techniques for recoveries of certain compounds is generally lower recoveries observed for endrin aldehyde and chlorothalonil during sonication extraction (SW-846 Method 3550) when compared with results from automated Soxhlet extraction (Method 3541) or closed-vessel MAE during acetone/hexane extraction of 10 gram samples (sand, clay, or sediment)[2]. MAE (101%) equaled automated Soxhlet (98%) for chlorothalonil at a high spiking level (100 µg = 10µg/g) and both were superior to sonication (69%). At a lower spiking level (500 ng = 50 ng/g) sonication recovered no chlorothalonil from sand or clay, whereas automated Soxhlet and MAE produced equal recoveries (69% each). Endrin aldehyde recoveries were similar for all techniques at both high (17% MAE, 25% SOX, 22% SON) and low (26%, 32%, 29%) levels. This work studies effectiveness of open-vessel MAE for recovery of analytes known to be easily lost at low trace levels. Results were not available at the time the manuscript was prepared.

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BIAS FACTORS IN RECOVERY OF SPIKED ORGANIC COMPOUNDS FROM AQUEOUS SAMPLES

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ABSTRACT

In organic trace analysis, spiking experiments are system checks (i.e. can you recover what you put in) but don't necessarily reveal whether a technique recovers incurred residue from a matrix. Analysis of standard reference materials (known matrix that is analyzed multiple times using a reference method) provides more accurate assessments of whether bound contaminants are recovered. Nevertheless, judgement based on spike recoveries is widely used when comparing techniques for analytical equivalency. This is particularly so for aqueous samples, since reference materials are not available, have inadequate shelf life, or cannot be homogeneously subsampled.

This work describes occurrence and prevention of bias during separatory funnel (SF), continuous liquid/liquid (CL), and electrically assisted extraction (EA). The degree of bias observed can be affected by: 1) choice of extraction technique, 2) choice of solvents used for preparation of spiking solutions, 3) method of introducing spiking solution to the sample, and 4) the atmospheric pressure of the laboratory. For example[1], 56 BNA analytes spiked into seven replicates of reagent water at 10 µg/L and processed with EA extraction produced average recovery of 77% when the spiking solutions were composed of methanol, versus an average of only 61% when they were composed of methylene chloride (DCM). The corresponding figures for the same experiment but with CL extraction were 72% for both cases. These results were assigned to a *wall effect* during EA extraction, wherein spiked compounds were carried onto an upper surface of the glass sample bottle in the presence of DCM only, rather than dispersed into the water sample in the presence of methanol. In another bias example, a *surface layer volatility* effect was observed when two laboratories performing EA extraction obtained similar results, but only after the one at higher altitude (ca. 5000 ft. elevation) began injecting spiking solution under the surface of the water instead of on top of the sample. Average recoveries for seven chlorinated compounds at the higher altitude laboratory were 26%, versus 78% recovered at the lower altitude laboratory under similar extraction conditions. Average recoveries for those analytes at the higher laboratory rose to 73% after the change in spiking procedure.

INTRODUCTION

All liquid/liquid extraction techniques are based on some equilibrium process which partitions extractable materials between aqueous phase (sample) and organic phase (extraction solvent). This is especially true of *batch-sequential* extractions such as separatory funnel (SF) (e.g. SW-846 Method 3510). Continuous liquid/liquid extraction (CL) also depends on such equilibria, but for

many small droplets of solvent introduced over a long time. This is still batch-sequential in a sense, but what is non-equilibrium about CL is that recovered droplets are *recycled* by distilling solvent and thus reintroducing fresh organic phase throughout the extraction.

For spiking recoveries to be an accurate measurement of extraction efficiency, it is necessary that spiked compounds participate in whatever liquid/liquid equilibria are essential to that technique. Procedural artifacts which prevent this from happening can invalidate a spiking experiment. At levels typically used to evaluate extraction techniques most analytes are above their solubility in water and prone to biases resulting from failure to participate fully in establishment of phase equilibria. Some possibilities include (Type 1): *wall effects* - hydrophobic analytes adsorb to portions of glassware and become more difficult to recover; (Type 2): *surface layer volatility* effects - analytes having substantial vapor pressure at room temperature, when trapped in a layer on a liquid surface, can evaporate more rapidly from mixtures of water and organic solvent than they do from solutions in solvent alone; and (Type 3): *non-equilibrium bias effects* - which can occur when water and solvent are both present at the beginning of an extraction, analytes are offered an opportunity to pass directly into a solvent aliquot, and that aliquot is removed from contact with the aqueous solution relatively quickly thus preventing the analyte from ever establishing equilibrium concentrations in the two phases. The purpose of this study is to report occurrences of bias, comment on possible mechanisms (and thus reveal ways to control it), and demonstrate the potential for bias present in three techniques (SF, CL, and EA extractions).

DISCUSSION

US EPA methods generally call for spiking solutions made up in a water-miscible solvent such as acetone or methanol[2]. These materials help relatively insoluble compounds to disperse into aqueous sample. Theoretically, liquid/liquid equilibria are *path independent.* In other words, whether compounds are dispersed into the aqueous phase when extraction begins is immaterial, provided all compounds somehow reach equilibrium between the two phases. In SF extraction it is easy to guarantee that condition, since all materials are present and exposed when the system is thoroughly homogenized. For the other two techniques, this is not a sure bet.

Type 1 effect: Immediately after spiking solution is introduced each compound may be present in more than one phase. Some may be dissolved or dispersed within the sample. There may also be globules of spiking solution solvent plus analytes, and if a bulk layer of extraction solvent is present some of a compound may migrate and dissolve in that as well. If there isn't opportunity to disperse or dissolve in aqueous or solvent layers, spiked compounds may conglomerate and form a separate layer, which may find a solid surface (e.g. glassware) upon which to deposit.

Consider how three extraction techniques accomplish mixing of aqueous and solvent phases. SF extraction takes place in a closed vessel and all surfaces are wetted during shaking, therefore the type 1 effects should not occur and equilibria should be path independent. This is not so for CL, since spiked material not dispersed in the aqueous phase or fallen into the solvent pool below the sample (or to the membrane, in the case of accelerated CL) may "climb walls" of the extractor barrel at the top of the sample. Even so, a CL system is nearly closed, with a condenser at the top, and through the long extraction time (at least 6 and possibly as long as 24 hours) and reflux action analytes that were not dispersed in the beginning may still be recovered . In contrast,

during EA extraction, the spiking compounds are introduced to sample residing in a glass bottle (see diagram). Then the water sample (plus solvent aliquot) is conducted through a PTFE tube (1/4 inch diameter) into a PTFE funnel where phase mixing takes place. Although the (now solvent saturated) water sample returns to the sample bottle along with a fresh aliquot of extraction solvent, extreme type 1 effects occurring in this system might not be completely corrected during subsequent extractions.

Type 2 effect: In addition to adsorption in inaccessible spots, another mechanism for loss of analytes is evaporation. During these investigations extraordinary losses were noted for a few of the more volatile compounds from the semivolatiles target list. The losses were more severe than and out of proportion to losses of other analytes close in order of GC elution (and therefore presumed to be similar in volatility). Typical compounds exhibiting such losses include di-, tri-, and hexachlorobenzenes, hexachloroethane, hexachlorocyclopentadiene, hexachlorobutadiene, and naphthalene. Some are solids with enough vapor pressure at room temperature to sublime.

The unexplained losses seemed only to affect samples processed using EA technique; however, it eventually was shown that such losses could also occur in SF extraction and could be avoided during EA extraction. The problem was traced to the way spiking solution was introduced to the sample. When it was dropped on top of a sample ("top spiking") a film layer was observed atop the water, and fragrant naphthalene was detected by smell. However, when the same spiking solution was *injected* directly into the sample ("direct spiking") no film layer was observed and no odor was detected. Any extraction method can be affected by this problem, but SF extraction is usually "forgiving", since materials are contained in a vessel with a narrow neck that is often sealed shortly after spiking. An experiment involving top spiking and leaving water samples in a jar in the hood for an extended time followed by SF extraction produced the same pattern of losses that had been seen during EA extraction (see Table 3). Such losses can also occur during CL extraction. Examination of the CL data in a published study[3] reveals a pattern of recoveries that is consistent with the type of volatility losses reported here.

Type 3 effect: So far we mentioned only negative factors; however, it's possible to have positive bias during extraction. This occurs if a portion of spiked compound, instead of dispersing within the sample, enters an extraction solvent aliquot that has no opportunity to participate in phase equilibria. In that case the percentage of the target compound contained in the recovered extract is not representative of the ability of the technique to extract compounds from water samples. This situation is most likely to occur during CL extraction, where there is generally a layer of solvent at the bottom of the extractor to ensure proper operation without introducing aqueous fluid into the boiling flask connected to the extractor.

EXPERIMENTAL

Facilities where these experiments were performed are identified as Lab 1 (US EPA Region 6 laboratory in Houston, Texas), Lab 2 (OI Analytical's laboratory in Columbia, Missouri), or Lab 3 (Rocky Mountain Arsenal laboratory near Denver, Colorado). SF and CL extractions were performed according to US EPA SW-846 methods 3510 or 3520, except some spiking solutions were dissolved in DCM instead of the methanol specified in EPA methods. All samples were dosed with 1 mL of each spiking solution used. For CL extraction the accelerated version was

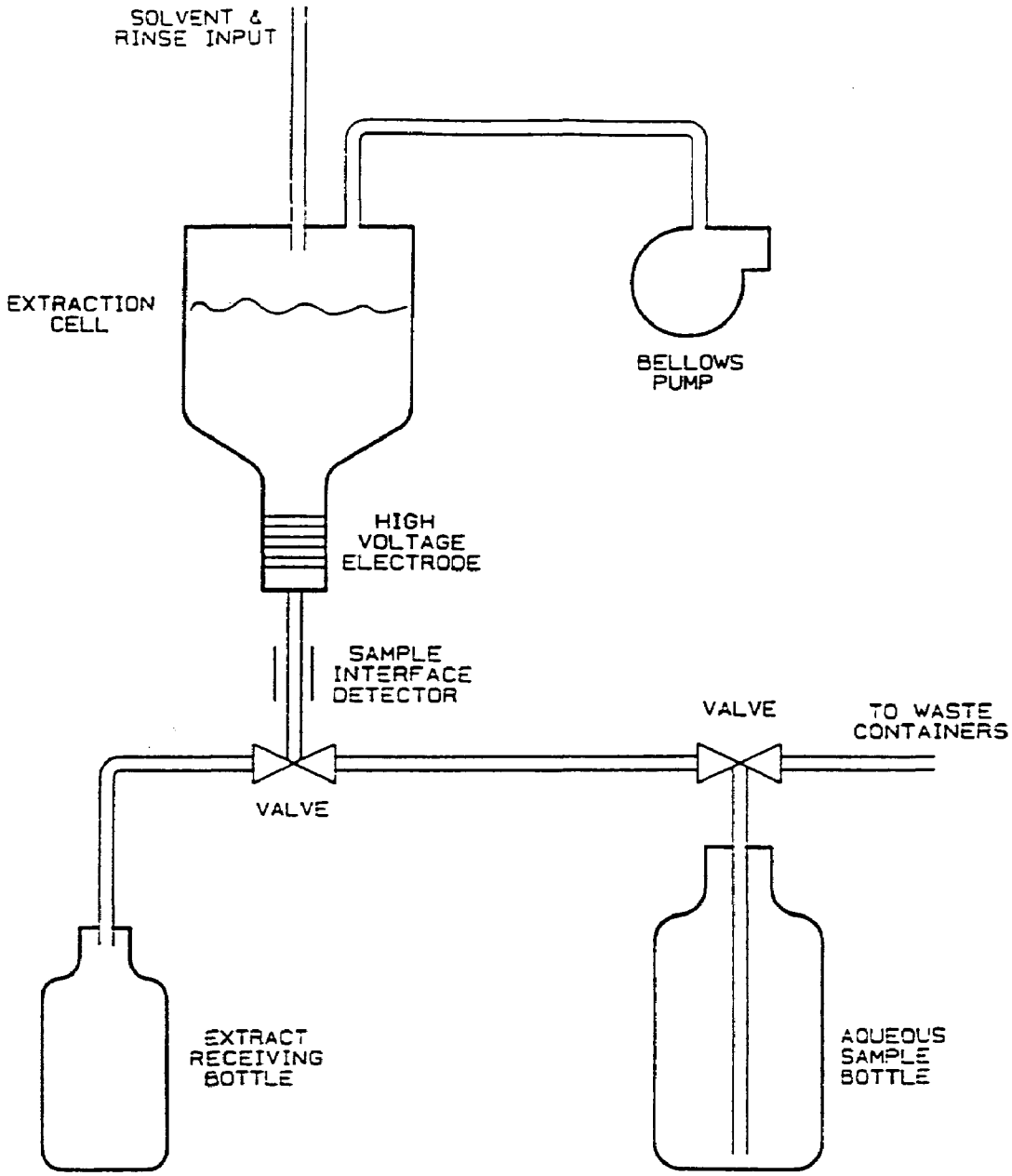

Figure 1. Schematic Diagram of ExCell Extraction Module

employed, using the One-Step system (Corning), wherein a polymer membrane retains water sample while allowing passage of solvent droplets. This modification eliminates the need for a solvent "pad" below the sample and allows extraction to be completed in about 6 hours. EA extractions were performed using the ExCell system (OI Analytical), which completes automated extractions in about 2 hours.

Extracts from SF or EA were evaporated using the RapidVap N_2 (Labconco). Extracts from CL were evaporated using the integrated Kuderna-Danish glassware of the One-Step system. All results reported from Laboratory 2 were obtained using GC/FID quantitation, while those from Laboratories 1 and 3 were obtained using GC/MS. Results from three groups of experiments (*A*, *B*, and *C*) are presented to demonstrate bias effects. Conditions for the sets of experiments are summarized in Table 1.

Observance of type 1 effect: Group *A* experiments were conducted in Lab 1 using either CL or EA extraction with a spiking solution containing fifty-six semivolatile analytes in either DCM or methanol. Matrix was 1-liter samples of reagent water, wastewater, or groundwater. Sequential extraction was performed at two pH values as per Method 3520. These results (Table 2) show a possible wall effect which had no significant impact on CL extraction, but which seemed to introduce negative bias during EA extraction. The results for EA using spiking solution in DCM at the 10 µg spiking level averaged 58% for all 56 analytes over the three matrices tested, versus 69% for CL. When the spiking solution was changed to methanol the CL results changed hardly at all, whereas the EA results jumped to an average recovery of 73%. At the higher spiking level (300 µg) there was no significant difference in EA recoveries from reagent water upon changing spiking solution solvent; however, the corresponding CL results dropped from 97% to 85%, suggesting that when DCM was used as spiking solvent at the 300 µg spiking level the CL method may have been subject to a positive bias from a type 3 effect.

Observance of type 2 effect: Group *B* experiments were performed in Laboratory 2 on acidified reagent water samples spiked with 25 µg each of eleven semivolatile analytes in DCM. This group shows how volatility losses were either produced or avoided using either EA or SF extraction depending upon conditions. Results are presented in Table 3. Note that recoveries of phenol and 2-fluorophenol, not susceptible to volatility loss, are determined by their water solubility and change very little between the three experiments. This serves as a control measure for validity of the extraction procedure. In contrast, recoveries of the compounds subject to volatility losses vary drastically depending on the spiking procedure. Top spiking produced poor results for both EA and SF (poor SF results were "forced" by top spiking one liter of water in a 1.25 liter jar and leaving the jar open in the hood for 80 minutes before the SF extraction). When EA was conducted with direct spiking, recoveries for susceptible analytes (marked with a "*" in the Table) rose from an average of 50% to 78% while recoveries of those not susceptible changed hardly at all.

Group *C* experiments were conducted in Laboratory 3 using EA extraction only for reagent water samples that were either top spiked or direct spiked with a methanol solution containing 50 µg/mL of numerous semivolatile compounds. Results are presented in Table 4 for compounds prone to type 2 effect and they show a dramatic improvement in recoveries for those analytes when top spiking was replaced by direct spiking. It is believed that altitude of the laboratory (above 5000 feet) played a role in the severity of the losses associated with top spiking.

SUMMARY & CONCLUSIONS

Three types of bias resulting from failure of the spiked analytes to completely participate in liquid/liquid phase equilibria were discussed. Examples of two types of negative bias, *wall effects* and *volatility losses*, were shown to occur by comparing: 1) average recoveries when using spiking solutions made from either methanol or DCM (Group *A* experiments); or 2) the average recoveries from experiments (Groups *B* and *C*) where spiking solution was either placed on top of the sample (top spiking), or injected directly into the sample (direct spiking). A third (positive) type of bias results from shunting off solvent into which a portion of the spiked analytes has dissolved so that they have no opportunity to reach equilibrium. This type of bias may occur during CL extraction, as is suggested by experiments where at a level of 300 µg of each compound CL produced significantly higher recoveries with spiking solution made in DCM than it did with a solution made of methanol.

Overall, the results indicate that all three extraction types, SF, CL, and EA, can be subject to bias (negative or positive) which derives from spiking technique or the type of solvent used to prepare spiking solutions. Logically, bias effects are more severe at higher spiking levels because spiked compounds become more difficult to disperse. SF, and less so CL, appear to be fairly "forgiving" of variations in technique. Valid EA spiking results seem to be more strongly dependent on use of correct technique.

Those laboratories which deviate from published methods by using spiking solutions prepared in a non-miscible solvent may wish to reexamine their procedures. Direct spiking is recommended over top spiking for superior recovery of spiked compounds which are subject to volatility losses. Although direct spiking is not aesthetically pleasing, since the instrument for delivering spiking solutions must be dipped into the sample, the use of a syringe with needle for adding the spiked compounds makes it a fairly simple procedure to wipe the tip clean with a tissue and remove matrix material before the next aliquot of spiking solution is drawn up.

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[3] C. A. Valkenburg et.al; "Evaluation of Modifications to the Extraction Procedure Used in the Analysis of Superfund Sites"; *J. AOAC 1989*, 72(4), pp. 602-608.

Table 1. Conditions Used for the Cited Extraction Experiments

Experimental group	*A*	*B*	*C*
Laboratory	1	2	3
Extraction Techniques	EA or CL	EA or SF	EA
Matrix	RW, GW, WW	RW	RW
Spiking Solution	methanol or DCM	DCM	methanol
Spiking Technique	direct	top or direct	top or direct
Spiking level	10 µg, 300 µg	25 µg	50 µg
pH	base then acid	acid	neutral
number of replicates	7, 3	5 or 2 (SF)	2

Table 2. Wall Effect (Group *A*): Comparison of Methanol and DCM Spiking at Lab 1

Average Recovery for 56 Semivolatile Analytes

Spiking Solution in ===>		DCM		Methanol	
Spike Level	**Matrix**	**EA**	**CL**	**EA**	**CL**
300 µg/L	**reagent water**	76%	97%	78%	85%
10 µg/L		61%	72%	77%	72%
	groundwater	55%	61%	75%	63%
	waste water	59%	75%	67%	65%

Table 3. Group *B*: Evaporative Losses in Lab 2 During EA or SF Extraction

Analyte	SF top	EA top	EA direct
2-fluorophenol	60	58	52
phenol	46	43	41
1,4-dichlorobenzene(*)	59	44	77
1,2-dichlorobenzene(*)	67	51	78
hexachloroethane(*)	45	27	75
nitrobenzene	90	94	81
bis-(2-chloroethoxy)methane	94	93	82
naphthalene(*)	75	71	79
hexachlorobenzene(*)	49	29	79
2-fluorobiphenyl(*)	71	75	81
acenaphthene	79	86	83

Table 4. Group *C*: Comparison of Top and Direct Spiking at Lab 3 Using EA Extraction

Analyte	Top Spiking	Direct Spiking
1,3-Dichlorobenzene	16	74
1,4-Dichlorobenzene	17	75
1,2-Dichlorobenzene	19	75
bis-(2-Chloroisopropyl) ether	55	77
Hexachloroethane	12	72
2,3-Dibromochloropropane	45	77
1,2,4-Trichlorobenzene	19	76
Naphthalene	36	81
Hexachlorobutadiene	10	76
2-Methylnaphthalene	45	83
Hexachlorocyclopentadiene	27	47
2-Chloronaphthalene	55	86
Acenaphthylene	76	87
Acenaphthene	68	88
2-Fluorobiphenyl	52	86

PAH EXTRACTION FROM RIVER WATER USING NEW NOVO-CLEAN C18 EXTRACTION MEMBRANES

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ABSTRACT

Novo-Clean C18 PTFE extraction membranes were evaluated, and a procedure based on EPA method 550.1 was developed for quantitating polycyclic aromatic hydrocarbons in river water.

INTRODUCTION

Novo-Clean C18 PTFE (Teflon) extraction membranes were evaluated, and a procedure based on EPA method 550.1 was developed for quantitating polycyclic aromatic hydrocarbons (PAHs) in river water. These 47 mm membranes are twice as thick (54 mil, about 1 mm) as the only other commercially available PTFE membrane and are 80% bonded silica by mass. Because of their greater thickness and high C18 content, they have more capacity than the other PTFE membrane. This was verified by measuring the volume of a PAH solution that could be passed through the membranes before analyte breakthrough.

The procedure for extracting PAHs from river water using these membranes was tested by extracting spiked Susquehanna river water (20 µg/L) and spiked reagent water (2 and 20 µg/L). The procedure has the advantage of not employing chlorinated solvents; only acetonitrile, *tert*-butylmethylether (MTBE), methanol, and water are required. Analysis is done with a gradient controlled HPLC pump, a Shandon hypersil PAH column, and a UV detector.

EXTRACTION PROCEDURE

Equipment, Reagents, and Consumables

- Novo-Clean C18 extraction membrane, 47 mm
- Kontes 47 mm membrane manifold
- HPLC grade acetonitrile, *tert*-butylmethylether (MTBE), methanol, and deionized water
- Alltech model 525 gradient HPLC pump with a UV detector and a Shandon hypersil green PAH column
- PAH standard solution (200 µg of 16 PAHs in 1 mL of methylene chloride diluted to 10 mL with acetonitrile)

Sample Preparation: For laboratory spiked samples, the appropriate amount of PAH standard solution was added to a 1 liter flask. To this, 5 mL of methanol were added and the solution was swirled to ensure homogeneity. Then 1 liter of river or reagent water was added to the flask. It was not necessary to filter sediment from river water samples.

Membrane Preparation: The membrane was placed in the filtration apparatus and 10 mL of methanol were added to the solvent reservoir. After the methanol had soaked into the membrane for 3 minutes, vacuum was applied to draw most of it through, leaving 5 mm of solvent above the membrane. Then 10 mL of MTBE were added to the reservoir, allowed to soak into the membrane for 3 minutes, and then drawn through by vacuum. The membrane was dried thoroughly by applying vacuum.

Extraction: The membrane was conditioned by adding 15 mL of methanol to the solvent reservoir and letting it soak into the membrane. Most of the solvent was drawn through and 15 mL of deionized water were added to the reservoir. After the water soaked into the membrane, most of it was drawn through. The water sample was applied and drawn through the membrane by vacuum in 10 to 20 minutes. The membrane was dried by vacuum for 3 minutes. At no time during the extraction procedure was the membrane allowed to dry until all of the sample had been drawn through.

Elution: Ten mL of methanol were placed in the solvent reservoir and allowed to soak into the membrane for 3 minutes. The solvent was drawn through the membrane at a rate of <5 mL/min and the eluent was collected. Then 10 mL of MTBE were added to the solvent reservoir and allowed soak into the membrane for 3 minutes. The solvent was drawn through the membrane and the eluent was collected. The extracts were combined and concentrated under an N_2 flush to a total volume of 1 mL. The solution was reconstituted to 10 mL using a 50:50 mixture of acetonitrile and deionized water.

Analysis: HPLC conditions for analysis of extract (chromatogram presented in Figure 1):

Column: Shandon Hypersil Green PAH 5μ, 100 x 4.6 mm

Mobile phase gradient: A = $CH_3CN:H_2O$ (1:99), B = $CH_3CN:H_2O$ (99:1)

Time (min)	0	5	25	27	30
% B	50	50	100	50	50

Flow rate: 2.0 mL/min

Detector: UV 254 nm

Sample size: 100 μL or less

DISCUSSION

Recoveries† for extractions from river water and reagent water are given in Tables I and II. The recoveries of five sequential extractions were used to calculate the mean recoveries from river water. The recoveries are within the limits specified as acceptable by EPA method 550.1.

Breakthrough of a solution of 0.5 μg/mL PAHs in 80:10:10 water:acetonitrile:methanol was determined for a Novo-Clean C18 membrane and the only other commercially available PTFE membrane. After 50 mL of solution was eluted through the other manufacturer's conditioned membrane, the eluent contained naphthalene, phenanthrene, and anthracene whereas the Novo-Clean membrane under identical conditions had no PAHs in the eluent. This greater capacity may be attributed to the increased thickness of the Novo-Clean membrane. HPLC chromatograms of each eluent are given in Figures 2 and 3.

SUMMARY

A procedure, based on EPA method 550.1, for extracting PAHs from river water using Novo-Clean C18 extraction membranes has been developed. Recoveries of each of the 16 analytes are within the limits specified as acceptable by the EPA method. The Novo-Clean membranes were shown to have a higher sample capacity over the only other commercially available C18 PTFE membrane by measuring the volume of PAH solution required to breakthrough the membranes.

Table I: Average Recoveries* of PAHs from Laboratory Spiked Susquehanna River Water

Peak Number	PAH	Mean Recovery	Standard Deviation
1	Naphthalene	75.7%	39.9%
2	Acenaphthylene	67.0%	10.5%
3	Acenaphthene	68.2%	10.4%
4	Fluorene	75.9%	6.8%
5	Phenanthrene	92.3%	3.3%
6	Anthracene	89.7%	1.3%
7	Fluoranthene	92.5%	4.9%
8	Pyrene	94.9%	5.4%
9	Benzo(a)anthracene	95.5%	4.1%
10	Chrysene	95.4%	3.8%
11	Benzo(b)fluoranthene	97.5%	6.3%
12	Benzo(k)fluoranthene	94.7%	3.8%
13	Benzo(a)pyrene	92.0%	8.4%
14	Dibenzo(ah)anthracene	93.6%	7.6%
15	Benzo(ghi)perylene	96.8%	3.9%
16	Indeno(123cd)pyrene	91.7%	2.8%

Table II: Recoveries of PAHs from Spiked Reagent Water

Peak Number	PAH	20 μg/L	2 μg/L
1	Naphthalene	92.2%	81.2%
2	Acenaphthylene	82.9%	62.4%
3	Acenaphthene	84.6%	55.6%
4	Fluorene	85.3%	79.4%
5	Phenanthrene	83.6%	83.5%
6	Anthracene	79.4%	85.1%
7	Fluoranthene	83.4%	78.6%
8	Pyrene	74.2%	69.9%
9	Benzo(a)anthracene	82.3%	77.8%
10	Chrysene	80.0%	79.1%
11	Benzo(b)fluoranthene	75.1%	72.4%
12	Benzo(k)fluoranthene	77.7%	78.5%
13	Benzo(a)pyrene	60.8%	74.1%
14	Dibenzo(ah)anthracene	83.7%	64.9%
15	Benzo(ghi)perylene	82.2%	66.9%
16	Indeno(123cd)pyrene	83.1%	69.0%

NOTES

* Average of five extractions, calculated using an external standard.

† (20 μg PAH/L ≈ 100 ppb) River water was sampled from the West branch of the Susquehanna River at Lock Haven, Pennsylvania, on 27 February 1996; acidified to pH=4.5 with 1.0 M $HCl_{(aq)}$ on the following day; and stored at 4°C until used. Samples were spiked immediately prior to extraction.

REFERENCE

J. W. Hodgeson, W. J. Bashe, T. V. Baker, "Determination of Polycyclic Aromatic Hydrocarbons in Drinking Water by Liquid-Solid Extraction and HPLC with Coupled Ultraviolet and Fluorescence Detection, Method 550.1." Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio, July 1990.

Figure 1: HPLC Analysis of PAHs Extracted from River Water

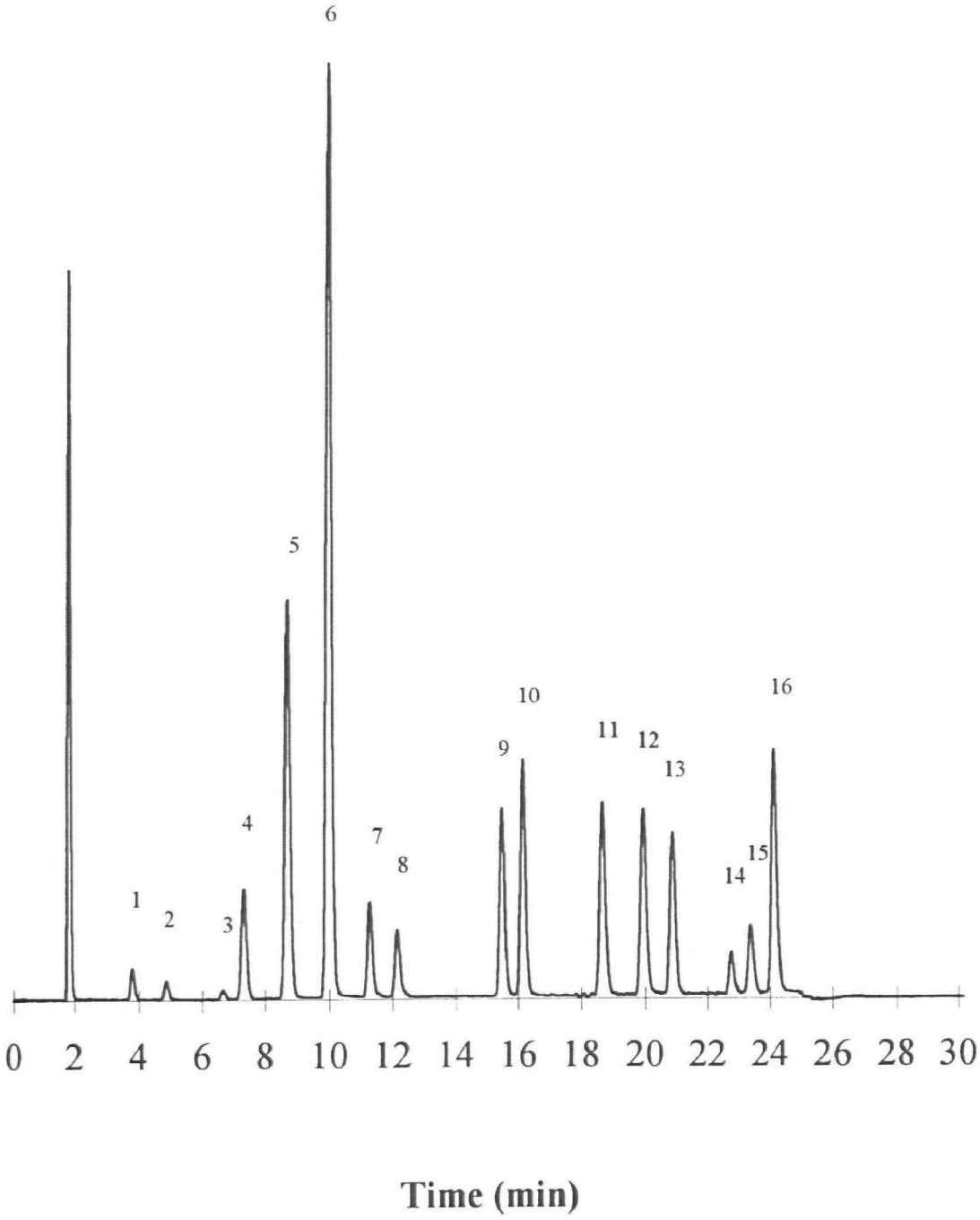


Figure 2: Breakthrough with Novo-Clean

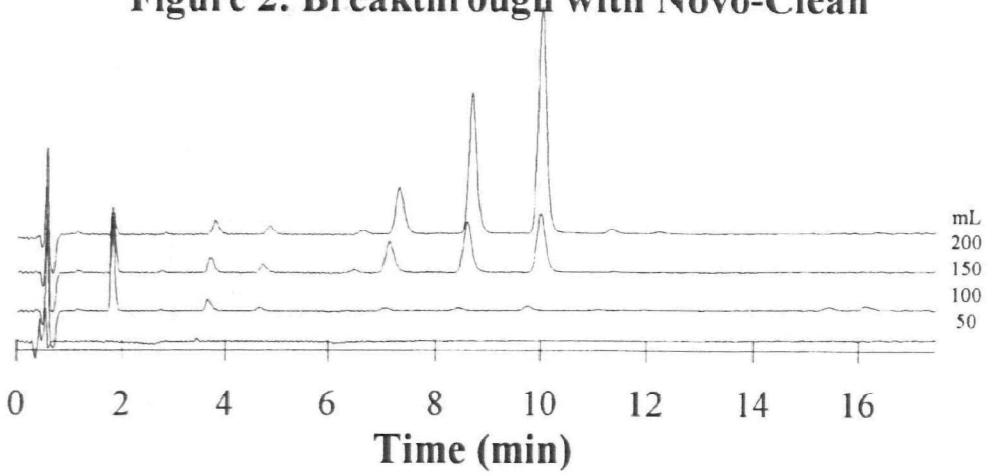
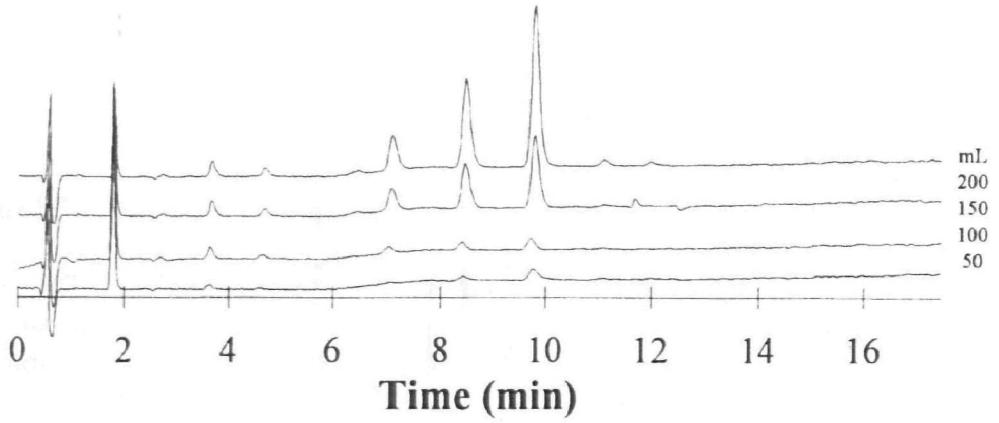


Figure 3: Other Membrane



SCREENING FOR SILVEX BY A MAGNETIC PARTICLE ENZYME IMMUNO-ASSAY IN TCLP EXTRACTS FROM SOIL AND WASTEWATER.

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ABSTRACT

Use of immunoassays as field-screening methods to detect environmental contaminants has increased dramatically in recent years. Acceptance of immunoassay methods by the EPA has accelerated, enabling their use in applications where SW-846 methods are required or desirable. Immunochemical assays are sensitive, reliable, cost-effective and can be used for lab or field analysis. A commercially available magnetic particle-based enzyme immunoassay (ELISA) kit has been adapted to screen the extracts of environmental samples prepared according to the Toxicity Characteristics Leaching Procedure (TCLP) at the 1.0 ppm regulatory level for 2-(2,4,5-Trichlorophenoxy) propionic acid (also known as Silvex or 2,4,5-TP). The enzyme immunoassay was originally designed to quantitate Silvex in water samples at concentrations around the MCL (50 ppb) established by the the Safe Drinking Water Act (SWDA). The kit includes calibrators at 5, 25 and 250 ppb. A simple one-step 1:40 dilution of a TCLP extract with diluent is performed to bring the analytical range of the immunoassay within the regulatory level of 1 ppm established by the EPA for Silvex TCLP leachate. Subsequent analysis by the magnetic particle-based ELISA indicates an absence of matrix effects on various environmental waste matrices. The method was found to be accurate, achieving 100% agreement between positive and negative samples around the regulatory level of 1.0 ppm on the samples tested. Comparison of 30 water samples using the Silvex ELISA versus an USEPA GC method gave a correlation (r) of 0.995. The application of this ELISA method in combination with the standard TCLP extraction permits cost-effective evaluation of samples without the solvent disposal required by traditional methods. Details of the studies to evaluate the results of combining the immunoassay with the TCLP extraction method are presented.

INTRODUCTION

Silvex was used as a plant growth regulator for the control of woody plants on uncropped lands; as a selective pre- and post-emergence herbicide used on crops, right-of-ways and golf courses; and as an aquatic herbicide in lakes, streams, and irrigation canals. Silvex has been banned in the U.S. since 1983 because of adverse effects to the liver and kidneys of laboratory animals (USEPA, 1991).

Silvex is persistent in soil at levels which can contaminate drinking water by runoff into surface water or by leaching into groundwater. It is regulated under the Safe Drinking Water Act (SDWA) which set a Maximum Contaminant Level (MCL) of 50 ppb in

drinking water and under the Resource Conservation and Recovery Act (RCRA) which set an MCL of 1.0 ppm for Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 1992).

The Methods Section of the EPA Office of Solid Waste (OSW) has stated a need for more rapid, less expensive, field screening procedures that do not compromise the accuracy of the analysis. The availability of commercial immunoassays, which are reliable, sensitive, and which can be utilize for inexpensively screening large sample loads of potentially contaminated samples, coupled with the subsequent confirmation of positive samples by established instrumental methods is an approach that addresses this need. The OSW has accepted a number of immunoassays (Series 4000) for inclusion in its SW-846 compendium of analytical and test methods.

The principles of enzyme immunoassays have been described (Hammock and Mumma, 1980). Magnetic particle-based ELISAs have previously been applied to the detection of environmental contaminants (Lawruk et al., 1996). The performance characteristics of a 2,4-D magnetic particle-based enzyme immunoassay on TCLP extracts have previously been demonstrated (Hayes et al., 1993); subsequently, the OSW validated and accepted the method as Method 4015 for use in hazardous waste analysis of water and soil matrices as required by federal, state and local governments.

The TCLP was designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. If the analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at a concentration equal to or above the regulatory level for that compound, then the waste is considered hazardous and should be disposed accordingly.

All wastewater and soils used to demonstrate the capability of the immunoassay for TCLP analysis were subjected to the Method 1311 extraction procedure prior to analysis. The Silvex RaPID Assay® kit, a magnetic particle-based immunoassay developed and manufactured by Ohmicron Environmental Diagnostics, Inc., for the determination of part per billion (ppb) Silvex in water and in soil, was used during this evaluation. This study shows that the immunoassay can be readily adapted for use as a screening method for the analysis of TCLP extracts for the presence of Silvex at the regulatory level of 1.0 ppm.

MATERIALS AND METHODS

Equipment and reagents: Silvex RaPID Assay kits, Silvex Sample Diluent, precision pipettes, magnetic separator, RPA-I photometric analyzer and vortex mixer are available from Ohmicron Environmental Diagnostics, Inc., Newtown, PA. Silvex for the gravimetric preparation of spiking stock solutions was obtained from Chem Service (Westchester, PA). All stock solutions were prepared in methanol.

Environmental Samples: Several water samples were studied for matrix effect. They included municipal water from Philadelphia, PA and surface water ("runoff") collected from Newtown, PA. Wastewater ("effluent") was collected from a wood treatment facility in North Dakota. Two soil types were evaluated: a sandy soil and an organic soil from New Jersey.

Procedures: TCLP extractions were performed on soils and wastewaters as described in Method 1311. Silvex spikes were made volumetrically into the final extract after filtration. The detailed TCLP extract screening procedure is published as an Application Procedure (T00077) and available from Ohmicron Environmental Diagnostics, Inc. All immunoassay results are converted to ppm Silvex in the waste extract for evaluation vs. the regulatory level. Detailed directions on use of the immunoassay kit are given in the kit package insert.

RESULTS AND DISCUSSION

Establishing a cutoff concentration for the screening procedure. To use the quantitative result obtained from the immunoassay in a qualitative way, a cutoff that could reliably discriminate the regulatory action level (1.0 ppm) from one half the concentration level (0.5 ppm) was established. The TCLP extraction buffer (sodium acetate, pH 4.9) and TCLP extracts of the sandy soil were diluted (1:40) with Silvex sample diluent and spiked with Silvex at 0.5, 1.0 and 2.0 ppm. Ten replicates of each solution were then tested in one immunoassay run. Figure 1 shows that the use of a cutoff concentration of 0.75 ppm provides excellent discrimination between 1.0 and 0.5 ppm. This cutoff concentration falls near the mid-point on the calibration curve where precision is optimal.

In a similar manner, the TCLP extract of a Silvex-free organic soil was spiked at 0.5, 1.0 and 2.0 ppm and tested at each level of interest in an immunoassay run. Figure 2 demonstrates a similar pattern of result distribution between the various spiked matrices: buffer, TCLP extracts of sandy and organic soils; no overlap of the regulatory level could be seen with half its concentration.

To test the utility of the method as a screening procedure for organic type of soils, ten replicates each of a TCLP organic soil extract and buffer spiked at 0.50, 0.75, 1.0 and 2.0 ppb Silvex were run in an immunoassay run, when the definition of "positive" as greater than 0.75 ppm and "negative" as less than 0.75 ppm are applied to this data (Figure 3), the utility of the method as a screening procedure can be demonstrated.

Matrix specific performance of the screening method. A variety of water and soil matrix types were studied to determine their interference, if any, with the immunoassay screening method. All matrices were first treated as solid or liquid waste according to the procedures given in Method 1311 (TCLP Procedure). Prior to spiking, each extract was diluted, tested in the immunoassay and determined to contain a non-detectable

concentration of Silvex. Aliquots of the extract were then spiked volumetrically with 0.5, 1.0 and 2.0 ppm Silvex, prior to the 1:40 dilution in Silvex Sample Diluent and subsequent analysis by immunoassay.

Table 1 shows that the screening method accurately discriminates negative and positive regulatory levels in all matrices tested. All results on matrices spiked at one-half the regulatory level (0.50 ppm) were less than 0.54 ppm Silvex, showing no false positives (results > 0.75 ppm). Results on matrices spiked at the 1.0 ppm regulatory level ranged from a low of 0.76 to a high of 1.75 ppm with no false negatives (results < 0.75 ppm). Samples spiked above the regulatory level at 2.0 ppm gave quantitative results from 1.96 to 2.72 ppm Silvex (no false negatives).

Correlation with a Reference Method. Results from a method comparison performed in 30 samples (7 groundwater, 9 municipal, 13 surface, TCLP extract) using GC by EPA Method 515.1 (x) and the Silvex RaPID Assay (y) is illustrated in Figure 4. The methods agreed well; the regression analysis yielded a correlation coefficient (r) of 0.995 and a slope of 1.17.

SUMMARY

A magnetic particle based enzyme immunoassay for Silvex has been evaluated for use as a screening method with TCLP extracts of some commonly encountered forms of liquid and solid waste. Using a 0.75 ppm cutoff concentration, the method was found to be accurate, achieving 100% agreement between positive and negative samples around the regulatory level of 1.0 ppm. No interferences were exhibited by the method when TCLP extracts from an organic soil, effluents and runoff water samples were tested. The immunoassay compares favorably to GC Method 515.1. The Silvex RaPID Assay provides real-time data for on-site decisions and permits timely initiation of corrective process control measures in compliance situations. Fifty results can be available in less than one hour compared to conventional methodology which requires several days to weeks to provide results. The test is easy to use and can be performed in the laboratory or in the field by non-laboratory personnel and technicians. Extraction, derivitization and cleanup are not required, making the immunoassay safe to handle and easy to dispose of.

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Lawruk, T.S.; Lachman, C.E.; Jourdan, S.W.; Fleeker, J.R.; Hayes, M.C.; Herzog, D.P.; Rubio, F.M. Quantitative Determination of PCBs in Soil and Water by a Magnetic Particle-Based Immunoassay. Environ. Sci. Technol. 1996, 30, 695-700.

USEPA, National Primary Drinking Water Regulations; Final Rule, Federal Register 40 CFR Parts 141, 142 and 143, Washington DC, January 30, 1991.

USEPA, Method 1311: Toxicity Characteristic Leaching Procedure, 40 CFR Ch. 1, July 1, 1992.

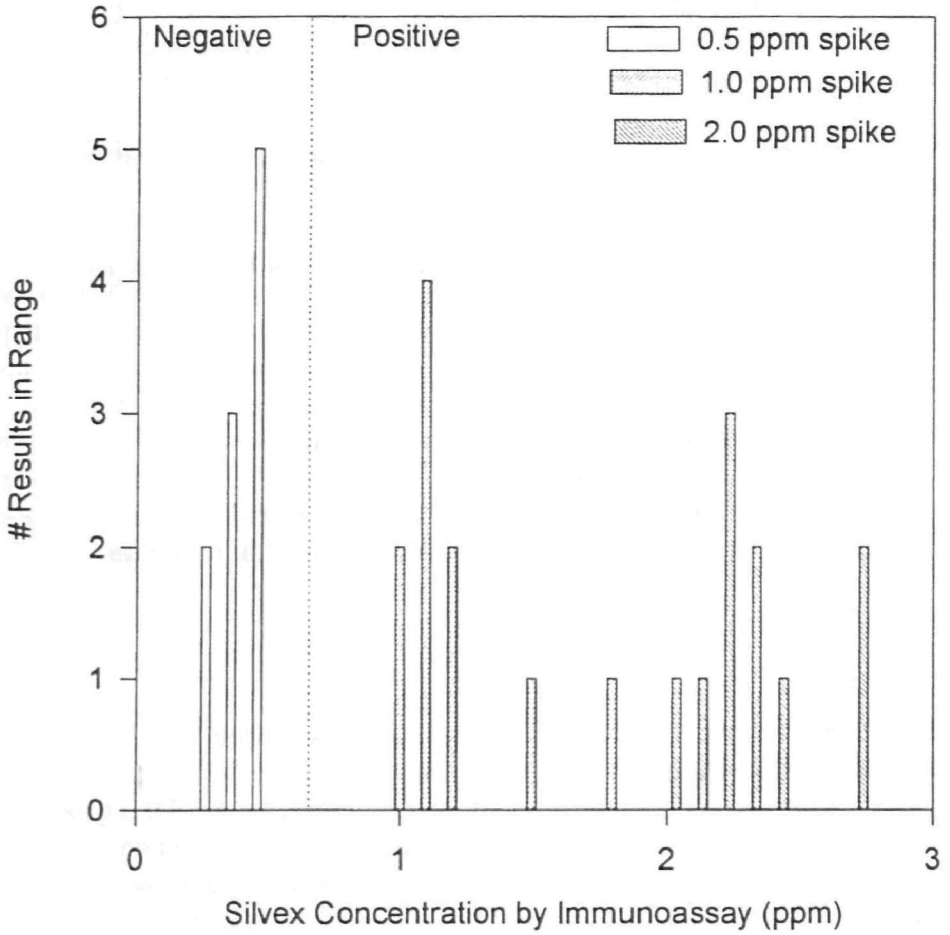

Figure 1. Demonstration of the sensitivity of the selected cutoff for Silvex in TCLP Buffer Matrix and Sandy Soil TCLP Extract. Silvex was spiked into TCLP extraction buffer and sandy soil TCLP extract at concentrations of 0.5, 1.0 and 2.0 ppm. Each spiked solution was then diluted 1:40 in Silvex sample diluent. Ten immunoassay determinations were then made on each diluted solution. The frequency of occurence of the results is plotted against the range of Silvex concentration measured.

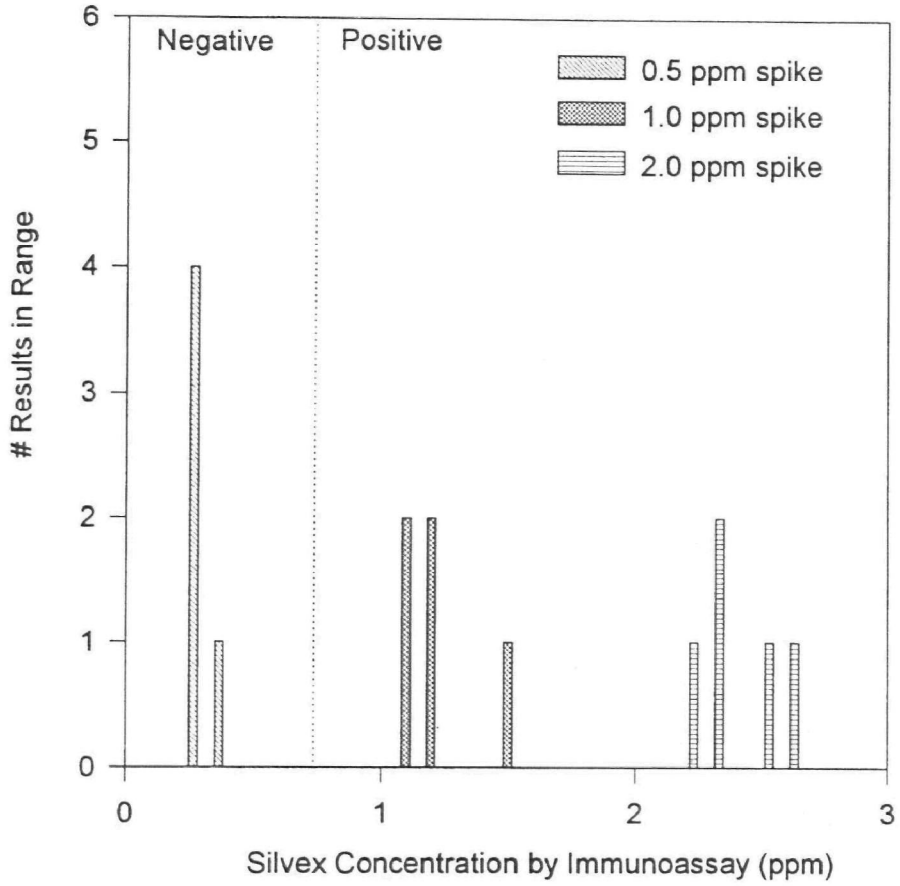

Figure 2. Demonstration of the sensitivity of the selected cutoff for Silvex in TCLP extract of an organic soil. Silvex was spiked into TCLP extract of an organic soil TCLP extract at concentrations of 0.5, 1.0 and 2.0 ppm. Each spiked solution was then diluted 1:40 in Silvex sample diluent. Ten immunoassay determinations were then made on each diluted solution. The frequency of occurence of the results is plotted against the range of Silvex concentration measured.

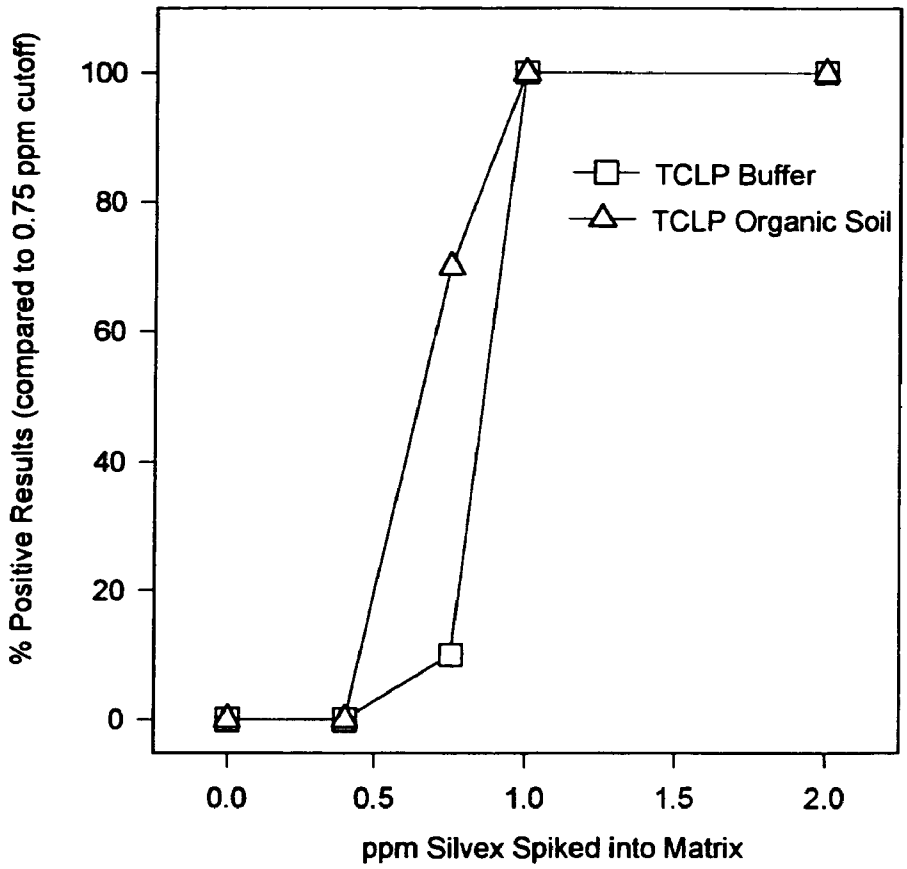

Figure 3. Break point of the Silvex screening test in buffer and TCLP organic soil extract. Spiked buffer or TCLP soil extracts from an organic soil were graded for positivity and negativity based on a 0.75 ppm cutoff. In both matrices the 1.0 ppm regulatory level is distinguishable from the 0.5 ppm (one-half the regulatory level) 100% of the time.

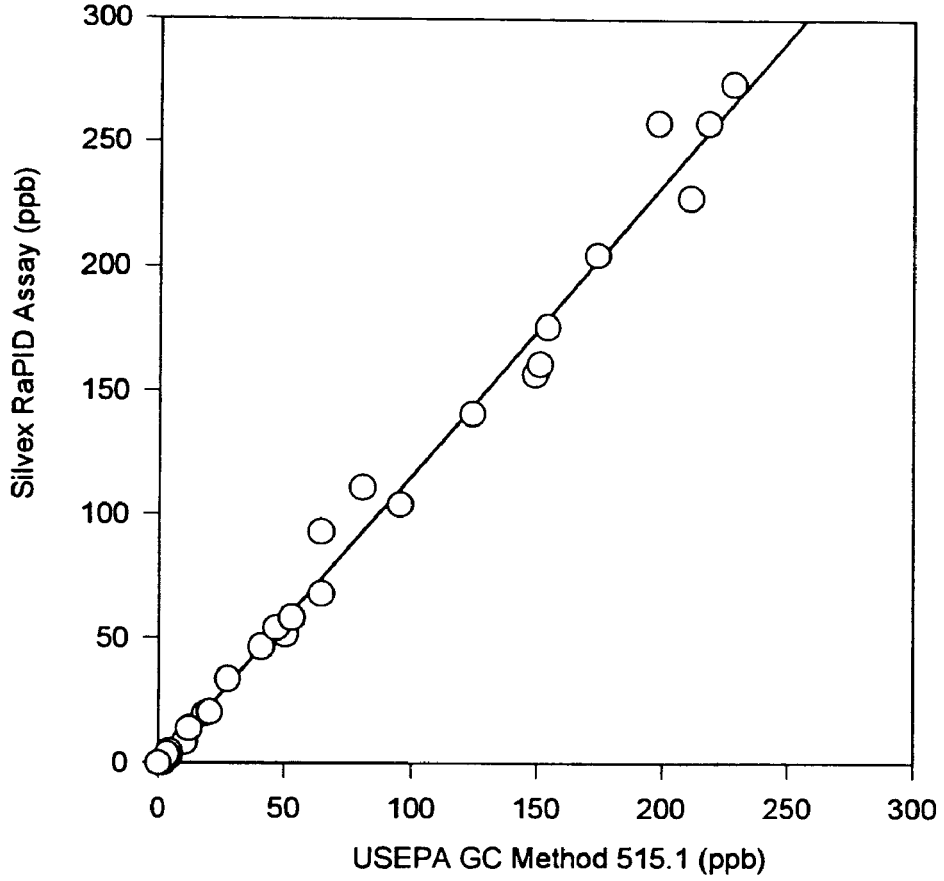

Figure 4. Correlation of the Silvex RaPID Assay with method 515.1. Regression analysis yields the following equation: $y = 1.17x - 1.45$ ppb, correlation coefficient (r) = 0.995, n = 30.

Table 1. Silvex spiking results on TCLP extracts of environmental waste matrices.
Silvex was spiked into buffer, water or a TCLP extract of the matrices shown after the final filtration step. Each matrix was diluted 1:40 and tested by the immunoassay five times. Each result was then compared with the 0.75 ppm cutoff to determine if its status was positive or negative.

		Silvex concentration by immunoassay (ppm)							
		Determination #							
ID	Matrix/Spike	1	2	3	4	5	Mean	% POS	%NEG
1	TCLP buffer	nd	nd	nd	nd	nd	-	0	0
2	TCLP buffer + 2.0 ppm	2.21	2.12	2.23	2.66	2.37	2.32	100	0
3	TCLP buffer + 1.0 ppm	1.16	1.01	1.05	1.08	1.07	1.07	100	0
4	TCLP buffer + 0.5 ppm	0.51	0.54	0.47	0.48	0.52	0.50	0	100
5	Sandy soil extract	nd	nd	nd	nd	nd	-	0	100
6	Sandy extract + 2.0 ppm	2.30	1.96	2.20	2.72	2.30	2.30	100	0
7	Sandy extract + 1.0 ppm	1.11	0.98	1.18	1.49	1.75	1.30	100	0
8	Sandy extract + 0.5 ppm	0.35	0.40	0.29	0.34	0.35	0.35	0	100
9	Organic soil extract	nd	nd	nd	nd	nd	-	0	100
10	Organic extract + 2.0 ppm	2.26	2.22	2.58	2.33	2.48	2.37	100	0
11	Organic extract + 1.0 ppm	1.07	1.06	1.16	1.50	1.23	1.20	100	0
12	Organic extract + 0.5 ppm	0.34	0.32	0.38	0.33	0.27	0.33	0	100
13	Effluent #1	nd	nd	nd	nd	nd	-	0	100
14	Effluent #1 + 2.0 ppm	1.60	1.43	1.54	1.55	1.57	1.54	100	0
15	Effluent #1 + 1.0 ppm	0.81	0.89	0.79	0.78	0.76	0.81	100	0
16	Effluent #1 + 0.5 ppm	0.43	0.47	0.40	0.46	0.46	0.44	0	100
17	Effluent #2	nd	nd	nd	nd	nd	-	0	100
18	Effluent #2 + 2.0 ppm	2.11	2.13	2.08	2.10	2.24	2.13	100	0
19	Effluent #2 + 1.0 ppm	1.10	0.95	0.86	1.05	1.06	1.00	100	0
20	Effluent #2 + 0.5 ppm	0.53	0.48	0.48	0.51	0.54	0.51	0	100
21	Runoff	nd	nd	nd	nd	nd	-	0	100
22	Runoff + 2.0 ppm	1.82	1.76	1.66	1.60	1.68	1.70	100	0
23	Runoff + 1.0 ppm	0.75	0.81	0.81	0.86	0.88	0.82	100	0
24	Runoff + 0.5 ppm	0.44	0.41	0.37	0.49	0.49	0.44	0	100
25	Municipal water*	nd	nd	nd	nd	nd	-	0	100
26	Municipal + 2.0 ppm	2.17	1.99	1.83	1.85	1.85	1.94	100	0
27	Municipal + 1.0 ppm	0.85	0.81	0.79	0.76	0.90	0.82	100	0
28	Municipal + 0.5 ppm	0.50	0.39	0.47	0.45	0.44	0.45	0	100

* Not applicable to wastewater regulatory limit

EVALUATION OF THE ACCELERATED SOLVENT EXTRACTION SYSTEM™ FOR THE EXTRACTION OF ENVIRONMENTAL MATRIX REFERENCE MATERIALS

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ABSTRACT

The Accelerated Solvent Extraction (ASE) System™ was evaluated for extraction of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides from the following certified reference materials: Standard Reference Material (SRM) 1649a (Urban Dust/Organics), SRM 1941a (Organics in Marine Sediment), SRM 1944 (Highly Contaminated Marine Sediment), SRM 2974 (Organics in Freeze-dried Mussel Tissue), and CARP-2 (Ground Whole Carp). The materials were extracted using methylene chloride, acetonitrile, and a mixture of hexane/acetone (1:1, v:v). For the three solvent systems evaluated, the ASE™ system showed comparable extraction efficiency to Soxhlet extraction for selected PAHs, PCB congeners, and chlorinated pesticides in a variety of matrices.

INTRODUCTION

Accelerated solvent extraction (ASE)™ is a new extraction procedure that uses elevated temperature (50-200 °C) and pressure (500-3000 psi) for solvent extraction of solid matrices [1]. It has appeared as proposed EPA Method 3545 in Update III of EPA's SW-846 manual [2,3]. Two of the method's advantages are: (1) it uses less solvent than traditional Soxhlet and sonication extractions and (2) it is automated [4]. Richter and co-workers [1] investigated the effect of experimental parameters on recovery of total petroleum hydrocarbons, PAHs, and PCBs from a variety of samples.

This paper details an evaluation of ASE™ for the extraction of PAHs, PCBs, and chlorinated pesticides from several certified reference materials: SRM 1649a (Urban Dust/Organics), SRM 1941a (Organics in Marine Sediment), SRM 1944 (Highly Contaminated Marine Sediment), SRM 2974 (Organics in Freeze-dried Mussel Tissue) and a Carp reference material (Carp-2). The solvents used for extraction were methylene chloride, hexane/acetone (1:1,v:v), and acetonitrile.

EXPERIMENTAL

Materials. SRM 2260 (Concentrated PAH in Toluene), SRM 2261 (Concentrated Chlorinated Pesticides in Hexane), SRM 2262 (Concentrated PCB Congeners in Iso-octane), SRM 1941a (Organics in Marine Sediment), SRM 1649a (Urban Dust/Organics), and SRM 2974 (Organics in Freeze-dried Mussel Tissue) were obtained from the Standard Reference Materials Program, NIST. Candidate SRMs 2269 (Perdeuterated PAH-I), 2270 (Perdeuterated PAH-II), 2275 (Supplemental Pesticides), and 1944 (Highly Contaminated Marine Sediment) were also used. Perdeutered 4,4'-DDT was obtained from Cambridge Isotope Laboratories (Andover, MA) while PCB 103 (2,2',4,5',6-pentachlorobiphenyl) and PCB 198 (2,2',3,3',4,5,5',6-

octachlorobiphenyl) were obtained from Ultra Scientific (New Kingston, RI). The carp sample was obtained from the National Research Council of Canada. All solvents were HPLC-grade.

Sample extraction. The conditions used for ASE™ are similar to those given in proposed EPA Method 3545 [2] and used by Richter and coworkers [1]: 100 °C, 5 min equilibration, 5 min static time, 2000 psi. Since dead volume of the cells can be a problem, precleaned sodium sulfate was used to fill the cell volume and to dry the wet samples. Two samples each of SRM 1944 (2-3 g dry) and SRM 1941a (3-5 g dry) were extracted with methylene chloride using the above conditions. Also extracted using methylene chloride were one sample of SRM 1649 (1.78 g dry), two samples of SRM 2974 (1-1.5 g dry), and two samples of the Carp-2 material (5-7 g wet). One sample of each of the above mentioned materials was also extracted using acetonitrile and one sample of each using hexane/acetone (1:1, v:v). At least one of the samples for each of the materials was extracted a second time using the same conditions. None of the second extracts contained measurable quantities of the analytes of interest. The internal standard solution (containing PCB 103, PCB 198, and perdeuterated 4,4'-DDT, naphthalene, acenaphthene, biphenyl, phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, benzo[*a*]pyrene, perylene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene) was added directly to the cells prior to extraction. The extracts were concentrated to approximately 0.5 mL using an automated evaporation system.

In the case of the sediment samples, copper powder that had been activated using hydrochloric acid and then washed with methanol and methylene chloride was added to the extracts. The sediment extracts and the urban dust extracts were then eluted through a silica solid phase extraction cartridge that had been precleaned with the eluant, 15 mL of 10% methylene chloride in hexane. This fraction was then concentrated using an automated evaporation system to approximately 0.8 mL. This 0.8 mL was divided into two 0.4 mL portions, one portion for the determination of the PCB congeners and pesticides and the other portion for the determination of the PAHs.

In the case of the mussel tissue and carp extracts, size exclusion chromatography (SEC) on a preparative-scale divinylbenzene-polystyrene column (10 μm particle size, 100 Å pore size, 2.5 cm i.d. x 60 cm, PL-Gel, Polymer Labs, Inc., Amherst, MA) was used to remove the majority of the lipid and biogenic materials. Using a mobile phase of 100% methylene chloride at 9.9 mL/min for the SEC, the majority of the lipid and biogenic material elutes immediately after the void volume of the column while the compounds of interest are retained longer. The eluant (approximately 70 mL) was concentrated using an automated evaporation system to approximately 0.8 mL for the mussel tissue samples, one 0.4 mL portion for the determination of the PCB congeners and pesticides and the other 0.4 mL portion for the determination of the PAHs, and to approximately 0.4 mL for the carp samples for the determination of the PCB congeners and pesticides.

Determination of the chlorinated pesticides and PCB congeners. One 0.4 mL portion was subjected to normal-phase liquid chromatography (LC) on a semi-preparative-scale aminopropylsilane column to isolate two fractions containing (1) the PCB congeners and the lower polarity chlorinated pesticides and (2) the more polar chlorinated pesticides. For the normal-phase LC fractionation, *n*-hexane was used as the mobile phase for the isolation of the

PCB and lower polarity pesticide fraction, and 5% methylene chloride in *n*-hexane was used for the isolation of the second fraction. The two fractions were analyzed using gas chromatography (GC) with electron capture detection (ECD). GC-ECD was performed using a 0.25 mm x 60 m fused silica capillary column containing a 5% phenyl-substituted methylpolysiloxane phase (DB-5), 0.25 μm film thickness.

Determination of the PAHs. The other 0.4 mL portion was concentrated and further fractionated using LC on a semi-preparative-scale aminopropylsilane column for GC/MS analysis. The mobile phase used for the normal-phase LC fractionation was 2% methylene chloride in hexane. A similar GC column (DB-5 MS) as above was used for the GC-MS analysis. The major ions monitored during different time periods were 128, 136, 142, 152, 154, 156, 164, 166, 170, 176, 178, 184, 188, 190, 192, 202, 212, 228, 240, 252, 264, 276, 278, 290, and 292.

RESULTS AND DISCUSSION

The concentrations for selected PAHs, PCB congeners, and chlorinated pesticides determined using ASE™ with methylene chloride as the solvent are summarized in Table 1 for a variety of reference materials and are compared to the certified concentrations where available or to concentrations determined using Soxhlet extraction. The concentrations determined using the ASE™ are comparable to those determined using Soxhlet extraction for the analytes of interest. The sediment samples (SRM 1944 and SRM 1941a), the urban dust sample (SRM 1649), and the freeze-dried mussel tissue (SRM 2974) contain very little water (<10% by mass). The Carp-2 sample is a whole carp tissue sample and therefore contains approximately 85% (by mass) water [5]. The sodium sulfate that was added to the sample was sufficient to handle this amount of water. Losses were not observed for the most volatile compounds of interest, naphthalene and hexachlorobenzene. Similar extraction efficiencies were obtained using hexane:acetone (1:1, v/v) and acetonitrile.

SUMMARY

ASE™ showed comparable extraction efficiency to Soxhlet extraction for the PAHs, PCB congeners, and chlorinated pesticides in a variety of environmental matrices. The advantages of ASE™ over Soxhlet extraction include speed of extraction and concentration of the extracts, automation, and reduced solvent usage.

ACKNOWLEDGEMENT AND DISCLAIMER

We wish to thank Dionex for the loan of an Accelerated Solvent Extractor System™ for a period of one month.

Certain commercial equipment, instruments, or materials are identified to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are the best available for the purpose.

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Table 1. Concentrations (μg/kg) of Selected PAHs, PCB Congeners, and Chlorinated Pesticides in Various Reference Materials extracted using ASE™ with Methylene Chloride

Compound	SRM 1944		SRM 1941a		SRM 1649a		SRM 2974		Carp-2	
	Soxhlet[a]	ASE[b]	Certificate[c]	ASE[b]	Certificate/Soxhlet[d]	ASE[e]	Soxhlet[f]	ASE[b]	Soxhlet[a]	ASE[e]
PAHs										
Naphthalene	2152 (34)	2224	1010 ± 140	1114	ND	ND	9.7 ± 1.5	9.25	ND	ND
Phenanthrene	4896 (77)	4906	489 ± 23	460	4140 ± 370	4494	20.8 ± 1.6	25.5	ND	ND
Anthracene	2570 (56)	2257	184 ± 14	180	432 ± 82	405	6.49 ± 0.45	6.25	ND	ND
Fluoranthene	8954 (233)	8953	981 ± 78	1005	6450 ± 180	6674	159 ± 10	164	ND	ND
Pyrene	9721 (301)	9781	811 ± 24	849	5290 ± 250	5223	146 ± 9	156	ND	ND
Benzo[*a*]pyrene	4082 (85)	4281	628 ± 52	639	2509 ± 87	2375	16.5 ± 1.6	15.7	ND	ND
Perylene	953 (42)	925	452 ± 58	393	646 ± 75	642	7.60 ± 0.59	8.09	ND	ND
Benzo[*ghi*]perylene	2749 (91)	2818	525 ± 67	528	3990 ± 890	3795	20.6 ± 0.9	22.8	ND	ND
PCB Congeners										
PCB 28	75.8 (2.2)	77.8	ND[g]	ND	18.0 (0.4)	19.2	74.8 ± 5.2	75.3	31.6 (1.4)	30.4
PCB 52	78.9 (1.7)	80.8	6.89 ± 0.56	6.90	24.4 (0.5)	24.7	118 ± 5.8	107	139 (6)	133
PCB 101/90	73.3 (1.5)	72.5	11.0 ± 1.6	10.9	51.7 (0.6)	52.4	120 ± 3.3	119	142 (8)	143
PCB 118	57.6 (1.3)	62.1	10.0 ± 1.1	10.5	26.0 (0.4)	25.0	115 ± 6.5	114	148 (7)	155
PCB 138/163/164	59.7 (1.5)	62.9	13.38 ± 0.97	12.4	70.8 (1.2)	72.7	111 ± 8.6	99.7	124 (3)	121
PCB 153	73.5 (1.5)	76.9	17.6 ± 1.9	16.9	86.8 (1.0)	84.5	145 ± 9.8	138	104 (5)	101
PCB 170/190	23.2 (0.8)	24.1	3.00 ± 0.46	3.16	30.0 (1.3)	32.5	6.38 ± 0.37	5.49	20.6 (0.6)	21.2
PCB 180	41.7 (1.0)	44.5	5.83 ± 0.58	5.67	84.0 (1.7)	85.0	16.4 ± 0.82	17.6	51.3 (0.9)	53.1
Chlorinated Pesticides										
4,4'-DDE	95.6 (1.9)	95.3	6.59 ± 0.56	6.26	40.3 (0.7)	42.8	40.2 ± 1.8	44.6	147 (4)	148
4,4'-DDD	120 (8)	118	5.06 ± 0.58	4.65	72.1 (1.3)	73.0	44.9 ± 3.3	38.0	97.1 (1.8)	99.2
4,4'-DDT	125 (6)	121	ND	ND	1120 (54)	1187	4.00 ± 0.31	3.93	4.31 (0.15)	4.32
cis-chlordane	15.7 (0.5)	15.3	2.33 ± 0.56	2.09	10.1 (0.8)	9.89	15.5 ± 0.59	17.0	7.56 (0.21)	7.78
trans-nonachlor	7.36 (0.25)	7.41	1.26 ± 0.13	1.35	8.88 (0.7)	8.56	14.5 ± 1.1	16.4	10.8 (0.7)	11.3
hexachlorobenzene	5.54 (0.45)	5.68	70 ± 25	67.5	ND	ND	ND	ND	4.20 (0.08)	4.14

[a] Three samples were extracted using methylene chloride and analyzed in duplicate. Concentrations are the means, and the numbers in parentheses are one standard deviation of a single measurement.

[b] Two samples were extracted using methylene chloride and analyzed in duplicate. Concentrations are the means.

[c] The values are as reported in the Certificate of Analysis for SRM 1941a [6]. The uncertainty is based on a 95% confidence interval of the true concentration.

[d] The PAH values are as reported in the Certificate of Analysis for SRM 1649a with the uncertainty based on a 95% confidence interval. The chlorinated values are the means from six samples Soxhlet extracted using methylene chloride and analyzed in duplicate. The numbers in parentheses are one standard deviation of a single measurement.

[e] One sample extracted using methylene chloride.

[f] Eight samples were extracted using methylene chloride and analyzed in duplicate. Concentrations are the means, and the numbers in parentheses are one standard deviation of a single measurement.

[g] ND=not determined

METHODS OF PREPARING SOIL SAMPLES FOR HEADSPACE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS: EMPHASIS ON SALTING OUT

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ABSTRACT

Three equilibrium and two solvent extraction methods of preparing and analyzing volatile organic compounds (VOCs) in soil by headspace gas chromatography (HS/GC) were compared. The samples studied were triplicates of four different soil types spiked with an aqueous solution containing BTEX and four chlorinated compounds. Solvent extraction was found to be superior for recovering spiked VOCs, followed by: direct heating; an aqueous solution preserved with $NaHSO_4$; and lastly, an aqueous solution saturated with NaCl and acidified with phosphoric acid. The findings indicated that correction factors may be necessary for equilibrium HS/GC determinations of VOCs in soils.

INTRODUCTION

This study evaluated several different methods by which discrete soil ("grab") samples can be prepared for headspace gas chromatography (HS/GC) analysis of volatile organic compounds (VOCs). In all, two solvent extraction methods and three equilibrium HS procedures were assessed. Of particular interest among the HS equilibrium methods is one that calls for soil samples be placed into an aqueous solution saturated with sodium chloride (NaCl) and acidified phosphoric acid (H_3PO_4). This salting-out method of HS/GC analysis was recommended in the initial draft of Method 5021. This method, *Volatile Organic Compounds in Soil and other Solid Matrices using Equilibrium Headspace Analysis*, is currently scheduled for the third update of the Test Methods for Evaluating Solid Waste (1).

Indeed, salting out has long been recognized as a means of increasing the sensitivity of HS/GC analysis of VOCs in aqueous samples (2), and acidification is an effective means of limiting biodegradation of labile compounds in water (3), soil and soil-water slurries (4–5). However, none of the experiments addressing the matrix effects of soils and soil-water slurries on HS analysis (6–7), studied or recommended salting out.

To assess soil matrix effects and potential confounding effects due to salting out during equilibrium HS/GC analysis, a comparative sample preparation study was performed. Recoveries of VOCs from four different soil types, as determined by HS/GC analysis, were compared after the samples were heated, dispersed in water saturated with NaCl and acidified with H_3PO_4, dispersed in water acidified with sodium bisulfate ($NaHSO_4$), extracted

with methanol (MeOH), or extracted with tetraethylene glycol dimethyl ether (tetraglyme). Merits and potential problems when using these various sample preparation methods, and the trends established in physical characteristics of the soil matrices and organic compounds tested, are discussed.

EXPERIMENTAL

a. Soil Subsample Preparation

A spiking solution was prepared by adding microliter volumes (3.1–5.8 μL) of neat analytes benzene (Ben), toluene (Tol), ethylbenzene (E-Ben), p-xylene (p-Xyl), o-xylene (o-Xyl), trans-1,2-dichloroethylene (TDCE), cis-1,2-dichloroethylene (CDCE), trichloroethylene (TCE) and tetrachloroethylene (PCE) to a 100-mL volumetric flask containing about 103 mL of groundwater. Once all the analytes were transferred, this aqueous solution was mixed for 48 hours using a stirring bar. The target concentration for each analyte was 50 mg/L; however, some volatilization losses occurred.

Table 1. Soil characteristics.

Ottawa sand	>99% sand, 0.035% organic carbon
Fort Edwards clay	>90% clay, 0.5% organic carbon
CRREL loam	silty/sand, 1.5% organic carbon
Point Barrow, Alaska peat	silty/clay, 7.1% organic carbon

Laboratory samples were prepared from four soils that varied in texture (clay, silt, and sand) and organic carbon content (Table 1). The method of laboratory subsample spiking and handling has been presented elsewhere (5). Briefly, 15 air-dried 2-g subsamples of each soil type were first transferred to 1-mL glass ampoules. Then, placing one ampoule at a time in a metal tension clamp, they were spiked with the aqueous solution. After transferring a 0.200-mL aqueous spike using a 0.500-mL glass syringe (Hamilton), each ampoule was quickly heat-sealed with a propane torch. All spike aliquots were taken from well below the water-air interface, and the stainless steel needle was wiped prior to insertion into the ampoule's neck. In addition to preparing the soil subsamples, 0.200-mL aliquots of the spiking solution were placed into three separate auto sampler headspace vials (22 mL, Tekmar) containing 10 mL of Type 1 water, and immediately capped with crimp-top caps and Teflon-faced butyl rubber septa (Wheaton). These autosampler vials with 10 mL of water were spiked at the beginning, middle and end of the soil subsample spiking process, and served as a means of establishing the spike concentration and homogeneity. These three autosampler vials containing spikes of the aqueous solution were analyzed within 24 hours of preparation.

All of the 60 sealed ampoules containing treated soil were placed in a refrigerator for two days to allow the analytes to sorb to the matrix. Then all of the ampoules were removed from the refrigerator and triplicates of each soil type (3 X 4) were randomly taken for each of the five sample preparation and analysis protocols. All of the soil subsamples were dispersed into the appropriate solutions at this time, then returned to the refrigerator for storage until analysis. By using this procedure, VOC losses due to volatilization and/or biodegradation were minimized.

b. Preparation for Subsample Analysis

Heated equilibrium HS/GC analysis: Ampoules containing the spiked soil subsamples were transferred to empty autosampler vials and capped. Once the vials were hermetically sealed, the ampoules were broken and the soil completely dispersed by carefully hand-shaking the autosampler vials. Sample analysis was performed the same day the ampoules were broken, after heating the sample to 60°C for 50 minutes and removing a HS vapor sample. This procedure is consistent with that described in the Draft Statement of W*ork for Quick Turn-around Analysis* (8).

Aqueous dispersion in a NaCl-saturated solution acidified with H_3PO_4, equilibrium HS analysis: The aqueous dispersion solution was prepared by acidifying 500 mL of water with H_3PO_4 to pH 2, then adding 180 g of NaCl. Ten mL of this aqueous solution was transferred to 12 autosampler vials and an ampoule of spiked soil was added to each. Once the vials were sealed, the ampoules were broken and their contents completely dispersed. These samples were analyzed one day after the ampoules were broken, after heating the sample to 85°C for 60 minutes and removing an HS vapor sample. This analysis procedure is consistent with that currently described in draft Method 5021.

Aqueous dispersion in a solution acidified with $NaHSO_4$, equilibrium HS analysis: Ten mL of water and 0.25 g of $NaHSO_4$ were placed into twelve autosampler vials, then an ampoule was placed in each vial. Once the vials were sealed, the ampoules were broken and their contents completely dispersed. Samples were analyzed two days after the ampoules were broken. HS vapors were removed after samples had been held for at least 20 minutes at 25°C.

MeOH extraction: Five mL of HPLC grade MeOH was transferred to twelve autosampler vials and an ampoule was placed in each vial. After capping the vials, the ampoules were broken, and the soil was completely dispersed by hand shaking. Five days after initiating the extraction process the autosampler vials were opened and a 100-mL aliquot was removed and transferred to another autosampler vial containing 10 mL of Type 1 water, which was then capped. HS vapors were removed after the aqueous MeOH solutions had been held for at least 20 minutes at 25°C.

Tetraglyme extraction: Samples were extracted with tetraglyme using the same procedure as described for MeOH (5 mL/ampoule). Six days after initiating the extraction process the auto sampler vials were opened and a 0.500-mL aliquot was transferred to another autosampler vial containing 9.5 mL of Type 1 water saturated with NaCl. HS samples were removed from the aqueous tetraglyme solution saturated with NaCl after they had been held for at least 20 minutes at 25°C.

HS ANALYSIS

All samples were analyzed with an HS autosampler (Tekmar 7000) coupled to a GC (SRI model 8610-0050) equipped with a 15-m DB1 0.53-mm capillary column and sequential PID/FID detectors. Just prior to placing auto sampler vials in this system, each was shaken for approximately 2 minutes. Appropriate settings for the autosampler were used for the expected in-vial pressures obtained during the equilibration period. For each sample prepa-

ration procedure, analyte amounts were established relative to HS standards prepared by adding small (≤ 2 μL) quantities of an MeOH stock solution to autosampler vials containing the same solution composition and volume as the samples. However, since the 2 g of soil and broken glass ampoules were present for the three equilibrium methods, these samples contain three phases (air, water, and soil), as opposed to only one or two for the standards (air, and air and water). In addition, the samples for the three equilibrium HS methods had less air space (i.e., the glass ampoule and soil occupied approximately 2 cm^3) than the standards. Although not presented here, this decrease in vapor phase volume causes a significantly (5–10%) different analyte response for samples in the heated HS and salting-out method of HS analysis.

RESULTS AND DISCUSSION

Spike amounts and recovery from the different soil matrices, as achieved by the five different subsample preparation and analysis protocols, appear in Table 2. The means and standard deviations of the analyte determinations (μg VOC) demonstrate that each sample preparation and analysis procedure was precise. A one-way analysis of variance test (ANOVA) was performed at the 95% confidence level for each sample preparation and analysis method,

Table 2. Octanol-water partition coefficients of analytes, and means and standard deviations of triplicate determinations. For each analyte with the same method of sample preparation and analysis, values with the same letter (or no letter at all) are not significantly different from each other.

Compound (Abbreviation)	Octanol-water partition coefficient
trans-1,2-dichloroethylene (TDCE)	2.09
cis-1,2-dichloroethylene (CDCE)	—
benzene (Ben)	2.13
trichloroethylene (TCE)	2.53
tetrachloroethylene (PCE)	2.60
toluene (Tol)	2.65
o-xylene (o-Xyl)	2.95
ethylbenzene (E-Ben)	3.13
p-xylene (p-Xyl)	3.18

	Analyte Concentration (μg)				
Analyte	*Spike*	*Ottawa*	*Ft. Edwards*	*CRREL*	*Pt. Barrow, Alaska*
I. MeOH extraction					
TDCE	8.26 ± 0.25	8.23 ± 0.21	8.57 ± 0.10	8.23 ± 0.46	8.33 ± 0.17
CDCE	8.45 ± 0.24	8.15 ± 0.41	8.70 ± 0.16	8.42 ± 0.44	8.53 ± 0.28
Ben	5.83 ± 0.18	5.60 ± 0.21	5.93 ± 0.11	5.75 ± 0.30	5.86 ± 0.20
TCE	9.98 ± 0.29	9.58 ± 0.46	9.75 ± 0.14	9.64 ± 0.40	9.82 ± 0.33
PCE	9.10 ± 0.28	8.66 ± 0.35	9.24 ± 0.16	8.95 ± 0.45	8.94 ± 0.46
Tol	6.54 ± 0.20	6.58 ± 0.28	6.69 ± 0.18	6.64 ± 0.43	6.56 ± 0.18
o-Xyl	6.71 ± 0.20	7.03 ± 0.57	7.20 ± 0.08	7.10 ± 0.29	6.92 ± 0.19
E-Ben	6.23 ± 0.26	6.08 ± 0.27	6.50 ± 0.16	6.38 ± 0.48	6.29 ± 0.40
p-Xyl	6.22 ± 0.14	6.27 ± 0.20	6.50 ± 0.16	6.55 ± 0.65	6.34 ± 0.31

Analyte	Analyte Concentration (μg)				
	Spike	*Ottawa*	*Ft. Edwards*	*CRREL*	*Pt. Barrow, Alaska*
II. Tetraglyme extraction					
TDCE	8.26 ± 0.25a	8.30 ± 0.12a	7.76 ± 0.03b	7.68 ± 0.32b	8.02 ± 0.28a,b
CDCE	8.45 ± 0.24a	8.28 ± 0.10a,b	7.93 ± 0.16b	7.87 ± 0.40b	8.17 ± 0.18a,b
Ben	5.83 ± 0.18	5.82 ± 0.12	5.57 ± 0.06	5.55 ± 0.17	5.62 ± 0.19
TCE	9.98 ± 0.29a	10.0 ± 0.26a	9.42 ± 0.10b	9.56 ± 0.40a,b	9.38 ± 0.35
PCE	9.10 ± 0.28a	8.87 ± 0.16a,b	8.42 ± 0.36b	8.39 ± 0.10b	7.64 ± 0.51c
Tol	6.54 ± 0.20a	6.42 ± 0.14a,b	6.13 ± 0.15b,c	6.14 ± 0.15b,c	5.87 ± 0.27c
o-Xyl	6.71 ± 0.20a	6.58 ± 0.18a	6.32 ± 0.42a	6.32 ± 0.04a	5.03 ± 0.35b
E-Ben	6.23 ± 0.26a	5.87 ± 0.14a	5.48 ± 0.20b	5.47 ± 0.08b	4.56 ± 0.25c
p-Xyl	6.22 ± 0.14a	6.02 ± 0.13a,b	5.67 ± 0.25b,c	5.53 ± 0.12c	4.64 ± 0.28c
III. Heated-headspace analysis					
TDCE	8.26 ± 0.25a,b	8.68 ± 0.22a	8.12 ± 0.41b	8.22 ± 0.20a,b	8.09 ± 0.20b
CDCE	8.45 ± 0.24b	9.24 ± 0.16a	8.56 ± 0.38b	8.30 ± 0.27b	6.94 ± 0.08c
Ben	5.83 ± 0.18a,b	6.10 ± 0.14a	5.75 ± 0.26b	5.73 ± 0.09b	4.47 ± 0.06c
TCE	9.98 ± 0.29a,b	10.5 ± 0.15a	9.72 ± 0.44b,c	9.28 ± 0.42c	7.17 ± 0.07d
PCE	9.10 ± 0.28a,b	9.74 ± 0.32a	8.86 ± 0.46b,c	8.45 ± 0.39c	5.38 ± 0.29d
Tol	6.54 ± 0.20b	7.00 ± 0.23a	6.18 ± 0.39b	6.15 ± 0.05b	3.84 ± 0.10c
o-Xyl	6.71 ± 0.20b	7.38 ± 0.16a	5.98 ± 0.28c	5.48 ± 0.04d	2.24 ± 0.13e
E-Ben	6.23 ± 0.26b	6.93 ± 0.20a	5.68 ± 0.40c	5.58 ± 0.18c	2.72 ± 0.06d
p-Xyl	6.22 ± 0.14b	6.80 ± 0.16a	5.70 ± 0.16c	5.40 ± 0.13d	2.57 ± 0.14e
IV. Headspace analysis of soil-water slurry preserved with $NaHSO_4$					
TDCE	8.26 ± 0.25a	8.35 ± 0.09a	5.56 ± 0.37d	7.81 ± 0.21b	6.54 ± 0.21c
CDCE	8.45 ± 0.24a	8.37 ± 0.06a	5.58 ± 0.41d	7.83 ± 0.17b	6.40 ± 0.24c
Ben	5.83 ± 0.18a	5.83 ± 0.02a	3.95 ± 0.25c	5.41 ± 0.12b	4.03 ± 0.13c
TCE	9.98 ± 0.29a	10.2 ± 0.21a	6.60 ± 0.74c	8.71 ± 0.21b	5.21 ± 0.10d
PCE	9.10 ± 0.28a	9.10 ± 0.07a	5.71 ± 0.34b	5.85 ± 0.13b	2.32 ± 0.06c
Tol	6.54 ± 0.20a	6.51 ± 0.05a	4.34 ± 0.28c	5.46 ± 0.17b	2.95 ± 0.08d
o-Xyl	6.71 ± 0.20a	6.62 ± 0.16a	4.37 ± 0.20b	3.91 ± 0.15c	1.46 ± 0.08d
E-Ben	6.23 ± 0.26a	6.37 ± 0.08a	4.09 ± 0.23b	3.99 ± 0.18b	1.53 ± 0.05c
p-Xyl	6.22 ± 0.14a	6.00 ± 0.16a	3.87 ± 0.26b	3.51 ± 0.14c	1.31 ± 0.07d
V. Headspace analysis of soil-water slurry saturated with NaCl and acidified with H_3PO_4					
TDCE	8.26 ± 0.25a	8.85 ± 0.46a	6.74 ± 0.69b	6.67 ± 0.10b	4.58 ± 0.09c
CDCE	8.45 ± 0.24a	8.66 ± 0.29a	6.45 ± 0.75b	6.10 ± 0.21b	3.42 ± 0.04c
Ben	5.83 ± 0.18a	6.33 ± 0.31a	4.71 ± 0.55b	4.24 ± 0.17b	2.09 ± 0.20c
TCE	9.98 ± 0.29a	10.8 ± 0.61a	7.37 ± 0.95b	5.91 ± 0.39c	2.51 ± 0.15d
PCE	9.10 ± 0.28b	9.99 ± 0.51a	5.39 ± 0.34c	3.45 ± 0.37d	1.24 ± 0.13e
Tol	6.54 ± 0.20b	7.16 ± 0.28a	4.69 ± 0.32c	3.20 ± 0.22d	1.18 ± 0.08e
o-Xyl	6.71 ± 0.20a	6.93 ± 0.32a	3.33 ± 0.27b	1.60 ± 0.10c	0.53 ± 0.02d
E-Ben	6.23 ± 0.26b	6.94 ± 0.30a	3.40 ± 0.18c	1.84 ± 0.16d	0.62 ± 0.02e
p-Xyl	6.22 ± 0.14a	6.54 ± 0.37a	3.07 ± 0.29b	1.61 ± 0.14c	0.54 ± 0.03d

and for each analyte, to determine if there were any significant differences between the theoretical (spiked) and measured concentrations for the various soil matrices tested. In addition, a Fisher's Protected LSD was performed to determine which values were significantly different from each other. Table 2 is arranged with analytes of increasing octanol/water partition coefficient going down a column, and soil matrix with increasing organic carbon content going across a row.

Independent of sample preparation and analysis method, there was good recovery of all the analytes from the Ottawa sand. However, MeOH extraction was the only sample preparation method that was able to achieve quantitative recoveries of all of the spiked analytes from the other three soils. Tetraglyme showed good recoveries of TDCE, CDCE, and Ben; however, recovery of the other analytes from the three other soils was significantly lower than expected. This discrepancy between the expected and measured amounts often increased with increasing percent organic carbon in the test soil, and with increasing octanol/water partition coefficients (Table 2). To compensate for the extraction deficiencies of tetraglyme, correction factors up to 1.34 would be necessary. The greater extraction efficiency of MeOH in comparison to tetraglyme for VOCs in soils is consistent with a previous study (9).

In general, the pattern established for tetraglyme was followed by each of the equilibrium HS sample preparation and analysis methods, except that the number and magnitude of correction factors increased. For the heated HS method, correction factors as great as 3.00 would be necessary. Likewise, correction factors as great as 4.75 and 12.7 would be necessary for the aqueous dispersion acidified with $NaHSO_4$, and the aqueous dispersion saturated with NaCl and acidified with H_3PO_4, respectively.

During equilibrium HS/GC analysis, the partitioning of VOCs into the vapor phase from solution is more strongly increased by salt addition than by increases in temperature (2). Usually, in the analysis of aqueous solutions by equilibrium HS/GC, both parameters are used in concert for optimal conditions. Accordingly, the standards prepared for equilibrium HS/GC analysis that used a saturated NaCl solution acidified with H_3PO_4, and were analyzed after heating to 85°C, had analyte responses some 2 to 5 times greater than the others (all three procedures used the same detector and signal attenuation). However, this salting-out approach to preparing soil samples for equilibrium HS analysis failed to achieve a similar enhanced analyte response. Instead, the matrix-analyte interactions cited previously increased. A possible explanation for this phenomenon is that organic carbon, which serves as a separate phase into which VOCs can partition, is more favorable than the vapor state under salting-out conditions.

Method 5021 and Method 5035 (also under consideration for the third update of the SW-846) both recommend in-vial methods to solve the volatilization and preservation issues that plague VOC determinations in solid waste matrices. These two loss mechanisms have been shown to cause up to 99.9% reduction in VOCs between collection and analysis (10–11). Clearly, in-vial methods are necessary for obtaining site-representative VOC concentrations for vadose-zone samples. These two methods, along with the currently used Method 5030, recommend an aqueous dispersion/extraction method for low-level (< 1 μg/g) and MeOH extraction for high-level (> 1 μg/g) VOC determinations in soils. The water-based sample analysis procedure for Methods 5030 and 5035 is performed by dynamic purging, while static headspace is used for Method 5021. Studies have shown that MeOH is a superior solvent, in comparison to water, for extracting VOCs from soils (6, 12), and that dynamic purging by mass transfer may be more efficient than the static equilibrium methods described here (6).

The findings of this study should make users of equilibrium HS/GC methods aware of potential matrix-analyte interactions. On a site-per-site basis, these interactions can easily be identified and corrected for by surrogate analyte and/or matrix spike recoveries. Often, these interactions will be small, perhaps even insignificant, because vadose-zone soils rarely have high (> 1%) organic carbon contents.

SUMMARY

Except in the case where there are no matrix effects (i.e., little or no organic carbon or clay content), such as was shown for Ottawa sand in this study, correction factors are likely to be necessary either when purging a soil-water slurry or performing an equilibrium HS analysis of a soil or soil-water slurry for determining VOC concentrations in soils. Appropriate correction factors for soil matrices can be established by either surrogate analytes or matrix spike recoveries. In general, soil matrix effects will increase with the analyte octanol/water partition coefficient and the organic carbon content of the soil. Furthermore, because analyte-organic carbon matrix effects increase with increasing solution electrolyte concentrations, using salting out for equilibrium HS is not recommended.

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Detection of Cyclodiene Insecticides in Water and Soil Using a Magnetic Particle-Based Immunoassay

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Abstract

Although banned in most countries, the cyclodiene insecticides still cause concern because of their high toxicity and environmental persistence. Half-lives ranging from two months to ten years have been reported for various cyclodienes in soil and water. A method for the quick and simple determination of cyclodiene insecticides in water using a magnetic particle based enzyme linked immunosorbent assay (ELISA) is described. Results are reported in parts per billion dieldrin. Recovery from dieldrin spiked waters averaged 97%. A comparative study of dieldrin recovery from water using immunoassay versus EPA Method 505 showed good correlation yielding an $r^2 = 0.958$. An extraction method for use on soil is also described. Soils fortified with the various cyclodienes and extracted using a methanolic solution containing stabilizers and surfactants averaged 97% recovery.

Introduction

The cyclodiene insecticides comprise a large group of polychlorinated, cyclic hydrocarbons including two pairs of stereoisomers: aldrin and isodrin, dieldrin and endrin. Until the discontinuance of production and limitations on domestic usage, the cyclodiene insecticides most commonly used in the United States were heptachlor, chlordane, aldrin, dieldrin, endrin, toxaphene and benzene hexachloride (BHC) (Stanker, 1994; Smith, 1991). Though usually considered to be nonsystemic insecticides, they have been shown to be absorbed by root tissue like carrots and potatoes (Felsot and Pederson, 1991).

The previous widespread use of these compounds has led to concern about the persistence of these pesticide residues in foodstuffs and the environment. These highly lipophilic compounds have soil half-lives ranging from 2 - 10 years (Kidd and James, 1991; Stanker, 1994) which has resulted in severe environmental contamination. Although banned from use, bioaccumulation has resulted in their prevalent distribution in milk and human fat. Fish also have accumulations of these compounds in their bodies as a result of contaminations in the water (Stanker et al., 1994).

Traditional methods for the determination of cyclodiene insecticides in water and soil matrices require lengthy extraction procedures. Magnetic particle based ELISAs for the determination of pesticides in water and soil have been previously reported (Itak et al., 1993 and Lawruk et al., 1993). Described within is a quick and easy-to-use method for the determination of cyclodiene insecticides in water based on the use of a magnetic

particle ELISA. Also described is a short method for the extraction of the cyclodiene insecticides from soil.

Materials and Methods

Reagents

a. Cyclodienes RaPID Assay ®, RaPID Prep® Soil Collection Kit, RaPID Prep Cyclodienes Sample Extraction Kit, Cyclodiene Water Stabilizer and Sample Diluent, (Ohmicron Corp, Newtown, PA).
b. Dieldrin was purchased from Chem Service (West Chester, PA).
c. Compounds Tested for Cross Reactivity: Heptachlor, toxaphene, lindane, perthane, DDT, DDE and DDD were also purchased from ChemService. Chlordane, α-endosulfan, aldrin, endrin, isobenzan and heptachlor-endo-epoxide were purchased from Cresent Chemical (Hauppauge, NY). Isodrin was purchased from Aldrich (Milwaukee, WI).

Apparatus

a. RaPID Magnetic Separation Unit (Ohmicron Corp, Newtown, PA).
b. RPA-I Analyzer™ (Ohmicron Corp, Newtown, PA).
c. Vortex Mixer (VWR Scientific, South Plainfield, NJ).
d. Adjustable pipettes, Gilson P-1000 and P-200 (Rainin, Woburn, MA).
e. Eppendorf Repeater pipette 4780 (Hamburg, Germany).

Water Preparation

Water samples were collected in glass vessels with teflon cap liners. Immediately upon collection, samples were diluted with Cyclodienes Water Stabilizer (1 part Water Stabilizer: 3 parts water sample) to prevent adsorptive losses. After samples dilution, those samples containing gross particulate matter were centrifuged in order to remove particles.

Soil Extraction

Ten grams of soil were weighed or measured by packed volume into a Soil Collection tube. The contents of one vial of Cyclodienes Extraction Solution was poured into a collector. The sample was capped and shaken for one minute. The collection tube was positioned upright in the rack and the contents were allowed to settle for 5 minutes. The cap was removed from each tube and a filter cap was secured onto each collector. The soil collector was inverted over a collection vial; the plunger was attached, and pressure was applied to the handle. The collection vial was filled with a minimum of 30 drops (1.5 mL) of extractant and capped. Using a pipet, 250uL of the soil extract was transferred directly into a vial of Cyclodienes Extract Diluent (12.25mL). The samples were then assayed according to Cyclodienes RaPID Assay protocol (see below).

The actual Cyclodienes concentration expressed as ng/g dieldrin (ppb) was calculated by using the following equation.

(1) (assay result) x (dilution) x $\frac{\text{volume of extract (mL)}}{\text{weight of sample (g)}}$ =

(2) (ug/mL) x (50) x (20mL/10g) = assay result x 100 =

(3) cyclodienes concentration (ng/g or ppb dieldrin)

RaPID Assay Protocol

250uL of the standard, control, or sample to be tested was added to a disposable test tube along with 250uL of enzyme labeled cyclodiene analog and 500uL of magnetic particles with cyclodiene specific antibodies attached. After mixing, the samples were incubated for 30 minutes at room temperature. The reaction mixture was separated using the magnetic separation rack and washed twice with washing solution. 500uL of color solution was then added and allowed to develop for twenty minutes at room temperature. The color reaction was stopped with 500uL of stopping solution. Photometric analysis of the final colored product was made using the RPA-I Analyzer set at 450nm to determine ppb levels of cyclodienes (as dieldrin) in the samples.

Results and Discussion

The Cyclodienes RaPID Assay is calibrated to dieldrin but detects ten of the main cyclodiene insecticides. Table 1 summarizes the reactivity of the Cyclodienes RaPID Assay to dieldrin and other cyclodienes in buffer. The percent cross-reactivity was determined as the amount of dieldrin analog required to achieve 50% B/Bo divided by the amount of cross reactant analog required to achieve 50% B/Bo.

Recovery studies were performed using four water samples collected from creeks and wells from the east coast of the United States. Each water was treated with water stabilizer and spiked with four levels of dieldrin (0, 3, 6, 10 and 15 ppb). The mean recovery from water was 97% (n=16). The recovery data is summarized in Table 2.

Inter and intra assay precision studies were performed with four surface and ground water samples diluted 1:3 with water stabilizer and fortified with one level of dieldrin. Dieldrin samples were analyzed over 5 days, 5 assays each per day, in singlicate (n=25). The within- and between-day and total variations were determined according to the method of Bookbinder and Panosian (1986). Results are shown in Table 3. Coefficients of variation (%CV) for within day and between day were less than 13%.

Twenty dieldrin fortified water samples were analyzed by immunoassay and EPA Method 505. The coefficient of correlation was r^2 = 0.958, with a best fit line equation of y =

0.778x + 1.15. The correlation graph is shown in Figure 1. The immunoassay recoveries ranged from 80 - 99% while the GC reported recoveries ranging from 66 - 170%.

The reactivities of the cyclodiene insecticides in soil have been characterized for the described soil method. The least detectable dose (LDD) for the extraction method was estimated at the first standard which is equivalent to 100 ng per gram dieldrin in soil. Table 4 shows the analyte specific soil equivalents for each of the 3 assay standard levels. While the assay reports results as ppb dieldrin, the soil equivalency table can be used to semi-quantitate or rank the other cyclodienes. For example, if a heptachlor soil sample gives an assay response equivalent to 750 ppb dieldrin, it can be estimated to contain approximately 1200 ppb heptachlor.

In a soil precision study, ten samples of two soils fortified with dieldrin were weighed on a balance or measured by packed volume in the soil collector prior to analyzing. Results are shown in Table 5. The overall coefficient of variation for cyclodienes measurement using the Soil Collection and Sample Extraction Kits for both cases was less than 17%.

Fourteen neat and spiked soil samples collected from around the world were extracted with the RaPID Prep Cyclodienes Soil Extraction Kit and run in the Cyclodienes RaPID Assay. Out of the fourteen samples, four were found to be positive (greater than 100 ng/g dieldrin). Dilutions of these positive readings showed them to be linear. One positive sample was also confirmed by GC for 700 ppb chlordane.

Conclusions

This study demonstrates the feasibility of applying magnetic particle-based immunoassays to the detection of pesticide residues in water and soil. The speed of the described protocol makes it suitable as a screening method for large numbers of samples in short periods of time. This assay also compares favorably with the EPA recommended method for the determination of cyclodienes in water.

Table 1. Cross reactivity in the Cyclodienes Immunoassay

COMPOUND	90% B/Bo LDD (ppb)	IC_{50} (ppb)	% CROSS REACTIVITY
Dieldrin	0.45	9.91	100.0
Aldrin	0.22	7.88	125.4
Isodrin	0.32	9.54	103.9
Heptachlor-endo-epoxide	0.47	17.8	55.7
Heptachlor	0.50	15.9	62.3
Endrin	0.51	12.3	80.6
Chlordane	0.81	26.9	36.8
αEndosulfan	0.87	44.6	22.2
Isobenzan	1.04	45.8	21.6
Toxaphene	1.95	116.0	8.5
Lindane	15.2	846.0	1.2
p.p'-DDD	2040	NR	<0.001
p.p'-DDT	6562	NR	<0.001
p.p'-DDE	NR	NR	<0.001
Perthane	NR	NR	<0.001

Table 2. Dieldrin recovery from water.

Dieldrin Added (ppb)	Mean (ppb)	S.D. (ppb)	% Recovery
3.0	3.20	0.72	107
6.0	5.72	0.78	95
10.0	9.57	0.76	96
15.0	13.68	1.08	91
Average			97

Table 3. Immunoassay precision for the recovery of dieldrin from water.

Sample	+ 3.0 ppb	+ 6.0 ppb	+ 10.0 ppb	+ 15.0 ppb
Replicates	5	5	5	5
Days	5	5	5	5
N	25	25	25	25
Mean ppb	2.90	6.03	10.00	14.49
% CV Intra	12.8	11.8	8.4	9.8
% CV Inter	10.9	<0.1	<0.1	3.8
% CV Total	16.2	11.6	8.3	10.4

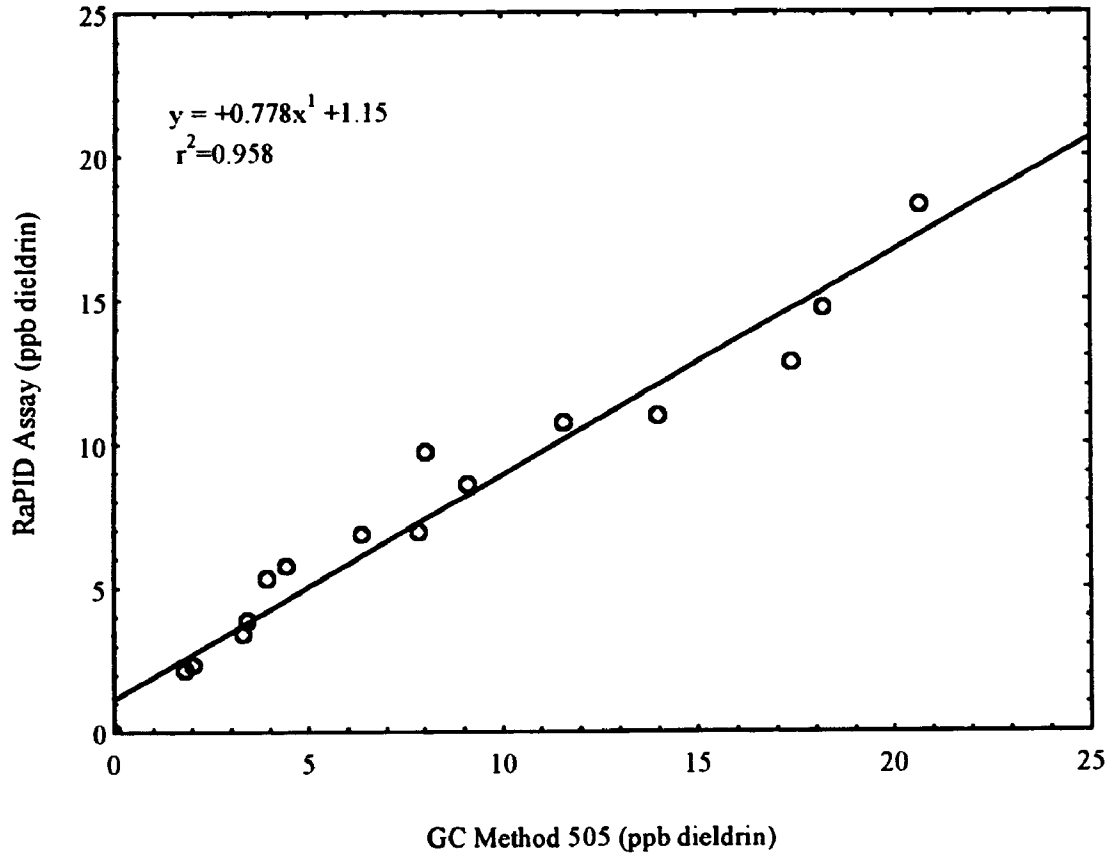
Table 4. Cyclodienes in Soil Equivalents.

Analyte	STANDARD 1 (ppb soil)	STANDARD 2 (ppb soil)	STANDARD 3 (ppb soil)
Dieldrin	100	750	2000
Aldrin	100	600	1700
Isodrin	100	700	2000
Endrin	125	900	2500
Heptachlor	150	1200	3400
Heptachlor-endo-epoxide	150	1300	4000
Chlordane	200	1550	5000
Isobenzan	300	3200	10,600
∝Endosulfan	300	3100	10,700
Toxaphene	830	8700	28,000

Table 5. Cyclodienes in Soil Precision by Weight and by Volume.

	Collection by Weight		Collection by Volume	
Soil	Holland	Mars Bluff	Holland	Mars Bluff
replicates	10	10	10	10
assayed soil concentration (ppb)	971	761	748	626
C.V. (%)	13.8	11.6	16.0	11.5

Figure 1.: Cyclodienes Correlation: Method 505 vs. RaPID Assay



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The Determination of Specific Polychlorinated Biphenyl Congeners in Fish Samples by Gas Chromatography and Electron Capture Detection

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Because of the persistence of Polychlorinated Biphenyls (PCBs) in the environment, the detection and accurate quantitation of PCBs remain an integral part of many environmental studies and remedial actions. In classical USEPA methodology, PCBs are reported as technical Aroclor mixtures which are recognized by their distinctive peak pattern on the gas chromatogram. PCB congener specific analysis, which has been made possible by advances in high resolution gas chromatography and the availability of all possible 209 PCB congeners as pure standards, allows for the individual detection of the specific more toxic planar congeners, has been shown to be less biased in quantifying PCBs than the classical Aroclor methods, and permits better tracking of PCBs in the environment because of weathering which occurs to Aroclor patterns.

In this study a gas chromatographic method was developed to separate and quantify all PCB congeners. Two dual capillary columns (a non polar Supelco SPB-Octyl 60 m x 0.25 mm, df 0.25 μm and a more polar J&W DB17 60 m x 0.25 mm, df 0.25μm) connected to a short length of guard column were used to separate the congeners; dual electron capture detectors (ECDs) were used for detecting and quantifying the congeners. Tetrachlorometaxylene (TCMX) and Decachlorobipheny (DCB) were added to all standards and samples as retention time markers for calculating relative retention times and as surrogate standards. Quadruplicate spiking studies (56 congeners) using Soxhlet extraction showed overall recoveries of 114% with an overall average RSD of 5.4%. Fish samples (approximately 30) collected from the Trenton Channel between Canada and the United States by the US Army Corps of Engineers were analyzed for these 56 PCB congeners. After the fish samples were Soxhlet extracted, the extracts were cleaned up using gel permeation chromatography, sulfuric acid, and florisil solid-phase cartridges. PCB congeners were found in all of the fish samples and ranged from the detection limit (less than 1 ppb for most congeners) to a high of 210 ppb for congener 153 in a Carp sample.

Composites of the fish sample were made to compare the efficiencies of the Soxhlet extraction, the sonication extraction, Accelerated Solvent extraction (ASE), and Supercritical fluid extraction. The recoveries and precisions for the PCB congeners in the fish tissue using these extraction techniques (n = 3 for each method) were compared.

NEW AND SPECIALLY DEVELOPED BONDED SILICONE PHASES FOR PESTICIDES TRACE ANALYSIS WITH CAPILLARY GC.

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Pesticides can be quantified at concentrations down to ppt levels using special sensitive detectors such as an Electron Capture Detectors. As the absolute amount of component that is injected on the column is in the order of picograms, the inertness of the chromatographic system is extremely important.

It is already known that certain pesticides will decompose in a hot injection port. p,p'-DDT and Endrin are such components.
Also the column must have a high degree of inertness to be able to elute picograms of pesticides as symmetrical peaks. A very popular column for pesticides analysis is the **CP-Sil 8 CB for Pesticides**, which separates the most important pesticides with excellent resolution. polysiloxane.

In many environmental applications a second, more polar column is often used to confirm the separation and identification of the apolar column.The commercially available OV-1701 phases and columns turned out to be quite irreproducible, especially for the recovery of pesticides like the p,p'-DDT.

A special high purity polymer was synthesized and the polarity was adjusted to be close to the polarity of OV-1701. This new polymer turned out to be very inert and it makes the quantitative elution possible of p,p'-DDT at sub-picogram levels. This new phase is called **CP-Sil 19 CB for Pesticides**, as it shows unique applications for these types of compounds.

In this poster the chromatographic behavior of this new phase will be discussed.

A NEW HPLC STATIONARY PHASE FOR THE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH'S).

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A new stationary phase has been developed to meet specific requirements towards PAH-analysis according to EPA- and ASTM methods: CP-EcoSpher 4 PAH.
On this phase the EPA-PAH's are well spread over the chromatogram due to it's specific selectivity. Using optimum conditions the "peakcapacity" is over 40, which means that there is enough space left for other PAH's to elute between the EPA-PAH's. For instance, this enables better quantification of for instance the components perylene and benzo(e)pyrene.
Besides that, because of the higher bonding percentage and efficiency of the material, it is possible to use methanol/water mixtures instead of the more "popular" acetonitrile/water mixture without a drastic decrease in separation power. As methanol is less expensive and less toxic than acetonitrile, the use of methanol offers some nice advantages.
The day to day deviation of the retention factor k is less than 1% and the day to day deviation of the selectivity factor α is less than 0.2%
The optimum temperature range for the new phase is lower and wider (15-35 °C) compared with most other phases as will be shown by a selectivity test.

Overview of the Current Status of the RCRA Organic Methods Development Program.

B. Lesnik

ABSTRACT NOT AVAILABLE AT TIME OF PUBLICATION

FREON ALTERNATIVES FOR THE ENVIRONMENTAL LAB

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ABSTRACT
The Accelerated Solvent Extractor (ASE) has been used to extract total petroleum hydrocarbons (TPH) from solid matrices with tetrachloroethene. The extraction conditions were 200°C and 1500 psi for 10 minutes. Analysis was performed with an infrared filter photometer following the procedure described in EPA SW-846 Method 8440. ASE extraction typically recovered 50% more TPH than Soxhlet extraction with Freon-113®. The exceptions were a group of wet clay samples. For many of these samples, the result from the initial ASE extract was significantly lower than the Soxhlet extract. A second ASE extraction of the same sample aliquot yielded high levels of hydrocarbons. Some secondary extracts actually had higher TPH results than the initial extracts. This illustrates the extraction problem caused by water when only a non-polar extraction solvent is used. Using hexane in the ASE provides an alternative for gravimetric analysis of TPH in solid matrices.

INTRODUCTION
As Freon-113® usage is being phased out many people within the environmental testing community have been searching for alternative solvents and test procedures. Unfortunately no single alternative solvent has been able to match all the key characteristics that have made Freon-113® so popular. It has been the primary solvent for the extraction and analysis of "Oil & Grease" and "Total Petroleum Hydrocarbons" from both aqueous and solid matrices. The extraction is usually performed in a separatory funnel (waters) or Soxhlet (solids). The most common analysis methods are gravimetric or infrared measurement around 2950cm^{-1}. Selecting the best alternative solvent and extraction procedure depends on the matrix and type of analysis.

Infrared analysis can be carried out in high purity tetrachloroethene (PCE). This nonpolar solvent is similar to Freon-113® in polarity and IR background around 2950cm^{-1}. It's boiling point (121°C) is much higher than the boiling point of Freon-113® (48°C) which makes it unsuitable for use in most Soxhlet systems. The higher boiling point is not a problem when using Method 3545, Pressurized Fluid Extraction.

Many gravimetric analyses are switching to hexane. This nonpolar solvent can also be used in the Accelerated Solvent Extractor system. After removing water from the extract, silica gel may be added to remove polar extracted materials. The hexane can then evaporated for gravimetric analysis similar that described in Method 1664.

EXPERIMENTAL
Pressurized fluid extraction (PFE) will be included in SW-846 Update III as Method 3545. The extraction time is 10 minutes, with sample-to-sample cycle time of about 13 minutes. The required solvent volume ranges from 15 to 50mL depending on the amount of sample extracted. Sample amounts up to 20g can be routinely extracted. If the sample is dry enough that very little drying agent is required then 30g quantities can be extracted.

The Accelerated Solvent Extractor system (ASE) has been described previously at this symposium (1,2). In this application the ASE has been used to extract total petroleum

hydrocarbons (TPH) from solid matrices with tetrachloroethene or hexane. The extraction conditions were 200°C and 1500 psi for 10 minutes unless stated otherwise. Analysis was performed with an infrared filter photometer following the procedure described in EPA SW-846 Method 8440. Hexane was investigated as an alternative for gravimetric analysis of TPH in solid matrices. A few matrix spiked clay samples were studied. Also, 72 real TPH samples were extracted and analyzed. Most samples were only processed once. The exceptions being the wet clay samples discussed below.

RESULTS and DISCUSSION

Figure 1 shows the results from several matrix spiked petroleum hydrocarbon samples. Hydrocarbon recovery from wet samples is more difficult when only non-polar extraction solvents (such as Freon-113® or tetrachloroethene) are used. It is necessary to dry the sample either before or during the extraction to achieve good analyte recovery. Both wet and dry sample matrix spikes of diesel and motor oil were sequentially extracted until quantitative recovery was achieved. The two dry samples were quantitatively extracted with a single 10 minute extraction with tetrachloroethene at 200°C.

The wet samples were more difficult to extract. The fresh diesel spiked sample required a second 10 minute, 200°C extraction to reach quantitative recovery. The aged motor oil spike although easy to extract when dry became very difficult to extract when the moisture content of this clay sample was brought to 50%. Three 10 minute extractions were required to achieve quantitative recovery. The first extraction had very little hydrocarbons recovered, but the extract contained significant amounts of water. Subsequent extractions of the same clay sample aliquot recovered more hydrocarbons and less water. These wet clay results illustrate the problem encountered when extracting wet samples with nonpolar solvents. Fortunately most real samples were not this difficult, as described below.

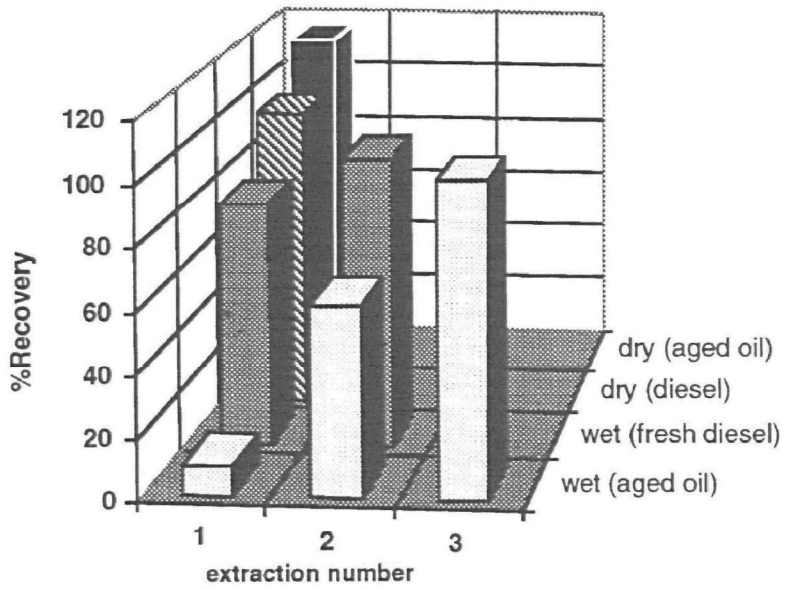

Figure 1 Recovery of TPH from spiked clay

A wide range of real samples were extracted with both Soxhlet and ASE. The IR analysis results are shown in Figure 2. ASE extraction typically recovered 50% more TPH than Soxhlet extraction with Freon-113®. The diagonal line in the center indicates the region where the ASE concentration data corresponds exactly to the Soxhlet data. The shaded region covers the area from ASE results being 50% higher to 50% lower than the Soxhlet results. The X and Y axes are shown in log-log space since the concentration data cover many orders of magnitude.

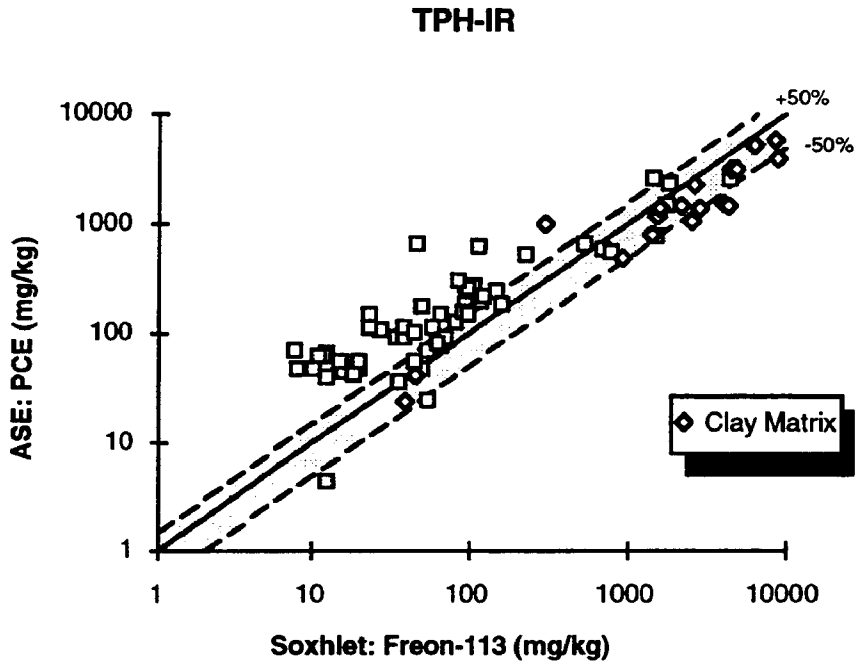

Figure 2 Comparison of TPH Results for ASE and Soxhlet Extractions

The exceptions to the general trend of higher recovery with the ASE were a group of wet clay samples. For many of these samples, the result from the initial ASE extract was significantly lower than from the Soxhlet extract. A second ASE extraction of the same sample aliquot yielded high levels of hydrocarbons. Some secondary extracts actually had higher TPH results than the initial extracts. The average Soxhlet data and the sum of the two ASE results are shown in Figure 3. With one exception, the combined ASE results were equivalent or higher than the Soxhlet results. Usually the first ASE extraction yielded 1-2mL of water and 30-70% of the TPH. The second extraction had no water and the remainder of the hydrocarbons. This illustrates the extraction problem caused by water when only a non-polar extraction solvent is used. The water reduces analyte recovery until it is removed from the surface of the sample. It is possible the water forms an insoluble barrier between the analytes on the particle surface and the non-polar extraction solvent.

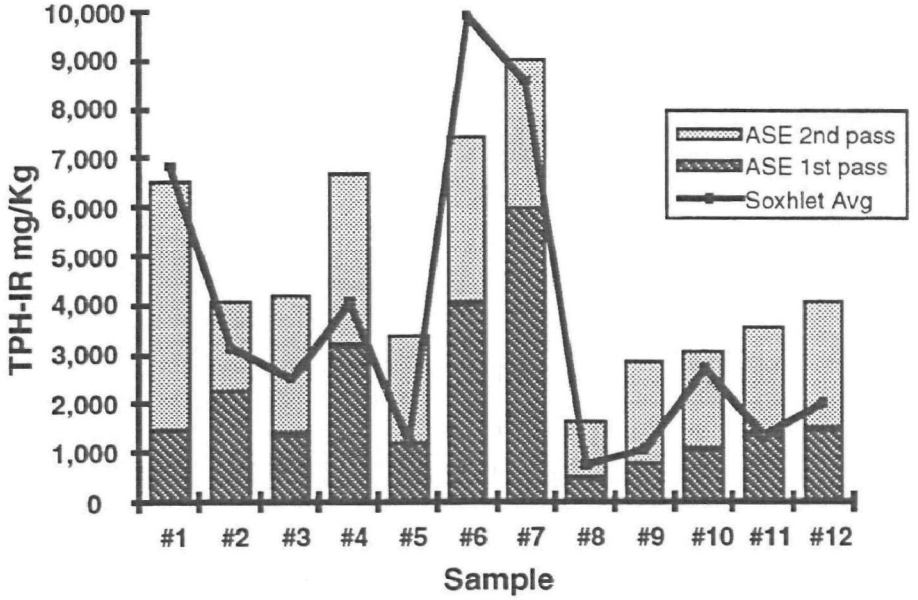

Figure 3 Comparison of Wet Clay TPH Results for ASE and Soxhlet Extractions

Unfortunately the 200°C ASE extractions wear out the polymeric seals of the extraction vessel more quickly than the usual 100°C extractions (1,2). A few of these wet clay samples were repetitively extracted at 100°C for 10 minutes. Figure 4 illustrates that TPH recovery was significantly lower at 100°C than it was at 200°C. The amount of water in the initial passes of the 100°C extractions was much lower than in the first pass of the 200°C extraction. It appears that water was not being efficiently removed from the surface of the sample and thus inhibited recovery of the hydrocarbons. The single 200°C extraction after 5 extraction passes at 100°C demonstrates that significant levels of hydrocarbons were still available for recovery. Presumably water elimination (and thus TPH recovery) was enhanced by the increased solubility of water in tetrachloroethene at 200°C relative to 100°C. This water interference effect was very pronounced even though all samples had been mixed with at least an equal amount of sodium sulfate drying agent.

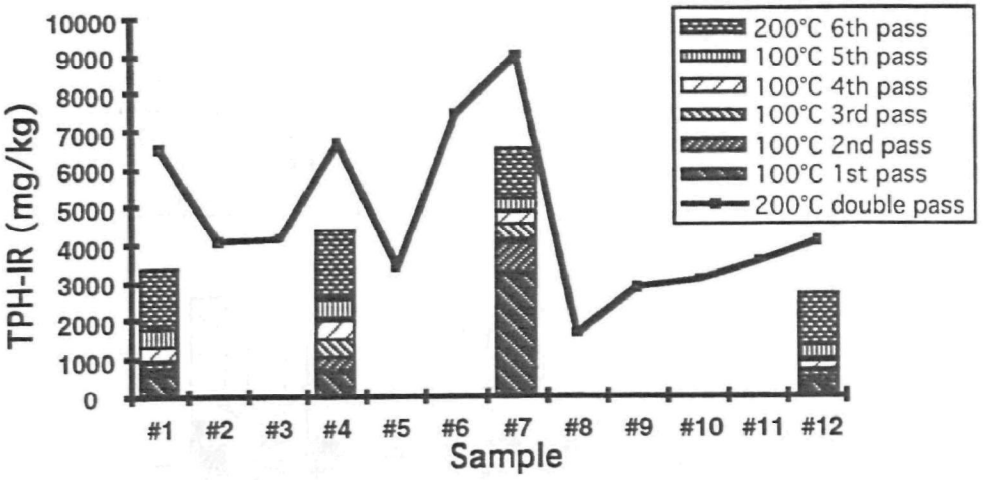

Figure 4 Comparison of Wet Clay ASE TPH Results for 100°C and 200°C Extractions

Eight of the wet clay samples were extracted with hexane at 200°C for 10 minute passes. Analysis was performed gravimetrically. Figure 5 shows the results were similar to the tetrachloroethene extraction results. However, the hexane extraction with gravimetric analysis was not equivalent to the tetrachloroethene extraction with IR analysis. This was expected since the solvents and analysis methods were quite different.

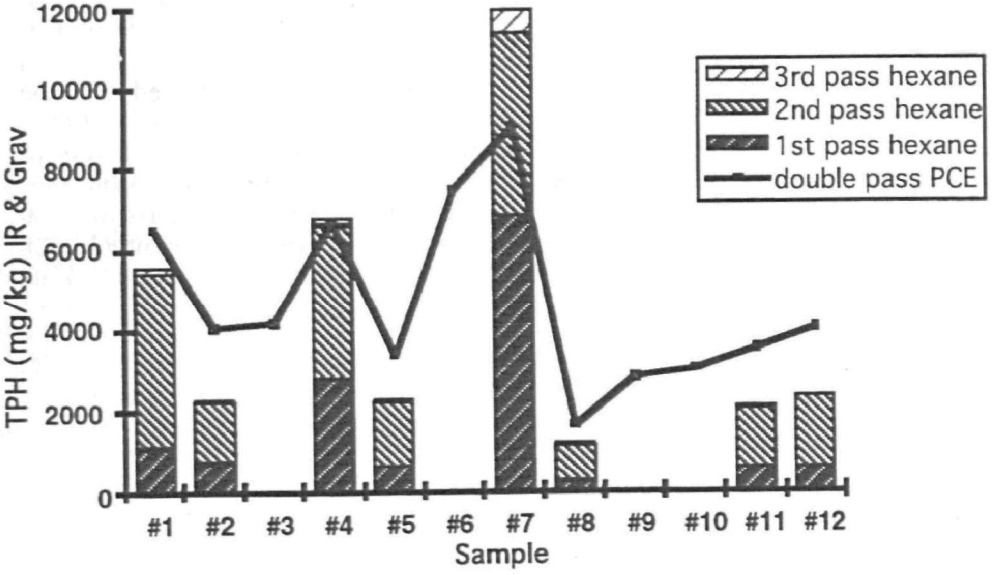

Figure 5 Comparison of Wet Clay ASE TPH Results for Gravimetric and IR Analysis

Figure 6 summarizes the results from Soxhlet extraction with Freon-113® and IR analysis, ASE extraction with PCE and IR analysis and ASE extraction with hexane and gravimetric analysis. The trends in the analytical data are similar but are sufficiently different to demonstrate that the three combinations of extraction and analysis methods are not likely to produce equivalent results for all samples.

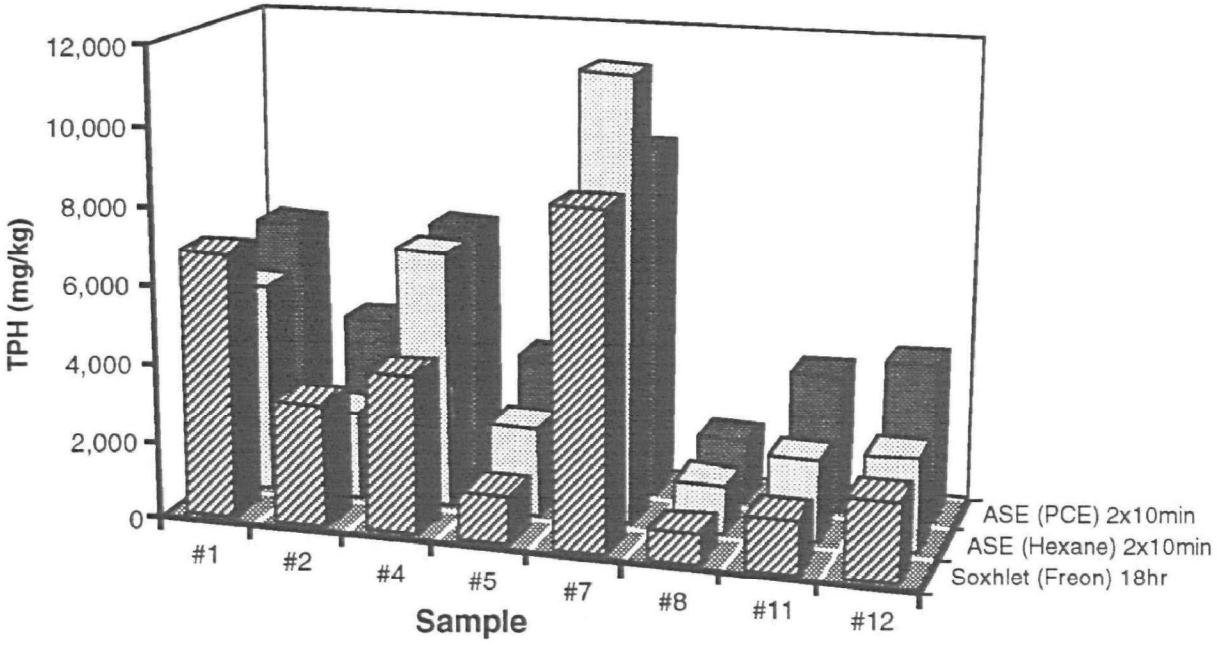

Figure 6 Summary of Wet Clay TPH Results for ASE IR & Grav and Soxhlet IR

CONCLUSION

ASE extraction efficiency is generally equivalent or better than the traditional Soxhlet techniques. A single 10 minute, 200°C extraction is sufficient for most soil samples. The difficult to extract wet clay samples require two extraction passes at 200°C to complete the extraction. The ASE PCE-IR results are similar but not equivalent to the ASE hexane-gravimetric results. There do not appear to be any replacement solvents or methods which will produce equivalent results to the Soxhlet extraction with Freon-113® followed by IR analysis for all sample types. Since Freon-113® is being phased out changes to alternative solvents/methods will necessitate changes in the way the data are interpreted and used.

ACKNOWLEDGMENTS

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EVALUATION OF SOLID PHASE EXTRACTION FOLLOWED BY SUPERCRITICAL FLUID ELUTION OF SEMI-VOLATILE ORGANIC COMPOUNDS IN TOXICITY CHARACTERISTIC LEACHATES.

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ABSTRACT

The Environmental Protection Agency (EPA) developed the toxicity characteristic leaching procedure (TCLP) to determine the potential for unknown wastes to leach hazardous constituents into the environment. Current methods being used for the extraction of semi-volatile organic compounds from aqueous TCLP leachates involve acid/base partitioning into methylene chloride. The concentrated extract is then analyzed by gas chromatography/mass spectrometry (GC/MS). Continuous liquid/liquid extractions require up to 48 hours for completion and consume up to 500 mls of methylene chloride. Separatory funnel extractions are faster and require less solvent but are labor intensive and prone to forming emulsions, resulting in poor recoveries. Ironically, the wastes generated from these extractions are themselves a listed hazardous waste. Methylene chloride has also been targeted for production elimination due to its ozone depleting properties.(1) Considering the hazards associated with exposure to chlorinated solvents and the disposal costs of methylene chloride wastes, great interest has been elicited by the EPA in other extraction techniques which would reduce the volume of solvent wastes being generated by environmental laboratories. A hyphenated technique utilizing solid phase extraction (SPE) followed by elution with supercritical fluid carbon dioxide (SFE) has been developed. Method development included the optimization of both the SPE and SF elution variables. The modified method has been found to show comparable detection limits, accuracy, and precision for most of the TCLP compounds while drastically decreasing extraction time and virtually eliminating methylene chloride. Comparison of SPE/SFE extractions of fortified TCLP leachate solutions with currently used extraction procedures have been compared.

INTRODUCTION

Two extraction methods which offer the benefit of reduced solvent consumption are liquid-solid extraction or solid-phase extraction (SPE) and supercritical fluid extraction (SFE). In addition to reducing the amount of methylene chloride being used, these two methods may also offer drastically reduced extraction times, and reduction in the manual labor involved with liquid solvent extraction procedures.

Solid phase extraction has been widely used in environmental applications where a preconcentration and/or an isolation step is required prior to analysis. Reversed phase sorbents are the most applicable for extracting organic compounds from aqueous samples, with a variety of reversed phase sorbents available. Alkyl bonded silica's such as C_{18} and C_8 have been shown to exhibit quantitative extraction capabilities for large non-polar compounds such as polycyclic aromatic hydrocarbons (PAH) (2) and polychlorinated biphenyls (PCB) (3). However, polymeric sorbents such as styrene-divinyl benzene (SDVB) have been shown to exhibit retention values 20-40 times higher than C_{18} for moderately polar compounds in aqueous samples (4,5). Recent advances in solid phase technology has produced the solid phase extraction disks (6,7). The solid phase Empore™ disks were first introduced by 3M (St. Paul, MN) in 1990. The characteristics of a smaller particle size with a high surface area, combined with a uniform particle distribution within

the disk, results in extremely high flow capabilities while maintaining extraction efficiencies comparable to or exceeding conventional solid phase extraction cartridges. Solid phase extraction disks have already been examined for a variety of environmental applications and will also be utilized in proposed hazardous waste method 3535 in the up-coming third update of SW-846 (8). Other methods for wastewater and hazardous waste using solid phase disk extraction are currently being reviewed for validation by the EPA.

Supercritical fluid extraction (SFE) is an additional analytical technique which is being heavily evaluated by the EPA as a replacement for classical methods using liquid solvents. Supercritical fluids have intermediate properties of liquids and gases, providing perhaps the most influential characteristic of SFE; very high mass transfer capabilities. With viscosity's similar to that of gases and solute diffusivities higher than that of liquid solvents, supercritical fluids show much faster extraction kinetics than conventional liquid solvent extraction techniques. While CO_2 is the most commonly used fluid due to its mild critical constants (73 atm @ 31^0 C), the addition of polar modifiers is usually used to aid in increasing the extraction efficiencies of more polar compounds. SFE has been limited to mostly solid and semi-solid matrices. SFE applications for the direct extraction of organic compounds in aqueous matrices have been slow to gain acceptance. Although Hedrick and Taylor (9,10) have demonstrated the extraction of organic compounds directly from aqueous samples, only small sample volumes could be extracted. The mobility of the water through the extraction cell to the restictor outlet can result in restrictor plugging. A more widely accepted approach for extracting organic compounds from aqueous samples using SFE is performed by first immobilizing the analyte(s) on a stationary support and then extracting the support using SFE. This type of technique using solid phase extraction coupled to supercritical fluid elution (SPE/SFE) has also been used for the extraction and measurement of organics in aqueous matrices.(11) Recently, Messer and Taylor (12) reported the use of 47-mm C18 disks for the recovery of trace semivolatile analytes from water using a three step, acetone-modified SFE-CO2 elution technique. Quantitative recovery of over 90% of the EPA Method 525.1 analytes, including PNA's, PCB's, phthalates, and orgonochlorine pesticides (OCP's) were determined in fortified reagent water with the majority of the RSD's found to be below 15%.

In the following study, a method has been developed for the extraction of the TCLP-regulated semivolatile compounds in TCLP leachates by isolating the compounds onto a solid phase extraction disk followed by elution with modified supercritical fluid CO_2. The procedure required that the optimization of both the solid phase extraction and the supercritical fluid elution be examined separately. The two phases of solid disk extraction followed by supercritical fluid elution were sequentially evaluated, optimized, and then combined. This strategy simplified the approach by reducing the number of co-variate parameters involved when integrating the two methods. The main goal of the extraction procedure was to quantitatively recover the TCLP semi-volatile compounds from TCLP leachates while minimizing the amount of hazardous waste produced. Further requirements of the method that were deemed essential were that the extraction procedure must meet the detection limits, recoveries, and additional QC requirements mandated using current protocols. The extraction procedure was found to be completely compatible with the current method of quantitation (M8270) using gas chromatography/mass spectrometry (GC/MS).

Optimization of Solid Phase Extraction. Initial experimentation was performed to maximize the retention of the TCLP analytes on the solid phase extraction disk. The first portion of the SPE optimization was to establish the type of solid phase disk which had the highest retention for the TCLP analytes. Afterwards, optimum conditions of pH and ionic strength were evaluated as well. Determination of the capacity factor of the solid phase disk was also performed in order to prevent analyte loss when filtering larger volumes of the fortified leachate. A mass balance determination of eluent and filtrate extracts was also performed using all of the optimized conditions as a confirmation of the solid phase extraction efficiency.

Optimization of Supercritical Fluid CO_2 as an Elution Solvent. A Suprex Prepmaster supercritical fluid extractor with Accutrap module for sub-ambient trapping of the analytes was used for all SF-elutions. Evaluation of the trap desorption (efficiency of solvent elution of the compounds from the trap) was the initial task at hand. This was performed by spiking the top of the solid trapping material with the TCLP targets and surrogates prior to sealing the trap. After inserting the trap into the Accutrap module, solvent was pumped through the trap at 1 ml increments and collected into separate 2-ml autosampler vials until a total volume of 10 mls had been eluted through the trap. This initial procedure established the optimum type and amount elution solvent required for quantitative removal of the compounds from the trap. The next step in optimizing the trapping procedure was to evaluate the isolation of the compounds from the decompressing fluid onto the solid trapping media. A 1 gram portion of hydromatrix was fortified with the TCLP target and surrogate compounds prior to dynamic supercritical fluid extraction. The trap was rinsed with solvent after 10 volumes (10mls as fluid) of CO_2 had been used. This procedure was repeated using several trapping temperatures and flow rates. After the optimization of trapping and collection had been completed, the optimum conditions for supercritical fluid elution of the TCLP compounds and the related surrogates from a solid phase extraction disk were investigated. For this portion of the study, 47-mm disks using the previously determined, optimized-SPE conditions were used. The TCLP and associated surrogates were spiked at 50ug each into 50 ml aliquots of TCLP extraction fluid prior to filtering through the disk. The disk was then dried prior to SF elution. Disks were either dried by vacuum directly on the filtration assembly or by pressure drying using nitrogen gas. Pressure drying was performed by placing the disk between two stainless steel support screens which were then placed into a stainless steel zero headspace extraction assembly or ZHE (Associated Design and manufacturing, Alexandria, VA). Optimization of SF elution required evaluation of pressure, temperature, modifier addition, and volume of fluid required. The CO_2 flow rate was adjusted manually by manipulation of the expansion fitting on the Duraflow restrictor while modifier was injected directly into the extraction vessel prior to extraction. All other extraction variables were manipulated via direct programming of the extractor unit.

RESULTS AND DISCUSSION

Solid Phase Extraction. The initial evaluation of which phase of these two would be more efficient at retaining the TCLP analytes is summarized in figure1. The absolute peak areas were used as indicators of disk performance. 47-mm disks were used for extraction of TCLP leachates fortified with 50ug of the TCLP semi-volatile compounds prior to solvent elution with 1:4 ethyl acetate/methylene chloride. Quantitative recoveries were not of concern at this point in that other optimization variables had not yet been investigated. Overall extraction efficiencies were higher for the SDVB disk for most compounds. The SDVB disks showed surprising increases in extraction efficiences for the nitro-containing compounds relative to the C18 disks. A 24% and 28% increase in recovery for nitrobenzene and 2,4-dinitrotoluene respectively, were found using the SDVB disks. The strong electron withdrawing nitro-groups favor delocalization of the aromatic pi-electrons through resonance and inductive effects. This results in an increased pi-electron cloud area which may increase the availability of pi-pi interactions with the aromatic moiety of the SDVB ligand. In contrast, an almost quantitative loss of pyridine was observed using both disks. Effects of pH and ionic strength on extraction efficiencies were also evaluated. The salting-out caused by the addition of 10% NaCl resulted in an increase in the recoveries of all of the compounds. A significant increase in recoveries for the phenolic compounds was observed when

the pH of the extraction fluid was decreased. The lowered pH ensures that the acidic compounds exist mainly in their unionized forms, with a subsequent reduction in water solubility. The decrease in pH is especially important for pentachlorophenol; the most acidic of the phenolic compounds (pKa 4.9).

The data in table 1 shows the recoveries of the TCLP targets and base/neutral surrogates spiked at 100ug and acid surrogates spiked at 200 ug, in 50, 100, 250, and 500 mls of extraction fluid filtered through 90 mm SDVB disks. The non-polar, neutral organic compounds were found to have little break through. Conversely, some of the more polar compounds showed rapid break through between 250 and 500 mls of sample filtered. Establishment of the breakthrough volume is particularly critical here considering that a final extract volume of 1 ml results in a considerable concentration factor. This concentration factor will play an important role in maintaining method detection limits below the regulatory limits of the TCLP compounds. A mass balance evaluation was performed as a final evaluation of the effectiveness of the 90 mm SDVB disk using all of the optimized conditions and summarized in table 2. As was expected, a quantitative recovery of pyridine was recovered from the filtrate indicating that the sorbent failed to retain this compound. Poor retention was also found to be responsible for the discrepancies for the two acidic surrogates; phenol-d6 and 2-fluorophenol. A mass balance for each of the other compounds showed discrepancies to be within experimental error except for 1,4-dichlorobenzene and hexachlorobutadiene.

Supercritical Fluid Elution. Evaluation of trapping efficiencies for the TCLP analytes from a fortified inert solid (hydromatrix) are summarized in figures 2 and 3. Desorption from the trap was performed by gentle heating of the trap followed by rinsing with an appropriate solvent. A minimum trapping temperature of -5^0 C was needed in order to obtain quantitative recoveries for 1,4-dichlorobenzene and hexachloroethane while a trapping temperature of -20^0 C was required to achieve a semi-quantitative recovery of 86% for pyridine. The extreme trapping conditions required for pyridine recovery is believed to be due to the combined effects of its high vapor pressure and poor adsorption on the trapping media. The other compounds were quantitatively recovered at slightly higher temperatures although precision decreased with increasing trap temperatures for most compounds. Initial poor recoveries for some of the phenolic compounds were recovered upon an addition of a methanol modifier. Subsequently, a methanol modifier concentration of 3% was added directly to the extraction vessel prior to extraction. SFE extraction conditions of pressure and temperature were selected at 450atm and 50^{0}C to maintain high fluid densities at lower temperatures. Temperature limitations were mandated due to disk degradation and water plugging considerations. The conditions of lower temperatures and higher pressures equated to higher solvent densities which increased the solvating power of the fluid, decreased restrictor plugging, and decreased the potential of thermal degradation of analytes. The length of extraction time or total amount of fluid used was found to be vital to quantitative recoveries of analytes, with 3 to 4 extraction vessel volumes usually found to be sufficient to quantitatively sweep solubilized species from the vessel. A summary of the final, optimized conditions for the solid phase extraction and supercritical fluid elution procedures are given in tables 3a and 3b respectively.

CONCLUSIONS

Final evaluation of the optimized procedure is summarized in tables 4,5, and 6. A recovery comparison using typical liquid solvent extraction procedures on fortified TCLP leachates to the solid phase extraction procedure followed by solvent elution and SF-elution is found in table 4. The solid phase techniques were found to be comparable to the liquid solvent procedures for all of the TCLP semi-volatiles and surrogates except for pyridine. The optimized SPE/SFE procedure showed the greatest reduction in the extraction time and amount of solvent required. The

procedure was also found to show acceptable surrogate recoveries relative to current method QC requirements. Finally, a series of fortified samples were extracted at the 5ug level to determine the method detection limit. The calculated values are given in table 6 which show that the modified method not only met the quantification levels relative to the regulatory limits, but showed comparable detection limits relative to the liquid techniques as well.

The failure of the solid phase extraction to isolate pyridine realizes the importance of further evaluation of additional solid phase sorbents. As a matter of logistics, one disk with the capability of simultaneously extracting all of the semi-volatile compounds is preferable. To augment this study, current research is being performed on actual leachates using the modified method in order to evaluate if the method is robust enough for leachates with high organic loading. Finally, direct coupling of the supercritical fluid eluent to the GC inlet of the chromatographic system is the desired end-product. The future on-line method will allow for an extremely fast extraction, separation, identification, and quantitation procedure with a greater sensitivity and will literally eliminate the need for solvent.

ACKNOWLEDGEMENTS

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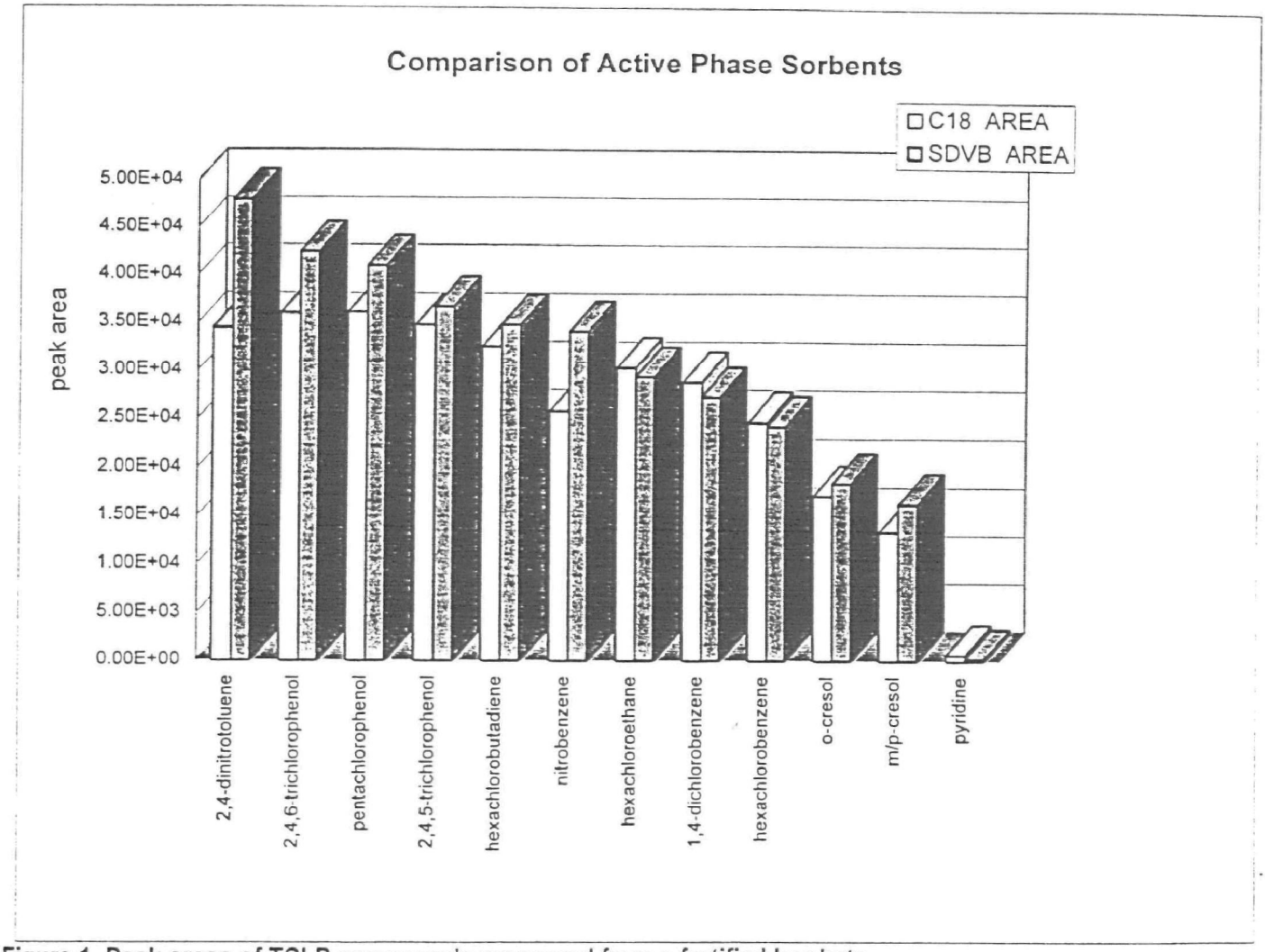

Figure 1. Peak areas of TCLP compounds recovered from a fortified leachate. Extractions performed on 47-mm disks with 1:4 ethyl acetate/methylene chloride used as the elution solvent.

TABLE 1 EXTRACTION EFFICIENCES OF 90MM SDVB DISKS

	% RECOVERY AS VOLUME FILTERED (MLS)			
BASE/NEUTRALS	50	100	250	500
Nitrobenzene-d5 (Surrogate)	89.2	84.6	82.6	78
Nitrobenzene	92.4	88.2	78.2	76
2-Fluorobiphenyl (Surrogate)	85.7	85.4	76.7	81
Terprenyl-d14 (Surrogate)	113.8	104.9	108.7	101
1,4-Dichlorobenzene	87.4	83.1	77	65
Hexachloroethane	80.8	76.5	75	65
Hexachlorobutadiene	81.7	78.8	76	77
2,4-Dinitrotoluene	98.7	95.5	96.6	76
Hexachlorobenzene	97.3	87.5	85	65
Pyridine	5.4	3	3.1	-
ACIDS				
2-Fluorophenol (Surrogate)	79.5	76.7	66.7	37
Phenol-d6 (Surrogate)	66.1	55.1	45.1	21
O-Cresol	86	80	76.8	37
M/P-Cresol	82.3	75.5	72.2	33
2,4,6-Trochlorophenol	99.8	75.8	68.5	53
2,4,5-Trichlorophenol	88.7	77.6	72.3	47
2,4,6-Tribromophenol (Surrogate)	99.3	93.8	83.5	74
Pentachlorophenol	99	94.8	89	75

Acid surrogates were spiked at 200ug, Base/neutral surrogates and TCLP compounds spiked at 100ug. Solvent elution with 1:4 ethyl acetate/methylene chloride.

Table 2

MASS BALANCE OF SPE

	% recovered 90mm SDVB solvent elution (RSD)	% unretained (recovered from filtrate) (RSD)	% balance
Nitrobenzene-d5 (Surrogate)	82.6(9.1)	12.7(3.7)	4.7
Nitrobenzene	78.2(7.7)	15(5.5)	6.8
2-Fluorobiphenyl (Surrogate)	85.4(5.7)	3.8(7.8)	10.8
Terprenyl-d14 (Surrogate)	108.7(11)	-	-
1,4-Dichlorobenzene	77(11)	3.6(2)	19.4
Hexachloroethane	75(10.4)	20.9(5.5)	4.1
Hexachlorobutadiene	76(5)	<1(6)	24
2,4-Dinitrotoluene	96.6(7.6)	4(3.8)	-
Hexachlorobenzene	84(13.2)	4.1(2)	11.9
Pyridine	3.1(67)	95(13)	1.9
2-Fluorophenol (Surrogate)	66.7(12.7)	30(9)	1.4
Phenol-d6 (Surrogate)	45.1(23)	44(10.1)	10.9
O-Cresol	76.8(9.9)	18.2(6.6)	5
M/P-Cresol	72.2(12.7)	24(4.7)	3.8
2,4,6-Trochlorophenol	68.5(15.6)	21.7(13)	9.8
2,4,5-Trichlorophenol	72.3(8.4)	24.8(8.8)	2.9
2,4,6-Tribromophenol (Surrogate)	83.5(9.6)	11(4.4)	5.5
Pentachlorophenol	89(15)	-	11

Three replicates of 250 ml aliquots of TCLP extraction fluid fortified with 200 ug of acid surrogates, 100 ug of base/neutral surrogates and TCLP target compounds. pH adjusted to 2, 10% w/v NaCl added.

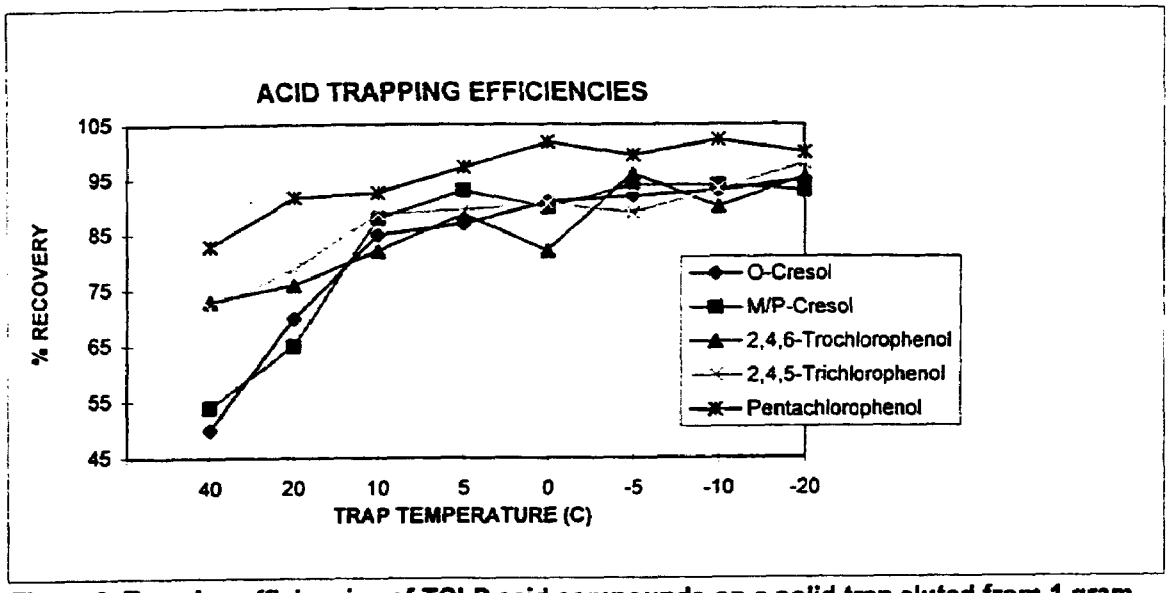

Figure 2. Trapping efficiencies of TCLP acid compounds on a solid trap eluted from 1 gram hydromatrix using 10 mls SFE-CO_2 at 80°C and 300 atm (d=.7495)

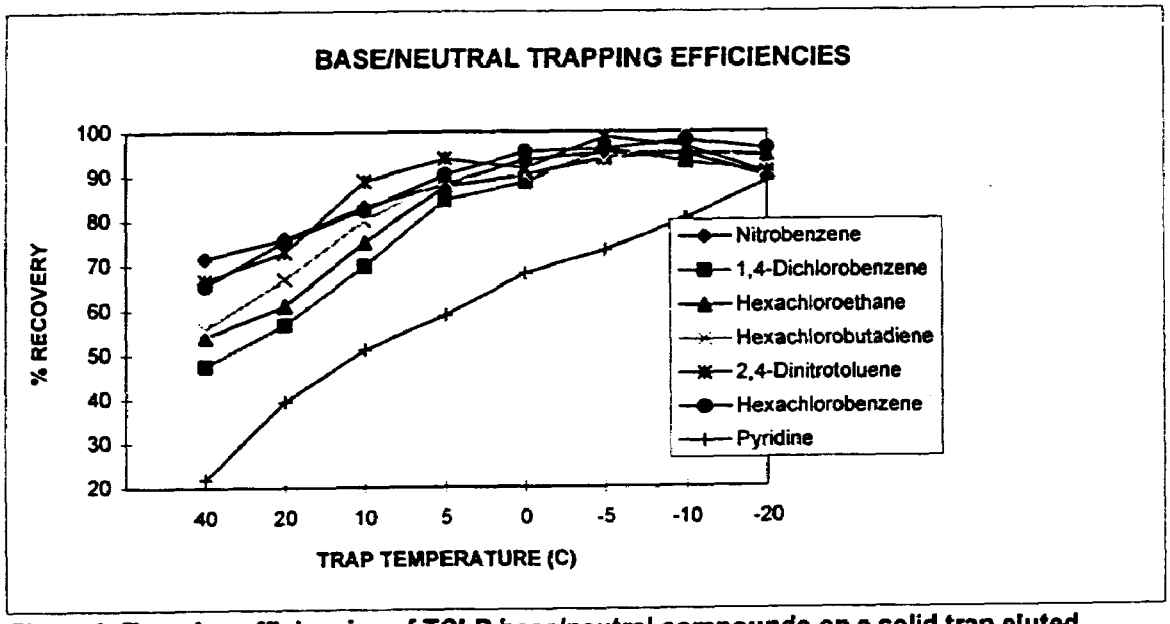

Figure 3. Trapping efficiencies of TCLP base/neutral compounds on a solid trap eluted from 1 gram hydromatrix using 10 mls SFE-CO_2 at 80°C and 300 atm (d=.7495).

Parameter	Values
Sorbent	SDVB Disk
Size	90-mm
Sample Volume	200 mls
Sample Conditions	pH=2, 10% NaCl
Drying	N_2 @ 10 psi, 5 min.

Table 3.a Optimum Conditions for Solid Phase Extraction

Parameter	Values
Extraction Conditions	
Vessel Size	10 ml
Temperature	50 ^{0}C
Pressure	450 atm (psi)
Density	0.987
Extraction Fluid	3% methanol-CO_2
Flow Rate	2 mls/min
Static Time	20 min
Dynamic Time	30 min
Trapping Conditions	
Solid Trap	1:1 Glass Beads/ ENVI-Chrom P
Trap Temperature	-5^{0}C
Restrictor Temp.	50^{0}C
Desorption Conditions	
Rinse Solvent	1.2 mls of 1:4 Ethyl Acetate/CH_2Cl_2
Rinse Flow Rate	1 ml/min
Trap Temperature	40^{0}C

Table 3.b Optimum Conditions for SFE Elution of SDVB Disk

Comparison of Extraction Procedures

% Recovery (RSD)

	90-mm SDVB solvent elution	90-mm SDVB SF elution	Sep. funnel EPA 3510	Cont. Liq./Liq. EPA 3520
O-Cresol	77(8.8)	72(2.2)	79(4.2)	88(3.9)
M/P-Cresol	82(12.1)	78(11.1)	88(9.8)	92(4.8)
2,4,6-Trochlorophenol	89(11.3)	88(2.3)	91(4.6)	88(1.5)
2,4,5-Trichlorophenol	75(8.2)	83(5)	90(5.8)	98(7)
Pentachlorophenol	93(15.4)	91(13.8)	88(10)	92(4.9)
Nitrobenzene	98(7)	108(12.8)	93(8)	102(4.2)
1,4-Dichlorobenzene	79(10.6)	79(5.1)	83(15.5)	90(3)
Hexachloroethane	85(7.8)	88(9.3)	88(5.5)	97(4.9)
Hexachlorobutadiene	83(5.3)	89(6.4)	85(14.7)	89.2(5.8)
2,4-Dinitrotoluene	97(7.1)	90(6.1)	100(2.9)	98(5.2)
Hexachlorobenzene	84(12.7)	82(7)	88(8.3)	94(3.9)
Pyridine	3(67)	n/a	64(14.3)	78(9.5)
Extraction Time	1.3 Hours	50 Minutes	5 Hours	36 Hours
CH_2Cl_2 Required	50 mls	1.2 mls	350 mls	500 mls

Table 4. Extractions of 200 ml, TCLP leachates fortified with 100 ug of base/neutrals, and 200 ug of acids as EPA Certified Reference Standards. (n=7)

Surrogate Recoveries

Surrogate	90-mm SDVB solvent elution	90-mm SDVB SF elution	Sep. funnel EPA 3510	Cont. Liq./Liq. EPA 3520	Recovery Criteria EPA 8270/Water
Nitrobenzene-d5	95.9	91.7	95	95.1	23-120
2-Fluorobiphenyl	86.4	88.4	89.2	98.2	30-115
Terphenyl-d14	108.7	77.5	105	101.4	18-137
Phenol-d6	61.3	69.2	73.7	83.2	24-113
2-Fluorophenol	75.6	78.8	76.1	89	25-121
2,4,6-Tribromophenol	88.3	98.6	100	95.4	19-122

Table 5. Mean surrogate recoveries for extraction procedures. (n=7)
Acid surrogates fortified at a concentration of 200 ug/L
Base/Neutral surrogates fortified at 100 ug/L

CALCULATED METHOD DETECTION LIMITS*
CONCENTRATIONS IN ug/L

	METHOD 3510B SEP. FUNNEL	METHOD 3520B CONT. LIQ./LIQ.	SPE WITH MECL2	SPE/SFE	*REGULATORY LIMIT*
PYRIDINE	71	29	-	-	5000
1,4-DICHLOROBENZENE	21	26	23	29	7500
O-CRESOL	21	27	35	35	200,000
HEXACHLOROETHANE	25	38	32	24	3000
NITROBENZENE	15	16	21	59	2000
M/P-CRESOL	51	42	19	35	200,000
HEXACHLOROBUTADIENE	18	8	27	46	500
2,4,6-TRICHLOROPHENOL	30	17	18	36	2000
2,4,5-TRICHLOROPHENOL	24	26	20	37	400,000
2,4-DINITROTOLUENE	48	27	23	45	130
HEXACHLOROBENZENE	32	16	20	43	130
PENTACHLOROPHENOL	50	70	45	42	100,000

Table 6.
*METHOD DETECTION LIMIT WAS BASED UPON SEVEN, 200-ML REPLICATE ANALYSES OF TCLP EXTRACTION FLUIDS SPIKED WITH 20ug EACH OF BASE/NEUTRAL TARGET COMPOUNDS AND 40ug OF THE ACID TARGET COMPOUNDS.
VALUES WERE CALCULATED BY MULTIPLYING THE STANDARD DEVIATION BY ONE-SIDED STUDENT'S t-VALUES DETERMINED BY N-1 DEGREES OF FREEDOM AT THE 99% CONFIDENCE INTERVAL.

EVALUATION OF THE MICRODISTILLATION METHOD (METHOD 5031) FOR MEASURING VOLATILE WATER-SOLUBLE COMPOUNDS IN PULP MILL TREATMENT INFLUENTS AND EFFLUENTS

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ABSTRACT

A variety of low boiling point, water-soluble compounds are produced as byproducts of the chemical pulping process. Analysis of these compounds has been complicated because they are too soluble to either extract or purge from water. Method 5031 - Microdistillation, which provides a simple method for concentrating these volatile water-soluble compounds from a water matrix, is proposed in the third update of SW-846. This report presents an evaluation of the microdistillation method using GC-FID analysis for analysis of pulp mill wastewater. General method performance was evaluated by determining recovery, precision, sensitivity and the operating range of the method. Specific studies examined the effect of sample pH, sample preservation, storage stability, choice of internal standard, optimization of GC column and injector conditions, and the effect of sample and distillate volume. Of the nineteen compounds studied, seventeen were found to be recovered and quantified with good precision at levels ranging from 5 µg/L to 20,000 µg/L. Several compounds in effluent samples were found to be unstable unless preserved at low pH. Distillation of samples at high pH was found to result in the loss of four compounds. When samples were neutralized before analysis, no loss was observed. The volume of the sample distilled (10 to 40 mL) had an effect on the results, while the volume of distillate collected (0.1 to 0.4 mL) had no observable effect. A summary of QA results and suggestions on how to analyze samples by direct aqueous injection is also presented.

INTRODUCTION

A variety of low boiling point, water-soluble compounds are known to be produced in the kraft pulping process (1). Among those identified, methanol, acetone, and 2-butanone are common and are often present at parts per million concentrations. Many of these compounds have been identified in regulatory statutes such as the Clean Air Act and RCRA. Components of these statutes may require the pulp and paper industry to perform analyses for these compounds in a variety of matrices and at levels in the parts per billion range. For low-level work, purge and trap methods have typically been employed. However, even with the benefit of isotopic dilution (EPA Method 1624), purge and trap methods perform poorly for water-soluble compounds, and for methanol, purge and trap will not work at all. Purge efficiencies are low and can be quite variable depending on sample matrix and purge conditions (2). Solvent extraction methods are not effective for the water-soluble volatile compounds because of the poor partitioning from water into immiscible solvents and volatile loss during solvent concentration steps. Direct aqueous injection is suggested in EPA Methods 8240 and 8260 and has been characterized by several researchers (3,4,5,6), but it has limited sensitivity and is prone to artifacts due to nonvolatile compounds dissolved in water. Therefore, a brief literature survey was conducted to search for alternative analytical approaches capable of yielding reliable low-level data for water-soluble volatiles.

One alternative that shows promise is microdistillation (7), which has been proposed as Method 5031 in the third update of SW-846. Microdistillation removes compounds from the sample which either distill zeotropically at lower boiling points than water (methanol), or that form azeotropes with water that distill below the boiling point of pure water. In the case of compounds present in low concentrations (<1%), it has been found that most of the water-soluble volatile organic compounds are present in the initial milliliter of distillate, resulting in concentration factors of between 70 and 230 for a 40 mL sample (7). As the distillate condenses, most water-soluble organics remain in the condensate, while the hydrophobic volatile organics escape into the atmosphere. This eliminates or reduces interferences from methylsulfides, monoterpenes and chloroform, which are hydrophobic volatile compounds present in some mill wastewaters. The concentrated condensate can be analyzed by direct aqueous injection GC-FID.

NCASI initiated an evaluation of the method as it pertains specifically to influents and effluents of pulp mill treatment systems. The goal of the project was to determine the accuracy, precision, and sensitivity for the target analytes. The presence of artifacts, interferents, matrix effects and sample instabilities was also investigated.

ANALYTICAL OPTIMIZATION

During method evaluation, the chromatographic procedures were optimized. The parameters that were investigated included the columns (megabore DB-Wax and DB-624), and injection parameters (temperature, purge time, and rinse solvent). The DB-Wax column was chosen because of key separations which could not be resolved using the DB-624 column. Target compounds which coeluted using the DB-624 column were: ethyl ether, ethanol, and acrolein; acetonitrile, 2-propanol, and methyl acetate; and 2-butanone and propionitrile. Since some of these analytes are known to be present in pulp mill wastewaters and others were of interest due to lack of data, the DB-624 column was not selected for this study. The DB-Wax column was not very stable and retained the water until midway through the elution of target analytes, but it separated a larger number of the target analytes than the DB-624 column. Only acetonitrile and MIBK were found to coelute using the DB-Wax. Based on the data available from purge and trap analysis, it seemed unlikely that acetonitrile would be detected in the matrices of interest. The DB-Wax column was chosen for this study because it was best suited for the target analytes. Other applications may be better suited by a different column.

The injection of water on the DB-Wax column was found to be critical. Water elutes during the analysis of the target analytes, rather than before as is common with most solvents. The water acts as a moving phase on the column, and selectively affects both the retention time and peak width of the target analytes. The amount of water introduced onto the column was controlled by the injection port temperature and the purge vent time. While conditions were selected to minimize the amount of water on column, some water was necessary to resolve some target analytes. Injecting water with the automatic injector periodically resulted in freezing of the syringe plunger. An organic solvent (dimethyl formamide and, later, ethyl ether) was added as a second rinse to help lubricate the syringe plunger between analyses. At the end of the sequence, a methylene chloride rinse was used to keep the syringe from freezing. Table 1 lists the optimized GC conditions used for the study.

The choice of internal standard for the microdistillation method is critical, because the internal standard is spiked into the sample before distillation. This resultes in correction for standard recovery. Therefore, it is important that recovery of the internal standard correlates well with the recovery of target analytes. During this study 2,2,2-trifluoroethanol, 2,2,2-trichloroethanol, 1-propanol, 2-chloroacetonitrile, methyl heptafluoropropyl ketone, and hexafluoroethanol were tested as internal standards. 1-Propanol was found to work well with effluents, but is a native component in some influents. Methyl heptafluoropropyl ketone and hexafluoroisopropanol were not acceptable because of coelution with methanol and low water solubility, respectively. 2-Chloroacetonitrile elutes well after the target analytes, and an interferent was found in one of the three mill influents tested. 2,2,2-Trifluoroethanol eluted in the middle of the chromatographic run and did not interfere with any target analytes. However, an unidentified interferent was found to be native in five of the eighteen mill influents tested. 2,2,2-Trichloroethanol eluted after all the target analytes and no interferent was found for the three mills checked using this standard. As the method states, each new matrix must be checked for interferences before an internal standard can be used, and it is wise to calibrate with several so a standby is available when interferences are encountered. 2,2,2-Trifluoroethanol was used as an internal standard for most of this study, with 2-chloroacetonitrile used as a backup and surrogate for later studies. 2,2,2-Trichloroethanol is added after distillation and is used as a recovery standard for the internal standard.

METHOD EVALUATION

Microdistillation was performed as described in Method 5031, with the exceptions described in each section below. A collection volume of 300 mL was used because of difficulties encountered with 100 mL

volume collection. The changes were made either to study the effect of the method parameter (e.g. condensate volume) or to optimize the procedure (e.g. preservation techniques).

Distillation Recovery - For the microdistillation method to be effective for a particular compound, a significant percentage of the compound should be distilled and collected in the initial drops of the condensate. The percent of each target compound distilled was calculated by comparing the distilled response to standards prepared without distillation and correcting for the internal standard's absolute recovery. Table 2 lists the recoveries found for each analyte compared with those reported by Bruce (7). The recoveries were similar to those found previously, and the recoveries found for compounds not previously reported were above 20 percent, except for ethyl ether. Ethyl ether was found to give highly variable recoveries, and was eliminated from the target analyte list.

Effects of Sample pH on Microdistillation - Untreated pulp mill wastewaters can be quite variable in pH. Standard preservative techniques for biologically active samples such as pulp mill effluents include pH adjustments. Some of the target analytes are known to be susceptible to hydrolysis when heated at extreme pH. Therefore, the effects of pH on microdistillation were investigated. The native concentrations and matrix spike recoveries were compared for a mill influent analyzed at its native pH of 10.6 and after pH adjustment to 7. The same comparison was made for an influent that was preserved at a pH of 2. The results of this comparison are shown in Table 3. Methyl acetate and ethyl acetate showed a large decrease in matrix spike recovery at pH 10.6 with a smaller decrease found at pH 2. Percent recovery for acrylonitrile and acrolein were found to be lower in the pH 10.6 analysis compared to pH 7, but were not affected by the lowest pH distillation. Acrolein was not recovered well in the pH 7 analysis of the pH 10.6 influent. Native concentrations did not show a significant effect with analysis pH, possibly because compounds that are not stable at extreme pHs are not likely to be found in these influents. Similar experiments were performed for calibration standards using DI water (pH 5), DI water pH adjusted to 7 with strong base, and DI water buffered at pHs 4, 7, and 9.2. The acetate and acrolein recoveries decreased as the pH increased. The levels of methanol and ethanol increased when the acetates decreased.

To prevent both the loss of target analytes due to hydrolysis and the interference of other target analytes such as methanol and ethanol, a neutralization step was added to the procedure to bring the pH to between 6 and 7 using diluted NaOH or H_2SO_4. No neutralization is recommended for preparing standards in DI water. If alkaline water is used for calibration, a pH adjustment should be made when preparing standards.

Storage and Preservation of Samples - Storage and preservation of effluent and influent samples for microdistillation are critical because some of the target analytes are known to be chemically and biologically unstable. Standard volatile collection and storage techniques require storage at 4°C and a sample free of headspace. For biologically active samples, adjustment to pH 2 is recommended. Headspace-free sampling can be difficult to accomplish when samples foam and when adjustment to a specific pH is required. The need for headspace-free samples was investigated, as well as preservation of samples by several methods.

The effect of headspace was investigated by spiking a pH 2 preserved effluent and storing it at 4°C with no headspace, with a 10 percent container volume of headspace, and with a 20 percent container volume of headspace. Each sample was analyzed in duplicate at day one and at day eight. The difference in the recovery at day eight and day one was found to be smaller than the range in the duplicate determinations, which indicated no measurable volatile loss during storage. These results indicate that headspace in the sample for these compounds does not have a significant effect on the analysis.

The need for preservation of samples was demonstrated with a spiked mill effluent stored for 23 days, both preserved at pH 2 and unpreserved . After 23 days of storage, six analytes could not be detected in the unpreserved effluent, and six more analytes' recoveries were less than 40 percent. Acetone recovery increased to 159 percent, while only acrylonitrile and propionitrile had recoveries between 70 and 130

percent. All but three compounds had recoveries between 70 and 130 percent in effluent preserved at pH 2 for 23 days. Acrolein and ethyl acetate had recoveries of 12 and 69 percent, respectively. Methanol recovery was 135 percent, but the methanol spike level was 60 percent of the native level, which would result in a greater variability in the recovery values.

In unpreserved influent after 24 days, three compounds (methyl acetate, acrolein and ethyl acetate) could not be detected, and acrylonitrile recovery was less than 25 percent. All other analytes' recoveries were between 70 and 120 percent. In the pH 2 preserved influent stored for 24 days, all analytes' recoveries were between 70 and 120 percent except acrolein, which was not detected.

Most of the target analytes were not stable in unpreserved effluent, while four of the analytes were not stable in unpreserved influent. Acrolein was not stable under any storage condition in either matrix. It was observed that acetone recovery increased with storage in the unpreserved effluent. Both influents and effluents could be preserved at pH 2 for up to three weeks for all target analytes except acrolein.

Sample Size and Dilution - The concentrations of components found in pulp mill influents and effluents ranged from nondetect to over 100,000 µg/L for methanol. The distillation and GC-FID method was found to be linear over the range of 10 to 200,000 µg/L. However, at the highest concentration, column overloading caused an unacceptable shift in retention times and a loss of compound resolution. A more practical upper response range would be 20,000 µg/L. Because a typical influent has methanol values above this range, a practical method for dilution was needed. The approaches investigated were varying the sample volume, diluting the sample before distilling, and varying the distillate volume. An influent was spiked with the target analytes and three volumes were analyzed (10, 20, and 40 mL), the sample was diluted twice (1:1 and 1:3), and 100, 200, 300, and 400 µL of distillate were collected.

The volume of sample distilled correlated (r^2 >0.95) with the measured concentration for ten of the compounds. Table 4 shows the results of this study. Of the ten analytes that showed a strong correlation, five were found to increase as volume increased, and five decreased. Methanol showed the largest change, with a decrease of 73 percent going from 10 to 40 mL sample size. When samples were diluted and analyzed at 40 mL each, no change in concentration was found except for methanol, which was above the practical range of the method (200,000 µg/L).

Distillate volume is difficult to control because drop size is relatively large compared to volume collected. If distillate volume is a critical factor in the analysis, control of the volume collected must be improved. During this study a volume of 300 µL was routinely collected, rather than the 100 µL specified in the method, to minimize fluctuations in the volume collected. To study the effect of distillate volume, spiked influent was distilled and 100, 200, 300, and 400 µL were collected. A recovery standard was spiked into the distillate to determine the recovery of internal standard at each volume. No concentration change was noticed in the results, but the recovery of the internal standard was 30, 58, 87, and 96 percent for the 100, 200, 300, and 400 µL distillate volumes, respectively. Because internal standard recovery is proportional to the volume collected, sensitivity of the method does not decrease as distillate volume increases up to a volume of 300 µL. Above 300 µL, internal standard recovery is no longer proportional with volume collected, so a dilution of the collected analytes occurs, decreasing the sensitivity of the method. This study shows that the volume collected is not critical between volumes of 100 and 300 µL, and 300 µL was chosen for this study because it was easier to collect.

METHOD PERFORMANCE

The optimized method was used to collect data for 18 mills representing a cross-section of the kraft and sulfite pulp and paper industry. The QA/QC data were compiled for this study to get an indication of the method performance. Sensitivity was determined for a single effluent using two procedures, the method detection limit (MDL) as defined in chapter one of SW-846 and a regression-based detection limit (RBDL) procedure (8). The precision was estimated by pooling duplicate sample analyses for each matrix. Accuracy was determined from percent recovery of matrix spike analyses.

Table 5 shows the detection limits for pulp mill effluent using microdistillation. The MDLs were determined twice, once during the initial method evaluation and again during an evaluation of the RBDL procedure. Effluent from the same mill was used, but the actual samples were collected at different times. Most of the detection limits range from 5 to 50 µg/L, with the higher levels found for the compounds eluting before water. The difference between MDL and RBDL were, in most cases, no greater than a factor of two.

Precision for the effluent and influent was estimated using the standard deviation from duplicate results. Some of the values were based on native levels, while others were based on duplicate spikes. Table 6 lists the relative standard deviations found and the number of duplicate sets used. The relationship between standard deviation and concentration was determined for one effluent sample during the RBDL study. Using this relationship, the relative standard deviation (RSD) at any concentration (C) can be calculated by solving for the equation $RSD = (Ae^{BC})/C$, where A and B are the exponential regression constants given in Table 6. Precision was estimated to be less than 25 percent for all compounds except acrolein. Most compounds had RSDs of less than 10 percent, except compounds that eluted before water, whose RSDs were generally >10 percent.

Method accuracy was evaluated by performing matrix spike experiments. Table 7 shows the mean recovery and standard deviations for effluents and influents. Mean recoveries were found to be within 75 and 125 percent for all target analytes except acrolein. The standard deviations of the recoveries were higher for the influents than for the effluents. The majority of the standard deviations in the effluent were 10 percent or less, while most influent standard deviations were above 20 percent. To investigate the effect of spike concentration on recovery in influent, the results of the RBDL study were used. Multiple spikes of the same effluent were made at levels covering the linear range of the method. Standard additions were used to determine the native level and estimate a true concentration. Most of the target analytes' recoveries fell between 70 and 130 percent recovery, with no observable trend with concentration. Five compounds had values that fell outside the 70 to 130 percent recovery range, and they are plotted in Figure 1. Acrolein shows a trend to lower recoveries at higher concentrations, while the other four compounds' recoveries are scattered. All five of these compounds elute before the water peak in the region where chromatographic performance is less than ideal.

SUMMARY

The microdistillation method provides a sensitive, rugged method for measuring water-soluble volatile organic compounds in pulp mill effluents and influents. Detection limits were found to be in the range of 5 to 50 µg/L, with RSDs of 30 percent or less, and mean recoveries of 75 to 120 percent for the target analytes. Method performance for acrolein and ethyl ether was found to be unacceptable.

Several changes or additions to the method should be made to improve its performance. Samples outside the pH range of 6 to 7 should be adjusted into this range before distillation to prevent the hydrolysis of labile compounds, which results in both poor recovery and addition of the hydrolysis products methanol and ethanol. Samples should be preserved by adjusting the pH to 2.0 and storing at 4°C to prevent both biological activity and chemical reactivity. Distillation volume has been found to be an important variable, and the volume of sample distilled should be the same as the volume of calibration standard distilled. When necessary, samples should be diluted before distillation so that the diluted sample volume distilled is the same as the calibration standards. Distillate volume collected is not a critical parameter, and collection volumes between 100 and 300 µL would result in the same sensitivity, while larger volumes would result in a loss of sensitivity. 2,2,2-Trifluoroethanol was shown to be a good internal standard when no native interferences were present. All new matrices should be screened before selecting an internal standard. Alternative internal standards 2-chloroacetonitrile and 2,2,2-trichloroethanol were shown to be recovered by the distillation process and did not coelute with any target analytes. These standards have been used as backup internal standards/surrogates and as recovery standards for the internal standard for a limited number of samples.

The major source of variability found with the method was due to chromatographic problems encountered with compounds which eluted before the solvent, water. Developing a more rugged chromatographic determination step for the method would provide a more consistent level of data quality for all the analytes.

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TABLE 1 METHOD CONDITIONS FOR MICRODISTILLATION ANALYSIS

Parameter	Setting
Sample Conditions[a]	
Sample storage	pH 2 at 4°C
Sample volume	40 mL
Distillation pH	between 6 and 7
Distillate collection volume	300 µL
GC Conditions	
Injection	Grob splitless, at 110°C with 0.35 purge vent
Column	DB-Wax, 30 m x 0.53 mm i.d. with 1.0 µm film
Carrier	He at 4 mL/min
Oven program	
Initial	10°C for 1 min
Rate 1	20°C/min to 20°C
Rate 2	6°C/min to 120°C
Rate 3	12°C/min to 200°C
Detector	FID with N_2 make-up at 250°C

[a] Unless otherwise specified as part of the experimental plan.

TABLE 2 DISTILLATION RECOVERIES FOR TARGET ANALYTES

Compound	Recovery (%)	
	Measured	Literature[a]
Ethyl ether	16.5	na
Acetaldehyde	21.1	na
Acetone	41.0	na
Methyl acetate	23.7	na
Acrolein	28.7	17
Ethyl acetate	22.6	20
2-Butanone	35.8	na
Methanol	39.9	35
2-Propanol	46.0	na
Ethanol	45.3	na
Acrylonitrile	27.1	28
MIBK	24.0	na
Propionitrile	37.0	48
1,4-Dioxane	33.0	38
Isobutanol	46.1	58
1-Butanol	51.5	58
Cyclohexanone	39.1	na
Acetophenone	38.5	na
2,2,2-Trifluoroethanol[b]	48.5	na

[a] Recoveries reported in reference 7.
[b] Internal standard

TABLE 3 EFFECT OF MICRODISTILLATION PH ON TARGET ANALYTE IN INFLUENTS

Compound	Concentration (mg/L)[a]			
	Mill A		Mill B	
	PH 10.6	PH 7	PH 2	PH 7
Acetaldehyde	2730 (115)	2430 (67)	185 (72)	258 (97)
Acetone	1280 (103)	1160 (85)	690 (98)	861 (99)
Methyl acetate	nd (14)	nd (64)	nd (73)	nd (102)
Acrolein	nd (0)	nd (32)	nd (79)	nd (86)
Ethyl acetate	nd (38)	nd (75)	nd (80)	nd (106)
2-Butanone	498 (105)	469 (87)	273 (55)	323 (56)
Methanol	59200 (89)	68000 (109)	89700 (68)	71400 (67)
2-Propanol	254 (84)	176 (106)	nd (91)	83.8 (86)
Ethanol	2890 (89)	3020 (103)	1710 (73)	1380 (81)
Acrylonitrile	nd (56)	nd (80)	nd (108)	nd (115)
MIBK	18.2 (122)	17.6 (88)	nd (93)	nd (108)
Propionitrile	nd (111)	nd (96)	46.4 (78)	42.9 (100)
1,4-Dioxane	nd (104)	nd (101)	388 (67)	286 (64)
Isobutanol	16.6 (104)	17.5 (100)	nd (73)	nd (85)
1-Butanol	47.3 (112)	49.4 (112)	10.3 (87)	8.7 (84)
Cyclohexanone	24.9 (102)	27.4 (111)	23.9 (62)	19.3 (76)
Acetophenone	21.4 (90)	21.5 (115)	na	na

[a] Matrix spike recoveries as percent are in parenthesis.
na Compound not analyzed.
nd Compound not detected.

TABLE 4 RESULTS OF DISTILLATION VOLUME EXPERIMENT STUDY FOR SPIKED INFLUENT

Compound	Concentration (mg/L)		
	40 mL Sample	20 mL Sample[a]	10 mL Sample
Acetaldehyde	2090	1840 (7.7)	1940
Acetone	3140	2840 (3.8)	2840
Methyl acetate	2310	1960 (3.2)	1940
Acrolein	1920	1700 (6.2)	1690
Ethyl acetate	2400	1980 (0.1)	1850
2-Butanone	2790	2350 (5.3)	2280
Methanol	134000	195000 (14)	232000
Isopropanol	2770	2810 (1.5)	3210
Ethanol	4840	5950 (16)	6120
Acrylonitrile	2210	1870 (3.0)	1810
MIBK	2460	1990 (5.4)	1800
Propionitrile	2320	2170 (3.6)	2140
1,4-Dioxane	2890	4050 (3.0)	4420
Isobutanol	2550	2470 (5.4)	2620
1-Butanol	2690	3800 (6.1)	2920
Cyclohexanone	2550	2970 (7.1)	3100
Acetophenone	2520	2920 (6.6)	3010

[a] Mean value of duplicate with the relative percent difference in parenthesis.

TABLE 5 MICRODISTILLATION DETECTION LIMITS FOR EFFLUENTS

Compound	MDL[a] (mg/L)	MDL[b] (mg/L)	RBDL[c] (µg/L)
Acetaldehyde	20.3	91.0	45.4
Acetone	11.4	34.1	26.6
Methyl acetate	17.7	17.2	35.7
Acrolein	14.5	28.3	na
Ethyl acetate	14.2	21.1	24.8
2-Butanone	7.0	6.9	6.9
Methanol	26.6	na	na
Isopropanol	9.4	8.0	5.9
Ethanol	16.0	8.0	7.8
Acrylonitrile	20.0	3.7	7.6
MIBK	15.2	9.3	7.8
Propionitrile	4.6	5.9	6.1
1-Propanol	na	4.1	5.1
1,4-Dioxane	14.9	9.7	12.8
Isobutanol	3.9[d]	5.4	5.8
1-Butanol	8.5	4.6	6.2
Cyclohexanone	8.9	3.4	6.2
Acetophenone	na	4.8	8.6

[a] Method detection limit as defined in SW-846 determined during method evaluation study.
[b] Method detection limit as defined in SW-846 determined during the regression based detection limit study.
[c] Regression based detection limit as described in reference 8.
[d] Mean concentration was greater than five times the MDL.
na is not available.

TABLE 6 METHOD PRECISION ESTIMATES FROM DUPLICATE RESULTS

Compound	Effluent precision				Influent precision	
	RSD[a]	n[b]	A[c]	B[c]	RSD[a]	n[b]
Acetaldehyde	21.5	7	19.3	.005	4.6	11
Acetone	11.4	8	8.79	.002	4.1	11
Methyl acetate	13.0	4	5.62	.009	8.4	7
Acrolein	na	na	6.50	.011	42.2	8
Ethyl acetate	11.6	4	6.40	.005	9.1	5
2-Butanone	5.3	4	1.85	.010	4.5	11
Methanol	21.7	9	na	na	9.1	11
Isopropanol	2.3	4	1.52	.008	10.9	10
Ethanol	4.4	4	2.64	.011	12.0	11
Acrylonitrile	5.7	4	1.94	.013	5.2	5
MIBK	9.1	4	2.32	.014	14.3	5
Propionitrile	3.5	6	1.53	.010	2.3	9
1,4-Dioxane	10.0	4	3.04	.010	11.9	9
Isobutanol	2.4	4	1.81	.007	1.7	11
1-Butanol	3.9	4	2.08	.008	11.0	11
Cyclohexanone	6.5	4	2.14	.009	14.5	11
Acetophenone	8.0	5	2.86	.011	16.0	6

[a] Relative standard deviation expressed as a percent.
[b] Number of duplicate sets where not all compounds were detected in every sample and some represent spike duplicates.
[c] Regression variables for the exponential regression of standard deviation versus concentration in the form $SD = Ae^{(BC)}$.

TABLE 7 MATRIX SPIKE RECOVERY DATA

Compound	Effluent Recovery Mean (%)	Effluent Recovery SD[a] (%)	Effluent Recovery N[b]	Influent Recovery Mean (%)	Influent Recovery SD[a] (%)	Influent Recovery N[b]
Acetaldehyde	86.9	5.8	7	99.0	21.1	12
Acetone	93.4	9.3	7	89.4	22.8	11
Methyl acetate	75.8	29.5	7	77.6	26.1	12
Acrolein	65.7	36.0	7	32.5	31.4	12
Ethyl acetate	83.1	23.3	7	99.8	21.7	11
2-Butanone	89.2	7.2	7	85.6	24.2	12
Methanol	105	19.4	6	100	32.7	11
Isopropanol	105	11.5	7	83.0	36.3	11
Ethanol	112	8.7	6	88.4	19.1	11
Acrylonitrile	87.8	9.0	6	77.9	28.1	10
MIBK	101	10.0	7	124	35.8	12
Propionitrile	91.5	7.7	7	98.4	9.0	12
1,4-Dioxane	99.6	8.9	7	85.1	27.3	12
Isobutanol	98.4	8.2	7	94.9	15.1	12
1-Butanol	102	10.1	7	92.8	26.1	12
Cyclohexanone	102	11.0	7	96.1	19.2	12
Acetophenone	102	2.7	2	105	8.1	6

[a] Standard deviation expressed as a percent.
[b] Number of recovery determinations.

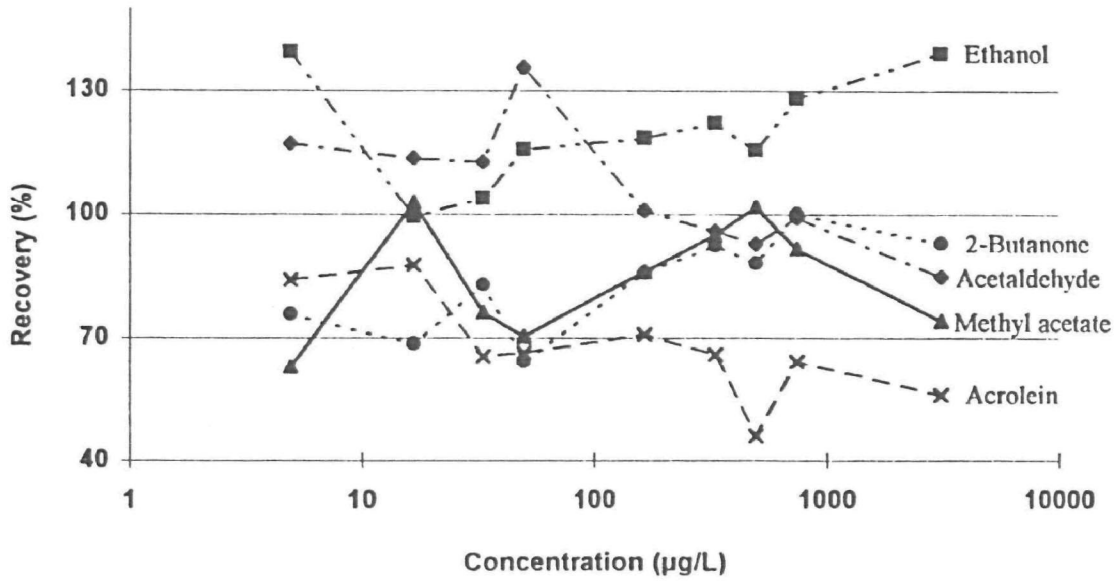

Figure 1 Percent recovery versus concentration for microdistillation for pulp mill effluent

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Extraction of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzo-Furans from Environmental Samples Using Accelerated Solvent Extraction (ASE)

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Method 3545 is a new extraction method that utilizes accelerated solvent extraction (ASE) to perform rapid and efficient extractions of analytes from solid and semi-solid matrices. The method applies to the following analytes: organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), semivolatiles (BNAs), organophosphorus pesticides (OPPs), polycyclic aromatic hydrocarbons (PAHs), and chlorinated herbicides. The only extraction techniques that have applicability and acceptance as broad as ASE are Soxhlet, automated Soxhlet and sonication.

ASE applies temperature and pressure to accelerate extraction processes and improve the efficiency of solvent extraction. Sample extractions can be done faster and with less solvent than by current methods. Since organic solvents are used in ASE, method development can be very rapid, and no significant matrix effect is seen with ASE. This paper reports on a study to compare the results obtained with Soxhlet to those obtained by ASE for various samples containing polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs). Contaminated samples (soil, sediments, chimney brick, urban dust and fly ash) were extracted by ASE and Soxhlet. A review of the data indicates that ASE gives essentially equivalent data to Soxhlet extraction. However, ASE extractions are performed in less time and with less solvent than by the classical extraction techniques (about 15 mL and less than 25 min for 10-g samples by ASE as compared to 250 mL and 18 hours for Soxhlet).

A CONFIRMATORY HOLDING TIME STUDY FOR PURGEABLE VOCS IN WATER SAMPLES

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Abstract

Analyte stability during pre-analytical storage is essential to the accurate quantification of contaminants in environmental samples. This is particularly true for volatile organic compounds (VOCs) which can easily volatilize and/or degrade during sample storage. Recognizing this, regulatory agencies require water samples be collected in vials without headspace and stored at 4°C, and that analyses be conducted within 14 days, even if samples are acid-preserved. Since the selection of a 14-day holding time was largely arbitrary, the appropriateness of this requirement must be re-evaluated. The goal of the study described here was to provide regulatory agencies with the necessary data to extend the maximum holding time for properly preserved VOC water samples to 28 days. An extensive stability experiment was performed on freshly-collected surface water spiked with a suite of 44 purgeable VOCs. The samples were contained in 40-mL glass vials with no headspace, preserved with 250 mg of $NaHSO_4$ and stored at 4°C. For a majority of the 44 VOCs included in this study, concentration changes were <10% of the initial values after 28 days of storage. Maximum holding times calculated from the stability data using the "practical reporting time" approach [Bayne et al., 1994] were predominantly greater than 28 days. This study showed that a 28-day holding time for properly preserved VOC water samples would not jeopardize the measurement of target VOCs. This holding time extension would benefit the regulated community, particularly government agencies with large-scale compliance sampling programs such as the Department of Defense and Department of Energy. The suggested modification of holding times can also improve the efficiency of commercial laboratories through simplified sample management. Application of this study's results to data review would also improve the analytical data validation process by providing an alternative to the currently "one-size-fits-all" accept or reject approach that is very costly but not technically defensible.

Introduction

Analyte stability during pre-analytical storage is essential to the accurate quantification of contaminant levels in environmental samples. This is particularly true for volatile organic compound (VOC) analysis, since some of these target analytes can volatilize and/or degrade during sample storage. To reduce the impact of these transformation mechanisms on VOC analyses, regulatory agencies require that water samples be collected without headspace in 40-mL vials with Teflon-lined septum caps, acidified to pH~2, and stored at 4°C. Furthermore, analytical data are considered valid only if the analyses are conducted within 14 days of sample collection (7 days if samples are not acidified). This maximum

holding time was arbitrarily set and specified in 40CFR Part 136 [1979], and has since been adopted by other regulatory programs and for application to other environmental media [40CFR Part 136, 1984; EPA, 1986]. The appropriateness of this requirement must be re-evaluated since compliance with this 14-day holding time can and has been difficult and costly for sample collectors, data users and analytical laboratories. Recent Superfund Guidance [EPA, 1994] attempts to address the problem by relying on data validators' judgment to assess the impact of missed holding times on analytical measurements. However, this has still led to unequivocal rejection of data when prescribed holding times are missed, and more specific guidance backed by scientific data is needed from regulatory agencies [Bottrell, 1995].

Previous stability studies [Maskarinec et al., 1989; Bottrell et al., 1989] have demonstrated that a majority of purgeable volatile organic compounds in properly preserved VOC water samples (acidified, no headspace, 4°C storage) are stable for time periods well over 14 days. The goal of this study is to confirm these previous studies, as well as to provide regulatory agencies with the necessary data to extend the maximum holding time for properly preserved VOC water samples to 28 days.

Experimental Methods

The stability study was performed on surface water collected from a tributary of the Clinch River in Oak Ridge, TN. Water samples were prepared following the procedure described by Maskarinec et al. [1989]. A clean 3-L Tedlar bag was filled with two liters of surface water. Measured aliquots of VOC standard solutions were injected into the water-filled Tedlar bag through the bag's septum port. The water-filled Tedlar bag was shaken for 1-min, and allowed to equilibrate at room temperature for 20 min. After equilibration, the spiked water was distributed into an appropriate number of pre-cleaned 40-mL VOA vials with Teflon-lined (0.010-in thick) silicone septum caps. Two hundred-fifty milligrams of $NaHSO_4$ were placed in each vial prior to filling. Each vial was completely filled (i.e., with no headspace) and stored at 4°C prior to analysis. Two sets of samples were prepared, one set was spiked to 20-ppb (W1) while a second set was spiked to 200-ppb (W2). At 1, 8, 15, 22, 29, 35, and 71 days after sample preparation, four samples from each set were analyzed for VOCs. Analyses followed the purge-and-trap (PT) method in SW846-8260A [EPA, 1986], except that all calibrations were performed in reagent water that had been acidified to pH~2 with reagent-grade $NaHSO_4$ (resulting pH was 2.4-2.6). Further experimental details are given in a forthcoming report and publications [West et al., 1996].

Results

Regression lines were fitted to the data for concentration vs analysis day (see Table 1 for a select number of compounds). Measurement variability [i.e., relative measurement error (*%RME*)] for each compound within each sample set was estimated as follows:

$$\%RME = \frac{S_o \times 100\%}{C_o}, \quad (1)$$

where S_o is the square root of the mean-square error for the linear regression residuals, and C_o is the extrapolated concentration on Day 0. Calculated values for *%RME* were predominantly less than 15% in both sets W1 and W2, with values being lower in set W1 (20 ppb spike). These low values indicate that scatter in the data was generally minimal, and that concentration trends with time were less likely masked by measurement variability. Such masking of concentration trends may have occurred with *vinyl chloride*, which exhibited the highest %RME in both sample sets (43% and 33%). Statistically insignificant changes in *vinyl chloride* concentration with time may have been due to large measurement variability. However, a statistically significant negative slope was observed in *vinyl acetate* in both sets W1 and W2, despite a relatively large %RME (21% and 29%). For this compound, the concentration change with time was large enough to offset the masking effects of data scatter.

Changes in concentration after 28 days of storage (last column in Table 1) were predominantly low relative to the initial concentrations. Out of 44 analytes, concentration changes exceeded 10% for only three compounds in set W1 [*vinyl acetate* (42%), *cis-1,3-dichloropropene* (11%), and *trans-1,4-dichloro-2-butene* (20%)]. Concentration changes exceeded 10% for a larger number of compounds in set W2, including *trichlorofluoromethane* (15%), *acrolein* (25%), *carbon disulfide* (17%), *vinyl acetate* (42%), *cis-1,3-dichloropropene* (14%), *trans-1,3-dichloropropene* (12%), *tetrachloroethene* (16%), and *trans-1,2-dichloro-2-butene* (26%). For compounds exhibiting non-significant slopes (Table 2), maximum holding times (*MHT*s) were set to 71 days, i.e., the duration of the stability experiment. For compounds with significantly negative slopes, *MHT*s were calculated from the stability data using "practical report time" analysis [Bayne et al. 1994]. Results of the analysis are presented in Table 2; details of the analysis are given in [West et al. 1996]. The compounds were subdivided into 3 groups (see Table 2): (1) VOCs which have *MHT*s greater than 28 days (Group 1), (2) VOCs which have *MHT*s less than 28 days but for which the relative change in concentration on the 28th day was <10% of the initial value, and (3) VOCs which have *MHT*s less than 28 days and the relative change in concentration on the 28th day was >10%.

Table 1. Summary of linear regression on stability data for select compounds.

	No. of data points	Regression parameters		Significant Negative Slope (1-sided 5% significance)	Relative Meas. Error	Change in conc. at 28 days (ppb)	%Change in conc. at 28 days
		Intercept (ppb)	Slope (ppb/day)				
SAMPLE SET W1							
Acetone	16	21.2	0.0124	NO	10%	–	–
Benzene	28	16.1	0.0033	NO	5%	–	–
Carbon disulfide	28	15.2	-0.0501	YES	6%	-1.4	-9%
Carbon tetrachloride	28	16.6	-0.0168	YES	6%	-0.5	-3%
Chlorobenzene	28	16.8	-0.0134	YES	5%	-0.4	-2%
Chloroform	28	18.0	0.0056	NO	6%	–	–
Dichloroethene, trans-1,2-	28	15.6	-0.0211	YES	5%	-0.6	-4%
Methylene chloride	28	17.5	-0.0007	NO	5%	–	–
Pentanone,4-methyl-2-	24	18.3	0.0082	NO	7%	–	–
Styrene	28	17.7	0.0099	NO	12%	–	–
Tetrachloroethene	28	18.1	-0.0654	YES	9%	-1.8	-10%
Toluene	28	15.2	-0.0005	NO	6%	–	–
Trichloroethane, 1,1,1-	28	15.6	0.0034	NO	8%	–	–
Trichloroethene	28	16.9	-0.0103	NO	5%	–	–
Vinyl acetate	20	23.5	-0.3486	YES	21%	-9.8	-42%
Vinyl chloride	24	10.9	0.0915	NO	43%	–	–
Xylene, m,p-	28	37.4	-0.0752	YES	10%	-2.1	-6%
Xylene, o-	28	18.7	-0.0268	NO	11%	–	–
SAMPLE SET W2							
Acetone	16	194.5	-0.2472	NO	9%	–	–
Benzene	27	177.7	-0.2523	NO	10%	–	–
Carbon disulfide	27	200.8	-1.2258	YES	8%	-34.3	-17%
Carbon tetrachloride	27	199.0	-0.6786	YES	13%	-19	-10%
Chlorobenzene	27	182.0	-0.3897	YES	9%	-10.9	-6%
Chloroform	27	194.0	-0.3069	YES	10%	-8.6	-4%
Dichloroethene, trans-1,2-	27	176.5	-0.5698	YES	9%	-16	-9%
Methylene chloride	27	179.3	-0.1591	NO	9%	–	–
Pentanone,4-methyl-2-	23	210.6	-0.0675	NO	5%	–	–
Styrene	27	174.7	-0.6391	YES	5%	-17.9	-10%
Tetrachloroethene	27	166.5	-0.9265	YES	8%	-25.9	-16%
Toluene	27	178.6	-0.1996	NO	16%	–	–
Trichloroethane, 1,1,1-	27	182.3	-0.5152	YES	12%	-14.4	-8%
Trichloroethene	27	193.7	-0.5018	YES	11%	-14.1	-7%
Vinyl acetate	19	235.4	-3.5267	YES	19%	-98.7	-42%
Vinyl chloride	23	144.0	-0.0040	NO	33%	–	–
Xylene, m,p-	27	343.6	-1.1289	YES	7%	-31.6	-9%
Xylene, o-	27	172.2	-0.4257	YES	6%	-11.9	-7%

Table 2. Maximum holding times for compounds in sample sets W1 and W2. Also includes relative change in concentration after 28 days of storage.

Compound	Sample Set W1 (20 ppb spike) Max. holding time (days)	%Change in conc. at 28 days	Sample Set W2 (200 ppb spike) Max. holding time (days)	%Change in conc. at 28 days
Group 1: Max. holding time greater than or equal to 28 days				
Acetone	71	–	71	–
Acrylonitrile	71	–	71	–
Benzene	71	–	71	–
Bromomethane	71	–	71	–
2-Butanone	71	–	71	–
Dichloroethane, 1,1-	71	–	71	–
Dichloroethane,1,2-	71	–	71	–
Dichloroethene, 1,1-	71	–	71	–
Dichloropropane, 1,2-	71	–	71	–
Dibromomethane	71	–	71	–
Pentanone, 4-methyl-2-	71	–	71	–
Tetrachloroethane, 1,1,2,2-	71	–	71	–
Toluene	71	–	71	–
Trichloroethane, 1,1,2-	71	–	71	–
Vinyl chloride	71	–	71	–
Bromodichloromethane	71	–	45	–
Carbon tetrachloride	43	–	28	–
Chlorobenzene	40	–	28	–
Chloroethane	71	–	34	–
Chloroform	71	–	44	–
Trichloroethane,1,1,1-	71	–	30	–
Trichloroethene	71	–	31	–
Methyl iodide	71	–	37	–
Group 2: Max. holding time less 28 days and %change at 28 days < 10%				
Chloromethane	25	-5%	22	-10%
Bromomethane	25	-4%	20	-9%
1,1-Dichloroethene	30	–	23	-10%
trans-1,2-Dichloroethene	24	-4%	20	-9%
Ethylbenzene	40	–	25	-8%
Dibromochloromethane	71	–	14	-6%
m,p-Xylene	36	–	14	-9%
o-Xylene	71	–	17	-7%
Styrene	71	–	9	-10%
Bromoform	71	–	15	-6%
2-Hexanone	71	–	7	-9%
1,2,3-Trichloropropane	71	–	12	-6%
Group 3: Max. holding time less than 28 days and %change at 28 days > 10%				
Trichlorofluoromethane	16	-8%	14	-15%
Acrolein	–	–	4	-25%
Carbon disulfide	13	-9%	9	-17%
Vinyl acetate	10	-42%	9	-42%
cis-1,3-Dichloropropene	12	-11%	13	-14%
trans-1,3-Dichloropropene	17	-9%	16	-12%
Tetrachloroethene	17	-10%	9	-16%
trans-1,4-Dichloro-2-butene	16	-20%	3	-26%

Calculated *MHT*s were very short for some analytes with very low measurement variability, even though concentration changes on the 28th day were relatively small (e.g., styrene in set W2: *%RME* = 5.0%, *MHT* = 9.4 days, %change on the 28th day relative to initial concentration = -10%). In such cases, factors other than calculated *MHT*s should be considered when assessing the effects of holding times on measurement validity. Statistical definitions of significant concentration change, such as the practical report time approach [Bayne et al., 1994], must be complemented with "practical" definitions of "acceptable" concentration change. Ideally, specifications for "acceptable" concentration changes should be tied into the eventual use of the analytical data. For example, "acceptable" concentration changes for analytical data used in quantitative risk assessments can be determined by the sensitivity of the risk assessment results to variations in the input analytical data. Since, the selection of a generic "acceptable" concentration change was beyond the scope of this study, 10% was chosen as a reasonable value to assess the holding time effects on analyses.

Based on calculated *MHT*s and an "acceptable" concentration change of 10% for low-variability analytes, the stability study showed that the measurement of 36 out of 44 purgeable VOCs in properly preserved water samples will not be affected by sample storage for 28 days. Larger changes in concentration (>10%) and low *MHT*s were observed for a few analytes (see Group 3 in Table 2). However, additional analytical problems for some of the latter compounds exist (e.g., inconsistent purging) which can confound the analytical process and which can not be addressed by restricting maximum holding times alone.

Summary

This study demonstrates that a 28-day holding time for properly preserved water samples would not jeopardize the measurement of VOCs. This holding time extension would benefit the regulated community, particularly government agencies with large-scale compliance sampling programs such as the Department of Defense and Department of Energy. Stringent holding times result in logistical difficulties further complicated by additional requirements for sample screening (e.g., for radioactivity). The suggested modification of holding times can also improve the sample through-put of commercial laboratories through simplified sample management. Application to data review of the database generated by this study would also improve the analytical data validation process by providing an alternative to the currently "one-size-fits-all" accept or reject approach that is very costly but not technically defensible.

This study also demonstrated a methodology for conducting a stability study and practical reporting time analysis of the stability data. The latter approach would be useful for establishing site-specific maximum holding times which, depending on the compounds of interest, can be longer than 28 days.

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How to Modify Existing Methods for New Applications.

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ABSTRACT NOT AVAILABLE AT TIME OF PUBLICATION

What To Expect From Immunoassay Methods And How To Obtain Their Benefits

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Abstract

Immunoassay testing can significantly reduce the cost and improve the overall quality of environmental projects when they are integrated into a comprehensive program that includes analytical testing. Unlike traditional methods they are able to generate reliable data within hours of sample collection.

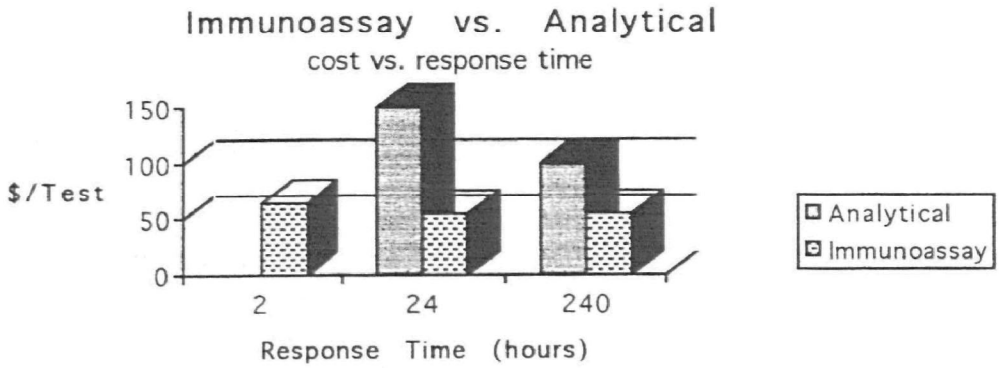
Claims regarding immunoassay simplicity, appropriate applications and general performance vary considerably. Those interested in using these tests must be willing to address the practical issues of labor, net cost calculations, training and product selection. A specialized immunoassay testing center has recently been established (Sylvanus Environmental, Pittsboro, NC) that provides the public a convenient way to access their benefits. Whether through self testing, or the services of a specialized laboratory, immunoassay methods can become the cornerstone of an efficient, state of the art, testing program.

Introduction

More than 50 compound-selective immunoassay methods have been developed by a number of manufacturer's. These tests are used to detect chemicals (e.g. PCB's, PCP, PAH's, TPH, pesticides, herbicides) that may be present in a variety of matrixes (e.g. soil, water, oil, sludge, surfaces). They provide data within hours of sample collection, and because they are portable, can be performed anywhere. They become the method of choice once the identity of a compound(s) has been established.

Immunoassay testing is used to improve the efficiency of site characterization (i.e. mapping), remediation and monitoring activities. They provide the data needed to produce a comprehensive map of a contaminated area rapidly. They can be used to help track a plume of contamination, direct excavation activities, assist in the design of an effective treatment process and monitor the treated waste. They provide the real time data needed to guide drilling activities and are used for the influent/effluent testing associated with drinking water and

industrial wastewater regulations. Once a compound has been identified testing using immunoassay methods if often beneficial. They promote overall project efficiency by providing the rapid data needed to keep field crews and equipment continuously, and productively, occupied. Their lower cost provides more data and improved quality.



Obtaining Immunoassay Benefits

The acceptance of immunoassay methods by the EPA began five year ago when OSW accepted an immunoassay for the detection of pentachlorophenol in water (Method 4010). A comprehensive program to review subsequent method submissions considered beneficial to RCRA activities has also been implemented. Developers submit documentation relating to the regulatory application of a method and justify performance claims with supporting internal validation and external field trial information. The time and resources required to complete the process are considerable, usually taking several years. The quality and reliability of the methods accepted has been well established.

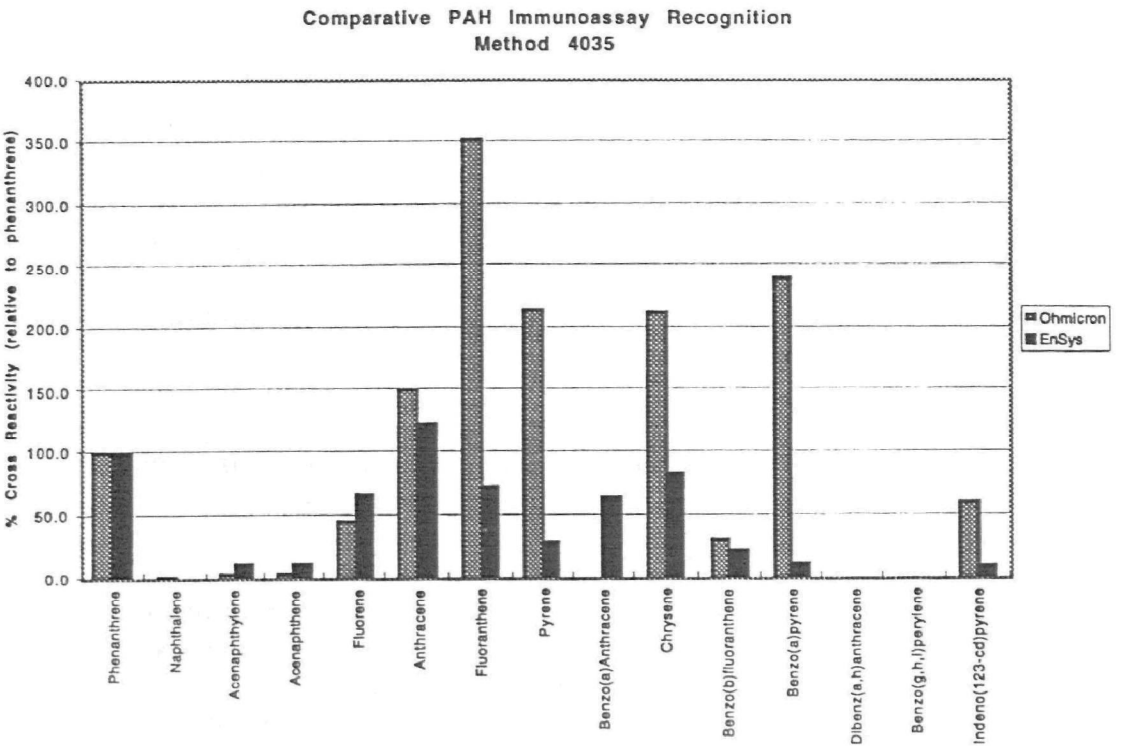
The performance of an EPA-accepted immunoassay method should be consistent with the claims made by the manufacturer in the package insert. EPA acceptance, however, does not suggest that competing products perform equivalently. Different "EPA-accepted " immunoassay methods for the same compound(s) exist (e.g. EnSys RISc PCB, Ohmicron RaPID PCB, EM Science DTech PCB, Millipore Envirogard PCB). They each contain different, and usually proprietary, reagents (i.e. antibody, conjugate, buffers, substrates, etc.) that influence the tests overall sensitivity, specificity, interference's and general performance. An evaluation of the claims made for a method will reveal performance variations that can determine the one that will work best for any given project.

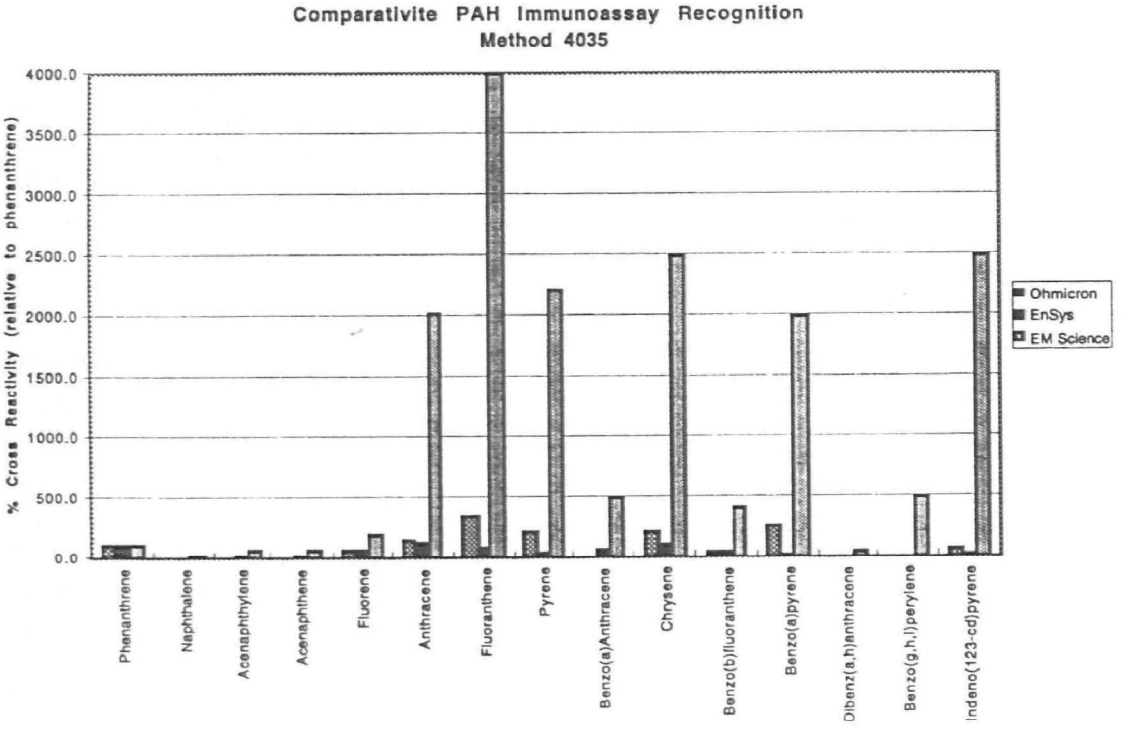
Quantitation and Specificity

Immunoassay methods are by nature quantitative procedures that can accurately and reproducibly quantify substances in a sample. Most of the available tests produce a signal that is inversely, and logarithmically, related to the concentration of the target compound. For example, the higher the PCB concentration in a sample the lower will be the intensity of color produced by the PCB test. By testing a series of reference solutions (i.e. standards), a dose-response curve of optical density (plotted on the ordinate) vs. concentration (plotted on the abscissa) can be developed and used to quantify the concentration of a sample. As an alternative, a single standard containing the compound at, or below, the action level can be tested and used as a comparative reference for the samples. The latter version does not provide the quantitative data of the former, but simply a "contaminated/not contaminated" interpretation at the action level of interest.

The sensitivity of an immunoassay is a function of the binding constant of the antibody population used. The maximum binding affinity of an antibody is approximately 10^{11}L/M. The limit of sensitivity for a competitive immunoassay method (i.e. without ligand concentration) is a function of the mass action equation and limited to approximately 10^{-11} M. Environmental immunoassay methods, because of the relatively small size of the molecules being detected, rarely attain a sensitivity greater than 10^{-8} - 10^{-9} M without prior concentration.

The compound detection profile of an immunoassay is also a function of the antibody used. Each manufacturer uses a proprietary reagent that provides performance unique to their product. The following chart illustrates the comparative detection characteristics of EPA method 4035 for PAH. A knowledge of the target compound and coexisting compound(s) at the site, action level(s) and comparative product performance will help ensure the selection of an appropriate method.


Comparative PAH Immunoassay Recognition
Method 4035
% Cross Reactivity (relative to phenanthrene)
400.0
350.0
300.0
250.0
200.0
150.0
100.0
50.0
0.0
Ohmicron
EnSys
Phenanthrene
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Anthracene
Fluoranthene
Pyrene
Benzo(a)Anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(a)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(123-cd)pyrene


Comparativite PAH Immunoassay Recognition
Method 4035
% Cross Reactivity (relative to phenanthrene)
4000.0
3500.0
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
0.0
Ohmicron
EnSys
EM Science
Phenanthrene
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Anthracene
Fluoranthene
Pyrene
Benzo(a)Anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(a)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(123-cd)pyrene

Immunoassay methods detect substances by means of an antibody binding reaction. Antibody binding can be either highly specific or selective to varying degrees. For example, an immunoassay that uses an antibody that specifically binds xylene(s) will reliably detect xylene to the exclusion of other compounds. An immunoassay using an antibody that detects both xylene(s) and toluene will detect both to differing degrees. If the intent is to specifically quantify xylene, the presence of toluene in the sample will cause a false positive response. The greater the recognition of toluene by the antibody, and the higher the concentration of toluene in the sample, the greater will be this incidence. On the other hand, if toluene is not present at the site the issue of cross reactivity becomes inconsequential and the immunoassay will provide the intended benefit.

Immunoassay methods are specific detection tools. They are used to detect either a single, or structurally-related group, of compounds. They differ from chromatographic methods that can fractionate, identify and quantify a variety of chemicals in a single sample simultaneously. Special care must be taken when using an immunoassay method to detect a family of molecules (e.g. PAH's, PCB's). Immunoassay's for PCB detection do not target a single congenor, but instead recognize the mixture of congenors found in the more highly chlorinated aroclor preparations. The sensitivity of a PCB immunoassay for different aroclors may vary significantly. If a specific aroclor is identified at a site, and other cross-reacting aroclors are absent, the assay can be calibrated appropriately. Similarly weathered aroclor samples can be analyzed if field references are incorporated.

The recognition of different polyaromatic compounds by a PAH immunoassay will also vary. These tests predominantly target the compounds having 3, 4 and 5 rings. They use this collective group of molecules as an indicator of total PAH contamination at a site. If the intent is to use a test to quantify a single PAH compound, reliable data can only be produced if the target compound is the only recognizable specie present in the sample, the assay can be effectively blanked for other detectable species and the test is calibrated appropriately.

Each of the group-specific immunoassay methods (i.e. PCB, PAH, TPH) have a unique detection profile. They need to be calibrated appropriately for the intended target. Positive field samples and field blanks, should be integrated into the testing routine whenever possible. Immunoassay methods from different manufacturer's will differ in their specificity, sensitivity and general performance characteristics.

Obtaining Immunoassay Benefits

Unlike the medical industry, where hundreds of different immunoassay tests are used to detect disease, substance abuse and pregnancy within a $20B/year industry, the amount of environmental immunoassay testing being currently performed is relatively low (i.e. appx. 500,000 tests in 1995). In part this reflects the different ages of the two industries. The medical immunoassay industry has matured over the better part of the twentieth century to a point where immunoassay products are routinely used. Environmental immunoassay technology, for the most part, has emerged this decade. A look at the evolution of the medical diagnostics industry, however, may provide insight into our future with this technology and guidance on the best way to obtain their benefits.

Immunoassay testing for medical applications is performed by trained laboratory professionals and the general public. Hundreds of millions of immunoassay tests are performed each year, but the Food and Drug Administration (FDA) allows the public to perform less than 5% of the methods available (i.e. pregnancy, streptococcus). The FDA mandates that the vast majority of immunoassay testing be performed by experienced professionals. Commercial laboratories, hospitals and doctors office laboratories provide the public rapid, reliable, cost-effective immunoassay data.

While environmental immunoassay methods are less complicated and more portable than analytical testing, claims that infer simplicity comparable to a "home pregnancy test" are exaggerated. Sample matrix heterogeneity dictate that environmental immunoassay tests contain protocols to process aqueous, solid, oily, and mixed wastes. Differing state and federal action levels require that dilution steps be added to address variations in regional regulations. Consider the additional complexity of a pregnancy test if soil had to be analyzed, or if each state had a different definition for pregnancy.

Immunoassay tests contain many components and use protocols that contain numerous steps. Some are sensitive to time, technique and temperature. The user of an immunoassay method must have a basic understanding of the elements that can influence performance. Training is necessary and proficiency should be demonstrated. For those considering the use of a quantitative immunoassay method the statistical conventions applicable to any analytical procedure, and those unique to immunoassay methods, should be understood and incorporated.

The use of a specialized immunoassay testing center (e.g. Sylvanus Environmental, Pittsboro, NC) can simplify the process of obtaining rapid, reliable, cost-effective data. Specialist select and perform the test most appropriate for a project and integrate their benefits into a program that includes the appropriate use of analytical methods. The result of an integrated

program of innovative and traditional testing is the significant reduction in the time and cost required to complete a project. Trained personnel can provide data on-site within hours of sample collection or produce data from a centralized laboratory within a day. The emergence of an immunoassay laboratory removes many of the obstacles that have complicated their use and provides a convenient, practical, way for individuals and corporations to obtain their benefits.

Summary

Immunoassay testing can benefit most programs. On-site testing can benefit projects in remote locations or those that need results within hours. Individuals who perform these methods should become familiar with the technology, proficient with the protocols and review the product claims in order to select the best testing method. The use of a specialized immunoassay laboratory should be considered as a convenient, cost-effective way to gain the benefits of this valuable new technology.

Method 4670: A Quantitative Immunoassay Method for the Determination of Triazine Herbicides as Atrazine

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While immunochemical reactions have been employed in the medical testing community for more than 20 years, recent efforts to expand the utility of immunoassay techniques into environmental testing have met with mixed success. Problems included lack of testing products for environmental contaminants of interest, lack of compound specificity for some testing products, and product formats that yielded semi-quantitative, or screening, results. Manufacturers of immunochemical testing products have worked on resolving these issues, resulting in the first set of EPA immunoassay methods proposed in the SW-846 methods manual from the Office of Solid Waste. These methods, the "4000 Series" methods, are specifically designed as semi-quantitative screening procedures.

The EPA Office of Ground Water and Drinking Water (OGWDW), in conjunction with the Office of Solid Waste (OSW), are about to propose an immunoassay method for Atrazine for use in monitoring compliance with the Safe Drinking Water Act. This method, Method 4670, represents several "firsts" for both OGWDW and OSW. It is the first truly cooperative methods development effort between these two EPA Offices and it represents the first truly quantitative immunoassay method to be proposed by EPA.

The adaptation of a screening immunoassay for quantitative determinations involves a variety of efforts. The testing product developers have to develop a product capable of the accurate and precise determination of the analyte of interest in a given matrix. They must also develop appropriate calibration standards and procedures that are consistent with the fundamentals of the immunochemical techniques. EPA's role has been to not only provide guidance on the matrices of interest, the regulatory levels of concern, and the validation data required, but also to develop written method documentation that incorporates the traditional quality assurance and quality control aspects of EPA methods and provides sufficient information to allow the data user to develop confidence in the results. Given the goals of allowing the use of as many testing products as possible without rewriting the method and minimizing the need for product-specific descriptions in the procedure, the development of the written method is not a trivial task.

In preparing Method 4670, EPA sought to provide the necessary level of quality assurance and written detail in several ways, including:

- Providing general background and guidance on the mechanics of immunoassay testing in the written method.
- Describing the potential limitations of the testing products relative to the intended use.
- Directing the user to product inserts and instructions provided by the manufacturer and reviewed by EPA for the details of the testing procedures.
- Incorporating modifications to the traditional EPA approach to quality control so that the analyst and the user can determine that the results are valid and usable.

Written in EPA's EMMC format and numbered for inclusion in SW-846, both Offices are planning to propose Method 4670 in late 1996. It's primary use will be in SDWA compliance monitoring, but it may find application is ground water monitoring associated with RCRA requirements. EPA hopes that the approach employed in Method 4670 will become the model for the incorporation of additional quantitative immunoassay methods.

METHOD 8085: PESTICIDES BY GC-AED

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Authors: Randy K. Cummings and Robert Rieck, chemists, EPA Region 10 Manchester Laboratory, Port Orchard, Washington; Norman L. Olson and Robert Carrell, chemists, Washington State Department of Ecology Manchester Laboratory, Port Orchard, Washington

ABSTRACT

Current EPA pesticide methodology focuses on a few target analytes using rigorous calibration techniques. Often a great deal of effort is used to demonstrate acceptable multi-point calibrations for compounds not present in the sample. The rigorous calibration techniques may discourage efforts to identify and quantitate non-target detections. Furthermore, the various clean-up procedures used in the methods limit the analysis to a few target compounds. Proposed RCRA's SW-846 Method 8085 specifically uses gas chromatography with atomic emission detection (GC-AED) for the general screening for hetero-atom containing pesticides in environmental samples. The screen monitors for nitrogen, sulfur, iodine, bromine, chlorine, phosphorous and carbon contained in the compounds. A single point calibration of expected pesticides at the limit of quantitation (LOQ) and a special AED compound independent calibration (CIC) mixture are utilized to assure that quantitation levels are met, identify and quantitate compounds detected, and provide dilution factors for further analysis if required. Quantitation of pesticides at levels above the LOQ that do not meet specific CIC criteria may require the use of traditional EPA methodology. Application of this technique is presented.

INTRODUCTION

Currently the EPA uses a myriad of analytical methods to cover the analysis of synthetic pesticides. These methods use an assortment of instruments and detectors. The primary instruments utilized are high performance liquid chromatography (HPLC) and gas chromatography (GC) of which GC is the most commonly used.

Of the available detectors for GC analysis the electron capture detector (ECD), the flame photometric detector (FPD), the nitrogen/phosphorus thermionic detector (NPD), Hall Electrolytic Conductivity Detector (ELCD) and mass selective detectors (MSD) are widely used in the various EPA methods. With the exception of the MSD, these detectors use their selectivity to analyze particular classes of pesticides. For this reason their target compound lists are limited to pesticides containing specific functional groups. The MSD is a universal detector. Its' non-specificity makes investigating every peak in the resulting chromatogram very time consuming and it is usually pursued in a cursory fashion. Thus the MSD is most often limited functionally to a targeted list of pesticides.

In addition to the limited scope of target compounds within each EPA method, these methods have a set of quality assurance/quality control (QA/QC) criteria that include multi point calibrations and rigorous calibration checks. The results obtained using these methods are usually accurate and precise. However, so much effort is put into quality control of a target list that investigation of unknown peaks is often neglected. Therefore the best use of these methods is when the target list of compounds is thoroughly known, i.e. all sources of pesticide contamination have been determined.

Currently a complete analysis for pesticide contamination of an environmental sample may require several EPA methods that cover an assortment of often overlapping pesticide target lists. In a restrictive senerio an investigator or laboratory client will request a "tried and true" method that may not apply to the different pesticide contamination possibilities in his/her samples. Method 8085 uses the selectivity of the atomic emission detector (AED) to screen for and quantitate an extended list of pesticides in an effort to address the previous situations using a single methodology. Where applicable the AED can also be used as the detector for any of the other EPA methods following an initial demonstration of capability.

The AED uniquely offers the combination of the following capabilities not offered by any other detector:

1) Multi-element response,

2) High selectivity for most elements common to pesticides,

3) and, compound independent calibration capability.

METHOD OVERVIEW

Method 8085 is proposed under the EPA's SW 846 RCRA methodologies. It is designed to provide a flexible approach to general pesticide screening in a manner similar to that used by the FDA. A minimum of QA/QC is used for non-detected target compounds whereas detected target and non-target compounds follow the conventional QA/QC requirements of the other EPA methods.

One function of the target list of compounds described in Method 8085 is to furnish information about a wide range of pesticides comprised of differing functional groups. Group characteristics can be used as a way to generalize method applicability. That is, compounds with similar functional groups should generally behave the same within the confines of the method. So even if a compound is not on the method list, method applicability can be assumed -- compound analysis can go beyond a routine list.

The method allows for the most efficient extraction procedures but priority is given to SW-

846 methods. Even with this flexibility, not all compounds that can chromatograph via GC can be extracted from a sample or remain stable during extract cleanup. Therefore, cleanup of the resulting extracts is kept to a minimum until the sample has been screened.

The sample is screened for compounds containing phosphorus, nitrogen, sulfur, iodine, bromine and chlorine. In addition, carbon is monitored for background assessment. These elements are common in most synthetic pesticides. Fluorine, oxygen and other elements can be monitored, if desired, but they require additional analysis steps. Since the AED is very selective to elements even in a difficult background matrix, the analyst has high confidence in the presence of a hetero-atom containing compound. Therefore, more time and effort can be dedicated to investigating or confirming the compound's identification and specific cleanup steps, focusing on isolating the target compound can be implemented. Monitoring the carbon channel aids in peak identification when mass spectral confirmation is desired. Even with the selectivity the AED provides, its use in combination with mass spectrometry optimizes this screening technique.

COMPOUND INDEPENDENT CALIBRATION (CIC)

It has been demonstrated that GC-AED provides a linear response to elements that is independent of molecular structure.(1,2) This phenomenon allows detector calibration based upon elemental response. Thus a compound independent calibration (CIC) mixture is used to calibrate the AED for all the elements of interest.

The suggested CIC mixture described in the method contains 15 compounds, but different CIC mixtures may be used. The compounds in the mixture were chosen for their elemental composition, solvent and GC stability, and retention times. Concentrations of the analytes were adjusted to define the calibration range of the elements determined.

To demonstrate an application of the CIC mix, the calibration curve for element chlorine in the following table shows that the AED response is linear and compound independent. Even though the six compounds describing the curve elute in random concentration order a high degree of linearity (RSD=2.5%) is observed. Area, not peak heights, must be used.

Compound	RT	ng/uL	area(3uL)	ngCl/uL		ERF
1,2,3-Trichlorobenzene	6.157	681.0	49558	4.00		12390
Dichlobenil	7.903	614.0	30648	2.54		12066
Silvex, methyl ester	15.067	40.0	1921	0.15		12807
PCNB	15.350	169.0	12512	1.01		12388
Chlorpyrifos	19.520	568.0	21605	1.72		12561
Decachlorobiphenyl	33.187	49.3	4202	0.351		11971
					AERF	12364
			StdDv	310	RSD	2.5%

The CIC is key to the implementation of Method 8085. Therefore the quality of this standard must be very high. After the CIC standard has been prepared, and during each analysis thereafter, the linearity for each element must be tested. First, the average elemental response factors (AERFs) are calculated for each element by averaging their elemental response factors (ERFs). Second, the standard deviation of the AERF is determined. Last, the relative standard deviation (RSD) is calculated by dividing the standard deviation by the AERF. The linearity, for each element other than phosphorus is considered acceptable if the RSDs are less than 10%. Phosphorus will be discussed in more detail later, but RSDs should be less than or equal to 20%.

The CIC must also be verified against a standard of high confidence. Certified standards from private companies make good reference standards. Most of the elements in the CIC are interrelated through common compounds, thus a standard containing only one element may be sufficient to provide quality assurance for the entire CIC. Once the CIC is verified, it can be used to measure the reliability of most other analytical standards, as well as quantitate analytes. In fact comparison of the single point calibration standard to the CIC is an ongoing part of analysis using Method 8085.

Even though the CIC is a versatile calibration standard, to obtain full quality assurance for an analysis, the compound specific standard (the single point calibration standard) must also be of high quality. Multi-component mixes can be checked internally against the assay of each compound. This provides information about the relative composition of the standard. If all of the components of the mix provide relatively equivalent proportional elemental responses, the only other error likely is the dilution of the entire standard. A dilution error can be checked using the CIC.

THE SINGLE POINT CALIBRATION

Method 8085 employs a single point calibration using several multi-component standard mixes. This single point calibration serves two purposes. The primary aim is to establish a calibration point at the practical quantitation limit (PQL) for a defined target list. The secondary goal is to provide a validation for CIC calculations.

The single point calibration is performed before and after sample analyses. When there is a non-detect of targets, the only purpose of the single point calibrations is to insure that the targets can still be detected. In this case no response criteria is required between the first and last calibrations. By performing the single point calibration, this method provides as much reliability as any EPA method of a compound's absence above a PQL.

A verified CIC mixture is used to calibrate the AED for carbon, phosphorus, sulfur, nitrogen, chlorine, bromine and iodine. Fluorine and oxygen can be calibrated as required. The calibration is used to determine dilution estimates, elemental ratios (empirical formula), or

quantitation. Elemental ratios may be used for compound identification confirmations (along with GC retention time). Quantitation can be made when:

1) the RSDs of the AERFs are less than or equal to 10% (except for phosphorous at 20%),

2) a minimum of five points is used to calculate the AERF,

3) a single point analyte calibration produces an elemental response factor within 20% of the AERF, before and after sample injection and,

4) the elemental concentration falls in the range defined by the CIC.

The GC system should be in a condition to meet all of the above criteria for most compounds on the target list before analysis begins. As a result of chromatographic difficulties some analytes do not always meet the third condition. This is not a problem when the compound(s) is not present in the sample and the minimum quantitation level can be achieved. If a compound is identified in the sample but does not meet the single point calibration criteria for response, then analyte calibration may be required if unqualified data is desired. System performance and degradation can be assessed from CIC comparisons to the single point calibrations. It should be emphasized that no other EPA method need be employed unless a positive detection is made above the PQL and calculations using the CIC cannot be made.

Information about retention time, matrix background, and hetero-atoms present are invaluable for mass spectral investigations of unknowns. If an unknown is identified with relative certainty it can be quantitated using the CIC AERFs. If extraction and GC performance for the compound is unknown, the measurement is only an estimate. However, this method provides the best estimate available without a reference standard.

METHOD DRAWBACKS

Quantitation limit requirements are occasionally too low for the AED to achieve. This is especially true for some of the SW 846-8080 chlorinated pesticides, particularly for Toxaphene and PCBs. In general multi-component analytes are not amenable to CIC calibration techniques. However, that does not preclude analyzing for them. Patterns derived from these analytes are often quite different from those found from ECD analysis, thus providing additional information for their identification.

Sample preparation/analysis methods may need modification if lower detection limits are required, i.e. use larger injection volumes, larger sample sizes, and/or smaller extract

volumes. Such measures can also increase matrix interferences. For instance, tissue samples may not be amenable to the method due to a combination of the lipids present and the low quantitation limits commonly required. Modified sample preparation/analysis techniques tend to concentrate the sample lipids that interfere with the gas chromatography portion of the analysis.

Very often it is the GC portion of the instrument that limits the scope of the method, not the detector.

Multiple injections are required to screen for all desired elements (see table). Each of these injections requires time. If the sample has already been characterized, more definitive methods may be cheaper and easier for a few target compounds.

Injection Sequence (element emission wavelength)

1st injection	2nd injection	3rd injection
193 carbon	478 bromine	186 phosphorous
181 sulfur	479 chlorine	178 phosphorous
174 nitrogen		
206 iodine		

Compounds containing phosphorus usually require extra effort when quantitating using phosphorus emission lines. This is due to bias resulting from interaction of phosphorus with the discharge tube.(3,4) If measures are not taken to reduce the interactions, RSDs for phosphorus may fall outside the CIC calibration criteria. This is because the interactions with the tube yield a disproportionate affect on the lower concentrate standards. Suppression of the tube interactions is required to obtain phosphorus quantitation with minimum bias. For screening purposes suppression of this effect is generally not necessary. However, if required, full suppression can be accomplished with addition of 0.1% gas oil to the standard and sample extracts. Partial suppression is obtained by introducing 2-methyl-naphthalene diffused into helium through the AUX gas line of the AED. But, the use of 2-methyl-naphthalene is not presented in Method 8085.

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VOLATILES PRODUCTIVITY ENHANCEMENT WITH AN XSD® DETECTOR

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ABSTRACT
The XSD is a new halogen specific GC detector based on thermionic emission from an alkali activated platinum electrode when interacting with chlorine, bromine and other halogens. This paper will present comparative results from ELCD and XSD® detectors for spike and real world volatiles samples. GC peak shape will be examined in particular as well as general performance characteristics such as accuracy and precision, linearity, analyte specificity and sensitivity to water. The impact of improved chromatographic performance on productivity measures such as turn-around-time and capacity will also be examined.

INTRODUCTION
Electrolytic conductivity detectors (ELCD) have been used for many years in the GC analysis of volatile organic analytes. Methods 8010 and 8021 list the ELCD as the detector of choice. While the ELCD is more specific than the electron capture detector (ECD), chromatographic performance is degraded by the liquid transfers involved. Thus, short term reproducibility may suffer and raise detection limits. The limited linear range of the detector can require frequent dilutions for common samples. Long term stability is limited and leads to more frequent recalibration than other common GC detectors. Transfer of water from the purge-and-trap system to the GC is a common problem and is particularly troublesome for the ELCD. General sensitivity declines and responses for early eluting compounds are especially impacted. A relatively new detector technology based on thermionic emission (Halogen Specific Detector, XSD®) promises improved performance for analysis of volatile organohalogen compounds based on methods 8010 and 8021.

An OI Analytical application note describes the XSD (1). "The ... XSD is a thermionic device based upon the work of Rice (2) and Roberts (3). The XSD requires a negatively biased platinum electrode (cathode) to be activated by an alkali, which lowers the work function of the platinum metal. Prior combustion is required to oxidize the sample [analytes] to carbon dioxide, water, and halogen atoms. Since halogen atoms are in the gas phase, they exist in an equilibrium towards the dissociated halogen atoms." The signal current is probably generated when halogen species adsorb onto the alkali activated cathode surface, emission of a thermal electron, followed by desorption of a neutral halogen atom or halogen ion or alkali-halide molecule.

Figure 1 shows the principle components of the detector. The GC column effluent is introduced through the jet tube into the reactor core. The analytes are oxidized at high temperature (1000°C) to produce the halogen atoms which interact with the platinum probe. Several types of interactions produce the detector signal which produces the chromatographic peak. The detector is reported to be linear from 10pg to 10ng. From 10ng to 1000ng the calibration response is quadratic (1). The detector is most sensitive to chlorine. Bromine response is about 9X less sensitive than chlorine. Since the XSD detection limits are much lower than required for normal environmental work this is not expected to be a problem.

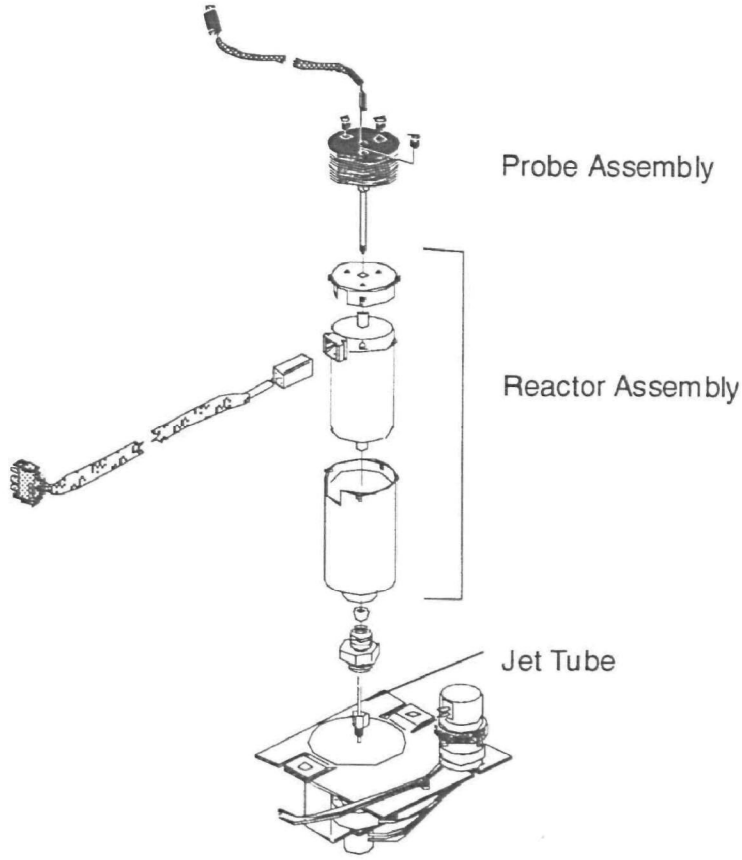

Figure 1 XSD Diagram.

EXPERIMENTAL

A Hewlett Packard 5890 Series II was equipped with both an XSD Model 5360 and an ELCD Model 5220 detectors. The injection port fed into a Valco Y splitter which was connected to two Restek RTX-502.2 105m, 0.53 mm ID, 3 µm film columns. One column was plumbed to the XSD and the other to the ELCD. An OI Analytical Sample Concentrator Model 4560 was used. An Arcon Model 5100 autosampler from Dynatech was attached to the sample concentrator.

RESULTS and DISCUSSION

This paper will present comparative results from ELCD and XSD® detectors for spike and real world samples. GC peak shape will be examined in particular as well as general performance characteristics such as accuracy and precision, linearity, analyte specificity and sensitivity to water. The impact of improved chromatographic performance on productivity measures such as turn-around-time and capacity will also be examined.

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(2) Rice, Chester W. U.S. Patent 2,550,498. June 24, 1951.
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Fast GC Capillary Columns applied to Environmental Separations and Analysis - Screening Methods

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There are some environmental analytical problems which would appear to benefit from additional speed. In some cases, this is a direct enhancement of sample throughput. In others, rapid screening of a potential hazardous sample area can aid in the decisions about the ultimate analysis plan.

Although narrow-bore capillary columns (100-200) have been available for some time, the narrow peak width was almost wasted because the time constant of the GC and GC detector could not keep up. Recently, faster GC equipment has become widely available providing the entire system desired for fast chromatography.

There are several commercial GC systems approaches for fast gas chromatography. They include ; cryofocus with fast desorption, cryogenic cooling and multidimensional separations with rapid column heating, miniaturized (micromachined) isothermal systems and small internal diameter columns with fast temperature programming. In this talk, we will discuss the last approach listed, small ID GC columns with fast temperature programming.

There are specific requirements in the hardware in order to take advantage of the speed and resolution of small ID columns. These requirements are listed in table 1.

Table 1. Requirements for Fast GC columns Screening Methods

Requirement	*Parameter values*
High speed injection	100 millisecond
High inlet pressures	up to 150 psi
Fast oven temperature programming	35-120 degrees per minute
High speed detectors	200 Hertz
High speed data acquisition	1-200 Hertz
Inlet flow conditions	Electronic Pressure Control

The gas chromatography applications presented here include data for the GC of volatile organic compounds (VOC), total petroleum hydrocarbons (TrPH), and organochlorine pesticides. The intent is to present very fast separations in each case to be used for screening methods.

The first example is a separation of 60 VOC's at the 40 ppb level in 10 minutes. This work was carried out with a 10 m X 100 um X 0.34 mm capillary column using the HP 6890 Series GC. The speed is accomplished using electronic pneumatic control (EPC). Both the FID and MSD detectors were utilized. This is seen in Figure 1.

The 100 um column provides a very adequate screening procedure that is perhaps 2-4 times faster than the conventional 250 um ID column. This will be extended to compare with a 25 m X 200 mm X 1.1 um column, with separation of most of the 60 VOCs at the 10 ppb level in 17 minutes. This larger bore, thicker film column provides a sensitivity optimized method especially for the early eluting most volatile compounds particularly for the mass spectral detector.

Figure 2 shows another example of the fast screening separation of the VOCs. In this case, 84 VOCs are separated in 14 minutes. In each of the two examples, the sample was introduced by purge and trap apparatus and the detection device was a GC/MSD. In the more conventional separation on a 250 um ID column where full quantitation would be accomplished, the separation time would be in the order of 35 to 40 minutes under analogous flow and temperature programs with the same phase ratio.

Figure 3 depicts the separation of 44 semi-volatile compounds with a 100 um ID column HP-1 column in 12 minutes. The HP 6890 GC with fast temperature programming and splitless injection utilized the electronic pressure control with constant flow starting at 48 psi inlet pressure.

In Figure 4, the fast screening separation of organochlorine pesticides was carried out in just 6 minutes. A small volume electron capture detector was used in this application. This detector has a wider than usual dynamic range, so quantitation on a 250 um ID column was carried out in the same linear dynamic region.

Finally, in the last chromatogram, Figure 5, we see the group separation of a diesel range of organic compounds resulting from the SFE of a soil sample. The entire group separation was carried out in seven minutes.

We will discuss the advantages of using these small diameter fast columns with the comparative larger ID columns used for the determinative methods. In summary, it will be shown that a current method used for determinations of environmental samples can be used as the templates for scaling to small ID fast GC columns for convenient screening of large numbers of samples in a short period of time. Illustration will be made of a method translation computer program which allows the conversion back and forth between screening methods and determinative methods while maintaining equivalent separation and identical elution order.

Figure 1. 60 VOCs separated in 9.5 minutes

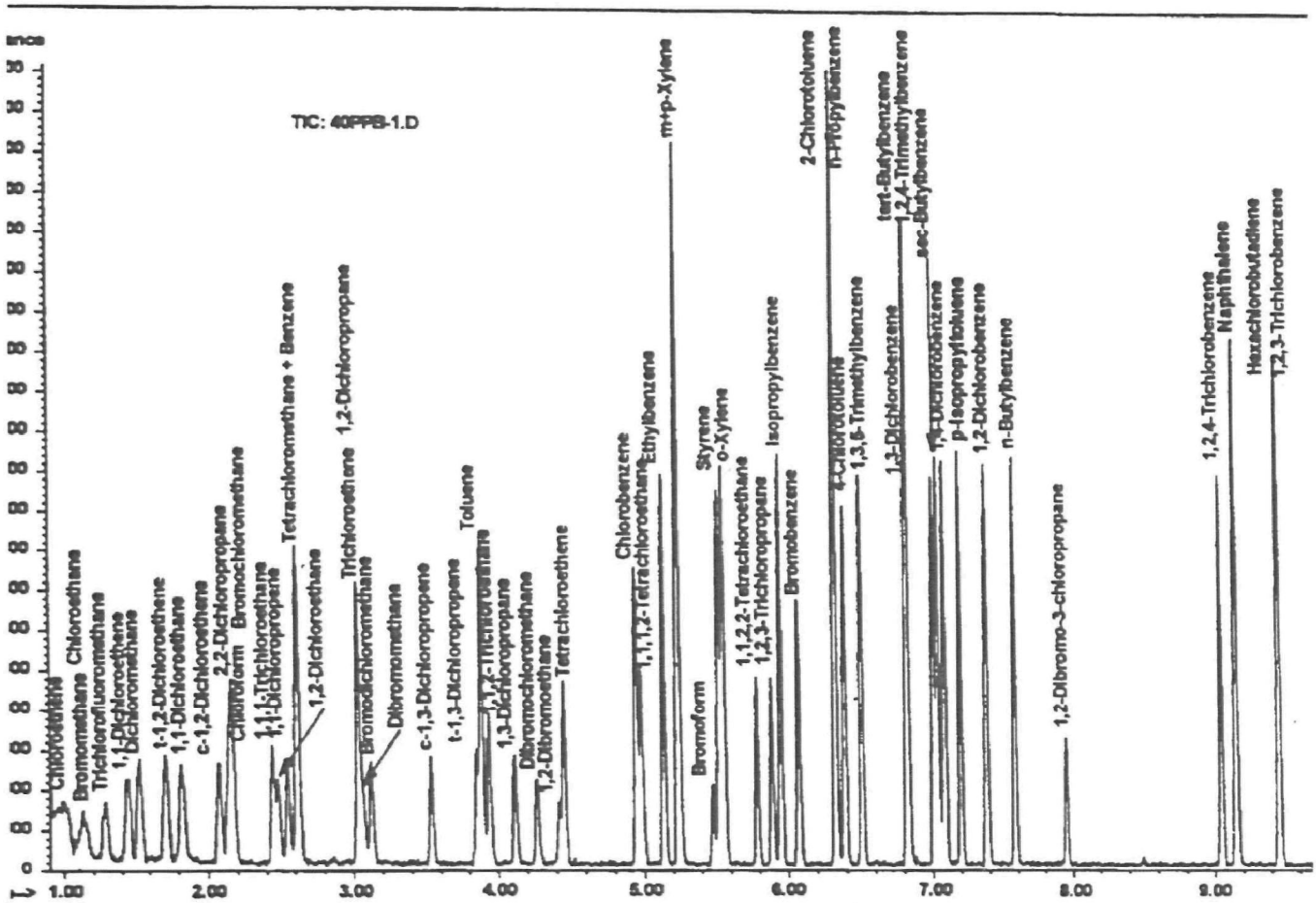


Figure 2. 84 VOCs separated in 14 minutes

Instrument : HP P&T, 5890 GC & 5972 MSD
Sample Name: 84 VOC
30 cm/sec He Carrier

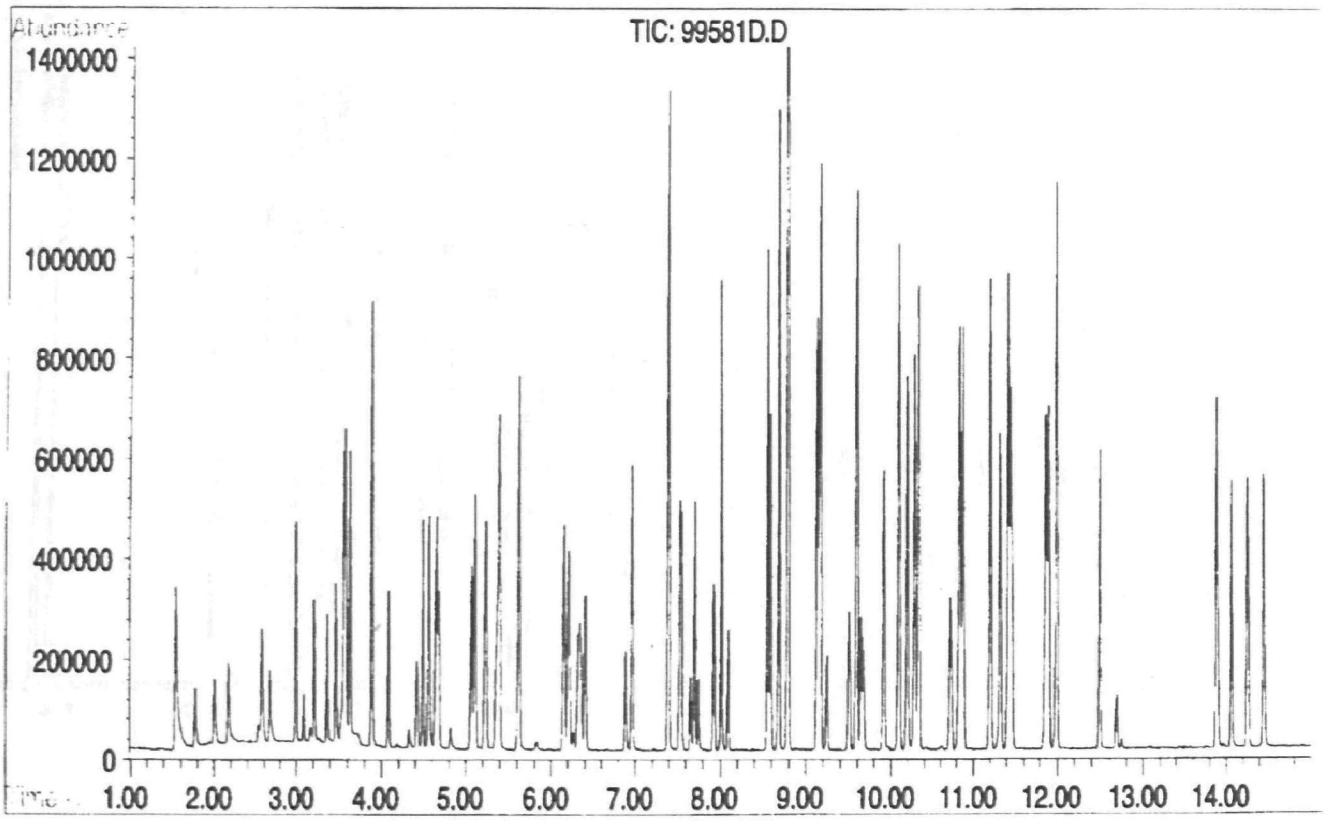


Figure 3.

40 Semi-Volatiles separated in 12 minutes

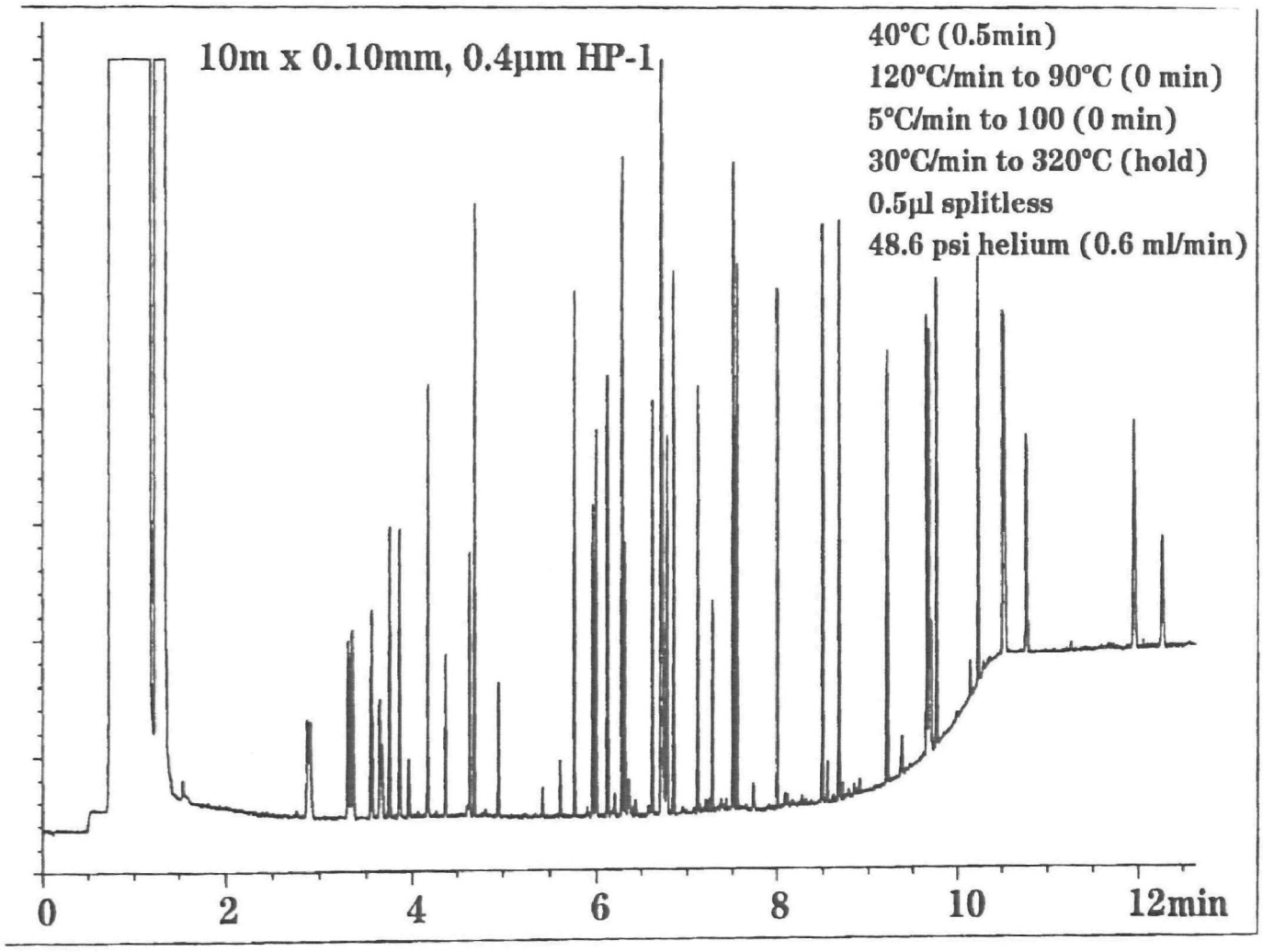


Figure 4. **11 Organo Chlorine Pesticides separated in 6 minutes**

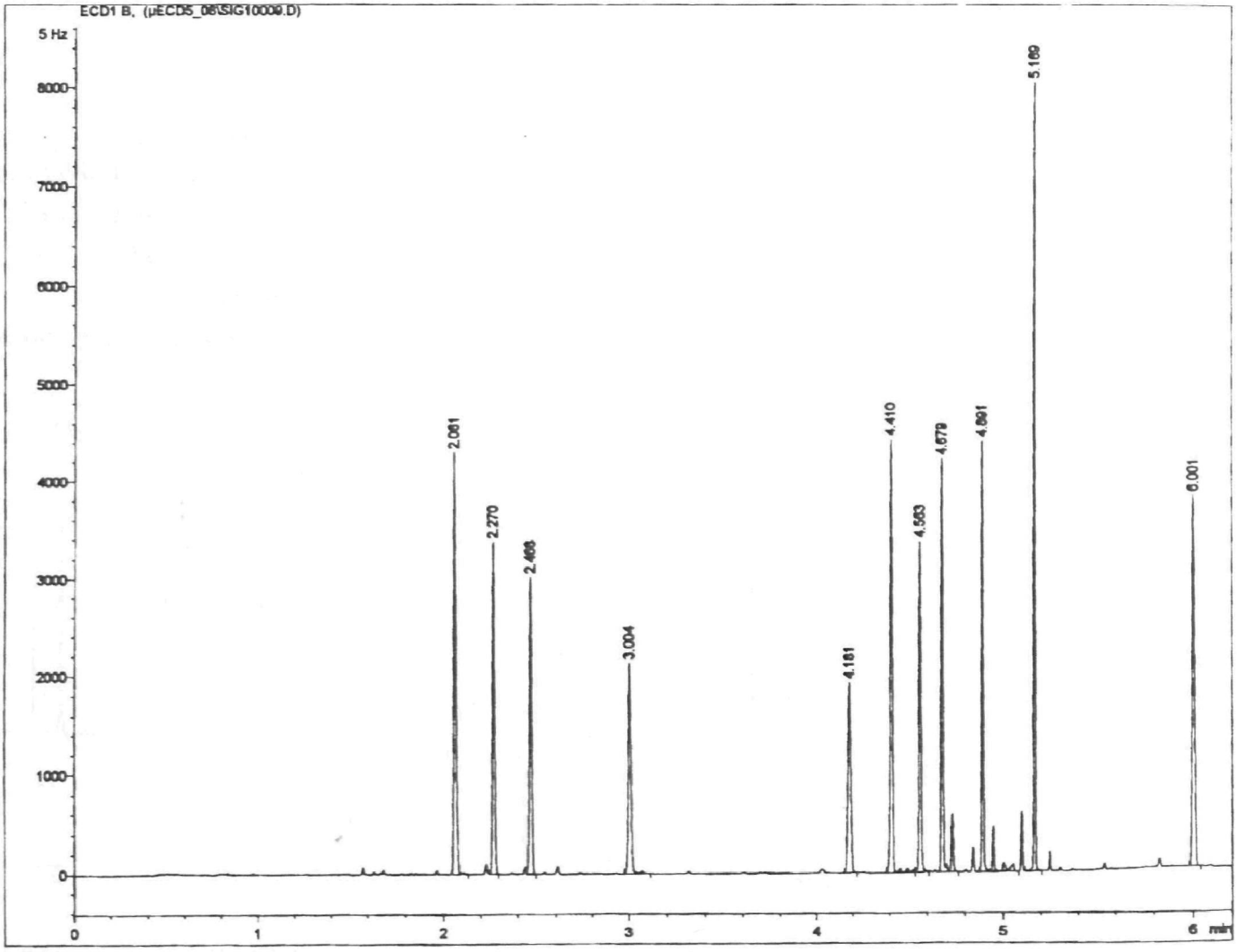
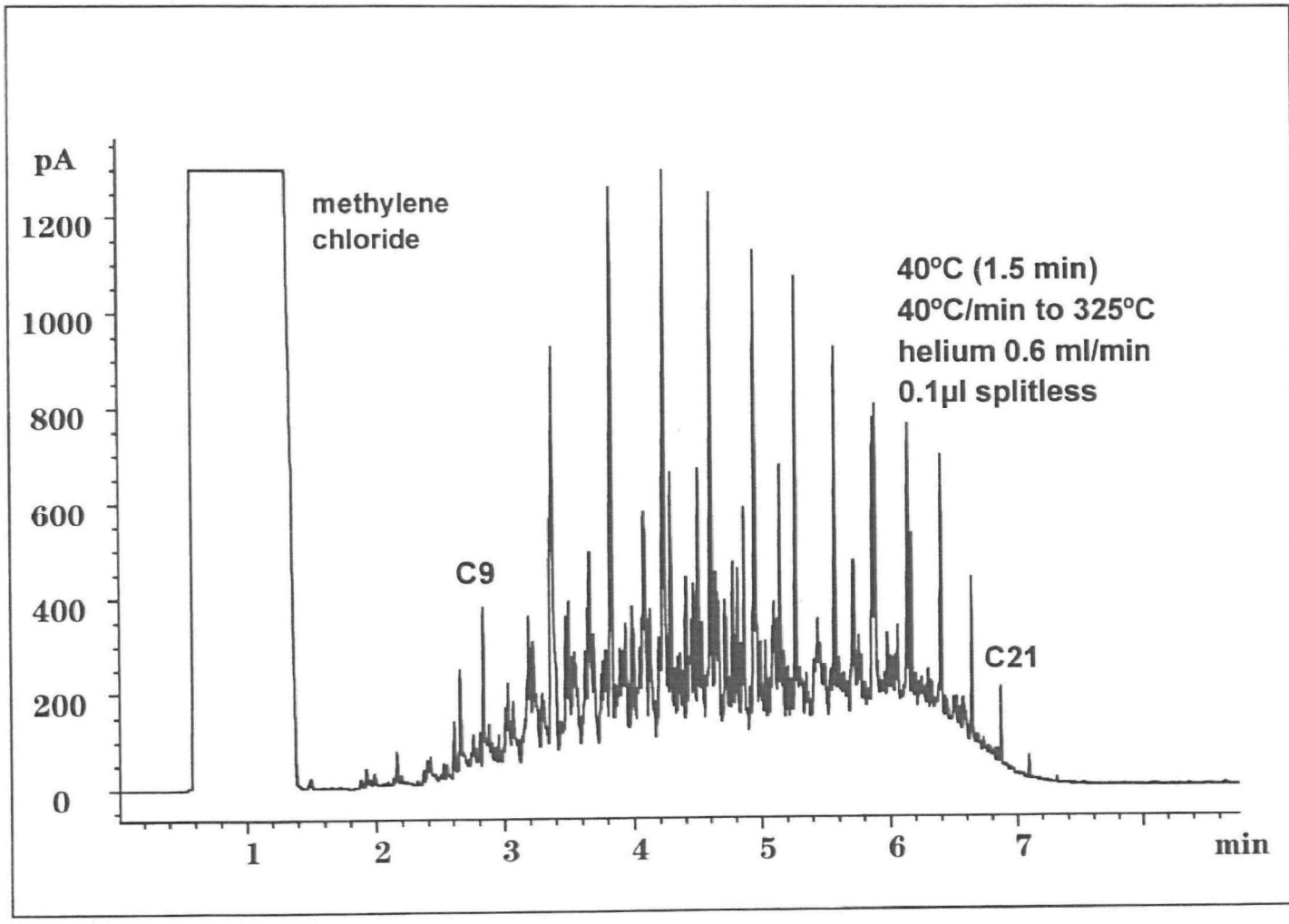


Figure 5. Diesel Range Organics TrPH group separation in 7 minutes

10 meter x 0.10 mm x 0.17 µm HP-5
µECD



GENERAL/AIR & GROUNDWATER

THE APPLICATION OF HIGH SPEED GAS CHROMATOGRAPHY TO AIR ANALYSIS

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ABSTRACT

The demand for frequent sampling (2 to 5 minutes) approaching a continuous mode has generated interest in high speed GC analysis. This paper describes an apparatus which produces a minimum injection bandwidth (10 to 50 msec) which provides the primary means of attaining good column efficiency while achieving High Speed GC Analysis. This *Fast*GC inlet which is mounted on a Varian 3400 Gas Chromatograph is described and its operation is detailed from the cryofocussing of the sample onto a short Nickel tube to the 100,000°C/sec desorption to the 8 Meter x 0.32 mm capillary column. The applications described in the paper include the analysis of chlorinated hydrocarbons, polar organics, an ozone precursor standard (C2 to C13), and BTEX's. Data regarding the recovery, response linearity, and retention time and area count precision are also reported.

INTRODUCTION

The demand for faster analyses and increased sample throughput when using High Resolution Capillary Gas Chromatography has traditionally required developing application specific chromatographic methods which sacrifice column efficiency in order to use shorter columns, higher oven temperatures, higher carrier gas flows, or less retentive coatings. The tremendous effort required to develop and modify numerous application specific methods has pointed up the need for more general methodology yielding fast GC analyses. This has lead to a re-examination of the means to preserve overall column efficiency while reducing analyses cycle times. This paper describes the general applicability of minimizing injection bandwidth as the primary means of retaining good column efficiency and simultaneously achieving High Speed GC analyses. The technology is applied to the chromatographic analysis of several classes of air pollutants.

THEORETICAL CONSIDERATIONS

Elution times can easily be reduced by shortening the length of the analytical column. However, the total resolving power of that column is also reduced. Approaches to High Speed GC have attempted to improve column efficiency in order to get useful performance from shorter columns. This can be seen mathematically in the Giddings-Golay Equations [1-3] , used to evaluate column efficiency in terms of minimizing plate height (H). Capillary column efficiency is related to longitudinal diffusion through the column (B term) and to resistance to mass transfer of the gas and liquid phases (C terms, Figure 1). For low volume columns, such as short columns, performance is better described by modifying the Golay equation by adding a D term [4] which accounts for band broadening by the system's dead volume.

One approach to obtain lower H values needed for short columns (<10M) has been to decrease column diameter (dc) in the Cg term. If a particular analysis uses 0.25 mm ID columns, typical of today's capillary work, then 0.05 mm or 0.1 mm ID columns (microbore) would be required to gain any significant speed reduction while maintaining resolving power. An example is shown in Figure 2. The

higher pressures needed for these columns increases f1 and decreases f2 (the pressure correction factors) working against the gains made by decreasing dc. These columns are also somewhat limited, having a decreased sample capacity, a smaller selection of available phases, and several additional instrument hardware requirements.

FastGC inlet technology uses sample introduction as a means to reduce the requirements of column efficiency to effect a usable separation. This technology improves column efficiency by significantly reducing t (unretained peak time) in the D term. The FastGC inlet system [5] cryofocusses the sample onto a short nickel trap and then desorbs the sample using heating rates up to 100,000°C/sec. This results in samples being introduced to the column in 2-10 msec bandwidths compared to the 50 to 500 msec bandwidths of conventional GC. The injection dead volume is thereby reduced by a factor of ten to several hundred. Theoretically, the D term is reduced, decreasing plate height, and the resolving power of the desired short column is now sufficient to effect the same separations obtained using longer columns with broader injections.

The reduction of injection bandwidth also permits minimizing analysis times by increasing carrier gas flow rates. With a conventional split injector, even a very fast 50 ms injection requires reduced column gas flow to obtain a low H value and good column efficiency (Figure 3).The 2 ms to 10 ms injection bandwidths obtained by the FastGC inlet provides more tolerance to column flow increases, almost as favorable as the theoretical minimum (0 ms). With these injections, column flow rates can be increased 2 to 4 times the standard rates.

APPARATUS AND ANALYTICAL CONDITIONS

All chromatograms were acquired using the following instrumentation and conditions:

Varian 3400CX Gas Chromatograph equipped with FastGC Accessory

Trap temp:	-70 to -90°C (LN_2 cryogenics)
Column:	8M x 0.25 mm ID x 0.25 μM film thickness DB-1 or specified
Oven:	50°C Isothermal or temperature programmed as specified
Carrier Gas:	H_2 ,150 cm/second
Inlet:	Direct Air Sample Inlet
Detectors:	FID at 300°C (50 ms Time Constant) PID at 250°C (50 ms Time Constant)

Data acquired using a Varian Star Workstation ADC Board running at 40 Hz.

*FAST*GC INLET OPERATION

The Varian 3400CX GC was configured with the low volume FastGC inlet system. The basic inlet system has been described previously [5]. As shown in Figure 4, samples may be introduced via a split injection or the special air inlet that was used in this study. The microsolenoid valves, V1 and V2, control the carrier gas flow pathway. The deactivated, fused silica tubing restrictors (R1, R2, R3) balance gas flows. In the Standby mode, V1 and V2 are closed allowing carrier to flush the trap, restrictors and inlet line. During sampling (Figure 4), V1 is opened and carrier gas flows from the GC injector with the injected sample to the trap, or in the case of air sampling, air is drawn through the trap to the vacuum source for a user-specified time interval. Sample vapor is condensed in the trap, which may be held at temperature to -99°C. Next, carrier purges any remaining sample from the restrictors and purges any air from the trap.

For the sample desorption onto the column, V1 is closed (Figure 5) reversing the gas flow direction through the trap which is then heated rapidly (at approximately 100,000°C / second) by applying a current pulse from a capacitive discharge circuit. The desorbed sample flows with the carrier gas onto the head of the analytical column.

RESULTS AND DISCUSSION

Several standards and one sample were analyzed using this new approach to High Speed Gas Chromatography. Most of these separations would require at least 20 to 40 minutes using standard GC columns and injectors. But with the FastGC inlet, analyses times are approximately one minute.

In Figures 6 and 7 are shown the chromatographic separations of an ozone precursor standard by traditional capillary chromatography and FastGC. In both cases, recoveries of 100% were obtained through C10 and fell off to approximately 60% for C12. Retention time precisions were similar at approximately 0.05% . Peak area count precisions were approximately 1% and 3% for the traditional and FastGC separations.

Figure 8 is a 0.65 mL sample of 10-20 ppm each paint booth standard in air. This mixture of polar components was cryofocussed at -70°C on the nickel trap for approximately 30 seconds, desorbed to the 8 M x 0.25 mm DB-1 column, and chromatographed in less than one minute. Peak tailing normally associated with polar components was not observed.

Figure 9 exhibits a mixture of ten halocarbons focussed at -70°C and subsequently chromatographed with an initial column temperature of 35°C, programming immediately to 80°C. An air sample was drawn into the FastGC module during carpet installation with the resulting chromatogram shown in Figure 10. It can be seen that toluene was an obvious solvent in the carpet glue.

In the last figure, Figure 11, 0.16 mL of 50 PPBV BTEX's are detected on a PID. The sample was concentrated over a 30 second time interval. Since samples of up to 2 mLs at 100% humidity are possible this chromatogram shows that FastGC has application to industrial hygiene as well as ambient air analysis where high ppb sensitivity is required.

SUMMARY

Dramatic reductions of elution times while maintaining good resolution and peak shape were observed using shorter columns, faster carrier gas flows, and the reduced injection dead volume provided by the FastGC inlet system. This was accomplished with standard 0.25 mm ID columns and standard GC hardware.

Several gaseous standards including air toxics and a wide range of hydrocarbons from ppb to ppm levels were preconcentrated on the FastGC cryotrap over fixed timed intervals and resolved in very short analysis times.

$$B = 2D_g f_1 f_2$$

$$C_g = \frac{(11k^2 + 6k + 1)}{96(k + 1)^2} \frac{d_c^2 f_1}{D_g f_2}$$

$$C_l = \frac{2}{3} \frac{k}{(k + 1)^2} \frac{d_f^2}{D_l}$$

$$D = \frac{\Delta t^2}{L(k + 1)^2}$$

Figure 1. Modified Golay Equations for High Speed GC

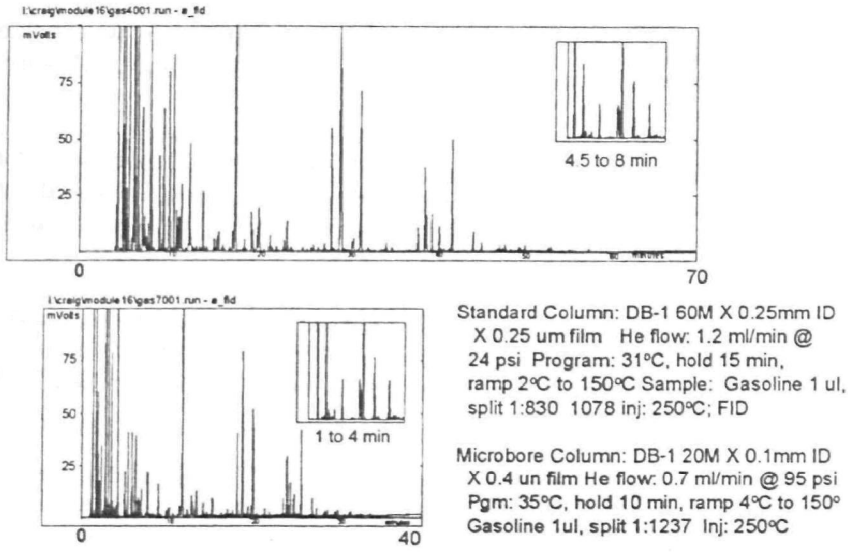

Figure 2. Standard Column (0.25 mm ID) vs. Microbore (0.1 mm ID) Analysis of Gasoline

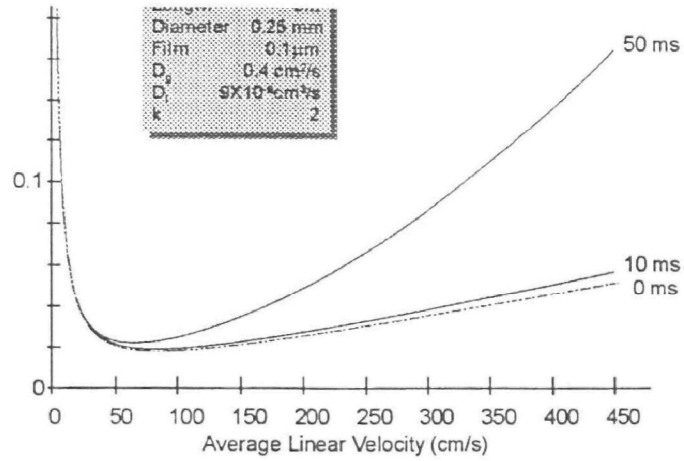

Figure 3. Dead Time Effect on Column Efficiency

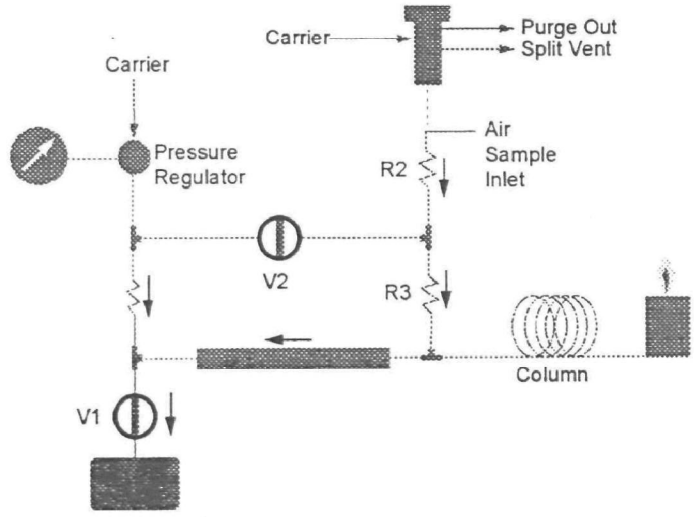

Figure 4. Sample mode for FastGC

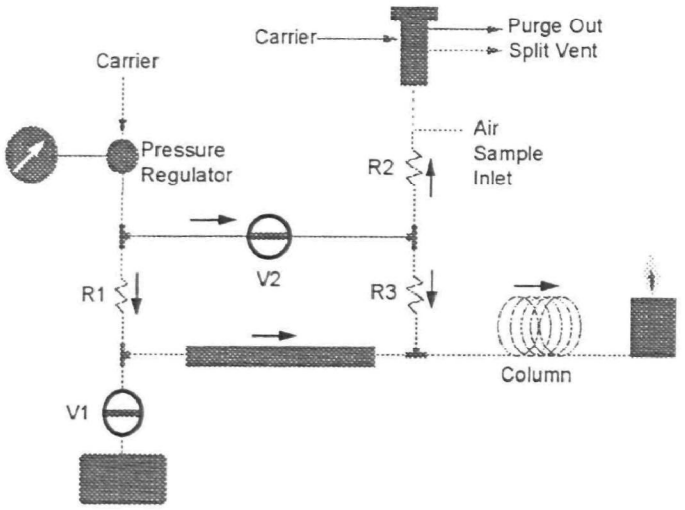

Figure 5. Analyze Mode on FastGC

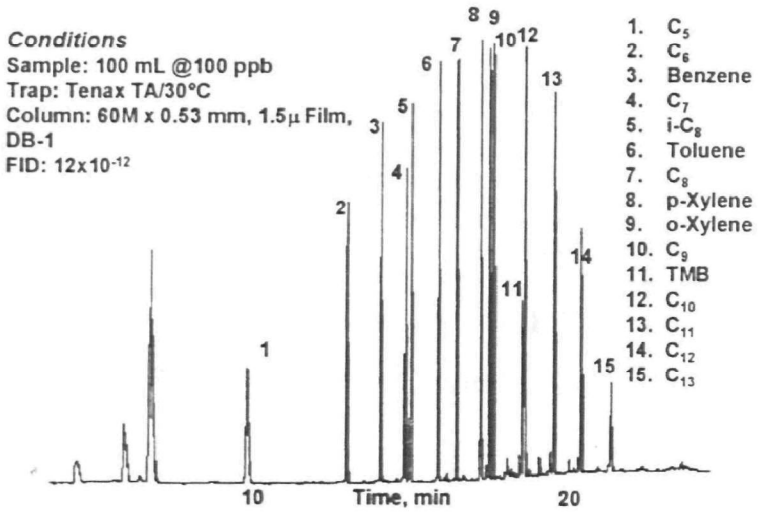

Figure 6. Ozone Precursor Standard by Standard GC

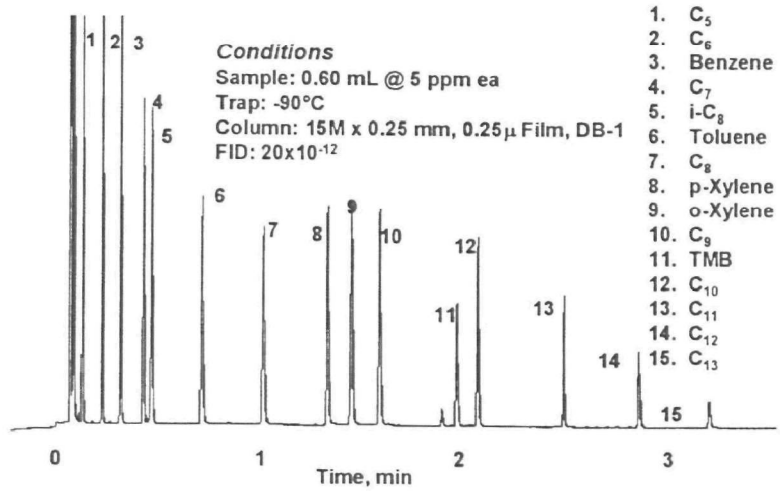

Figure 7. Ozone Precursor Standard by *Fast*GC

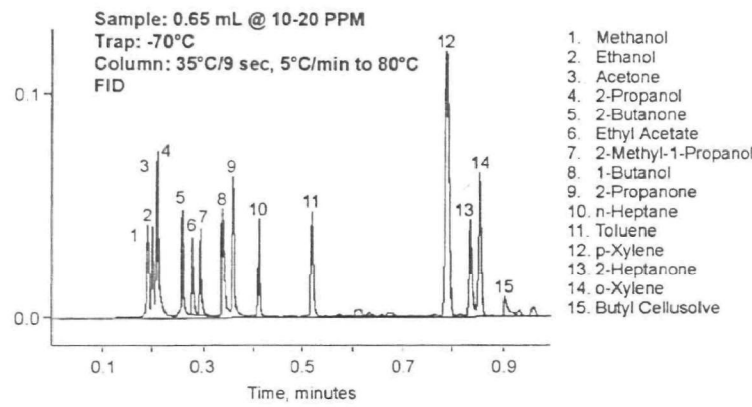

Figure 8. Polar Organics by *Fast*GC and Flame Ionization Detector

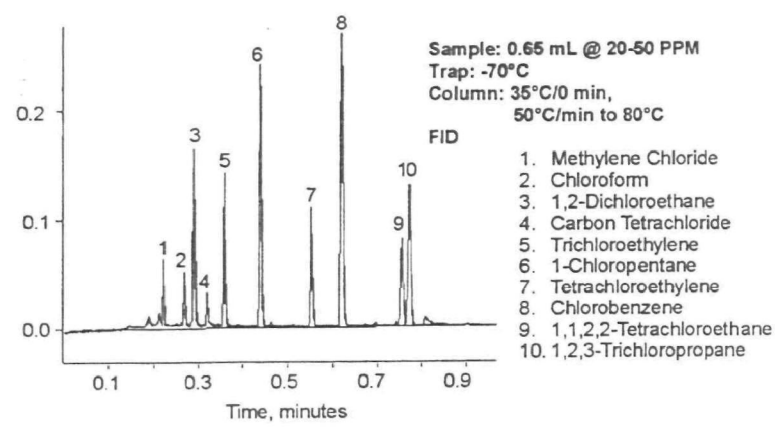

Figure 9. Chlorinated Hydrocarbons by *Fast*GC and FID

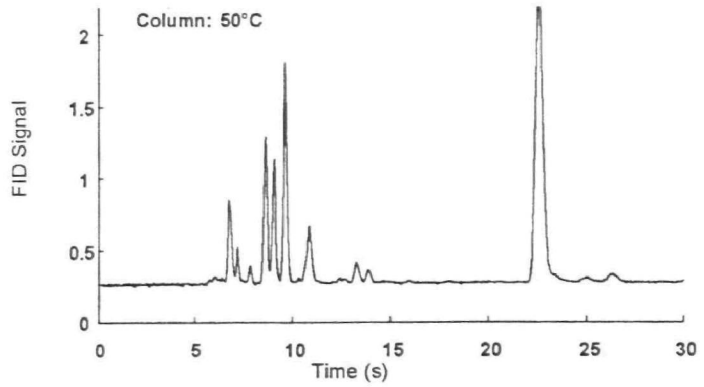

Figure 10. Direct Lab Air Sample During Carpet Installation

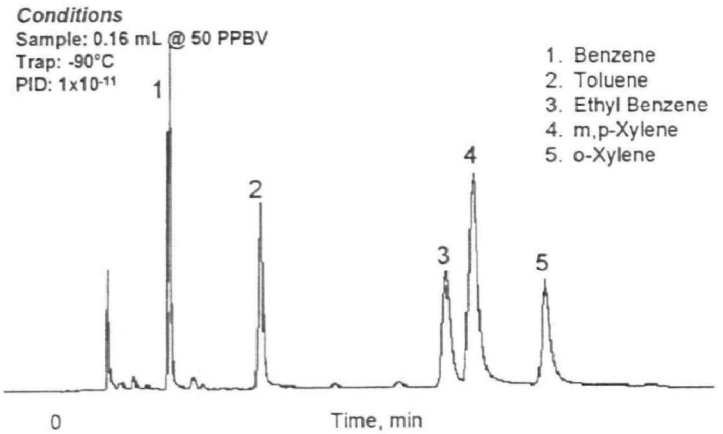

Figure 11. BTEX's by FastGC and Photoionization Detection

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A RAPID, COST-EFFECTIVE METHOD FOR DETECTION OF TRIHALOMETHANES IN DRINKING WATER

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Research Triangle Park, North Carolina 27709

ABSTRACT

EnSys Environmental Products, Inc. has developed the first commercially available, simple, colorimetric technology that can supplement trihalomethane (THM) testing using EPA methodology. This rapid, low-cost method enables water treatment facilities to respond quickly to changes in water quality. The test method and required resources will be described demonstrating its usefulness as a rapid, inexpensive and easy-to-use method for in-plant total trihalomethane (TTHM) determinations. Conventional analysis of TTHM require the use of gas chromatography methods, which require expensive equipment, extensive user training, and significant run time (30-45 minutes). The data presented will demonstrate the comparability of sensitivity, precision and performance to GC methods.

INTRODUCTION

Trihalomethanes (THMs) have been found to be the most widespread organic contaminants in drinking water, and occur at higher concentrations than other disinfection by-products. The four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) are formed when chlorine-based disinfectants are added to source water with fairly high organic content, such as surface water. THMs are included among the 25 volatile organic compounds regulated under the Safe Drinking Water Act (SDWA) of 1987. These compounds are persistent and mobile, and pose a cancer risk to humans.[1,2]

Regulations for the control of THMs in drinking water were promulgated by the EPA in 1979, setting the maximum contaminant level (MCL) of 100 μg/L (ppb) for systems serving populations of greater than 10,000 people. Since then, the increasing awareness of microbial risks in drinking water have caused disinfection and disinfection by-products to become more of an issue. Stage 1 of the proposed Disinfectants/Disinfection By-Products (D/DBP) Rule represents a lowered TTHM regulatory limit of 80 μg/L. Recently the AWWA Water Industry Data Base reported that a safety margin of 15% below the regulatory limit for total trihalomethanes (TTHMs) should be targeted; therefore, compliance with an 80 μg/L TTHM standard would require that a treatment process achieve < 64 μg/L to reliably stay below the regulatory limit. The stage 2 proposal, which will be

reevaluated in a second negotiated rule-making process, currently includes lowered MCLs of 40 μg/L for TTHMs.[3]

Because TTHMs are formed in proportion to the amount of organic matter in the source water, changes in TTHM concentrations may indicate changes in source quality. Timely measurement of TTHM concentrations can be a valuable tool in monitoring source water quality and making relevant adjustments to treatment processes.

CURRENT ANALYTICAL METHODS

TTHMs are analyzed in the laboratory using gas chromatography methods. The most widely used is EPA Method 502, volatile organohalogens by purge and trap/electrolytic conductivity detection. Two other methods, EPA Method 501 and the new Information Collection Rule Method 551 for determination of disinfection by-products, employ solvent extraction/electron capture detection. Use of GC methods requires expensive equipment, extensive user training, and significant run time (30-45 minutes). Furthermore, these EPA methods are relatively expensive, typically $40-100 per sample, and may involve laboratory turnaround times (including data analysis and recordkeeping) of 2-4 weeks.

TTHM WATER TEST SYSTEM

A number of investigators have studied simple spectrophotometric methods for determining THMs or other chlorinated organic compounds.[4-8] These colorimetric methods all involve in the color-forming step the Fujiwara reaction, which is a reaction between organic halides and pyridine (or a pyridine derivative) in an alkaline medium. The analytical challenges in developing a viable method using Fujiwara chemistry included extracting THMs from the water sample, concentrating them in an appropriate medium, and developing reaction conditions specific for the detection and quantitation of THMs in the presence of other chlorinated organic compounds. EnSys Environmental Products, Inc. has developed the first commercially available, simple, colorimetric technology, which can supplement THM testing using EPA methodology. The test is simple to use and does not require sophisticated equipment or chemistry training. Twelve samples can be tested in one batch generating results within 15 minutes of sample collection.

In the EnSys TTHMs Test System, trihalomethanes are extracted from a water sample using an Empore™ active carbon filter developed by 3M Corp., (St. Paul, Minn). Active carbon is a ubiquitous sorbent for the removal of organic contaminants from water. There are also a number of analytical devices, referred to as solid-phase extraction devices, filters, or membranes, that consist of a non-polar (reverse) organic phase covalently bound to an immobile surface, and that are effective in the removal of certain organic compounds from water. However, such reverse-phase sorbents are not as efficient as active carbon, and the use of active carbon in solid-phase extraction devices of the type used in the TTHMs Test System has not been explored extensively. Other extraction techniques reported in conjunction with Fujiwara chemistry deliver poorer sensitivity.[7,8]

The sample is collected either by attaching the Empore filter directly to a tap and using line pressure to filter the sample, or by collecting the sample in a suitable container (bottle or vial) and pressure-filtering using a syringe and either manual pressure or a peristaltic pump. After filtration, excess water entrained in the filter is removed by aspiration. The extraction method provides a separation of analyte from some potential interferents and cross-reactants, including inorganics and halogenated carboxylic acids, which are typically poorly adsorbed to the filter. THMs are then eluted from the filter with pyridine, using a manual dispenser. A developer reagent (containing hydroxide ion) is then added to the eluent, the mixture is incubated in boiling water for two minutes, then the solution is cooled to room temperature. A pink color indicates the presence of THMs; its intensity is proportional to the concentration of THMs.

The Fujiwara reaction and its modifications involve the reaction of pyridine, hydroxide, and chlorinated hydrocarbons to give products that absorb strongly in the visible or long ultraviolet regions. The ultimate product in all reactions is (colorless) glutaconaldehyde, obtained by N-alkylation of pyridine followed by complete ring hydrolysis.[9] However, depending on the analyte and on the specific reaction conditions, a number of Schiff base derivatives of glutaconaldehyde may form as reaction intermediates, and more than one molecule of glutaconaldehye may be obtained per molecule of analyte.

In the case of trihalomethanes a pink solution may be formed under certain conditions; the structure of the compound responsible for the color has been determined by Uno *et al.*[10] Although the compound is a reaction intermediate, its stability can be controlled. Conditions in the EnSys method have been optimized to yield the pink solution so that an approximately equivalent, linear response *on a weight basis* is obtained for each of the four THMs. Under the conditions of the present method, other chlorinated compounds give less response; most give little or none.

Sample concentrations are determined by reference to a single kit calibrator or a standard curve. A standard curve is obtained by analyzing a freshly prepared aqueous THM standard in the method. Absorbance is measured in a spectrophotometer at a wavelength of 531nm.

TEST SYSTEM PERFORMANCE

SENSITIVITY

The minimum sensitivity is expressed in terms of the method detection limit, which is the concentration at which 95% of the samples are correctly reported at that concentration. This concentration was determined as three standard deviations above a mean blank sample. The method detection level is usually regarded as the lowest concentration that could be measured under ideal circumstances and for the TTHM Water Test System is 5 μg/L.

SELECTIVITY

The complete set of disinfection by-products (DBPs) and selected Method 502.1 volatile organohalogens were tested for chemical cross reactivity with the EnSys method. The cross-reactivity was determined relative to the chloroform kit calibrator. In addition to the four individual THMs, the method detects (>10% response relative to an identical concentration of chloroform) the following organic compounds: trichloroacetonitrile, trichloroacetone, chloral hydrate, trichloroethylene and trichloroacetic acid. These compounds are typically not present or found in very low concentrations in treated water. As shown in Table 1 the test exhibits little cross-reactivity (<5%) with other organic compounds.

TABLE 1

Organic Compound	Response %
Chloroform	100
Chlorodibromomethane	92
Bromoform	79
Bromodichloromethane	74
Trichloroacetonitrile	70
Trichloroacetone	61
Chloral hydrate	43
Trichloroethylene	28
Trichloroacetic acid	15
Other Chlorinated Compounds	<5

Overview of Air Sampling and Analysis Methods

Gale G. Sutton, CIH -- Galson Corporation

The benefits of understanding the different sampling and analyses methods available for air contaminants should not be underestimated. Methods were developed for specific air matrices; although some methods can be modified for alternative applications, others have limited use. This paper will discuss the different validated methods presently published, their original purpose, and some alternative applications.

The NIOSH and OSHA methods of air sampling and analysis were developed to evaluate personal exposure to workplace chemicals and nuisance particles. The sample trains are designed to be worn by an employee and collect air within his/her general breathing zone. The sampling volume and collection media are designed to simulate the breathing capacity of an individual during a normal working day.

Air sampling methods in SW846 were designed for stack or emission sampling. As an example, method 0050 was written for the heated and/or humid matrix characteristic of stack emissions. But SW846 is fairly limited in the types of compounds it includes. The Federal Register, 40-CFR Part 60 and 61, contains not only on-site methods of contaminant determination, but also contains additional laboratory methods that cover a broader variety of analytes.

Still other publications, such as the EPA Methods for Determination of Toxic Organic Compounds in Air (TO Methods) and those listed in 40-CFR-Parts 50 and 51 were designed to evaluate ambient air; generally designed to target very low detection limits.

The California Air Resource Board (CARB), EPA Methods Manual for compliance with the BIF Regulations also contain air sampling and analyses methods. There are several commercially available data basis (as well as some produced by EPA) which can be utilized to select the proper method.

Each type of method has distinct advantages and disadvantages. Understanding the effects of humidity, air sampling volume and co-contaminants can help you choose the correct method modification when a specific procedure is not available.

In conclusion, the choice of method can affect usability of the data. Selecting the best method for a project is essential in obtaining usable and meaningful data from the laboratory.

PRECISION

The TTHM Water Test System was validated to ensure precision of results over the range of regulatory interest. The precision of the test was measured by spiking twenty replicate blank water samples at 5µg/L and 80µg/L and analyzed as two batches of ten each.

TABLE 2

Individual THM	Relative Standard Deviation (%)	
	5µg/L	80µg/L
Chloroform	3.8	1.6
Bromodichloromethane	10.2	3.2
Chlorodibromomethane	5.7	4.3
Bromoform	9.1	3.9

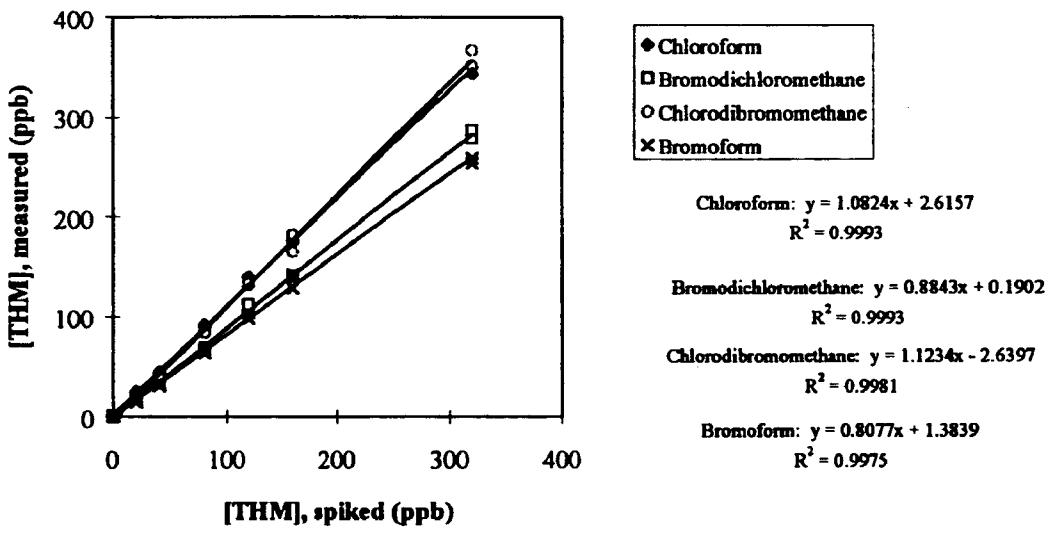
As shown here the method reproducibly (RSDs $\leq$ 10%) detected concentrations between 5 and 80 µg/L.

RECOVERY

Blank water was spiked with each of the four THMs at various standard concentrations. The graph below represents the concentrations measured after conducting the TTHM Water Test method. The concentrations were calculated relative to the chloroform calibrator provided in the EnSys procedure.

FIGURE 1

Spike Recovery of Trihalomethanes



The EnSys TTHMs test has a somewhat different response factor for each of the THMs, however the response factors of individual THM spikes are within 15% of the mean response.

Chloroform was selected as the basis for calibrating the test because most treatment plants disinfect with chlorine, and as a result chloroform is the predominant analyte in the finished water. Analyses of such samples using the EnSys procedure will correlate well with results using gas chromatography (GC) methods.

Certain source water and/or water that has been treated with oxidants other than chlorine will tend to contain more of the brominated THMs. As shown in the figure above, a bromoform sample must contain greater concentrations of THMs to give the same amount of color (absorbance) as the calibration sample. The method can be calibrated using a standard curve representative of the relative concentration of each of the THMs in a particular distribution system to account for this response factor difference. Alternatively, the chloroform calibrator concentration can be multiplied by a correction factor to reflect the different THM composition of the samples. For example, if water from a treatment system tends to have a mixture of similar amounts of each analyte, then a correction factor can be used that reflects an average response of the EnSys method to the four THMs.

CORRELATION WITH STANDARD ANALYTICAL METHODS

The TTHM Water Test can provide a high degree of accuracy when used to analyze water samples contaminated with TTHMs. To evaluate the relative accuracy samples were analyzed by the EnSys method; analysis by EPA GC Methods 501.1 and 502.2 was performed on concurrently collected same samples utilizing two different certified labs. The data presented below represent samples collected from 10 different water systems (71 observations) with variable treatment processes and a range of concentrations from not detected to 116 ppb. Results for the same sample show average percent differences of about 20% between each method. The difference between the EnSys method and each GC method is approximately the same as the difference between the two GC methods. On average the EnSys method has not given higher or lower concentration values than either GC method.

The *absolute percent difference* between methods for all observations in the four trials are displayed in Table 3 below. For each pair of observations the magnitude of the percent difference between concentration values was calculated; the mean of these values is the *absolute percent difference*. The GC method is used as the reference method to calculate the percent difference between the TTHM method and each GC method. For the comparison between GC methods, the percent difference was calculated relative to the mean of the two values. The results indicate that the percent difference between the EnSys method and each GC method is approximately the same as the difference between the two GC methods.

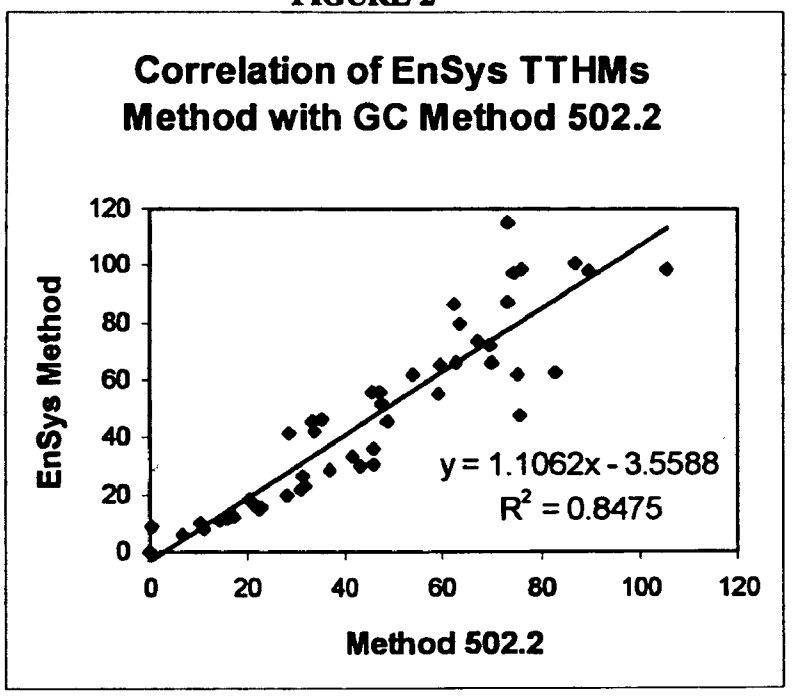
The absolute difference between each method was examined for all observations in the four trials. Percent differences for each pair of observations was again calculated, but this time the actual difference (positive or negative) was used in calculating the mean; this is the *relative percent difference*. The following results indicate that none of the three THM methods is biased - high or low - relative to another.

TABLE 3

	502.2 - 501.1 (n=23)	501.1 - TTHMs (n=30)	502.2-TTHMs (n=50)
Absolute Percent Difference	21.5%	19.0%	22.4%
Relative Percent Difference	- 2.8%	0.0%	+1.4%

Field data show excellent correlation with laboratory methods on real samples. As demonstrated by the slope of the regression line in Figure 2, there is a 1:1 correspondence between the EnSys method and Method 502.2 with a correlation coefficient of 0.85.

FIGURE 2



SUMMARY

EnSys Environmental Products, Inc. has developed an accurate, rapid, low-cost method for measuring total trihalomethane concentrations in drinking water. The results demonstrate good comparability of sensitivity, precision and accuracy to GC methods. The data further show that the TTHMs Water Test can be used as an in-plant alternative to the conventional laboratory-based methods. The method enables water treatment facilities to respond quickly to changes in water quality and serves as an effective monitoring tool on a routine basis.

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DETERMINATIONS OF N-NITROSODIMETHYLAMINE (NDMA) AT PART-PER-TRILLION (ng/L) CONCENTRATIONS IN CONTAMINATED GROUNDWATERS AND DRINKING WATERS FEATURING CARBON-BASED MEMBRANE EXTRACTION DISKS

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DETERMINATIONS OF N-NITROSODIMETHYLAMINE (NDMA) AT PART-PER-TRILLION (ng/L) CONCENTRATIONS IN CONTAMINATED GROUNDWATERS AND DRINKING WATERS FEATURING CARBON-BASED MEMBRANE EXTRACTION DISKS

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ABSTRACT

A new solid phase extraction procedure extracts *N*-Nitrosodimethylamine (NDMA) at part-per-trillion (ng/L) concentrations from aqueous samples using a C_{18} (reversed-phase) membrane extraction disk layered over a carbon-based extraction disk. The reversed-phase disk removes nonpolar water-insoluble neutrals and is set aside; the carbon-based disk is extracted with a small volume of dichloromethane. NDMA is quantitated in the organic extract using a gas chromatograph equipped with both a short-path thermal desorber and a chemiluminescent nitrogen detector (CLND). The Method Detection Limit for the procedure is 2 ng of NDMA/L; the analyte recovery is approximately 57%. A related procedure substitutes a standard automatic sampler for the short-path thermal desorber, and is suitable for determining NDMA in heavily-contaminated aqueous samples. The Method Detection Limit for the "high-level" procedure, which employs an automatic sampler, is 180 ng of NDMA/L, with an analyte recovery of approximately 64%.

The detection limits and measured recovery values are comparable to those observed in earlier work in which a conventional continuous overnight extraction with dichloromethane was used to remove NDMA from the aqueous samples. The newer procedures described herein offer a fiftyfold savings in extraction time and a one-hundredfold reduction in dichloromethane consumed per sample, while maintaining the wide range (three to four orders of magnitude concentrations of NDMA) observed for the original procedures used in a tandem.

The proposed procedure was challenged during a sampling campaign in which 100-200 groundwater samples were analyzed. In most cases, concentrations ranging between <5 to 200 ng NDMA/L were measured without difficulty, and were confirmed by GC/MS operated in the single-ion monitoring mode. Some samples required an extra C_{18} membrane extraction disk to reduce the concentrations of neutral contaminants. High concentrations of sulfur-bearing species present in groundwater samples may suppress NDMA recovery.

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INTRODUCTION

In previous work[1], we demonstrated that *N*-nitrosodimethylamine (NDMA, CAS Registry No. 62-75-9) can be quantitated readily at the part-per-trillion (ng/L) level in groundwaters after they are extracted continuously overnight with dichloromethane[2]. Briefly, a substantial portion of the resulting dichloromethane concentrate is then spiked onto a dual-sorbent carbon trap and dried before the residues (including NDMA) are desorbed onto a fused-silica gas chromatographic column. These residues are then separated in the usual manner; NDMA is detected selectively using a chemiluminescent nitrogen detector (CLND) optimized in its nitrosamine-selective mode. This procedure, while effective, exhibits a lengthy sample turnaround time (approximately three days per batch of eight samples, including a blank and appropriate QA/QC sample) and generates a substantial volume (approximately 300 mL per 1-L aqueous sample) of dichloromethane waste. For these reasons, it was most desirable to develop alternate procedures which would be effective, rapid, and generate smaller volumes of dichloromethane waste[3].

Both Taguchi *et al* [4,5] and Jenkins *et al* [6] have described extraction procedures for NDMA in which a small mass (200 mg) of Ambersorb 572, a carbonaceous sorbent, was used to extract NDMA effectively from 500 mL drinking water. We have extended this procedure by employing a carbon-based membrane extraction disk for removing NDMA from aqueous samples[7]. The procedure described herein employs a preconditioned C_{18} membrane extraction disk, laid over the carbon-based disk, to remove the unwanted neutral water-insoluble species. The former disk is set aside; the latter is dried and extracted with a small volume of dichloromethane. NDMA may then be quantitated using the various procedures described in Reference 1. Both the extraction time for a 1-L aqueous sample and the volume of waste dichloromethane are reduced approximately one hundredfold when the membrane disks are used instead of the continuous overnight extraction procedure. The calculated Method Detection Limit (MDL)[8] concentrations are 2 and 180 ng NDMA/L for the "low-level" (manual injection) and "high-level" (automatic injection) procedures, respectively. The use of the two procedures in a tandem permits the quantitation of NDMA concentrations ranging over approximately three orders of magnitude, from ng/L to the µg/L levels.

EXPERIMENTAL

Sample Collection and Storage. Groundwater samples should be collected in commercially available precleaned 1-L narrow-neck amber glass bottles, stored at 4°C, and extracted within 7 days of sampling.

NDMA Standard Solutions. Stock solutions with certified concentrations of NDMA in methanol may be purchased from several vendors. These include NSI Environmental Solutions, Inc. (Research Triangle Park, NC; 5000 µg NDMA/mL); AccuStandard (New Haven, CT; 1000 µg NDMA/mL); Polysciences (Niles, IL; 1000 µg NDMA/mL); and Ultra Scientific (North Kingstown, RI; 100 µg NDMA/mL). Aliquots are diluted sequentially to final concentrations ranging between 2 and 240 ng of NDMA/mL in highest purity dichloromethane (GC^2 grade, Burdick & Jackson, Muskegon, MI, or equivalent) to form

calibration standards for the "low-level" method, which employs the short-path thermal desorber, or between 50-4000 ng of NDMA/mL dichloromethane, prepared similarly, for the "high-level" method, which employs the automatic sampler. Fresh standards should be prepared every 60 days.

Preparation of Blanks and Spiked Samples for Method Certification and Quality Assurance. Aliquots (1-L) of synthetic groundwater are prepared from HPLC-grade water (Burdick & Jackson, J. T. Baker (Phillipsburg, NJ), or equivalent) which is fortified to 100 mg/L each in sulfate and chloride, as described elsewhere[9]. These are spiked to concentrations ranging between 2 and 40 ng of NDMA/L using a master spiking solution containing 0.1 µg of NDMA/mL of water for the "low-level" procedure. Spiked samples for the "high-level" procedure are prepared from a master spiking solution containing 10 µg of NDMA/mL water; the final concentrations range between 100-4000 ng of NDMA/L. Water produced from typical "on-demand" systems may not be used, as described in Reference (1).

Sample Preparation and Extraction. Aqueous samples are filtered through Empore C_{18} filter disks (47 mm diameter, J. T. Baker or Varian Sample Products Division, Harbor City, CA) layered over a carbon-based Empore disk[10,11]. An all-glass funnel/support assembly (DELTAWARE, with a 1-L filtering flask and a 300-mL reservoir, handles 47 mm diameter disks, VWR, part no. KT 93825-47 or equivalent) is used to support the disk and hold the filtrate. The two disks are preconditioned simultaneously with two 10-mL portions each of methanol and water. Each aliquot remains on the disk for 1 min prior to removal. *Do not permit the disk to become dry during the conditioning sequence.* A separate all-glass funnel/support assembly should be arranged for drying the carbon-based disks. Here, the 1-L flask is replaced with a custom-prepared "cap" fashioned from an "inner" Ŧ (standard taper) 40/35 glass joint; dimensions are 37 mm o.d., 60 mm high. These "caps" are large enough to accommodate pre-cleaned tared 20-mL screwcap vials.

Desorption Equipment. The sorbent trap contains 125 mg each of Carbotrap and Carbotrap C (Supelco, Inc., Bellefonte, PA), which are packed and conditioned as described in Reference 1. The short-path thermal desorber (SPTD), Model TD-1 (Scientific Instrument Services, Ringoes, NJ), is installed and arranged as described in Reference 1. Sample residues are first dried at room temperature using ultrapure (99.9999%) helium for 2 min at 25-30 mL/min, then desorbed for 5 min at 150°C using ultrapure helium (3 mL/min).

Gas Chromatograph, Automatic Sampler, Chemiluminescent Nitrogen Detector (CLND), and Data System. An Antek Model 705D pyro-chemiluminescent nitrogen detector was retrofitted to a gas chromatograph (described below), with details given in Reference 1.

A Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a split/splitless injector both supported and was physically interfaced to the SPTD ("low-level" procedure), CLND, data system, and automatic sampler ("high-level" procedure). One of the existing data interface boards was replaced with a Hewlett-Packard analog input board so that the output from the CLND could become part of the overall system network. The gas chromatographic parameters and conditions were optimized and are reported in Reference

(1). All gas chromatography was performed with a fused-silica capillary column, Rtx®-200 (Crossbond trifluoropropylmethyl), 3.00 µm film thickness, 0.53 mm i.d. x 30 m (Restek Corp., Bellefonte, PA) connected to a deactivated and uncoated fused silica guard column, 0.53 mm i.d. x 5 m using a Universal Press-Tight connector (Restek).

When the "high-level" procedure was used, a Hewlett-Packard Model 7673 Automatic Sampler replaced the short-path thermal desorber and injected 2 µL sample on column. The gas chromatographic operating parameters are the same as those described above with the exception of the purge valve settings, which are "OFF" at 0.00 min and "ON" at 0.25 min.

The presence of NDMA in contaminated groundwaters was verified using a Hewlett-Packard Model 5972 GC/MS equipped with a DB-5 analytical column (30 mm x 0.25 mm i.d., 1 µm film thickness). The column oven temperature was programmed from 40°C (hold for 4 min) to 310°C (hold for 14 min) at 10°C/min. Dwell time was maintained at 1000 msec. The presence of NDMA was established by its retention time (8.3 min) and two major m/e ratios (74 and 42). The presence of the surrogate d_4-dichloromethane was verified using its retention time (14.7 min) and major m/e ratios (150 and 152).

Procedure: Aqueous samples are filtered simultaneously through C_{18} and carbon-based Empore disks under vacuum at approximately 40-50 mL/min (a 1-L sample such as drinking water or filtered groundwater, which contains little or no particulate matter, is typically finished in approximately 20 min). The extraction apparatus is then dismantled; the C_{18} disk is set aside or may be used for related independent analyses. The carbon-based Empore disk is transferred to the second all-glass filter support where the "cap" has replaced the normal 1-L filtration flask, then dried for 10 min under vacuum. When the disk is thoroughly dry, a precleaned tared 20-mL screwcap vial is placed in the "cap," which is then reattached to the all-glass filter support. A 3-mL aliquot of highest-purity dichloromethane is added to the reservoir. After the solvent remains over the carbon-based disk for 1 min, it is drawn through the disk under vacuum (*slowly*, if at all possible); approximately 2 mL is collected in the screwcap vial. The vial is then reweighed to determine the mass (and later, the accurate volume) of the dichloromethane extract.

The determination of NDMA at ultratrace concentrations (between 2 and 40 ng of NDMA/L water) proceeds in the manner described in Reference 1. A 100 µL aliquot of the dichloromethane concentrate is added slowly to the Carbotrap C end of the dual sorbent trap, allowing sufficient time for the liquid to soak into the trap bed. The trap is then mounted into the short-path thermal desorber (Carbotrap C end is connected to the "top tube" without the needle attached) and dried with ultrahigh purity helium for 2 min at 25-30 mL/min. This procedure is repeated, leaving the residues from 200 µL of concentrate on the trap. The trap is then disconnected from the "top tube" and inverted. The needle is connected to the Carbotrap C end of the trap, and the remaining Carbotrap end is screwed into the "top tube." The residues present on the trap are then desorbed directly from the sorbent trap onto the guard and analytical gas chromatographic columns, both maintained at 35°C, using a 150°C desorption temperature maintained for 5 min and a helium desorption flow rate of 3 mL/min. The column oven temperature program commences immediately after completion of

desorption.

The extraction procedure for "high" levels of NDMA, typically exceeding 300 ng of NDMA/L water, is the same as that described above. Upon completion of the carbon disk extraction, the dichloromethane extract is transferred to a 2-mL amber autosampler screwcap vial equipped with a Teflon®/Silicone/Teflon® septum (National Scientific Co., Lawrenceville, GA). A 2 µL aliquot is injected onto the column using the automatic sampler, and analyzed using the gas chromatographic conditions described above.

RESULTS AND DISCUSSION

The MDL values for both the "low-" and "high-" level procedures were calculated as described in Reference (8). In the "low-level" procedure, eight (minimum seven required) 1-L synthetic groundwater samples were fortified to 10 ng NDMA/L and analyzed as described above. The standard deviation, which was calculated for both seven and eight replicates, was then multiplied by the appropriate one-tailed Student's-t statistic for 99% confidence. The resulting value is the MDL, approximately 2 ng of NDMA/L when all eight experimental data points. When the "best seven" values were employed (that is, those with the smallest spread), were employed, the MDL was reduced to 1 ng of NDMA/L groundwater. A similar approach was taken for the "high-level" procedure, where the eight groundwater samples were fortified to 1000 ng NDMA/L. The MDL calculated using all eight data was 180 ng of NDMA/L; that using the "best seven" data (that is, those with the smallest spread) was 100 ng of NDMA/L. All raw and calculated data are presented in Table 1.

The performance of the disk-based procedure was evaluated initially by quantitating NDMA in two small batches of drinking and contaminated groundwater samples. In both cases, additional QA/QC samples were analyzed to ensure the quality of the results. The latter included dichloromethane solvent blanks (no detectable NDMA), synthetic groundwater blanks (NDMA detected at levels at or below the MDL), and synthetic groundwater samples which had been fortified to 10 ng of NDMA/L (NDMA detected at a minimum recovery of 55%). These results were deemed sufficient to consider the resulting NDMA concentration data valid.

This procedure was challenged rigorously during a sampling campaign at a military defense site during the fall of 1995. Approximately 100-200 individual groundwater samples, with accompanying blanks and matrix spikes, were withdrawn from monitoring wells and analyzed. While most of these samples were processed without difficulty, a modest number required additional modifications to the procedure described above. Heavily-contaminated samples frequently required an additional C_{18} Empore disk to reduce the number of extraneous peaks. Furthermore, the presence of mustard gas by-products and degradation products, such as dithiane and thioxane (oxathiane), in substantial concentrations in the groundwater samples suppressed the chemiluminescent signal for NDMA. The reasons for this effect are not well understood at this time.

The concentration of NDMA in most of the samples examined was below the MDL calculated

above. A number of the monitoring wells were resampled in February 1996. The resulting groundwaters were not only re-analyzed, but the presence or absence of NDMA was confirmed by GC/MS in the single-ion monitoring (SIM) mode. The resulting data are presented in Table 2. In general, there is good agreement between the chemiluminescence and GC/MS-SIM data, particularly for the resampled data set. Furthermore, the agreement between all data for a given site (Fall 1995 and February 1996) is generally acceptable if NDMA was detected above approximately 20 ng/L.

SUMMARY

The above discussion demonstrates that analytical procedures based on carbon-based extraction membrane disks are capable of quantitating NDMA in aqueous samples with recoveries equal to or greater than existing procedures which employ conventional overnight dichloromethane extractions. The detection limits using the disks were calculated using a procedure given in the *Code of Federal Regulations*; the values were virtually interchangeable with those obtained previously[1]. When the "low-level" (2-40 ng of NDMA/L) and the "high-level" (100-4000 ng of NDMA/L) procedures are used in a tandem, it is possible to quantitate NDMA over approximately three to four orders of magnitude. In cases where the aqueous NDMA sample concentration falls between the upper bound of the "low-level" procedure and the lower bound of the "high-level" procedure, an accurate quantitation may be performed by simply spiking dichloromethane concentrate volumes smaller than the usual 200 µL on the dual-sorbent trap. It has been demonstrated[1] that the trap performance is independent of the volume of dichloromethane applied to it, up to at least 200 µL. Procedures which employ the membrane extraction offer considerable savings in both labor and the volume of hazardous waste organic solvent produced compared to conventional methodology. In this case, the volume of dichloromethane employed was reduced ***one-hundred fold*** compared to that required by conventional continuous extractions. Furthermore, the overall turnaround time for a lot of eight samples was improved from three days to a single day. It was also feasible to process a single "emergency" sample within three hours.

ACKNOWLEDGMENT

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Table 1. Calculation of MDL Values for the "Low-Level" and "High-Level" Procedures for NDMA in Groundwater

Replicate No.	"Low-Level" Procedure[a] Calculated NDMA (ng/L)[b]	"High-Level" Procedure[c] Calculated NDMA (ng/L)[b]
1	7.4	710
2	7.0	680
3	6.8	660
4	6.6	710
5	8.6	680
6	7.0	740
7	7.0	560
8	7.6	750
Standard deviation, all samples	0.6	60
MDL, all samples[d], ng/L	2	180
Standard deviation, "best seven" samples	0.3	30
MDL, "best seven" samples[e], ng/L	1	100

[a]Spiked water concentration is 10 ng NDMA/L.

[b]Values not corrected for recovery

[c]Spiked water concentration is 1000 ng NDMA/L

[d]Student's t-value (one-tailed) at 99% confidence, eight samples = 2.988.

[e]Student's t-value (one-tailed) at 99% confidence, seven samples = 3.143.

Table 2. Summary of NDMA Results on U. S. Geological Survey Resampling by Chemiluminescence (CLND) and by GC/MS in the SIM Mode

Sample ID	Original Sampling	Resampling		
	CLND ng NDMA/L[a]	CLND ng NDMA/L	GC/MS SIM, ng NDMA/L, by area	GC/MS SIM, ng NDMA/L, by height
Method blank	<5	1	<5[b], *1*[c]	<5, *1*
50 pptr spike/H_2O	40	29, 32	52, *74*	81, *120*
A	20	2	<5, *2*	<5, *3*
B	20	2	<5, *3*	<5, *3*
C	<5	4	5, *9*	5, *10*
D	<5	5	5, *8*	5, *10*
E	<5	1	<5, *2*	<5, *2*
F	<5	1	<5, *1*	<5, *1*
G	29	24	33, *54*	38, *85*
H	34	27	27, *39*	33, *65*
I	26	19	24, *41*	25, *54*
J	<5	2	<5, *2*	<5, *2*
Matrix spike	42	26	41, *61*	49, *100*
K	21	11	12, *18*	11, *17*
Method Blank	<5	1	<5, *1*	<5, *1*
50 pptr spike/H_2O	39	35	50, *68*	50, *61*
L	21	12	14, *17*	14, *19*
M	43	68	104, *178*	134, *225*
N	<5	2	<5, *<5*	<5, *2*
O	<5	1	<5, *1*	<5, *1*
Matrix spike	36	26	31, *40*	30, *34*
40 ng/mL standard	Not performed	Not performed	53, *86*	47, *75*

[a] Chemiluminescence method employs method of external standards exclusively for calculation of NDMA concentrations

[b] First number given uses the method of external standards to calculate NDMA concentration by GC/MS SIM.

[c] Italicized number uses the method of internal standards to calculate NDMA concentration by GC/MS SIM.

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8. Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11. *Code of Federal Regulations: Protection of the Environment,* Parts 100-149; Title 40; U. S. GPO: Washington, DC, Revised Jul 1, 1990.

9. *Program Manager for Rocky Mountain Arsenal: Chemical Quality Assurance Plan.* Version 1, Sep 1993.

10. The carbon-based Empore disks are currently not available through normal vendors. They should be ordered directly through: Mr. Chuck Haskins, National Sales Manager; 3M; Building 220-9E-10; St. Paul, MN 55144-1000.

11. Physical parameters of the disks: Carbon type, acid-washed coconut charcoal. Surface area > 1000 m^2/g. Nominal particle diameter, 15-20 µm. Weight of carbon in the disk, ca. 90% w/w of the disk (about 400-450 mg). Pore size distribution is proprietary.

Limited Life Cycle Analysis

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ABSTRACT

Limited Life Cycle Analysis (LLCA) is a technique for developing a quantitative estimate of the environmental impact of any action which affects the environment in a positive or negative manner. It is generally used to compare the environmental impact of various possible actions such as remediation alternatives for contaminated soil or water, for control options for emissions sources in various media, or even manufacturing processes. LLCA is based on a European model developed by Schaltegger and Sturm (S&S) and has been successfully used in several countries. This paper gives a brief overview of the LLCA process, the mechanism of the S&S model, and summarizes the results of two case studies where this technique has been implemented.

INTRODUCTION

The technique considers both direct and indirect emissions created by a given action in a comprehensive way and examines the environmental impact of each step of the process to be evaluated from "cradle to grave". LLCA incorporates the elements of full life cycle analysis (raw materials and energy balances), except it is limited in scope and can be applied to a set of potential alternative solutions to an environmental problem. The S&S model used is a ***quantitative*** assessment, based upon regulatory limits.

LLCA estimates the impact of each pollutant released to the environment by multiplying the mass of each pollutant released by a Pollution Factor (PF) for that pollutant. The product is the impact of that release in dimensionless Environmental Impact Units (EIUs). For a given action, the EIUs for all pollutants are summed to find the overall environmental impact of the action. EIUs are directly additive and comparable across pollutants and across environmental media. The PFs are specific for each pollutant and for each environmental medium (air, water, or soil) and are calculated from the legally or socially accepted limit of concentration of the pollutant in that medium.

This section provides an overview of how the LLCA process is applied. The most important step in performing this analysis is to define the boundaries of the process to be tested. Listed below are the types of information necessary to complete a successful LLCA for a soil or water remediation project.

- the pollutants of interest
- the total mass of pollutants to be remediated
- the total mass of pollutants produced during construction, operation, and decommission (the amount of pollutants produced from vehicular emissions, materials manufacture, electric power generation, etc., are published in various national and international reference documents)
- the required pollutant cleanup levels in soil and/or water
- regulatory limits for emissions in all media

- a flow diagram with equipment specifications
- all process and construction materials
- process energy flows

For example, emissions generated by the following are considered in analyzing an excavate and thermal treatment soil remediation option:

- transportation of materials and equipment to and from the site
- installation of equipment
- soil excavation (emissions from equipment and contaminants from the soil to air)
- production of fuels consumed in the treatment process
- generation of electrical power used in the treatment process
- production of materials consumed by the remediation
- release of pollutants to groundwater during and after the remediation

SUMMARY

Mechanism

The Schaltegger & Sturm model, which is used as the basis for all LLCA efforts described in this paper, compares each step of the process for environmental impact using regulatory-derived discharge, ambient, or emission limits. This section provides a brief overview of the process with example calculations.

- Pollution factor values are calculated for each compound of interest for all appropriate media. Compounds of interest include the site contaminants as well as emissions produced as a result of transportation, construction, and operation of the process.

- PFs are derived from regulatory limits in all appropriate media, and are converted to mass/mole of substrate. This conversion is quite simple for air and water media; calculation of mass/mole in soil is particularly difficult, since the molecular weight of soil is not well defined. However, if the soil in the test area is well characterized, an empirical molecular weight of the soil can be estimated. Once this has been done, the PF (a dimensionless number) is calculated based upon the normalization to a reference compound. The compound used as a reference in the Schaltegger & Sturm Model is carbon dioxide; however, any reference will produce PFs which are inversely proportional to their regulatory limits, i.e., the lower the allowable concentration, the higher the PF. The table below illustrates this concept:

Media & Compound	Limit Value	Standardization (mg/mole)	PF = EIU/Kg
AIR			
Carbon dioxide	579 mg/M^3*	13.7	1
SO_x	0.08 mg/M^3	0.00192	7,140
WATER			
Mercury	0.002 mg/L	0.000036	381,000

* The carbon dioxide limit value is the mid 1960's normal sea level concentration in air.

Conversion from the limit value to mg/mole for each compound is calculated as follows:

For air: Mg/mole = limit value in $mg/M^3/42.3$ (number of moles in one cubic meter of air at 15° C & 1 atmosphere)

For water: Mg/mole = limit value in mg/L/55.5 (number of moles in 1L water @ 15° C)

Standardization of the limit value for each compound is calculated as follows:

PF = 13.7/limit value in mg/mole = PF units = EIU/Kg

- In those cases where federal, state, or local emission or discharge limits have not been established, alternate sources may be utilized. For example, for a compound for which there are no ambient air limits, US industrial hygiene threshold limit values (TLVs) may be utilized with modification. Although TLVs have been established for industrial workers exposed over a nominal eight-hour time weighted average, some state regulatory agencies have adopted these modified TLV values (divided by 42 to "normalize" them for a 7-day, 24 hr/day week with a 10-fold safety factor) as an acceptable emission alternative in the absence of federal ambient standards. As another viable alternative, site-specific cleanup limitations derived as part of ongoing investigations may be used in the same manner.

Once pollution factors are determined for each compound, environmental impact units can be determined for each discharge or emission source based upon the total mass of component. The following worked hypothetical example of pollution present in groundwater illustrates this concept:

Compound	US (NJ) H_2O Cleanup Level	US Cleanup Level (mg/mol)	PF , or EIU/Kg	Quantity in Ground (Kg)	Impact (EIU)
Carbon Dioxide	579 mg/M^3 (Air)	13.7	1		
Benzene	0.2 ug/L	$3.61X10^{-6}$	$3.80X10^6$	8.2	$3.12X10^7$
Toluene	1,000 ug/L	0.018	761	2860	$2.18X10^6$
Total Impact					**$3.34X10^7$**

Note that the PFs derived for each compound are based upon the molar concentration in the medium of interest, e.g., the ambient limit for CO_2 in air is converted to mg/mole as are limits for compounds in aqueous media. This ensures that equal comparison of the PFs can be made for air, water, and soil (when appropriate) for each compound of interest. Unless the soil in the cleanup area is well characterized, molecular weights are not usually assigned. Rather, it is assumed that the mass of contaminants present in the soil will be completely transferred to groundwater or air, based upon the remediation mechanism under investigation. In this manner molecular weight assignments to these media are known.

Case Studies - Site A

Site A is a manufacturing facility in which soil contamination was discovered beneath a former building. Due to the possibility of groundwater contamination by organic materials, remediation of the area was required.

Four remediation technologies were considered: 1) cap & containment, 2) *in-situ* aerobic bioremediation, 3) *in-situ* anaerobic bioremediation, and 4) excavation and thermal treatment. LLCA was performed on each remediation alternative and compared to the do nothing or no action as a baseline.

Major assumptions made during the LLCA included the following:

- PF soil = PF groundwater because a) soil cleanup levels were not established, b) it was assumed that all pollutants would be transferred to the groundwater, and c) the molecular weight of the soil in the area was not well established
- the remediation area consisted of an area approximately 200' X 150' X 30'
- Total mass of the pollutants in the area = 3,660 Kg
- remediation times vary with technology

The final results of the study are summarized in the table below; total and local environmental impacts were also determined. (Local impacts occur at the site itself).

Site A Results
[Million EIU]

Component	No Action	Cap & Contain	Aerobic In-situ Bio	Anaerobic In-situ Bio	Excavate & Thermal
Total Impact	**167**	**25**	**61**	**75**	**182**
Release to GW	167	17	17	17	0
Electric consumption	0	0	42	56	49
Fuel consumption	0	5	<1	<1	132
Process materials	0	0	<1	<1	0
Construction materials	0	3	2	2	1
Local Impact	**167**	**21**	**17**	**17**	**132**
Release to GW	167	17	17	17	0
Electric consumption	0	0	0	0	0
Fuel consumption	0	4	<1	<1	131
Process materials	0	0	0	0	0
Construction materials	0	0	0	0	1

Based upon the results of the LLCA, cap & containment provides the lowest overall impact, but not the lowest local effect. However, since this option will not remove the contaminants, the preferred option is *in-situ* aerobic bioremediation.

Data was also examined in two ways: 1) a sensitivity analysis was performed on the three most prevalent EIU contributors and varied by $\pm$ 10%. The slope of the resulting lines indicate which components are the most sensitive to change (see example on page 7). 2) a breakeven analysis for operating times was performed on each option. That is, the impact for each option was determined on an annual basis and plotted against time. The breakeven operating time is defined as the point where the total (or local) environmental impact intersects the EIU for the no action option, i.e., operating times shorter in duration than the breakeven time less negatively impact the environment than the no action alternative (see example on page 8).

Examination of data from the sensitivity analysis shows electricity consumption to be the most sensitive to change for the *in-situ* bioremediation options; fuel consumption was the most critical to excavation followed by thermal treatment.

For the breakeven analysis, the bioremediation options could operate for >15 years before more negative environmental impact is realized. This time, however, is well beyond the expected cleanup times of 5 and 7 years for aerobic and anaerobic systems respectively. The thermal treatment option exhibits an operational breakeven time of approximately 90 days, which is less than the expected remediation time of 100 days.

Case Studies - Site B

Site B is an abandoned hazardous waste landfill in which organic compounds were leaching into a public drinking water supply. A series of purge wells contain the contaminated plume for onsite remediation.

Two remediation technologies are feasible: 1) vacuum steam stripping and 2) granulated activated carbon (GAC) adsorption. LLCA was performed on each option and compared to the do nothing or no action as a baseline.

Major assumptions made during the LLCA included the following:

- operations annualized since the total mass of pollutants in the area is unknown (annual mass = ~12,500 Kg)
- no air emissions observed for either treatment option
- construction was not considered (already built)
- well pumping power was not considered (common to all options)

The final results of the study are summarized in the table below; total and local environmental impacts were also determined.

Site B Results
[Million EIU]

LLCA Component	Baseline (Annual, Reg Agency limits)	Vacuum Steam Strip (Annual)	GAC (Annual)
Total impact [million EIU]	**17**	**214**	**46**
from groundwater	17	0	0
from process materials	0	2	5
from operating electricity (incl C regen)	0	198	35
from organics destruction	0	0.5	0
from carbon regeneration	0	0.8	7
from operating fuel consumption	0	12	0
Local impact [million EIU]	**17**	**12**	**0**
from groundwater	0	0	0
from process materials	0	0	0
from operating electricity (incl C regen)	0	0	0
from organics destruction	0	0	0
from carbon regeneration	0	0	0
from operating fuel consumption	0	12	0

Although the baseline (no action) scenario exhibits the lowest EIU value, this option is unacceptable. Therefore, based upon the LLCA results of the remaining alternatives, GAC provides the lowest overall impact with essentially no local impact, and was chosen as the preferred option.

Examination of data from the sensitivity analysis shows electricity consumption to be the most sensitive to change for both alternatives.

Since the total mass of contaminants at Site B is not reliably known, a true breakeven analysis in the strictest sense could not be performed. However, when annualized, it can be demonstrated that the vacuum steam stripper shows breakeven occurring at approximately 4 weeks operation; GAC at approximately 19 weeks operation.

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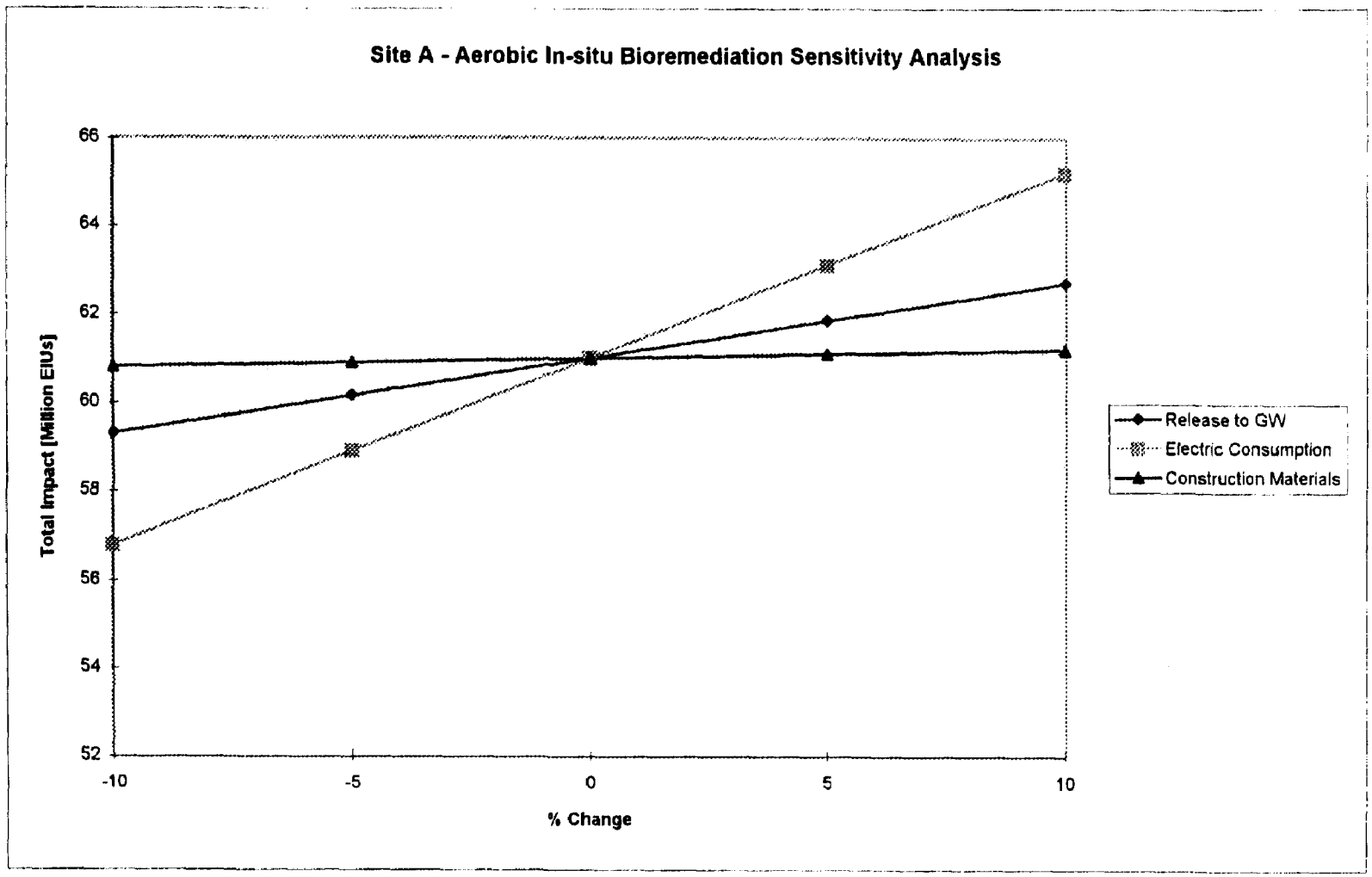
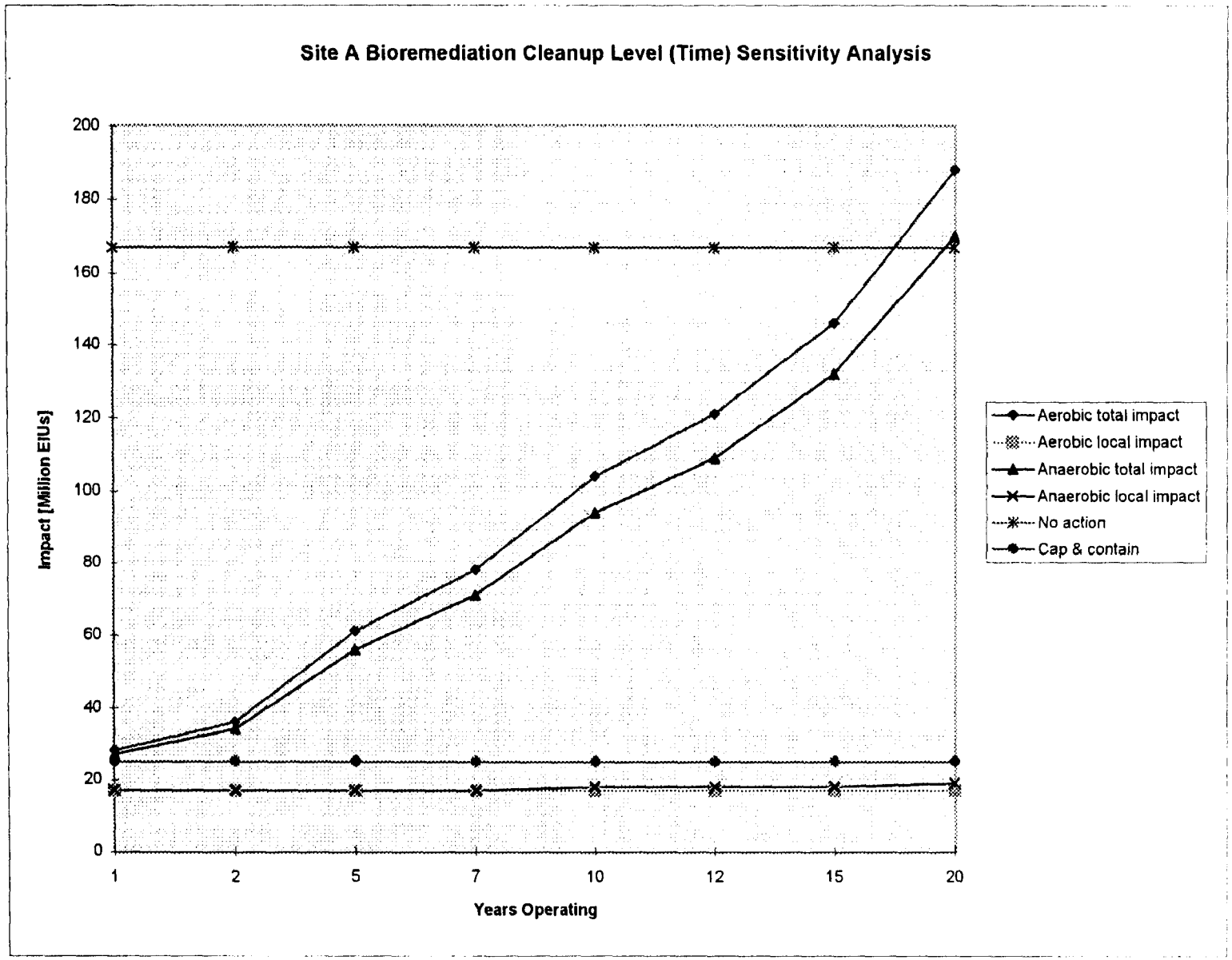

Site A - Aerobic In-situ Bioremediation Sensitivity Analysis
Total Impact [Million EIUs]
66
64
62
60
58
56
54
52
-10
-5
0
5
10
% Change
Release to GW
Electric Consumption
Construction Materials


Site A Bioremediation Cleanup Level (Time) Sensitivity Analysis
Impact [Million EIUs]
200
180
160
140
120
100
80
60
40
20
0
1
2
5
7
10
12
15
20
Years Operating
Aerobic total impact
Aerobic local impact
Anaerobic total impact
Anaerobic local impact
No action
Cap & contain

91

REDUCING WASTE GENERATION AND RADIATION EXPOSURE BY ANALYTICAL METHOD MODIFICATION

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SUMMARY

The primary goal of an analytical support laboratory has traditionally been to provide accurate data in a timely and cost effective manner. Added to this goal is now the need to provide the same high quality data while generating as little waste as possible. At the Savannah River Technology Center (SRTC), we have modified and reengineered several methods to decrease generated waste and hence reduce radiation exposure. These method changes involved improving detection limits (which decreased the amount of sample required for analysis), decreasing reaction and analysis time, decreasing the size of experimental set-ups, recycling spent solvent and reagents, and replacing some methods. These changes had the additional benefits of reducing employee radiation exposure and exposure to hazardous chemicals. In all cases, the precision, accuracy, and detection limits were equal to or better than the replaced method. Most of the changes required little or no expenditure of funds. This paper describes these changes and discusses some of their applications.

INTRODUCTION

Our laboratory provides analytical support for many different types of research programs within SRTC and throughout the Savannah River Site. A wide variety of sample types including ground water, organics, laboratory waste, process control, sludge, soils, and others are received for many different analyses. These samples are both radioactive and non-radioactive and may contain hazardous materials such as RCRA metals, organics, and flammable solvents. The sample size is often limited by these chemical hazards or by the level of radioactivity. Hazardous substituents present in the sample may prohibit its disposal to the laboratory drain system and therefore may limit the size of the sample or, in some cases, may prevent its analysis entirely.

The nature of an R&D support organization is to perform accurate analyses on unknown and uncharacterized samples and to be able to adapt analysis methods to compensate for difficult or hazardous sample matrixes. To enable analysis of all samples received while minimizing hazardous waste generation and radiation exposure, we performed a systematic evaluation of all methods performed in our Wet Chemistry and Ion Chromatography Laboratories. Evaluation of the more than thirty methods performed in these labs took approximately two years and is still continuing. Each method was evaluated for reagent content, detection limits, sample size, and its necessity in being offered. Improvements were tested and evaluated on both standards and actual samples. Method changes were implemented once the validity of the method was proven and documented. The changes that were made fell into three categories: method modification, reagent recycle or replacement, and method replacement.

DISCUSSION

Modification of Existing Methods

- **Ion Chromatography**
  Ion chromatographic analysis is one of the most frequently requested analyses in our laboratory, with over 7000 samples being submitted in 1995. This method is used to determine common anions and cations in aqueous sample matrixes. In this analysis, a sample is introduced into a flowing stream (mobile phase) which carries the sample through an ion exchange resin. Ions in the sample are separated by differential interaction with the resin and quantified through conductivity detection. Originally, the analysis took approximately 20 minutes per sample run and generated approximately 100 mL of aqueous waste per run. On average, complete determination of the commonly requested anions (fluoride, formate, chloride, nitrite, nitrate, phosphate, sulfate, and oxalate) required three different dilutions (three runs) so a typical sample analysis generated 300 mL of aqueous waste. Cation analysis followed a similar pattern. Several method changes were tested and implemented which lowered the waste generated to 20 mL per sample.

  The existing suppression system, which was used to decrease or "suppress" the conductivity of the eluent mobile phase, was a counter-current ion exchange system. Once the sample had passed through the anion exchange resin (for anion analysis) and the anions in solution were separate, the eluent stream was passed through a cation exchange resin. The separated anions passed through unaffected, but the cations in the eluent (predominantly sodium) were exchanged for hydrogen ions contained in a counter-current (regenerant) stream. This converted the eluent to a weak acid with very low conductivity. The regenerant stream flowed at 4 to 5 mL per minute and represented 80% of the liquid waste generated.

  This suppression system was replaced with an electrochemical suppression system which produces a regenerant stream by electrochemically reducing the waste from the eluent stream. The self regenerating suppressor (SRS) employs a self-contained electrochemical membrane and thus requires no preparation of reagents. It is therefore less time consuming and less costly that the previous system. The cost of the SRS membranes is the same as that of the counter current suppressor membranes. Minimal instrument and procedural modification was required. The suppressor system is more effective at decreasing the background conductivity and so enhances detection limits. The lower background conductivity enabled modification of the detector to increase the sensitivity of the analysis by an order of magnitude. This lower detection limit decreased the required sample volume by 90% with a corresponding decrease in radiation exposure.

  The separation of ions is effected by passage through a low capacity ion exchange column. The existing columns required 20 minutes for complete separation of anions and 15 minutes for complete separation of cations. These columns were relplaced by lower capacity ion exchange columns (called "fast-sep" columns) which effect the same separation in 5 minutes. Since the instrument generates waste based on the length of an analysis run, this change decreased the waste generated per sample by 75%. The precision of the data, +/- 3 to 5% depending on the sample matrix, is equal to that of the original columns. Since the column is of lower capacity that the previous column, column damage was of concern when running concentrated samples. However, the column has proven to be fairly resilient and can be easily cleaned and regenerated after poisoning by concentrated samples. The column lifetime, 12 to 18 months on average, is comparable to the previous column. Currently, our lab is testing a smaller diameter

column which effects the same separation using one fourth the eluent flow rate and one fourth the sample volume.

The combined effect of these changes was to decrease the liquid waste generated by 95%, decrease the required sample volume by 90% with a corresponding decrease in radiation exposure, lower the detection limits by an order of magnitude, and cut the analysis time by 75%. The precision and accuracy were virtually unchanged.

- **Titrations - Microelectrodes and Buffer Volume Reduction**
  Many of the analyses performed in the wet chemistry laboratory are titrations which use either potentiometric, pH, or ion selective electrodes to determine the titration endpoint. Waste reduction can be accomplished by decreasing the size of the analysis system and by using smaller, more sensitive electrodes (microelectrodes).

  The most common titrations performed in the lab are pH titrations to determine acid and base concentrations and halide determinations using ion selective electrodes. The standard sample cup used required a minimum sample volume of 25 mL to adequately cover the surface of the electrode. This cup was replaced with a narrower cup which required only 10 mL to cover the electrode surface. Data validation tests on standards and samples showed the precision and detection limits to be comparable to that of the 25 mL volume method. This change, which decreased the liquid waste generated by 60%, was simple to make and required minimal procedure modification and virtually no analyst training.

  Microelectrodes are small working surface electrodes, anywhere from 5 mm to less than 1 mm in diameter. A standard size electrode, which is usually 12 mm in diameter, typically requires clearance in solution of twice the electrode diameter in order to obtain accurate data. If a smaller solution volume is used, the electrode experiences electrochemical feedback from the sides of the reaction vessel. This feedback distorts the electrochemical response and corrupts the aquired data. Smaller electrodes require proportionally less clearance in solution and thus smaller volumes of solution. In addition, reducing the size of the electrode surface decreases the electrochemical noise caused by the unequal distance of all points on the surface of the electrode to the reference or counter electrode. For these reasons, smaller electrodes offer lower detection limits and require correspondingly lower sample volumes. Micro pH electrodes have been implemented in pH measurements, as described in the next section. They are still being evaluated for routine use in the titrations performed in the laboratory.

- **pH Determinations**
  The measurement of pH, hydrogen ion concentration, is one of the simplest laboratory measurements to make. It is also one of the easiest to do incorrectly, particularly with unbuffered samples. The most frequently made error is not allowing the electrode to equilibrate sufficiently in the sample. Therefore it is important to measure an adequate sample volume (20 to 25 mL with a standard size 12 mm electrode) and to repeat the measurement with fresh volumes of sample until successive measurements agree within 0.1 pH unit. In general, 50 to 100 mL of sample are required to accurately determine pH.

  We replaced the standard size pH electrode which had been in use in the lab with a smaller 5 mm diameter electrode. This electrode requires only 5 mm clearance to obtain accurate data. Using a 10 mL vial, accurate pH measurements can be made using 1.5 mL of sample. The waste generated by this analysis was reduced by 95%. A wide variety of samples between pH 2 and pH 14 was measured using both the standard size

electrode and the microelectrode. The pH results agreed within 0.1 pH unit and so were essentially equivalent.

Reagent Substitution and Recycle

- **Karl Fisher Titrant**
  Determination of volume percent water in liquid samples is accomplished by a potentiometric titration commonly known as the Karl Fisher method. An aliquot of sample is introduced into anhydrous methanol and titrated with a pyridine containing titrant. The titrant complexes with water, thus changing the solvent potential which is measured electrochemically. Pyridine is a RCRA listed waste and cannot be introduced in to the 773-A high or low activity drain systems. To reduce the hazard of the waste generated, we replaced the pyridine containing Karl Fisher Titrant with a pyridine-free titrant, hydranal. Hydranal contains a non-hazardous amine which complexes with water in the same manner as pyridine does in the Karl Fisher titrant. No method modification or instrument reprogramming was required and so the transition to this new solvent was essentially effortless. The precision and accuracy of the titration using hydranal is the same as that obtained using the pyridine-containing solvent. The relative standard deviation of the method is 3% in both cases.

  The solvent used in the Karl Fisher Method, methanol, is also hazardous from a flammability standpoint. However, less than 20% of the waste from the method is methanol, so the total waste stream from the method contains less than 10% total organic carbon. The total waste stream therefore is non-hazardous. Development work in progress on this method involves reducing the volume of methanol required by employing a microvoltammetric system.

- **Strontium Chloride**
  Determination of carbonate and free-hydroxide is accomplished by first precipitating the carbonate out of solution and then determining the carbonate and free hydroxide concentrations separately with pH titrations. The standard method in use involved precipitation of the carbonate with excess barium chloride. Barium is a RCRA listed waste due to its toxicity and can no longer be introduced into the laboratory's high or low activity drain system. We replaced the barium chloride with strontium chloride which is non-hazardous. Method validation experiments showed the strontium to be equivalent in a variety of sample matrices. Samples commonly run for carbonate and free-hydroxide were analyzed in duplicate using both methods and the results were found to be equivalent in all cases. As with the Karl Fisher titrant replacement, no method changes or instrument modifications were required.

- **Freon Recycle**
  The standard analysis method for determining total petroleum hydrocarbons (commonly known as oil and grease determination) involves solvent extraction of the hydrocarbons using Freon followed by quantitation using infrared detection. This had been the method of choice because it was simple, rugged, inexpensive, and applicable to solid and liquid samples and radioactive samples. Due to its deleterious effect on the ozone layer, the use of Freon and other chloro-fluorocarbons (CFCs) has been greatly restricted. Freon has become very expensive ($800/liter) and will soon be unavailable entirely. Proposed replacement methods include solid-phase extraction, solvent extraction, and supercritical fluid extraction all of which use gravimetric determination or infrared analysis of the extracted hydrocarbons. These methods are not as precise or as sensitive as the Freon extraction method, they require a larger amount of sample due to the decreased sensitivity, and the solid phase extraction method cannot be used with solid samples. Supercritical fluid extraction requires expensive instrumentation

($100,000), facility services (high pressure ultrapure carbon dioxide), and a lot of bench top and hood space. This method is therefore not feasible for radioactive sample analysis. All replacement methods would require procurement of new equipment and analyst training.

We opted to keep the existing Freon method and recycle the solvent. An inexpensive solvent reclamation system was procured to reclaim the spent Freon. This reclaimer removes hydrocarbons from the Freon solvent by passage through an activated carbon bed. The operation is simple: spent Freon is poured into the top of the instrument and clean Freon is obtained from a tap at the bottom. The hydrocarbon content of the reclaimed Freon is measured to ensure its purity. The capacity of the carbon bed is 5 g of hydrocarbon. This bed is changed out routinely every 3 months or if the hydrocarbon content of the reclaimed Freon is above 0.2 ppm (twice the minimum detection limit of the analyzer).

Using the carbon bed unit, 95-97% of Freon can be reclaimed and reused. The reclaimer has been used successfully for non-radioactive sample analyses for over two years. A contained unit is currently being tested for radioactive samples.

Instrument Replacements

- **High Temperature TOC**
  The existing instrument for determining total organic carbon (TOC) and total inorganic carbon (TIC) used a persulfate oxidation method. A sample was oxidized with sodium persulfate and the carbon in the sample was evolved as carbon dioxide gas. The evolved gas was quantified using infrared detection. This method had several undesirable characteristics. First, it used a flow cell reaction chamber which required a large sample volume (50 to 100 mL) per analysis. The instrument could only accommodate liquid samples, so the frequently requested analyses on sludges and soil samples could only be accommodated by making a slurry of the sample and then aspirating this slurry, while stirring, into the instrument. Sampling variability and absorption of carbon dioxide while the sample was stirring had a deleterious effect on both the precision and the accuracy of the data. In addition, the aspirated particulates frequently clogged the flow cell which contributed to a high percentage of down time while the instrument was being cleaned and repaired. The analysis method required hazardous chemicals (sodium persulfate) and generated a high volume of hazardous and radioactive waste. The instrument was also ten years old and was at the end of its useful life.

  We replaced this system with a Rosemount DC-190 High Temperature Total Organic Carbon Analyzer. This instrument oxidizes samples by combustion in a 900°C furnace, so there are no reagents to prepare or dispose. The analyzer is automated and requires only 50 microliters per analysis. In addition, ADS reconfigured the instrument by placing a small sampling system and analysis chamber in a radiologically contained hood. This enabled the analysis of radioactive samples, using as little as 25 microliters of sample. The contained module can accommodate solid samples so the need to dilute the samples into a slurry, and the accompanying detection limit and instrument damage problems, is eliminated. The detection limits of this instrument are 0.1 parts-per-million, which represents an order of magnitude improvement over the previous system. The instrument is also capable of determining purgeable organic carbon and non-purgeable organic carbon, methods which were unavailable with the previous instrument.

The overall benefit from this instrument change was a 98% reduction in the total liquid waste generated, a thousand fold decrease in the required sample size, and an order of magnitude decrease in the detection limits. The precision was slightly improved, from +/- 5% to +/- 3% RSD. The contained module is approximately one third the size of the previous system's contained module. This compactness is a huge benefit considering the scarceness of radioactive hood space. Unlike the previous instrument, in which 100 mL of radioactive sample was placed in an open flask while being aspirated into the instrument, the new contained analysis requires that 25 microliters of sample be introduced into a sealed furnace. This smaller sample volume combined with the shielding provided by the furnace significantly decreases radiation exposure to the analyst.

- **Flashpoint Tester**

Flashpoint is a frequently requested waste characterization analysis. Liquids which have a flashpoint below 140°F are considered hazardous due to flammability and must be treated as hazardous waste. We had a Pensky-Martens closed cup flashpoint tester which is the standard method for flashpoint determination. The temperature of the sample was raised at a specified rate and a flame was periodically introduced into the space just above the sample. The flash was detected by a heat sensor and recorded. This open cup system required 60 mL of sample. Since many of the samples received for flashpoint are organic, such as diesel fuel and solvents, this method presented a particular waste disposal problem, especially with radioactive samples. As with the TOC analyzer, the flashpoint tester had been put into service in 1980 and was at the end of its useful life. When the unit was taken out of service in 1993, it had failed and could not be repaired.

This instrument was replaced by a Petrolab multi-position mini-flashpoint tester. This unit is an open cup flashpoint tester requiring only 1 mL of sample per analysis. The flash is sensed by a pressure transducer which monitors the pressure change when the sample flashes. The system is much smaller (approximately one fourth the bench top footprint of the previous instrument) and requires no facility services other than 110 V electrical power. The unit has an autosampler which can accommodate eight different samples and can be programmed to perform different analysis protocols on each sample. The single sample unit is even smaller than the multiposition unit and one of these smaller units has recently been procured to be placed in a radiologically contained hood.

Open cup flashpoint values are slightly higher than closed cup values. For example, the closed cup flashpoint of dodecane, which is the check standard used with the analysis method to ensure that the instrument is functioning properly, flashes at 165°F in a closed cup tester and 174°F in an open cup tester. The standard laboratory method, upon which all hazard data is based, requires a closed cup value. The programming in the open-cup tester was therefore modified to give closed cup values. The accuracy of this modified temperature program is verified before each set of samples is analyzed. The precision of the method is +/- 1 to 3% when analyzing standards and samples. Reducing the sample size had no effect on the precision or accuracy of the data as long as the sample cups in the tester are well cleaned between samples.

The overall benefit was a 98% reduction in the amount of waste generated. The automated system greatly reduced the hands-on analysis time which decreased the analyst's exposure to chemicals and increased productivity.

CONCLUSION AND PATH FORWARD

We have successfully decreased the waste generated by these methods and decreased the total waste generated by the Ion Chromatography and Wet Chemistry laboratories by 60%. In all cases, the analytical precision and accuracy remained the same or improved and in most cases the detection limits were improved. The cost per sample decreased not only by streamlining methods but also by decreasing the costs associated with chemical procurement and waste disposal. The benefits of waste reduction and minimizing radiation exposure were achieved. Current efforts to further decrease waste generated include additional implementation of microelectrodes and buffer volume reductions in titrations and solvent recycling.

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