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QUALITY ASSURANCE

DISTRIBUTED INTEGRATED SUPERFUND ENVIRONMENTAL SYSTEM (DISES) - EPA'S WEB-BASED ENVIRONMENTAL DATA REPOSITORY

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The Environmental Protection Agency's Environmental Analytical Results Repository serves as one of the largest databases of its kind - containing analytical results for three to four hundred thousand environmental samples collected over a nine year period under the national Contract Laboratory Program (CLP). Plans are underway to extend this repository to ultimately contain all other environmental analytical results, including those from non-CLP programs, thus making this one of the most complete repositories for all Superfund analytical programs.

Such a repository will be an ideal target for data mining ventures, exploratory data analyses, and other statistical studies. The EPA is currently migrating this entire data system to a client/server environment, and redesigning the interfaces to the system. Users will be able to access these data repositories through the internet with the help of web-based intelligent interactive interfaces. The application of data warehousing technologies interfaced with web-based data analysis tools provide the ideal environment for state-of-the-art research on analytical procedures, environmental chemical behavior, and classical statistical methodologies. Web-based decision support systems interfacing these repositories will provide decision makers with the tools to conduct "drill-down" analyses of the data.

While the internet has geared itself to be the largest source of information, it is far from being the best source of information in any one field primarily due to the lack of an organized means of information delivery. Information on a particular subject is scattered the world-over! The EPA's new Distributed Integrated Superfund Environmental System (DISES) serves to provide the one most complete and generic interface to the Agency's distributed environmental data repository.

QUALITY ASSURANCE PROJECT PLAN FOR STUDIES USING SOLID PHASE MICROEXTRACTION (SPME) WITH GAS CHROMATOGRAPHY (GC)

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ABSTRACT

Solid Phase Microextraction (SPME) is a technique developed recently for sampling target organic analyses in liquids, solids and vapor headspace. Though the technique is only several years old, it is getting wide acceptance for use in combination with analytical instruments based on chromatography e.g., gas chromatography (GC) high performance liquid chromatography (HPLC), and ion mobility spectrometry (IMS). Potential applications are many including those dealing with sampling and analysis of water and environmental waste. The Quality Assurance Project Plan (QAPjP) described in this paper focuses on cocaine, its sampling with SPME and its analysis with GC. Sampling and analysis of cocaine in various environmental matrices represent major technology challenges and have high visibility in drug interdiction. Though the focus is on cocaine, the QAPjP can be translated to use with more classical environmental pollutants by taking into account properties of the target analyses.

INTRODUCTION

The goal of the present paper is to write a Quality Assurance Project Plan (QAPjP) for research studies using solid

phase microextraction (SPME) with gas chromatography (GC). The specific example involves research on the conversion chemistry of cocaine. However, the QAPjP can be translated to SPME-GC use with environmental pollutants by taking into account properties of analyses of interest as later discussed. A QAPjP for sampling and analysis may vary considerably depending on whether the method to be applied is well established or whether the method is still in an exploratory stage. Irrespective of the method maturity, the QAPjP is meant to provide valid and defensible data. SPME-GC methodology is still evolving. Development of SPME-GC for a specific application is not routine and requires research. This QAPjP is being written accordingly.

The present QAPjP will follow, with some modifications, the Preparation Aids for the Development of Category III and Category IV Quality Assurance Project Plans.[1] Quality assurance categories are established to determine the degree of quality assurance that is required from a point of view of the end use of obtained data: "Category III Projects are those producing results used to evaluate and select basic options, or perform feasibility studies or preliminary assessments of unexplored areas which might lead to further work. Category IV Projects are those producing results for the purpose of assessing suppositions".[1]

Two concepts are involved in QAPjPs[2]:
- A quality assessment-mechanism which verifies that the system is operating within acceptable limits, and
- A quality control-mechanism established to control errors.

A treatment of these concepts in a research QAPjP includes preparation of a more flexible plan for corrective actions and modifications of the proposed analytical procedure in comparison to more defined plans for routine analyses. Since the QAPjP in this paper will frame the research concept and a specific method development, i.e., the use of SPME-GC system in studies of cocaine conversion chemistry, the quality assessment and quality control mechanisms in this plan reflect unknown and sometimes unpredictable pathways of analytical errors and method limitations.

This QAPjP will cover:
- The process being tested and the objectives of the test,
- The quality of data that will be required and how that quality will be obtained,
- Sampling and detection procedures, and
- How data will be calculated, recorded, reviewed and reported in a defensible manner.

PROJECT DESCRIPTION

GENERAL OVERVIEW

SPME description. Solid phase microextraction (SPME) is a solventless extraction technique. The idea is based on sorbtion of an analyte on a fused silica fiber coated with an organic polymer. Sorbed analyses are thermally desorbed from the fiber, for instance, in an injection port of a gas chromatograph (GC). A team from Waterloo University-Canada, Department of Chemistry introduced SPME technology a few years ago[3]. Commercialization of SPME has been led by Supelco. Descriptive information on SPME can be found in Supelco's SPME Highlights[4]. A typical SPME device consists a holder with a stainless steel plunger and a stainless steel shield (needle) for the fiber. The fiber, 1 cm length fused silica coated on its outer surface with a polymer, is connected to the plunger. The shield is used to pierce septa of sampling vials or an injection port of a GC. The height of the stainless steel shield is adjustable. By pushing in or pulling out the plunger, the fiber can be exposed or withdrawn into the shield, respectively. Many polymers are used as coatings for SPME fibers. Diffusion of analyte from the sample matrix into the fiber coating depends on the thickness and polarity of the coating. Examples of stationary phases are, for example, a polyacrylate that is recommended for semipolar compounds and a poly(dimethylsiloxane) that is used for nonpolar compounds. Generally the thicker is the coating, the more analyte can be sorbed onto the fiber. However, the desorption time to remove analyses from the fiber will be longer for thicker coatings[5,6]. SPME is thought to be a very convenient sample collection method for analytical laboratory applications especially in conjunction with GC, GC/mass spectrometry (MS), and high performance liquid chromatography (HPLC)[7,8,9]. Extraction of analyses from liquids and solids or vapors (headspace), can be performed with SPME[10,11]. Examples of using SPME can be found in Supelco Application Notes and in the scientific literature. SPME is used in the food industry for flavor analysis[12], in headspace analysis of accelerants in fire debris[13], analysis of amphetamine in urine[14], and as a fast screening method for pesticides and volatiles in environmental samples[15], giving several examples.

GC technique. GC is well established as an analytical tool and does not require extensive description. Details are available in many GC bibliographies, e.g.,[16,17]. Detailed information on GC parameter development will be given in the Section 3, paragraph 3.2 Process Measurements of the present QAPjP.

THE PROCESS

Studies on conversion chemistry of cocaine will be performed at a microscale level, i.e., nanogram to microgram amounts of cocaine freebase and cocaine hydrochloride. Cocaine will be deposited on zeolite powders and the samples will be heated. Expected conversion products such as methyl benzoate, methyl ecgonine, and methyl ecgonidine will be collected on a SPME fiber from the sample headspace (vapors). At the method development stage, standard (certified) solutions of cocaine will be used. The method development combines SPME for sampling and GC for analysis.

STATEMENT OF PROJECT OBJECTIVES

The objective of the overall program portion, that is presented in this QAPjP is to develop a sampling and analytical system (SPME-GC) to help elucidate the conversion chemistry of cocaine using various zeolites at diffe-rent temperatures. A second objective is to select the most effective zeolite for the conversion chemistry. Efficiencies of conversion reactions are unknown and can not be predictable *a priori,* however, a 50% reaction efficiency would be desirable to ensure that sufficient amounts of products are formed to be easily detectable.

EXPERIMENTAL DESIGN - LIST OF EXPECTED MEASUREMENTS

Planned experimental measurements are presented in Table 1. These will be addressed further in the Quality Assurance Objectives Section.

Table 1. Summary of planned measurements in SPME-GC method development for studying the conversion chemistry of cocaine.

Measurement	**Measurement classification**	**Measurement site**	**Measurement frequency**
Temperature of heating block	critical	sample insert	continuous
Mass of zeolite powder	critical	analytical balance	each sample preparation
Volume of standard cocaine solutions	critical	Eppendorf automatic pipette	each sample preparation
Time of sample incubation at various vial temperatures	critical	heating block, sample	each sampling period
Time of analyte sorbtion on the SPME fiber	critical	sample headspace	each sampling period
GC parameters	critical	HP-6890 gas chromatograph (GC)	established during instrument calibration
Time of analyte desorption from the fiber	critical	Split/Splitless injection port of the GC	established throughout method development
Other measurements as might arise during method development will be included. Those measurements which require blanks (control samples) are also classified as critical.			

It is planned that each zeolite-cocaine combination will be prepared as three individual samples with one corresponding blank. The total number of samples is unknown. The primary selection of zeolite-cocaine combinations to be tested will be obtained by using a screening method developed in our laboratory[18]. The method combines SPME and ion mobility spectrometry (IMS). IMS is known as a very rapid and sensitive technique for drug detection. Heights and positions of signals obtained from IMS relate roughly to reaction yield and specifically to identification of reaction products. The information gained will determine which zeolite-cocaine sample will be selected for more detailed analysis with the SPME-GC system.

SCHEDULE

The detailed schedule for the overall project would be given here. Though important for the Project performance the schedule is independent of data quality considerations.

PROJECT ORGANIZATION AND RESPONSIBILITIES

The list of key personnel and their assigned responsibilities would be given here.

QUALITY ASSURANCE OBJECTIVES

Quality Assurance Objectives - definition. The limits on bias, precision, comparability, completeness and representativeness defining the minimal acceptable levels of performance determined by the data user's acceptable error bounds.[19] QA Objectives must be defined in terms of project requirements, and not in terms of the capabilities of the intended methods."

DETERMINING QA OBJECTIVES

The QAPJP refers to the method development process. It is a nonstandard method, in the present case, thus, in-process data validation will determine the ability of the method to achieve the desired results. Data validation is given in a later section of the present QAPjP.

QA Objective #1. *Design experiments leading to conversion chemistry of cocaine freebase and cocaine hydrochloride. Identify reagents and experimental setups that will result in enhancing cocaine decomposition to methyl benzoate, methyl ecgonine, and methyl ecgonidine.*

Zeolites are chosen as possible catalysts in the conversion reaction. A list of zeolites selected for tests is given below. All zeolites arc in a powder form and they are commercially available. List of chosen zeolites:

- organophilic zeolite
- molecular sieves 3A
- molecular sieves 4A
- molecular sieves 5A
- molecular sieves 13X
- NH_4Y zeolite
- NaY zeolite
- montmorillonite KF10
- montmorillonite KSF
- Ag exchanged zeolite
- zeolite purchased from Sigma

The amount of required zeolite for the conversion reaction will be decided from results of the method development. The amount, however, should be no less than 1.0 mg due to minimum capacity of the available analytical balance. (Weighing limits of the laboratory analytical balance Denver model M-310 are: maximum capacity 310 g, minimum capacity 1.0 mg, and readability 0.1 mg.)

Cocaine freebase (1000 µg/mL) standard solution in acetonitrile, and cocaine HCl (1000 ug/L) standard solution in methanol will be used for sample preparation. Certificates for these solutions will be obtained at the time of purchase. The volume of cocaine solution that will be used in zeolite-cocaine tests is not determined, but can not be smaller than 2 µL when using an automatic pipette (Eppendorf). The smallest range of the pipette adjustment is 2-20 µL. Accuracy and precision of the pipette are as follows:

Range [µL]	Accuracy [%]	Precision [%]
2	± 6.0	≤ 5.0
10	± 1.2	≤ 0.6
20	± 0.8	≤ 0.3

If smaller volumes are needed, Hamilton syringes will be used.

Tests will be performed in GC vials with conical inserts of 0.1 mL volume. Vials will be sealed with septa screw cups. Sampling with SPME will be performed at various temperatures. For temperatures higher than ambient, a heating block will be used. Stability of the temperatures obtained with the heating block should be no lower than ±1°C.

QA Objective #2. *Optimize the conversion chemistry reaction parameters.*

The assumption, at the present time, is to relate the process yield to disappearance of cocaine upon the conversion reaction. However, the lowest concentration of cocaine that can be used in the reaction is not determined at this point, but it should be at the microgram level.

The process of optimization includes a choice of the most promising zeolite for further investigations, define the best sampling vials, time of sampling, and detection parameters (GC).

QA Objective #3 *Follow guidelines/definitions[2] for precision, accuracy, method detection limits, and completeness as given below:*

Precision - the degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. Precision is concerned with the closeness together of results. The precision of chemical measurements for this project will be defined from standard deviations of measurements of three samples. The precision of the physical measurements, for example, the stability of the temperature of the heating block will be defined with results obtained from several days of measurements.

Accuracy - the degree of agreement of a measured value with the true or expected value of the quantity of interest. The accuracy for this project is not know at the present time. The degree of agreement of measured values of the conversion chemistry will be related to the calibration curve obtained at the identical conditions as tested samples.

Detection limit - the smallest concentration or amount of some component of interest that can be measured by a single measurement with stated level of confidence. The confidence level for this project is chosen to be 95%. Detection limit for this project is the method detection limit. This can be determined after accomplishments in particular components of the method development processes. The reference and Quality Control of the detection limit for GC measurement will be the cocaine calibration curve obtained by direct injection (Autoinjector HP-6890) of cocaine standard solutions. The curve will be obtained by triplicate measurements for each cocaine concentration. The QC-check will be performed on a daily basis by using the lowest and the highest concentration of the cocaine calibration solutions. The detection limits for physical measurements (temperature, time, weight, etc.) are related to respective instruments. No regulatory threshold exists for detection of cocaine and its conversion products, but the desirable yield of the reaction is 50% of cocaine conversion to methyl benzoate, methyl ecgonidine or methyl ecgonine at nanogram levels.

Completeness[1] - for Category III projects, completeness is defined as the number of measurements judged valid compared to the total number of measurements. For this project, the completeness objective is 100% for at least three runs. For example, three samples of a particular zeolite-cocaine set have to provide valid data to be used as a basis for decision-making and direction in design of additional experiments. Summarized QA Objectives for precision, accuracy, method detection limit and completeness related to this QAPJP are presented in Table 2.

OTHER QA OBJECTIVES

Any additional QA objectives that may appear throughout SPME-GC method development will be added to this QAPJP at periodic reviews. QA Objectives of the presented project will be interpreted in a statistical manner - Approach to QA/QC

WHAT IF QA OBJECTIVES ARE NOT MET?

The chemistry of cocaine will be reviewed relative to the results obtained. The use of catalysts other than zeolites will be considered.

Table 2. QA Objectives for precision accuracy and method detection limits (MDL)

Critical measurements	Matrix	Method	Reporting units	MDL	Precision	Accuracy (% of cocaine decomposition)	Completeness
Temperature of heating block	air	thermocouple	°C	-	standard deviation		100
Mass of zeolite	powder	analytical balance	mg	readability ±0.01 mg	-	-	100
Volume of standard cocaine solutions	methanol, acetonitrile	automatic pipette	µL	2 µL	±	-	100
Sample incubation time	-	personal watch	min	1 sec	± 1 sec	operator related	100
Time of sampling (sorbtion on SPME fiber)	headspace	personal watch	min	1 sec	± 1 sec	operator related	100
Cocaine and its conversion reaction products	vapors	GC	ng	not defined at the present time	relative standard deviation lower than 5%	desirable 50%	100

SAMPLING AND ANALYTICAL PROCEDURES

SAMPLING AND MEASUREMENT

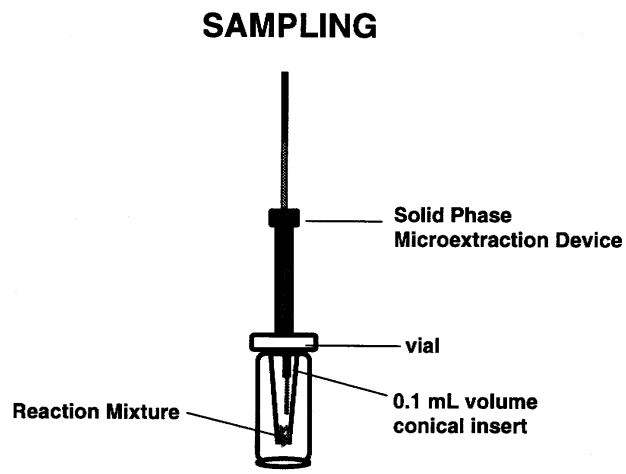

Figure 2. Schematic illustration of proposed sampling method using SPME.

Sampling procedure with SPME. Sampling experiments will be performed with a commercially available (Supelco, Inc.) SPME device for manual injection. Different fibers, ekonical vials with crimped aluminum caps with viton septa, temperature of a heating block, typical GC vials (2 mL) with screw-cap with PTFE/silicon septa, conical inserts and plastic self centered supports are selected for the method development. The sampling procedure involves placing reagents in the conical insert of a vial, sealing the vial and placing the vial into a heating block. After a certain time of the sample incubation, the SPME fiber will be introduced to the headspace of the sample or sampling will be processed immediately after location of the sample in the heating block. Times of analyte sorbtion on the fiber will be investigated. At the end of the sampling period, the fiber will be withdrawn into the needle and the needle will be removed from the vial. Analyses with GC will be performed immediately after the sampling. Cocaine solutions need to be stored in a freezer. Each sample will be prepared *in-situ* and processed immediately after preparation. Glass vials and inserts should have deactivated inner surfaces. Samples (vials) after sampling should be disposed in a designated container. The SPME fiber need to be conditioned before use. (The conditioning procedure is included in the instruction from manufacturer.) The height of the fiber immersion into a vial will be experimentally defined and then maintained through the sampling processes. The temperature stability of the heating block will be performed and presented in a form of a control chart. The monitoring of the temperature should be performed on a daily basis.

Sample detection with the SPME-GC and the SPME-GC/MS systems. A gas chromatograph (Hewlett Packard

model HP-6890) coupled with a flame ionization detector (FID) and a capillary column HP-INNOWax (15 m, 0.25 mm I.D., 0.25 µm film thickness) are chosen for the SPME-GC experiments. The fiber from the sampling process will be inserted into the split/splitless injection port of the GC. The analyses from the fiber will be thermally desorbed in the GC injection port. Detailed GC parameters will be established. GC response to 100 ng cocaine will serve for GC parameter optimization. A purge time will affect complete desorption of analyses from the fiber and their transfer to the head of the column and need to be properly determined. The exposed fiber should remain in the injection port after the purge valve is opened. These two parameters are considered to be of great importance. The first will affect the overall reaction yield estimation, and the later will be significant for identification of carry-over processes. Glass liners used in the GC injection port should be deactivated. For direct injection, the standard 4 mm diameter liner containing deactivated glass wool, and for SPME analyses, the 0.75 mm diameter liner will be used. The depth of the fiber immersion into the injection port will be chosen and then maintained for all performed measurements.

CALIBRATION PROCEDURE AND FREQUENCY

GC calibration. Cocaine standard solutions will be used. Verification of purity of these standards are included in certificates that are enclosed in shipping documents.

Cocaine HCl, 1000 µg/mL in methanol, will be purchased from Sigma. Cocaine freebase, 1000 µg/mL in acetonitrile, will be purchased from Radian. Preparation of diluted solutions in appropriate solvents will be performed in the laboratory. These solutions will be used for reaction experiments and calibration curves. It is proposed to use concentrations in a range from 5 ng to 1000 ng for preparation of calibration curves (direct injection of appropriate solutions) for cocaine HCl and cocaine free base. Each point will be the average of three measurements of the same solutions. Results will be collected in a data base using the computer software - Microsoft Excel. All calculations, graph drawings, and calibration curve equations will be processed with this software. The GC performance will be verified on a daily basis by checking the lowest and highest cocaine concentrations defined within the linear response of the instrument. Calibration curves for cocaine HCl and cocaine freebase using SPME sampling (as opposed to direct injection) need to be obtained after the methodology is developed. Relative Standard Deviation Errors (RSDE) of calculated averages should not exceed 5% for the direct injections, and 10% for sampling with SPME.

Analytical balance. The analytical balance Denver model M-310, has an automatic internal calibration with built-in NIST (National Institute of Standards and Technology) Traceable Weights. The calibration of the balance should be performed once a day before its use.

Eppendorf automatic pipettes. Accuracy and precision of a pipette should be checked at least once a week using gravimetric methods recommended by manufacturer. (See Appendix C.) When necessary the pipette should be re-calibrated to meet default criteria

APPROACH TO QA/QC

The operating characteristic of a method are called figures of merit.[20] Figures of merit such as: precision, detection level, sensitivity, bias, selectivity, and useful range are critical for selection methodology and need to be evaluated quantitatively. When a measurement system is in statistical control, i.e., variability of a measurement process is set, figures of merit describe the effectiveness of a method. In this paper a sampling-analysis method development is the object of QA/QC considerations, thus, values of figures of merit are unknown, or set a priori regarding to expected (desirable) results. However, they will be quantified within the method development process. It is also to be understood, that method modifications will be reflected in corrective actions upon data validation. This allows quality assurance of the measurements to be established. A systematic approach to statistical control of the measurements will be based on a calibration process. In chemical measurements, it refers to the process by which the response of a measurement system is related to the concentration or amount of analyte of interest. Measurement is essentially a comparison process in which an unknown whose value is to be determined is compared with a known standard.

CALCULATION OF RESULTS

All results (responses) obtained from GC measurements will be stored and undergo calculations, and graphical

presentations in a data base created with the computer software Microsoft Excel. The calibration curves for both the direct injection and SPME-GC, will he produced using diluted standard solutions of cocaine. At least five calibration points (cocaine concentrations) will be used to plot curves. Calibration curves (direct injection, and SPME-GC) based on at least three measurements for each concentration point, will be illustrated with corresponding graphical plots. The plots will be used to judge a linear relationship and to screen for outlying data points. The method of least-squares will be used for linear fit of data and will be reported as a correlation coefficient. The linearity test will be illustrated by error bars (standard deviation) for each plotted point. A linear fit will be justified when bars intersect the fitted line in a random manner. The slope and the intercept of the curve will be calculated and presented in the curve equation. The uncertainty of the calibration curve will be decreased by increasing the number of calibration points or increasing the number of independent measurements with each calibration solution. Yields of cocaine conversion will be calculated from the SPME-GC calibration curve equation.

STATISTICAL TREATMENT OF BLANKS

The blank measurements simulate the sample measurement process. Blank corrections are necessary for the proper data interpretation. In the present method a blank will be a methanol-zeolite or an acetonitrile-zeolite sample. It is not expected that cocaine may be present in any of zeolites, but some compounds present in zeolites may have the same retention times as cocaine or of cocaine conversion products. If this occurs the following statistical treatment for blank correction will be applied[20]:

Cm-mean of m measurements of the analyte concentration in the sample, with standard deviation δ_m
C_b-mean of b measurements of the analyte concentration in the blank, with standard deviation δ_b
C_s-best estimate of the analyte concentration in the sample, corrected for the blank
The statistical uncertainty of $C_m = \pm t\delta_m > \sqrt{m}$
The statistical uncertainty of $C_b = \pm t\delta_b / > \sqrt{b}$, where $t = t_{1-\alpha/2}$ is the value for m-1 degrees of freedom for the 100(1-α)% confidence level.

The blank correction will be calculated from the equation below:

The uncertainty of Cs ± $td_s = (C_m - C_b) + t\ \sqrt{[d^2_m/m + d^2_b/b]}$, where $t = t_{1-\alpha/2}$ is the value for m+b-2 degrees of freedom for the 100(1-α)% confidence level.

QC CHECKS FOR PROCESS MEASUREMENTS

Control Intervals. Frequency of measurements of control samples will depend on the stability of the GC performance, and the SPME-GC procedure. To estimate the stability runs of two cocaine standard solutions, one of the lowest and the other of the highest concentration used for the calibration curve preparation, will be chosen for analysis on a daily basis for a month. When the system shows good stability, the use of one cocaine solution is judged to be sufficient for a QC check.

DATA VALIDATION

Data validation is the process by which data are filtered and accepted or rejected based on a set of criteria. It is the final step before release of data[19,20]. Data validation for this project will be performed by peer review. The conclusions along with "raw" data will be reported and discussed with the project Principal Investigator.

DATA RECORDING

Sample preparations, and instruments used will be recorded in a Laboratory Notebook with dates indicated. Data, in the Laboratory Notebook, will be addressed with a file name under which they are stored in the HP-Chemstation for the GC measurements, and short sample descriptions. The Laboratory Notebook will have numbered pages and will include the table of contents on its first pages. Results of all measurements will be transferred to a data base created with the Microsoft Excel. Calculations and graphical data presentation will be performed with Microsoft Excel. A backup of each GC-Chemstation and Microsoft Excel files will be saved on floppy disks.

DATA REPORTING

Data presented in form of graphs and/or worksheets along with calculations will be reported to the Principal Investigator. After the data validation the Principal Investigator will report them in the form required by the overall Project. The overall Project progress and accomplishments will be reported periodically at review meetings to the appropriate management personnel.

GUIDELINES FOR PRACTITIONERS IN EXTENDING METHOD DEVELOPMENT TO ENVIRONMENTAL APPLICATIONS

SPME from the beginning of its invention[3] has been focused on extracting organic compounds from various matrices such as air, soil, and water, followed by their thermal desorption in a gas chromatograph injector, separation on a column and quantitation by the detector. The method has been applied to volatile and nonvolatile compounds. "Because SPME can attain detection limits of 15 ppt (parts per trillion) and below for both volatile and nonvolatile compounds, the technique can be used for the United States Environmental Protection Agency (EPA) methods and the Ontario Municipal/Industrial Strategy for Abatement (MISA) program".[5] Examples of organic pollutants sampled with SPME from different matrices and related literature references are given in Table 3.

Theoretical considerations of SPME processes are available.[3,5,10] The principle is the partitioning of analyses between the sample matrix and the extraction medium (coating of the fiber). The amount of an analyte sorbed on the fiber is illustrated by the following equation[10]:

$$n = K_{fs}V_fC_oV_s \,/\, K_{fs}V_f + v_s$$

where: n - mass of an analyte sorbed on the coating,
V_f - volume of the coating,
V_s - volume of the sample,
K_{fs} - partition coefficient of the analyte between the coating and the sample matrix, and
C_o - initial concentration of the analyte in the sample.

SPME can be used to extract organic compounds form virtually any matrix as long as target compounds can be released from the matrix. To overcome kinetic limitation one can use heat, and mixing processes, or modify the nature of a matrix by pH adjustment, and "salting out" procedures. These will increase the coating(fiber)/matrix partition coefficient, thus enhance sampling efficiency. Derivatization can be used for polar compounds such as phenols or carboxylic acids to improve their sorbtion on the fiber and their chromatographic separation. Derivatization can be performed *in situ,* i.e., fiber coating is covered with derivatization reagent. Compounds will be simultaneously extracted and derivatized. Also target compounds can be derivatized in their matrix and then sampled (extracted). Different groups of analyses can be extracted either by direct or headspace sampling with different sensitivity that is affected by a fiber coating and a sample matrix. Examples of sampling approaches are presented in Table 4.

Affinity of a target analyte to the fiber coating influences SPME sampling since both matrix and fiber coating compete for analyses. The basic principle of "like dissolves like" applies, so that nonpolar compounds are extracted by nonpolar coating, and vice versa. There are many different coatings (and coating thickness) offered by Supelco, that can be chosen depends on target analyses and sample matrices. A comparison of poly(dimethylsiloxane) and polyacrylate fiber coatings along with the rules of thumb for adsorption are presented in the paper of Yang and Peppard.[6] Unusual fiber coatings such as graphitized carbon black[24], and pencil lead[23] have been demonstrated for analysis of organic pollutants, as well. The primary factors affecting linear range and limit of detection using SPME-GC technique are fiber coating and GC detector.[5,10] The choice of the GC detector is limited to requirements of a certain EPA method for environmental analyses, whereas some consideration of the choice of the fiber coating have to be undertaken. With the increase of the fiber thickness more analyte is sorbed and the linear range increases, but the time of sampling has to be longer. Generally, it is most efficient to use thick fibers for analyses with low partition coefficient, and thin fibers for these with high partition coefficient. The octanol-water partition coefficients (K_{ow}) appeared to be useful to predict detection limits with SPME, and alternatively, SPME can be used for their estimation.[25] The determination of K_{ow} is important for the prediction of the fate of organic pollutants in the environment.

Table 3. Organic pollutants sampled with SPME

Compounds	Matrix	Ref.	SPME data compared with EPA method
Semivolatile insecticides, e.g.,: DDT(dichlorodiphenyltrichloroethane), BHC (benzene hexachlorides), hexachlorocyclohexanes, and others	water	15	508, 608, 625
Volatile Organic Compounds (VOC): chloroform, 1,1,1-trichloroethane, carbon tetrachloride, benzene, toluene, and others	environmental air	21	TO-14
BTEX: benzene, toluene, ethylbenzene, m,p-xylene, o-xylene	water, headspace	7	
BTEX, and volatile organic compounds listed in EPA method 624	water, headspace	11	624
Phenols	water	22	525
Lindane, methyl parathion, chlorophenol	water	23	604, 624, and Ontario MISA Group 20
PCB (polychlorinated biphenyls), PAH (polyaromatic hydrocarbons)	water	8	525
VOC, BTEX	water, headspace, air	24	

Table 4. SPME sampling techniques

SPME sampling technique	Approach	Analyte	Matrix
Direct	routine	most compounds	gaseous, liquid
	in situ chemical derivatization	polar compounds	"
Headspace	routine	volatile and semivolatile compounds	any matrix
	heating/cooling	volatile and semivolatile compounds with low partition coefficients	"

Future and state-of-the art developments of SPME. The development of new coatings will expand SPME technology. Recently a new coating for polar analyses has appeared on the market, The fiber coating is under evaluation among SPME users. This should expand environmental application. Bioaffinity coatings will allow to sample proteins and other biologically significant species from body fluids or cells.[10] An idea to use SPME with high speed GC[7] for field applications, including monitoring and process control for environmental applications seems to be very appealing. For example, *in situ,* screening of water samples should be time and cost effective. Two types of SPME devices are commercially available; for manual and autoinjection. The manual device can be used with any GC, whereas, the device for autoinjection is designed for Varian GC. Fully automated SPME consists a software that regulates an autosampler performance.[5] Extraction and analysis can be performed overnight, increasing sample throughput. The latest achievement in SPME automation is reported by Varian.[26] A new SPME III with sample agitation allows to reduce sorption and cycle times for semivolatile compounds. In addition to all Varian GC and GC/MS software programs, the SPME III is available for Hewlett Packard's 5890 GC Chemstation.

SUMMARY

Solid Phase Microextraction (SPME) is a technique developed recently for sampling target organic analyses in liquids, solids and vapor headspace. Though the technique is only several years old, it is getting wide acceptance for use in combination with analytical instruments based on chromatography e.g., gas chromatography (GC) high performance liquid chromatography (HPLC), and ion mobility spectrometry (IMS). Investigators are being challenged

with writing quality assurance plans for research and new concept studies using SPME. Due to the nature of research studies, few functions are followed repetitively in exactly the same manner, at least in the initial stages of the study and sometimes throughout the study. Writing QAPjPs for basic research and new concept studies was discussed at the 9th Annual Waste Testing and Quality Assurance Symposium.[27] The present paper on QAPjPs for SPME and GC draws from guidelines given in the earlier manuscript. Many environmental applications have followed naturally as SPME was being developed, however, no QAPjPs have been published to our knowledge. The present paper should be useful to both researchers and practitioners seeking information in writing quality assurance plans involving SPME.

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COMPARISON OF ONE-STEP ACID EXTRACTION VERSUS TWO-STEP BASIC AND ACIDIC EXTRACTION PROCEDURES FOR SEMIVOLATILE ANALYSIS OF WASTEWATER

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ABSTRACT

The Research and Development Department of the Metropolitan Water Reclamation District of Greater Chicago (District) is responsible for analyzing a significant number of industrial wastewater samples, collected within its jurisdiction, in order to document compliance with the United States Environmental Protection Agency's (USEPA) General Pretreatment Regulations.

The USEPA mandated method of analysis of base/neutral acid extractable compounds (BNAs) in wastewater samples is Method 625. This is a gas chromatographic/mass spectrometric (GC/MS) method that involves a two-step extraction with methylene chloride at a pH greater than 11 and then at a pH less than 2, using a separatory funnel or a continuous extractor.

The Contract Laboratory Protocol (CLP) of the USEPA's Superfund Program, requires an updated version of Method 625 when analyzing samples for BNAs. This updated method uses a one-step acid extraction with methylene chloride at a pH less than 2.

The feasibility of using the CLP method for analyzing Industrial Waste Pretreatment Program samples was investigated because of the time and the labor savings involved. Various laboratory evaluation studies were conducted to determine whether this alternate one-step acid extraction method would give comparable results to Method 625. These studies consisted of comparisons of method detection limits, spike recoveries in reagent water and actual field samples, and the precision between Method 625 and the alternate one-step acid extraction.

Over 60 BNAs (55 target compounds and 6 surrogates) were used in the comparative study of method detection limits and spike recoveries by the two procedures. Using reagent water the one-step acid extraction gave consistently better recoveries. Similar results were obtained with representative field sample matrices.

In all cases, the recovery values obtained by both methods were well within the established USEPA limits. In addition, the precision and sensitivity evaluation, as evidenced by method detection limit comparisons, also supports the use of one-step acid extraction.

Based upon the results of this investigation, the District submitted an application to the USEPA to have the one-step acid extraction accepted as an Alternate Test Procedure (ATP) for analyzing industrial waste samples. After thorough review, USEPA Region V approved the use of this alternate one-step acid extraction method.

INTRODUCTION

The Research and Development Department of the Metropolitan Water Reclamation District of Greater Chicago (District) is responsible for analyzing District water reclamation plant samples; namely, final effluent, raw sewage, and sludge for its National Pollutant Discharge Elimination System (NPDES) permits. The District performs specialized analysis in connection with pollution control of waterways and Lake Michigan. The District is frequently called upon to carry out specialized analyses in support of litigation, administrative hearings, and various research and technical assistance projects as well as analysis of emergency samples. The District is also responsible for analyzing a significant number of industrial wastewater samples, collected within its jurisdiction, in order to document compliance with the USEPA General Pretreatment Regulations. One portion of these regulations requires the determination of total toxic organics (TTOs) that may be present in the samples. The TTOs include volatile organic compounds (VOCs), BNAs, pesticides, and PCBs.

The USEPA-mandated methods of analysis of organic priority pollutants for the Pretreatment Program are the "600

Series". Method 625[1] is required for the analysis of BNAs. This is a GC/MS method that involves a two-step extraction with methylene chloride at a pH greater than 11 and then at a pH less than 2, using a separatory funnel or a continuous extractor.

The CLP of the USEPA's Superfund Program[2], requires an updated version of Method 625 when analyzing samples for BNAs. This updated method uses a one-step extraction with methylene chloride at a pH less than 2.

The feasibility of using the CLP method for analyzing Industrial Waste Pretreatment Program samples was investigated because of the time and labor savings involved.

DESCRIPTION OF STUDY

Two different methods of extraction were investigated in this study. The CLP one-step acid extraction and the two-step basic and acidic extraction procedures of Method 625.

Over 60 BNAs (55 target compounds for industrial waste monitoring and 6 surrogates) were analyzed in a comparative study. The study was done using 4 replicates of reagent water and 4 representative field samples; namely, final effluent, raw sewage, Lake Michigan water, and an industrial waste sample. Reagent water was used to evaluate the efficiency of the method on a sample free of interferences. The field samples were used to reveal the effects of the interferences on the method. A matrix blank was also extracted and analyzed for background concentrations of the tested analyses.

Precision and sensitivity were evaluated as well as quality assurance/quality control.

METHOD SUMMARY

For the one-step acid extraction[2], one liter of sample was extracted three times with 60 ml portions of methylene chloride at a pH less than 2.

For the two-step basic and acidic extraction[1], one liter of sample was extracted three times with 60 ml portions of methylene chloride at a pH greater than 11, then re-extracted three times with 60 ml portions of methylene chloride at a pH less than 2.

The collected extracts were passed through sodium sulfate, then concentrated to 1.0 ml. The concentrated extracts for each method of extraction were injected into the GC/MS instrument equipped with a 30 meter narrow bore DB-5 fused silica capillary column. The instrument met all daily performance criteria specified by Method 625[1]; namely, decafluorotriphenylphosphine[3], and column performance tests for BNAs.

RESULTS

The method detection limit (MDL) values in reagent water, determined from analyzing seven replicates extracted using both methods of extraction, showed that both extraction methods are capable of attaining the required USEPA MDLs. The results are shown in Table 1, in comparison to the USEPA Method 625 MDLs.

Matrix MDL values were also determined by analyzing seven replicate field samples, using both methods of extraction and the results are shown in Table 1. This data indicates that the sample matrix does not impact the sensitivity of Method 625, regardless of which extraction procedure is used.

Recovery studies were made using reagent water and different matrices. Representative field samples were chosen; namely, final effluent, raw sewage, Lake Michigan water, and an industrial waste sample (electroplating). These samples were analyzed using both extraction procedures to determine the background concentration before spiking. The results reveal that only trace levels of phenol, diethyl phthalate, di-n-butyl phthalate, and butyl benzyl phthalate were found, and both methods were comparable.

Table 2 compares the percent recovery of the spiked target compounds, and the surrogates in four replicates of reagent water using the two extraction procedures. This table also shows the average percent recovery in

comparison to Method 625, and the CLP limits.

In direct comparison of the two procedures, using reagent water (Table 2), the CLP one-step extraction gave consistently higher recoveries. Out of 244 observations, only four values gave more than 10% higher recoveries using the two-step extraction as compared to the one-step extraction, whereas 108 values gave more than 10% higher recoveries using the one-step extraction as compared to the two-step extraction, and 132 values had a difference in recovery of less than 10% in both methods. Based upon the average of four replicates (out of the 61 compounds) only one compound had more than 10% higher recovery using the two-step extraction as compared to the one-step extraction, and 24 compounds had more than 10% higher recovery using the one-step extraction as compared to the two-step extraction. Thus, the CLP one-step extraction gave higher recoveries than the two-step extraction of Method 625.

Table 3 compares the percent recovery of the spiked target compounds and the surrogates in four representative field sample types: final effluent, raw sewage, Lake Michigan water, and an industrial waste sample, using the two procedures of extraction. This table also shows the average percent recovery in comparison to Method 625, and the CLP limits.

In direct comparison of the two procedures, using the four sample types previously mentioned, a total of 244 comparisons were obtained. The data shown in Table 3 reveals that 54 values gave more than 10% higher recoveries using the two-step extraction as compared to the one-step extraction, whereas 120 values had more than 10% higher recovery by the one-step extraction as compared to the two-step extraction, and 70 values had a difference in recovery of less than 10% in both methods. Based upon the average of four replicates, only three recovery values were more than 10% higher using the two-step extraction as compared to the one-step extraction, and 33 values were more than 10% higher using the one-step extraction as compared to the two-step extraction. This would indicate that the CLP one-step extraction results in higher recoveries than the Method 625 two-step extraction over the range of compounds studied. It should also be noted that all recovery values for both procedures were well within the established USEPA limits.

Table 4 shows the duplicate spike recoveries of surrogates using one-step extraction versus two-step extraction in an industrial waste sample, and in the reagent water blank.

Percent recovery of duplicates were very reproducible using both procedures. However, percent recovery using one-step extraction were higher than those using two-step extraction, indicating the superiority of the one-step extraction. Percent recovery of these surrogates were also well within the CLP limits, at the spiking level of 50 µg/L. There are no limits for recovery of these surrogates under Method 625.

Table 5 shows the duplicate spike recoveries of representative organic priority pollutants (acid extractables at 100 µg/L and base/neutral extractables at 50 µg/L) using one-step extraction versus two-step extraction in an industrial waste sample, as compared to the limits under Method 625 and CLP. Percent recovery of duplicates was very reproducible. However, percent recovery using one-step extraction was higher than those using two-step extraction, again indicating the superiority of the one-step extraction. Percent recovery using both procedures was well within the Method 625 and the CLP limits.

USEPA APPROVAL FOR A LIMITED USE ALTERNATE TEST PROCEDURE

As part of its USEPA-approved Pretreatment Program, the District is required to sample and analyze the wastewater discharges from approximately 360 Significant Industrial Users (SIUs) to ensure their compliance with USEPA-promulgated categorical standards. These categorical standards regulate various toxic pollutants in the industrial discharges to the sewer system, and generally consist of various organic priority pollutants.

The USEPA specifies the exact analytical methods to be used for this type of analysis. Since 1984, the required methods for the pretreatment program have been the so-called "600 Series" of methods of which Method 625 is a part. In 1990, the USEPA proposed the use of an alternate extraction analytical procedure in the CLP, for analyzing environmental samples collected at Superfund Program sites. Their research showed that the CLP procedure, which uses one-step extraction, produced comparable precision and accuracy to the "600 Series" Methods, which use two-step extraction, and require fewer man-hours per sample to perform.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 1. METHOD DETECTION LIMITS (MDLs) OF ACID AND BASE/NEuTRAL EXTRACTABLES IN REAGENT WATER AND FIELD SAMPLES WITH ONE-STEP ACIDIC EXTRACTION VERSUS TWO-STEP BASIC AND ACIDIC EXTRACTION

	Compound	USEPA MDL in Water Method 625	MDL in Reagent Water		MDL in Field Samples	
			One-Step	Two-Step	One-Step	Two-Step
	ACID EXTRACTABLES					
1	Phenol	1.5	0.5	0.4	1.4	1.5
2	2-Chlorophenol	3.3	0.7	0.7	2.3	2.3
3	2-Nitrophenol	3.6	0.6	0.6	1.9	1.9
4	2,4-Dimethylphenol	2.7	0.9	1.0	1.4	6.4
5	2,4-Dichlorophenol	2.7	1.2	0.6	2.0	2.0
6	p-Chloro-m-cresol	3.0	1.3	1.0	1.4	1.7
7	2,4,6-Trichlorophenol	2.7	0.7	0.9	1.4	1.4
8	2,4-Dinitrophenol	42.0	5.4	3.7	11.2	20.0
9	4-Nitrophenol	2.4	3.1	3.0	4.4	6.2
10	4,6-Dinitro-o-cresol	24.0	9.9	10.3	8.0	15.0
11	Pentachlorophenol	3.6	7.9	6.3	7.2	14.5
	BASE/NEUTRAL EXTRACTABLES					
1	N-Nitrosodimethylamine	ND[1]	0.5	0.5	1.4	1.4
2	Bis(2-chloroethyl)ether	5.7	0.9	1.0	2.6	2.6
3	1,3-Dichlorobenzene	1.9	0.7	1.0	1.8	1.8
4	1,4-Dichlorobenzene	4.4	1.1	0.9	1.8	1.8
5	1,2-Dichlorobenzene	8.4	1.0	0.9	1.8	1.8
6	Bis(2-chloroisopropyl)ether	5.7	0.8	0.7	1.7	2.0
7	Hexachloroethane	1.6	1.3	1.0	1.6	1.6
8	N-Nitrosodi-n-propylamine	ND	0.8	0.8	1.8	1.8
9	Nitrobenzene	1.9	0.6	0.5	2.0	3.7
10	Isophorone	2.2	0.7	0.7	1.4	1.4
11	Bis(2-chloroethoxy)methane	5.3	0.6	0.7	1.8	1.8
12	1,2,4-Trichlorobenzene	1.9	1.1	1.6	1.6	1.6
13	Naphthalene	1.6	0.8	0.8	1.6	1.6
14	Hexachlorobutadiene	0.9	1.3	1.3	1.4	1.7
15	Hexachlorocyclopentadiene	ND	ND	ND	3.4	3.4
16	2-Chloronaphthalene	1.9	0.8	0.7	1.1	1.1
17	Acenaphthylene	3.5	0.7	0.9	0.9	1.0
18	Dimethylphthalate	1.6	1.3	0.5	0.5	1.9
19	2,6-Dinitrotoluene	1.9	0.7	0.6	0.8	1.2
20	Acenaphthene	1.9	0.9	0.8	0.9	1.2
21	2,4-Dinitrotoluene	5.7	0.6	0.6	0.8	1.4
22	Fluorene	1.9	0.9	0.8	0.8	1.5
23	Diethylphthalate	1.9	0.7	0.7	0.5	3.2
24	4-Chlorophenyl phenyl ether	4.2	1.0	0.9	0.8	1.1
25	N-Nitrosodiphenylamine	1.9	0.8	0.7	1.3	1.5
26	Diphenylhydrazine	ND	0.9	0.9	0.5	1.3
27	4-Bromophenyl phenyl ether	1.9	1.0	0.7	0.8	1.7
28	Hexachlorobenzene	1.9	0.9	0.7	0.6	1.8
29	Phenanthrene	5.4	0.7	0.5	0.4	1.3
30	Anthracene	1.9	0.7	0.7	0.5	1.2
31	Di-n-butylphthalate	2.5	0.8	1.2	1.4	1.4
32	Fluoranthene	2.2	0.5	0.6	0.4	1.5
33	Pyrene	1.9	0.8	0.7	0.5	4.6
34	Butyl benzyl phthalate	2.5	0.9	0.8	0.7	2.5
35	Benzo(a)anthracene	7.8	0.5	0.6	0.8	1.4
36	Chrysene	2.5	0.7	0.8	0.4	1.5
37	3,3'-Dichlorobenzidine	16.5	2.1	2.0	7.5	7.5
38	Bis(2-ethylhexyl)phthalate	2.5	12.3	28.7	15.8	35.3
39	Di-n-octylptthalate	2.5	1.4	8.7	2.3	2.7
40	Benzo(b)fluoranthene	4.8	0.9	0.5	0.9	2.0
41	Benzo(k)fluoranthene	2.5	1.5	1.0	0.8	2.2
42	Benzo(a)pyrene	2.5	0.4	0.4	0.6	1.6
43	Indeno(1,2,3-cd)pyrene	3.7	1.5	0.4	1.2	3.0
44	Dibenzo(a,h)anthracene	2.5	0.5	0.8	1.5	3.7
45	Benzo(ghi)perylene	4.1	0.7	0.4	1.4	4.0

[1]ND = Not determined.

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TABLE 2. PERCENT RECOVERY OF SPIKED TARGET COMPOUNDS AND SURROGATES OBTAINED BY ONE-STEP ACIDIC EXTRACTION VERSUS TWO-STEP BASIC AND ACIDIC EXTRACTION FROM REAGENT WATER (fOUR REPLICATES)

	Percent Recovery										Percent Recovery Limits	
	Recovery #1		Recovery #2		Recovery #3		Recovery #4		Average			
Compounds	One-Step	Two-Step	One-Step	Two-Step	One-Step	Two-Step	One-Step	Two-Step	One-Step	Two-Step	Method 625[1]	CLP
ACID EXTRACTABLES												
Phenol	46	42	46	45	48	42	52	46	48	44	5-112	12-110
2-Chlorophenol	72	67	69	72	74	68	77	74	73	70	23-134	27-123
2-Nitrophenol	79	73	78	80	83	75	85	80	82	77	29-182	NR[2]
2,4-Dimethylphenol	85	78	83	82	90	77	91	83	87	80	32-119	NR
2,4-Dichlorophenol	86	82	86	82	90	81	90	82	88	82	39-135	NR
4-Chloro-3-methylphenol	85	80	84	85	90	80	90	86	87	83	22-147	23-97
2,4,6-Trichlorophenol	88	83	88	81	93	84	92	86	90	84	37-144	NR
2,4-Dinitrophenol	76	68	81	74	80	72	81	78	80	73	D[3]-191	NR
4-Nitrophenol	44	38	46	42	48	42	48	42	47	41	D-132	10-80
4,6-Dinitro-2-methylphenol	91	79	89	85	90	81	90	84	90	82	D-181	NR
Pentachlorophenol	89	80	88	84	89	82	90	83	89	82	14-176	9-103
BASE/NEUTRAL EXTRACTABLES												
N-Nitrosodimethylamine	36	43	34	41	37	40	41	50	37	44	ND[4]	NR
Bis(2-chloroethyl)ether	80	70	76	62	82	64	86	80	81	69	12-158	NR
1,3-Dichlorobenzene	64	52	56	45	63	51	59	63	60	53	D-172	NR
1,4-Dichlorobenzene	66	54	59	48	65	54	61	64	63	55	20-124	36-97
1,2-Dichlorobenzene	66	52	59	48	65	53	62	64	63	54	32-129	NR
Bis(2-chloroisopropyl)ether	63	57	62	50	67	53	73	67	66	57	36-166	NR
Hexachloroethane	64	48	54	44	59	52	54	61	58	51	40-113	NR
N-Nitroso-di-n-propylamine	72	60	71	53	75	58	78	72	74	60	D-230	41-116
Nitrobenzene	80	67	74	60	81	63	84	74	80	66	35-180	NR
Isophorone	77	62	74	57	82	57	84	71	79	62	21-196	NR
Bis(2-chloroethoxy)methane	79	67	77	62	84	64	85	78	81	68	33-184	NR
1,2,4-Trichlorobenzene	76	63	70	57	78	63	73	72	79	64	44-142	39-98
Naphthalene Hexachlorobutadiene	81	70	75	63	83	66	81	76	80	69	21-133	NR
Hexachlorocyclopentadiene	79	65	70	57	78	67	72	74	76	66	24-116	NR
2-Chloronaphthalene	84	63	72	53	83	63	82	71	80	63	ND	NR
Dimethylphthalate	84	74	81	63	90	70	86	77	87	71	60-118	NR
Acenaphthylene	90	85	85	74	92	83	90	89	90	83	33-145	NR
2,6-Dinitrotoluene	94	82	92	90	97	78	92	78	92	82	D-112	NR
Acenaphthene	86	79	87	81	91	78	90	84	88	80	50-158	NR
2,4-Dinitrotoluene	84	77	86	73	89	76	88	81	90	77	47-145	46-118
Fluorene	98	93	102	94	103	94	104	99	98	95	39-139	24-96
Diethylphthalate	84	77	84	75	88	78	90	81	90	78	59-121	NR
4-Chlorophenyl phenyl ether	97	94	98	91	100	94	98	92	97	93	D-114	NR
N-Nitrosodiphenylamine	108	106	105	94	112	101	108	104	108	101	25-158	NR
1,2-Diphenylhydrazine	97	96	93	96	100	94	95	94	96	95	ND	NR
4-Bromophenyl phenyl ether	89	82	86	82	90	80	86	85	88	82	ND	NR
Hexachlorobenzene	95	84	91	85	95	83	94	88	94	85	53-127	NR
Phenanthrene	100	90	94	92	99	90	96	95	97	92	D-152	NR
Anthracene	93	87	91	89	94	86	92	91	92	88	54-120	NR
Di-n-butylphthalate	94	90	92	90	94	88	94	91	94	90	27-133	NR
Fluoranthene	95	94	93	93	97	90	93	92	94	92	1-118	NR
Pyrene	97	93	96	95	99	90	94	94	96	93	26-137	NR
Butyl benzyl phthalate	93	88	89	93	92	83	91	94	91	89	52-115	26-127
Benzo(a)anthracene	93	89	92	94	93	87	95	94	93	91	D-152	NR
Chrysene	93	88	92	94	93	95	95	94	93	93	33-143	NR
Bis(2-ethylhexyl)phthalate	94	88	96	94	93	86	95	94	94	90	17-168	NR
Di-n-octylptthalate	96	94	97	97	95	92	98	98	96	95	8-158	NR
Benzo(b)fluoranthene	89	85	96	87	92	88	97	94	95	88	4-146	NR
Benzo(k)fluoranthene	93	88	95	90	95	88	102	95	96	90	24-159	NR
Benzo(a)pyrene	91	87	94	90	94	89	96	91	94	89	11-162	NR
Indeno(1,2,3-cd)pyrene	90	86	93	90	94	87	95	92	93	89	17-163	NR
Dibenzo(a,h)anthracene	83	79	84	84	87	76	90	86	86	81	D-171	NR
Benzo(ghi)perylene	82	76	84	82	86	74	90	85	86	79	D-227	NR
	85	79	85	84	89	78	92	87	88	82	D-219	NR

Surrogates												
2-Fluorophenol	48	42	47	47	49	43	52	48	49	45	ND	21-110
Phenol-d5	41	36	40	40	43	38	46	41	42	39	ND	10-110
Nitrobenzene-d5	78	67	74	57	82	62	82	74	79	65	ND	35-114
2-Fluorobiphenyl	84	74	80	65	88	7	87	9	85	39	ND	43-116
2,4,6-Tribromophenol	92	81	90	80	95	84	94	86	93	83	ND	10-123
Terphenyl-d14	95	86	91	91	92	85	90	92	92	88	ND	33-141

[1]In reagent water.
[2]NR = Not required.
[3]D = Detected - results must be greater than zero.
[4]ND = Not determined.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 3. PERCENT RECOVERY OF SPIKED TARGEt COMPOUNDS AND SURROGATES OBTAINED BY ONE-STEP ACIdIC EXTRACTION VERSUS TWO-STeP BASIC AND ACIDIC EXTRACTION fROM FOUR DiffERENT FIELD SAMPLE MATRICeS

	Final Effluent		Raw Sewage		Lake Michigan		Industrial Waste		Average		Percent Recovery Limits	
Compounds	One-Step	Two-Step	One-Step	Two-Step	One-Step	Two-Step	One-Step	Two-Step	One-Step	Two-Step	Method 625[1]	CLP
ACID EXTRACTABLES												
Phenol	35	42	47	31	63	48	44	14	47	34	5-112	12-110
2-Chlorophenol	45	52	57	35	81	58	22	7	51	38	23-134	27-123
2-Nitrophenol	51	56	64	39	86	62	56	54	64	53	29-182	NR[2]
2,4-Dimethylphenol	33	26	75	49	77	57	8	6	48	35	32-119	NR
2,4-Dichlorophenol	52	63	72	50	86	68	63	22	68	51	39-135	NR
4-Chloro-3-methylphenol	57	69	78	66	88	72	78	8	75	54	22-147	23-97
2,4,6-Trichlorophenol	56	66	79	62	86	69	75	39	74	59	37-144	NR
2,4-Dinitrophenol	100	59	116	37	100	43	26	36	86	44	D[3]-191	NR
4-Nitrophenol	78	71	83	77	77	71	67	70	76	72	D-132	10-80
4,6-Dinitro-2-methylphenol	93	61	88	31	91	55	26	41	75	47	D-181	NR
Pentachlorophenol	92	82	106	65	90	73	82	47	92	67	14-176	9-103
BASE/NEUTRAL EXTRACTABLES												NR
N-Nitrosodimethylamine	27	42	32	27	55	50	33	34	37	38	ND[4]	NR
Bis(2-chloroethyl)ether	42	52	54	34	79	58	51	42	56	46	12-158	NR
1,3-Dichlorobenzene	37	46	49	29	64	47	39	29	47	38	D-172	NR
1,4-Dichlorobenzene	37	47	47	30	64	47	40	29	47	38	20-124	36-97
1,2-Dichlorobenzene	38	47	48	30	65	47	41	32	48	39	32-129	NR
Bis(2-chloroisopropyl)ether	44	53	56	34	78	59	59	42	59	47	36-166	NR
Hexachloroethane	26	35	34	18	53	37	32	23	36	28	40-113	NR
N-Nitrosodi-n-propylamine	46	56	60	38	82	63	54	45	60	50	D-230	41-116
Nitrobenzene	56	54	74	45	83	63	52	31	66	48	35-180	NR
Isophorone	46	55	61	37	83	64	58	41	62	49	21-196	NR
Bis(2-chloroethoxy)methane	48	57	61	38	85	65	61	48	64	52	33-184	NR
1,2,4-Trichlorobenzene	45	53	59	37	72	55	58	42	58	47	44-142	39-98
Naphthalene	45	54	60	37	76	58	46	42	57	48	21-133	NR
Hexachlorobutadiene	42	52	58	35	70	51	49	34	55	43	24-116	NR
Hexachlorocyclopentadiene	21	25	46	11	64	24	39	19	42	20	ND	NR
2-Chloronaphthalene	50	60	67	43	81	63	59	54	64	55	60-118	NR
Acenaphthylene	61	62	72	53	86	30	75	57	73	51	33-145	NR
Dimethyl phthalate	51	62	69	48	74	68	60	60	64	60	D-112	NR
2,6-Dinitrotoluene	59	68	70	51	85	70	58	64	68	63	50-158	NR
Acenaphthene	52	61	69	47	80	65	57	54	65	57	47-145	46-118
2,4-Dinitrotoluene	71	76	74	58	88	77	48	62	70	68	39-139	24-96
Fluorene	59	67	72	56	84	70	60	65	69	64	59-121	NR
Diethylphthalate 4-Chlorophenyl	67	71	93	73	85	64	73	72	80	70	D-114	NR
phenyl ether	59	69	72	59	85	72	73	74	72	68	25-158	NR
N-Nitrosodiphenylamine	77	57	91	84	29	42	49	87	62	68	ND	NR
1,2-Diphenylhydrazine	63	71	82	71	80	72	82	90	77	76	ND	NR
4-Bromophenyl phenyl ether	65	74	86	75	86	76	78	82	79	77	53-127	NR
Hexachlorobenzene Phenanthrene	64	73	83	73	83	76	67	69	74	72	D-152	NR
Anthracene	72	76	83	74	85	77	79	80	80	77	54-120	NR
Di-n-butyl phthalate	75	77	91	83	80	78	71	81	79	79	27-133	NR
Fluoranthene	84	81	94	84	85	82	81	85	86	83	1-118	NR
Pyrene	83	77	78	69	86	79	75	74	80	75	26-137	NR
Butyl benzyl phthalate	73	82	76	75	74	83	84	97	77	84	52-115	26-127

Benzo(a)anthracene	79	83	90	82	77	83	82	88	82	84	D-152	NR
Chrysene	86	85	84	79	84	86	78	83	83	83	33-143	NR
Bis(2-ethylhexyl)phthalate	87	85	88	82	85	87	83	86	86	85	17-168	NR
Di-n-octylptthalate	97	139	115	131	87	190	100	125	100	146	8-158	NR
Benzo(b)fluoranthene	82	95	86	83	76	95	110	107	88	95	4-146	NR
Benzo(k)fluoranthene	82	84	81	75	80	86	91	90	83	84	24-159	NR
Benzo(a)pyrene	84	84	84	81	80	87	92	92	85	86	11-162	NR
Indeno(1,2,3-cd)pyrene	83	74	82	78	64	75	70	80	75	77	17-163	NR
Dibenzo(a,h)anthracene	90	85	86	84	90	85	83	81	87	84	D-171	NR
Benzo(ghi)perylene	101	92	94	92	100	94	93	88	97	92	D-227	NR
	84	78	80	78	84	78	78	75	81	77	D-219	NR
Surrogates												
2-Fluorophenol	36	39	40	24	66	45	38	5	45	28	ND	21-110
Phenol-d5	35	41	44	28	63	47	39	11	45	32	ND	10-110
Nitrobenzene-d5	45	54	58	37	81	61	55	42	60	48	ND	35-114
2-Fluorobiphenyl	49	59	67	42	79	63	56	52	63	54	ND	43-116
2,4,6-Tribromophenol	71	80	91	79	90	78	69	40	80	69	ND	10-123
Terphenyl-d14	82	93	68	69	82	95	95	111	82	92	ND	33-141

[1]In reagent water.
[2]NR = Not required.
[3]D = Detected - results must be greater than zero.
[4]ND - Not determined.

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TABLE 4. DUPLICATE SPIKE RECOVERIES OF SURROGATES USING ONE-STEP ACID EXTRACTION VERSUS TWO-STEP BASIC AND ACIDIC EXTRACTION IN AN INDUSTRIAL WASTE SAMPLE AND IN REAGENT WATER BLANK

Surrogates[1]		% Recovery		
		One-Step	Two-Step	CLP[2] Limits
2-Fluorophenol	Sample	71, 72	51, 54	21-110
	Blank	74, 85	59, 69	
Phenol-d5	Sample	74, 77	55, 56	10-110
	Blank	79,87	61, 70	
2,4,6-Tribromophenol	Sample	123, 118	98, 116	10-123
	Blank	120, 123	102, 117	
Nitrobenzene-d5	Sample	104, 99	74, 77	35-114
	Blank	104, 112	85, 93	
2-Fluorobiphenyl	Sample	92, 93	65, 67	43-116
	Blank	91, 94	73, 90	
Terphenyl-d14	Sample	103, 100	90, 100	33-141
	Blank	105, 107	92, 102	

[1]Spiking concentrations were 50 µg/L.
[2]CLP limits were used in this table since there are no limits available under Method 625.

Realizing that increasing the sample processing efficiency of the District's organics laboratory was desirable, the work described in this report was begun in order to investigate the feasibility of using the CLP procedure for analyzing District Industrial Waste Pretreatment Program samples. In discussing the situation with the USEPA, the District was informed that the CLP procedure has not been approved for use in the pretreatment program, and that if the District wanted to use them instead of "600 Series" methods, the District would have to make a formal application to the USEPA for approval of a Limited Use ATP. The application would have to include a technical report demonstrating that the proposed alternate method gives comparable results to the current method under a variety of conditions.

Based upon the results described in this report, the District submitted an application for an ATP to the USEPA in June 1993. On February 17, 1994, the District received a letter from Valdas Adarnkus, USEPA Region V

Administrator, approving the District's application for the Limited Use ATP. Based upon this approval, the District has begun using the CLP procedure for analyzing industrial waste pretreatment program samples. By using the CLP procedure instead of the "600 Series" methods, the time required to process an industrial waste pretreatment sample has been reduced by about 20 %.

SUMMARY

Over 60 BNAs (55 target compounds and 6 surrogates) were used in a comparative study of method detection limits and spike recoveries by the two procedures.

Using reagent water, the one-step acid extraction gave consistently better recoveries. Out of 244 observations, only four values gave more than 10% higher recoveries using the two-step extraction as compared to the one-step extraction, whereas 108 values gave more than 10% higher recoveries using the one-step extraction as compared to the two-step extraction.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 5. DUPLICATE RECOVERIES OF MATRIX SPIKE COMPOUNDS USING ONE-STEP ACIDIC EXTRACTION VERSUS TWO-STEP BASIC AND ACIDIC EXTRACTION IN AN INDUSTRIAL WASTE SAMPLE

Spiking Compounds[1]	% Recovery Obtained		% Recovery Limits	
	One-Step	Two-Step	Method 625	CLP
Acid Extractables				
Phenol	59, 61	44, 44	5-112	12-110
2-Chlorophenol	75, 79	58, 60	23-134	27-123
4-Chloro-3-Methylphenol	87, 88	65, 88	22-147	23-97
4-Nitrophenol	76, 71	58, 64	D[2]-132	10-80
Pentachlorophenol	90, 85	70, 81	14-176	9-103
Base/Neutral Extractables				
1,4-Dichlorobenzene	72, 75	53, 54	20-124	36-97
N-nitrosodi-n-propylamine	78, 80	56, 60	D-230	41-116
1,2,4-Trichlorobenzene	77, 76	55, 58	44-142	39-98
Acenapthene	86, 86	60, 65	47-145	46-118
2,4-Dinitrotoluene	92, 89	71, 82	39-139	24-96
Pyrene	88, 88	79, 88	52-115	26-127

[1]Spiking concentrations for acid extractables and base/neutrals were 100 and 50 µg/L, respectively.
[2]D = Detected, result must be greater than zero.

Similar results were obtained with representative field sample matrices. Out of 244 observations, only 54 recovery values gave more than 10% higher recoveries with the two-step extraction, as compared to the one-step extraction, and 120 values gave more than 10% higher recoveries with the one-step extraction of field sample matrices as compared to the two-step extraction.

In all cases, the recovery values obtained by both methods were well within the established USEPA limits.

In addition, the precision and sensitivity evaluation as evidenced by the reproducibility results and by method detection limit comparisons also support the use of the one-step acid extraction procedure.

Based upon the results of this investigation, the District submitted a proposal to the USEPA to have the one-step acid extraction accepted as an ATP for analyzing industrial waste samples for its Pretreatnent Program. After thorough review, USEPA Region V approved the use of this alternate one-step acid extraction CLP method for analyzing TTOs in samples for the District's Industrial Waste Pretreatment Program.

ACKNOWLEDGMENT

We acknowledge Mr. Robert Booth, our consultant, for helping us in formulating the laboratory test procedures required to formally apply to the United States Environmental Protection Agency for Limited Use Alternate Test Procedure approval. We also acknowledge Mrs. Pragna Shah, Laboratory Technician II, for conducting the different extraction procedures needed for this study, and Mrs. Bonnie Bailey, Senior Clerk Typist, for typing the manuscript.

DISCLAIMER

Mention of proprietary equipment and chemicals in this report does not constitute endorsement by the Metropolitan Water Reclamation District of Greater Chicago.

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HOW TO ENSURE USABLE DATA UNDER PROGRAM SPECIFIC QUALITY CONTROL REQUIREMENTS

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Billions of dollars are spent yearly collecting environmental data for scientific research, regulatory decision making, and regulatory compliance. Much of this data is generated without taking into consideration project/program specific quality assurance (QA) criteria resulting in data that is noncompliant or does not meet project data quality objectives (DQO's). This can be prevented by implementing a QA Program that requires all project QA criteria, including validation, to be compared with analytical method requirements prior to any sampling activities.

Differences between standard analytical methods, program requirements, and project DQO's are noted in project specific Method Preparation and Analysis (MPA) Requirements. These requirements are to be met in addition to standard laboratory quality assurance/quality control (QA/QC) measures and are designed to enhance the specific standard published analytical method. Program QA criteria can often include validation guidelines that differ from procedural or QA requirements specified in the analytical methods. This can result in data that is accurate in the qualitative and/or quantitative sense but ii qualified as estimated or rejected based on program criteria. The usability of the qualified data is subjective and can vary based on the views of the validator.

This paper will illustrate that the implementation of specific procedures can reduce the instances where data is qualified. By providing project specific QC requirements to laboratories prior to analysis, this approach will minimize the probability of errors resulting from useability determination of qualified data.

VALIDITY OF LABORATORY INSTRUMENT COMPUTER PRINTOUTS AS DAILY RUNLOGS

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ABSTRACT
Daily instrument runlogs are traditionally handwritten, in bound, sequentially paginated laboratory notebooks. A column for comments provides space for the analyst to note, among others, unusual observations, such as

invalidated runs and aborted sequences and the reasons for such actions, high or low internal standard, surrogate or spike recoveries, return to control after instrument maintenance.

As prices for chemical analyses have plunged, environmental laboratories have been tempted to reduce real and perceived extra expenditures wherever they could. A favorite first target has been the daily instrument runlogs. Since the analyst has to input the information into the instrument computer for the dally run to start, some laboratories consider it superfluous to hand enter the information a second time in the daily runlog.

The significance and the essential elements of daily runlogs are discussed. Recent actual examples of computer printouts being substituted for hand-written runlogs are examined. The legal and scientific implications of generating runlogs using a non-tamperproof electronic data input system are considered and modifications proposed to current practices that may make it possible for computer runlogs to augment or eventually supplant the traditional runlog.

The unlimited and untraceable access of laboratory personnel to anonymously and repeatedly change computer field screens that hold daily runlog information makes the use of computer printouts unacceptable for daily runlog use at this time.

INTRODUCTION

As laboratories acquire more automated instrumentation, documentation by hand entry seems to be outmoded. Among the most important linchpins of laboratory documentation are daily instrument runlogs. Since the entry sequence in the computerized analytical instrument is the same as what would be in the hand entered logbook, some laboratories are trying to substitute the computer printout for the daily runlog. If proper safeguards are not in place from the very beginning of its implementation, this substitution may turn out to be an exercise in futility and an invitation to data fraud. "There is a significant difference between scientifically valid and legally defensible data".[1] Unlike runlogs, the process of data validation and qualification lends itself to automation and can end up being legally defensible and of known and documented quality.[2]

A review of recent guidance documents, protocols, quality assurance project plans (QAPP) by Federal and State agencies indicates that none addresses the issue of how should instrument runlogs be created and maintained.[3-11] To compound this confusion none of these documents addresses the issue of computerized runlogs in particular and computerized documentation in general.

EPA Region IX requires the submittal of "instrument analysis logs for each instrument" but is not clear as to its format.[7]

The most recent Contract Laboratory Program[8,9] states that:

- Entries on all laboratory documents be recorded in ink
- Instrument-specific run logs be maintained to enable the reconstruction of run sequences
- Logbook entries be recorded in chronological order

Similar statements by the U.S. Army Corps of Engineers (USACE)[4] seem to rule out the use of computer generated printouts as runlogs.

Only the U. S. Army Corps of Engineers' (USACE) draft SHELL document indicates that *"Computer logs can be used if all of the (preceding) information is captured".*[1].

Misunderstandings about runlogs are so prevalent because originators of QAPPs do not impose on the laboratory any restrictions up-front as to how the laboratory is supposed to be maintaining and documenting its runlogs.

THE SIGNIFICANCE OF DAILY RUNLOGS

The purpose of legally defensible documentation is to make it possible to recreate the events that yielded the specific data. This is heavily dependent on the scrupulous use of the method protocols, good automated laboratory practices,[13] good laboratory practices,[14] etc. Each analytical method, both organic and inorganic, has its specific

sequences of running the QC related tests, such as method blank, bromofluorobenzene tune, continuous calibration verification (CCV), etc. Properly maintained runlogs would indicate the actual run sequence of:[3]

- calibration checks
- QC checks, *e.g.* method blank, laboratory control sample (LCS), matrix spike/matrix spike duplicate (MS/MSD), etc.
- sample data

Figure 1 presents a typical runlog sequence for U.S. Environmental Protection Agency (EPA) Method SW8260A Volatile Organics by Gas Chromatography/Mass Spectrometry (GC/MS).[15]

The runlog should also contain a column for comments, that serves as a diary for recording:

- aborted or invalidated runs
- out-of-control events, such as internal standard, surrogate and/or spike compound recoveries outside control limits
- instrument malfunction
- abnormal sample conditions

The runlog comments column serves as a record of the corrective actions taken, *e.g.* when more than the permissible number of internal standards fail a rerun is indicated, or exceedance of the calibration range may require dilution and rerun, etc.

A properly documented instrument runlog serves dual purposes:

1. If assists data review and validation by providing an overview of possible QC problems for the daily run. Similar to Sample Delivery Group trend analysis,[12] checking for sudden significant shifts in internal standard area counts or in the percent recoveries of surrogates and spikes - even when all are within the prescribed control limits - gives insight into the "behavior" of the batch, the associated possible matrix effects, and instrument performance.
2. It serves as the performance record of the given instrument - this is important in determining the type and frequency of maintenance actions' as well as deciding when to replace the instrument with a newer or more modern one. It also familiarizes the new analyst with its "idiosyncrasies".

ESSENTIAL ELEMENTS OF DAILY RUNLOGS

No guidance documents or analytical protocols enunciate what are the essential elements of an instrument runlog.[16] Through experience, imitation and technical common sense a natural consensus has been arrived at that as a minimum the runlog should contain a record of the following:

1. Instrument ID
2. Sequence Number
3. Analyst's Name/ID
4. Analytical Method
5. Matrix and pH (if applicable)
6. Date
7. Time
8. Data File Identification
9. Sample Number or ID (Laboratory's and, if possible, Client's)
10. Batch Number
11. Dilution Factor
12. Client's Name or code
13. Rerun (Yes/No)
14. Comments

Initial Batch

- Tune (Method 8260A QC limits; every 12 hr before the ICal & CCV)
- ICal (5 standards; r ≥ 0.990 or %RSD ≤ 15%)
- ICB (Analytes ≤ MDLs)
- ICV (%R = 80% - 120%; use mid-level standard from independent source)
- Samples (≤ 10)
- CCV/LCS (%R = 80% - 120%; start of run, every 12 hr or 10 - 20 samples, and end of run)
- CCB/MB (Analytes ≤ MDLs)
- MS (LCS %R limits when spike ≥ 2X native analyte concentration)
- MSD/MD (LCS %R limits; RPD = 20%, 30%, or 40%)
- Samples (≤ 8)

Middle/Final Batch

- Tune
- CCV/LCS
- CCB/MB
- Samples (≤ 10)
- CCV
- MS
- MSD/MD
- Samples (≤ 8)
- CCV (Final Batch Only)

RUN SEQUENCE ABBREVIATIONS

CB	Calibration Blank
CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
ICal	Initial Calibration
ICB	Initial Calibration Blank
ICS	Interference Check Standard/Solution
ICV	Initial Calibration Verification
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MB	Method Blank
MD	Matrix Duplicate
MS	Matrix Spike
MSD	Matrix Spike Duplicate
PDS	Post-Digestion Spike

Figure 1. Sample Analytical Sequence For Method 8260A[15]

A supervisor should review, initial and date the runlogs. All pages must be sequentially numbered in a bound notebook. Empty spaces must be Z-ed out.

COMPUTER PRINTOUT RUNLOGS

From numerous on-site evaluations of laboratories, and reviews of various Sample Delivery Groups (SDG) it is evident that the consensus of the environmental laboratories is to use handwritten entries for CLP work.[8, 9] No computer printouts have been substituted for these. It seems this is the result of EPA's requirements for legal defensibility and traceability of all CLP-related documentation, and the strict evidentiary audits that the program entails.

With no guidelines for the use of computer printouts,[17] non-CLP analytical documentation has ended up in a free-for-all. This has resulted in four major problems:

- No ***real safeguards*** to limit access to computer files and restrictions to changes of the originally acquired data
- No information trail (paper, electronic, or otherwise) to archive the pre-change ("before") data for comparison with its later ("after") versions
- Presentation of "sanitized" data, where aborted or invalidated runs are never shown on the actual runlog
- Limited runlog elements with uninterpretable content.

Figure 2 presents a copy of a recent computer generated runlog for EPA Method 8020, Volatile Organics by GC from a major laboratory in the Eastern United States extensively involved in Federal Programs. It was substituted for the handwritten runlog and contains only sample name, method name, data file, amount injected, internal standard amount, dilution factor, and sample weight. No one can decode the Data File without the analyzing technician's personal help. In this instance, the **H** in the H:A1B4 is the server drive, **A1** the instrument ID, **B** is the week in the year (please see explanation in the endnote). The **4** denotes the fourth day of that week. There is no space for comments indicating terminated or invalidated runs. Moreover the runlog lacks any safeguards against further data tampering.

	SAMPLE NAME	METHOD NAME	DATA FILE	AMOUNT INJECTED	INT.STD. AMOUNT	DILUTION FACTOR	SAMPLE WEIGHT
1	WVG960716-01 BTEX CH	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
2	WVG960418-01 TPHV CH	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
3	BLANK	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
4	9609353-12¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
5	QC389158¦91126¦1¦VOA	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
6	QC389159¦91126¦1¦VOA	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
7	QC389163¦91127¦1¦VOA	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
8	QC389164¦91127¦1¦VOA	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
9	9609353-13¦91226¦10¦	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
10	9609353-14¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
11	WVG960418-01 TPHV CH	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
12	WVG960418-01 TPHV CH	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
13	WVG960418-01 TPHV CH	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
14	9609353-01¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
15	9609353-02¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
16	9609353-03¦91226¦10¦	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
17	9609353-04¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
18	9609353-05¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
19	9609353-06¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
20	9609353-07¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
21	9609353-08¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
22	9609353-09¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
23	9609353-10¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
24	9609353-11¦91226¦1¦V	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000
25	WVG960716-01 BTEX CH	G:ABTEX	H:A1B4	1.0000	1.0000	1.0000	1.0000

Figure 2. Computer Generated Runlog for EPA Method SW8020A, 23 September, 1996

Figure 3 presents a runlog for hydrazine from a western US laboratory, where the sequence had been sanitized to include only the "healthy" or acceptable runs - the Injection Cycle Numbers are not continuous. Although pasted in a sequentially paginated notebook, and properly signed across the edge by the analyst, it violates the letter and the spirit of what is legally considered defensible, by manipulating the original sequence of the run.

Figure 4 presents an Excel format inorganic prep logbook printout which contains almost all the elements necessary for a legally defensible document. The southeastern US laboratory that uses this has yet to implement safeguards against the alteration of the document screen.

During one on-site evaluation in 1995, it was discovered that an East Coast laboratory had 161 changes to just one day's computerized runlog for EPA Method SW8080 (Pesticides and Polychlorinated Biphenyls). No documentation existed as to who had changed what and when.

LEGALLY DEFENSIBLE SAFEGUARDS FOR COMPUTERIZED RUNLOGS

Computer printouts will become acceptable as daily runlogs when:

- the format of the runlog contains at least the minimum information necessary, as discussed above
- a *hardcopy* of the initially acquired data/screen is properly archived, reviewed and signed by the section

supervisor

- all subsequent changes to the initial screen are documented as to date and change, and, if necessary, approval of the change by the supervisor. This may work similar to the "strike-through" of word processing. Ascertaining that the properly authorized person had performed the actual change is more difficult but not impossible
- the data screens are tamperproofed so certain data, such as the sequence of the runlogs, will not be possible to modify *under any circumstance, e.g.* a permanent numerical fingerprint sequencing that can not be altered

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Notebook No. 94-693

PROJECT 411-JSC

Continued From Page

#95101 for Cal & QC Curve & data See pg 50 of Log 94-654

411-JSC.CSV

4/14/95

411-JSC

413-JSC

Sample Name	Date and Time	Injection Cycle Number	HZ Conc	HZ Area	MMH Conc	MMH Area	UDMH Conc	UDMH Area
AUTOCAL1R	4/13/95 11:03	2	0	0	0	0	0	0
AUTOCAL2R	4/13/95 11:16	3	1	51078	1	49358	1	20735
AUTOCAL3R	4/13/95 11:29	4	2	103677	2	107548	2	39699
AUTOCAL4R	4/13/95 11:43	5	5	217192	5	219383	5	82254
AUTOCAL5R	4/13/95 11:56	6	10	437724	10	432216	10	192026
AUTOCAL6R	4/13/95 12:09	7	20	882496	20	876284	20	380338
ICV	4/13/95 12:23	8	10.128	448061	9.99947	439775	9.90108	187222
ICB	4/13/95 12:36	9	0	0	0	0	0	0
LCS	4/13/95 12:49	10	9.75223	431620	9.88457	434792	10.3579	195934
PB	4/13/95 13:03	11	0	0	0	0	0	0
L4246-1	4/13/95 14:06	13	0	0	0	0	0	0
L4246-1 D	4/13/95 14:20	14	0	0	0	0	0	0
L4246-1 S	4/13/95 14:33	15	0	0	5.19087	231257	7.91334	149310
L4246-1 SD3	4/13/95 16:33	24	0	0	6.12951	271960	7.52921	141984
CCV	4/13/95 17:00	26	9.47248	419380	10.0576	442296	11.0813	209732
CCB	4/13/95 17:13	27	0	0	0	0	0	0
L4259-1	4/13/95 15:00	17	0	0	0	0	26	494087
L4259-1 D	4/13/95 15:13	18	0	0	0	0	26.7	506959
L4259-1 S	4/13/95 15:26	19	0	0	10.8319	475870	37.5806	715146
L4259-1 1:5	4/13/95 16:06	22	0	0	0	0	24.1811	90621
L4259-1 SD2	4/13/95 16:20	23	0	0	10.5236	462504	36.7007	698364
L4259-1 1:5 S	4/13/95 16:46	25	31.4942	280519	49.9696	439534	81.6314	309768

4/14/95

Continued on Page

Read and Understood By

Signed 4/14/95 Date

Signed 5/14/95 Date

Figure 3. Computer Generated Runlog for Hydrazine (pasted in logbook)

Rev. 7/1/96

ANALYST: FGD BATCH: 99991 MATRIX: Misc. -L Reviewed by:
DATE: 12/18/96 TIME: 15:00 METHOD: 3010 Review Date: 12/19/96

Facility ID	Sample	Client	Initial g/mL		Final Volume		Comments
Digestate	9612288-01	XXXX	1.00	ml	50.00	ml	
Digestate	9612288-02	XXXX	1.05	ml	50.00	ml	
Digestate	9612291-01	XXXX	1.02	ml	50.00	ml	
Digestate	9612291-02	XXXX	1.09	ml	50.00	ml	
Digestate	9612291-03	XXXX	1.02	ml	50.00	ml	milky white color
Digestate	9612291-04	XXXX	1.01	ml	50.00	ml	milky white color
Digestate	9612291-05	XXXX	1.10	ml	50.00	ml	
Digestate	9612291-06	XXXX	1.00	ml	50.00	ml	
Digestate	9612294-01	XXXX	1.07	ml	50.00	ml	
Digestate	9612295-01	XXXX	1.10	ml	50.00	ml	
Digestate	9612333-01	XXXX	1.11	ml	50.00	ml	
BLANK	QC406301	QC	50.00	ml	50.00	ml	BLANK
LCS	QC406302	QC	50.00	ml	50.00	ml	WATER
LCS DUP	QC406303	QC	50.00	ml	50.00	ml	QC406302
DUP	QC406304	QC	1.01	ml	50.00	ml	9612291-06
MS	QC406305	QC	1.03	ml	50.00	ml	9612291-06
MSD	QC406306	QC	1.00	ml	50.00	ml	9612291-06
SERIAL	QC406307	QC	1.05	ml	50.00	ml	9612333-01

Quality Control Information

HNO3- #K28067 LCS/MS - UI961031-02
HCL- #K25041 Volume - 250 UL
H202- NA LCS/MS - UI961031-03
HF- NA Volume - 250ul
HCL04- NA LCS/MS - UI961211-03
Volume - 250ul
LCS/MS - UI9601126-01
Volume - 50 UL

LCS- Water - NA

12-18-96 ED

For CLP use Only
MS NA
Volume NA
MS NA
Volume NA
SDG NA

Inorganic Prep Logbook Page# 27

Figure 4. Computer Generated Inorganic Prep Logbook
18 December 1996

Figure 4. Computer Generated Inoganic Prep Logbook, 18 December 1996

SUMMARY

The use of computer printouts for instrument runlogs can become a legally defensible reality as soon as the analytical instrument manufacturers and software designers are able to provide the laboratory industry with a tamperproof, traceable means of recording the changes to the runlogs.

The regulatory agencies, such as the EPA, as well as other Federal entities, such as the U.S. Department of Defense, U.S. Department of Energy, etc. *must immediately and clearly* enunciate the limits of acceptability for computerized documentation for analytical data - what is the minimum amount of information for each instance, and what is the minimum amount of tamperproofing safeguards that will be acceptable as legally defensible?

Until the above actions are thoroughly validated and vindicated in practice, all laboratories are strongly advised to adhere to the handwritten instrument runlogs as primary documentation, and most definitely as a backup.

ENDNOTE

Upon pointing out to the analyst that there should be at least two Bs in a 52 week year, he pulled out his small blackbook from his breastpocket and showed that *in this case* B was the 4th week of September 1996! ! !. This logic-defying record keeping practice may have been prompted by concerns of job-security and lifetime employment. Why it was tolerated by the laboratory for so long is itself worthy of an audit.

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OPTIONS IN DATA VALIDATION: PRINCIPLES FOR CHECKING ANALYTICAL DATA QUALITY

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ABSTRACT

US Environmental Protection Agency (EPA) Contract Laboratory Program National Functional Guidelines for Organic Data Review and EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (referred to as Functional Guidelines), along with regional modifications, provide guidance for validation of analytical data. However, these documents were written to accompany data analyzed under EPA Contract Laboratory Program Statement of Work methods (CLP SOW). Because analytical projects often use methods other than CLP SOW,

data validation in these situations must rely on a combination of principles found in the applicable Functional Guidelines (with regional modifications, if any), the particular method, and professional judgment.

In addition, data validation can be performed under different levels of effort, from a limited review of reported results to full review of raw data, transcriptions, and calculations. The scrutiny applied to data depends on several factors including data quality objectives, familiarity with the laboratory's quality, project budget, and time constraints. A focused approach of applying limited and full review to subsets of data, as appropriate, can be an effective solution to meeting the requirements of the data, saving time and money as well as satisfying regulatory requirements.

INTRODUCTION

A review of data completeness, laboratory precision, data quality, and error checks can be performed using the principles found in Functional Guidelines, even if the data are not presented in the CLP SOW format. Using these principles, the data validation can be focused to meet the data user's needs. The validation level of effort depends on the data quality objectives, the intended use of the data, and an understanding of how each quality control (QC) element affects the final result. For example, false-negative and false-positive results are of special concern for data used in risk assessment; and compound identification issues are important in polychlorinated biphenyl (PCB) congener analyses, gasoline weathering studies, and other chemical 'fingerprinting' projects. As users of environmental data require analytical results that are more sophisticated and focused to a specific need, data users must also focus the accompanying QC evaluations to meet the specialized concerns.

What Is Data Validation?

Data validation is used to determine if the available project data satisfy the project's data quality objectives and data use requirements. It is the process of comparing laboratory chemistry data against criteria established for the data through an independent review, performed after the laboratory has completed its own in-house quality control checks. Validation determines if the data are acceptable by evaluating, at a minimum, the following categories.

Data package completeness: This step confirms that the laboratory has provided the deliverables required by the contract, method, and/or project plan. During data validation, receipt and completeness of deliverables is checked and documented against the project requirements.

Laboratory performance: Laboratory performance can be evaluated from QC summaries provided by the laboratory. Elements of laboratory performance common to most methods are:

- Holding times (did the laboratory analyze the samples within the required time frame?)
- Calibration (were instruments calibrated at the correct levels and frequencies?)
- Blanks (did the blanks contain target analyses that indicate samples may be contaminated from laboratory procedures?)
- Bias (do laboratory spiking tests show high or low recoveries that may bias associated sample results?)
- Precision (are results reproducible when duplicated?)
- Other quality control (QC) results (did method-specific items meet the QC goals?)

Error checks: Checking for quantitative and qualitative error is performed using supporting instrument and source data (raw data). Data transcriptions of both sample and QC data are reviewed; analyte identifications are evaluated; and quantitation of analyte concentrations are recalculated.

After the validation is completed, qualifiers are assigned to the data points that are affected by QC outliers. Qualifiers indicate to the data user that analyte concentrations may be affected by laboratory or field contamination (in the case of blank contamination), unusable because of QC deficiencies, and/or estimated due to possible bias or reduced confidence in the results.

Functional Guidelines provides guidance for the technical review of data generated using methods found in the EPA Contract Laboratory Program Statement of Work (CLP SOW). Historically, Functional Guidelines has been applied to other methods or protocols but project- or method-specific criteria (such as regional or state requirements) are not specifically covered in Functional Guidelines.

Data Validation Principles From Functional Guidelines

Some examples of laboratory performance principles found in Functional Guidelines that may be applied to methods other than CLP SOW methods are summarized in Table 1.

Table 1: Laboratory Performance Principles

Laboratory Performance Item	**Functional Guidelines General Principle**	**Notes**
Blank Contamination	Qualify data as undetected (U) if concentration in sample is less than five or ten times the blank concentration.	Criteria of five or ten times the blank concentration depends on whether analyte is known as a common laboratory contaminant or not.
Bias • Matrix Spike (pre- preparation) • System Monitoring Compound (surrogate) Spike (post-preparation) • Laboratory Control Sample (blank spike)	If recovery is low (low bias), qualify both positive and not detected results as estimated (J/UJ). If recovery is high (high bias), qualify only positive results as estimated (J). Results that are not detected are not jeopardized by high bias.	Organic and Inorganic Functional Guidelines have different guidance for spike results.
Precision • Matrix Spike/Matrix Spike Duplicate • Laboratory Duplicate • Field Duplicates	If precision is poor, qualify positive results as estimated (J).	Organic and Inorganic Functional Guidelines have different guidance for precision results. Also, data may or may not be qualified based on field duplicates.

Focus And Extent Of Data Validation

Different levels of data validation can be performed using scrutiny ranging from a limited review of reported results to full review of raw data, transcriptions' and calculations. The scrutiny applied to data depends on several factors including data usage, familiarity with the laboratory's quality, and budget and time constraints. A focused approach of applying limited or full review to appropriate subsets of data can be an effective solution for meeting the project data review requirements. The two general levels of validation contain the following QC items and effort levels.

Focused data validation can emphasize efforts in a full review on items above that have the most impact on the data, and apply limited review to remaining items.

Full validation may be used in the following situations:

- When the laboratory quality is unknown to the data user or has a history of errors
- When the data are to be used for litigation purposes
- When the data are to be used for a risk assessment and
- When the project specifies full data validation.

Limited (QC summary forms only)	**Full** (raw data reviewed)
Laboratory performance, including: • Completeness • Chain-of-Custody, • Holding times • Instrument tuning and system performance • Calibration results • QC results reported on summary forms • Detection limits • Other contractual items	Error checks on: • Laboratory performance • Preparation of standards and samples • Analyte identification and quantification from raw data

Limited validation may be used if the above situations do not apply (for example, if the data are from routine monitoring of a known site). Limited validation may also be used in conjunction with full validation to reduce the time and cost of validating large sets of data. If the entire data set receives limited review, a specified percentage of data, data from certain sensitive sampling areas, and/or data that revealed analytical problems during limited review can further receive a full review.

SUMMARY

The needs of data users must be considered when planning data validation for an environmental project. The plan depends on the data quality objectives, intended use of the data, and prioritizing the QC elements affecting the data. Using principles from Functional Guidelines, the extent of data review can be performed using various levels and focus.

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LABORATORY ANALYST TRAINING IN THE 1990'S AND BEYOND

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INTRODUCTION

Within our industry there has been a proliferation of instant chemistry test kits. I refer to them as "pseudo-chemistry"" It takes no skill to generate numbers using these kits, I have taught my 8 year-old to use several. He is quite proud of his success, but I would never describe him as an analyst. He completely lacks any understanding of what he is doing or why. Although my example may be extreme, I think that many persons who work in laboratories in the United States can also be characterized as having little to no idea of what they are doing or why. It takes a lot of time and effort to learn all the skills necessary to be an expert laboratory analyst. The immense popularity of the test kits is a symptom of the shortage of trained analysts in our industry. Many people have an expectation of instant gratification, and the test kits provide both instant and gratification without any great expenditure of effort or time. Thus there is a very low level of professionalism in our industry.

Aside from the desire to raise the overall level of professionalism among laboratory analysts, there is also a legal necessity to have trained analysts perform tests in treatment plants and commercial laboratories. As described in a recent book[1] an important part of the foundation evidence used to support scientific evidence in court cases is

demonstration and documentation of the level of training of the analyst. Much scientific evidence has been refused admission or severely tainted due to a lack of documented training of the "expert". A recent example is the photographic analyst who testified in the O.J. Simpson civil trial that the pictures of the shoes presented by the plaintiffs were faked. It was subsequently brought out in cross-examination that the "expert" had absolutely no training in photographic analysis and was probably a fraud himself. The same can and has happened in court cases where laboratory results are submitted as evidence. Imwinkelried's standard reference[2] lists and discusses six known weaknesses in analyst training as tempting targets for legal challenge. They are:

I . The witness is unqualified to vouch for the theory's validity
    Lack of understanding of the theory
    Lack of theoretical background
    Insufficient theoretical background
2. The witness is unqualified to vouch for the instrument's reliability
    Unfamiliarity with the instrument or technique
3. The witness was unqualified to maintain the equipment
4. The witness was unqualified to operate the equipment and conduct the test
    Whether a credential is required
    Whether the witness possesses the credential
5. The witness did not use proper test procedures in conducting the test
6. The witness is unqualified to interpret the test result

It is important to remember that any result generated from a municipal or commercial laboratory in support of NPDES compliance monitoring requirements, hazardous waste characterization, industrial pre-treatment monitoring verification[3], or any of the other myriad regulatory programs, has the potential of ending up in court, sometimes in criminal court where the evidentiary requirements are much more stringent. This implies that all analysts need to be trained if legal defensibility of data is to be maintained.

This article is broken into three parts. The first is a discussion of the skill areas that analyst needs to know to be successful. The second part discusses a training program that addresses and meets these goals. The third part describes documentation of the analyst training.

TRAINING GOALS

Before we can address the issue of how to train an analyst, we need to examine what an analyst needs to know to function in a safe and responsible fashion. First and foremost is a knowledge of chemistry laboratory technique. I remember when I was in college there was only about 30 or so of my fellow chemistry undergraduates but in the biology department three buildings down the street there were over 100 students in the biology program. I often wondered what biology majors did for a living if they didn't go on to graduate school. Well now I know - many of them go to work in analytical chemistry labs. Which is strange because none of them ever take analytical chemistry as a course, most stop chemistry classes after general and organic. Which is also not to imply that chemistry majors learn any great amount of laboratory technique in analytical chemistry. Most persons graduating from college science majors have at best a smattering of proper laboratory technique that they picked up by accident during their studies. It's definitely not due to any systematic training program in lab technique.

Second, a detailed knowledge of chemistry laboratory safety is absolutely necessary. Colleges and universities are notorious for having a complete lack of awareness of safety in their laboratories. Sure they comply with the fire regulations and provide extinguishers, blankets, showers and eye-washes, but that's about it. Most college research laboratories are accidents on the verge of occurring. The cavalier attitude toward chemical toxicity and other health hazards, and especially toward responsible disposal (pour it down the sink) is prevalent. These attitudes and practices have to he changed to bring analysts into compliance with OSHA and other regulations dealing with work place safety, chemical exposure, and proper waste disposal practices. There is also a distinct need to develop common sense in the analyst with regards to chemicals and laboratory equipment.

Third, a detailed knowledge of environmental regulations is needed. The analyst operates within a compliance monitoring framework and certain test methods are approved while others are not. The mere possession of the most recent copy of *Standard Methods for the Examination of Water and Wastewater,* will not satisfy regulatory needs.

First, the most recent copy is probably not the approved edition for compliance monitoring methods, and second, not all the methods found in *Standard Methods* are approved for use. The analyst must be familiar with the *Code of Federal Regulations,* plus any State environmental regulations that govern the analyst's sphere of responsibility. The quickest way to have analytical results rejected as evidence in court cases is to use unapproved test methods to generate the data.

Fourth, an in-depth knowledge of the chemistry of the test is necessary. You can frequently recognize the untrained analyst when you hear the question, "is this step really necessary?" Persons writing test methods do not waste time and space by adding unnecessary steps to the procedure. Even though the chemist following the procedure may not know why each step is performed, they have enough trust and experience to recognize that each step is important to the successful generation of the result. On the other hand the analyst may find that the sample needing analysis is not completely amenable to the written test procedure and some modifications are necessary. Further, it is an advantage to know the chemistry of the test so that the analyst has an awareness of the limitations of the test. No test procedure works equally well for all samples and the analyst must know the symptoms that indicate when the test is not working. Learning to avoid or correct for test interferences is the hallmark of the expert chemist.

Fifth is a knowledge of the use and interpretation of quality control procedures. Without quality control there is no confidence in results. Quality controls are always part and parcel of every approved method. Knowledge of how to interpret the quality control results is needed to assist the analyst in making the determination of whether the test is working or not working for any particular sample. The knowledge of specific quality controls must also be accompanied by a knowledge of where they fit within the overall quality assurance program.

We can summarize these job knowledge goals as follows:

1. General laboratory technique
2. Safety and chemical hygiene
3. Regulatory requirements
4. Chemistry of specific test procedures
5. Quality control

TRAINING PROGRAM

When we consider training normally we have in mind a new employee, who we would have to make productive as soon as possible. It is not in our best interests to teach laboratory technique, then when that subject is finished move on to the next item on the list. We also can not sit the employee down in a class for one or two weeks, drill them with everything they need to even know, and then move them to the lab and expect them to remember or understand everything that was covered. Learning to be an analyst takes a long time and the most rewarding process occurs when the skills learned in the lab are supplemented with material discussed in the classroom.

Successful training can never be passive. The simple presentation of a block of information in a class is rarely sufficient by itself. It must be followed up with supervised practical application on the job and then the person receiving the training must be evaluated. Further, evaluation must be continued over the lifetime of the employee. This is especially true in the case of laboratory work, where overtime an analyst will introduce short-cuts in their work. Sometimes these short-cuts will introduce valuable savings in time and materials to the procedure, however the most common occurrence is that the quality of the work suffers. Periodic re-evaluation serves to identify when the product quality is deteriorating

We have taken the approach of tiered training. The levels can be characterized as introduction, development and maintenance. The introduction coexists of 8 hours of formal classroom lecture/demonstration that the new employee receives within the first 3 weeks of employment and on-the-job training by the immediate supervisor. The 8 hours of formal class contains 2 hours of chemical hygiene and safety training, 1 hour of radiation safety training, 3 hours of quality assurance training, 1 hour of LIMS orientation, and 1 hour of administration-personnel orientation.

The QA training is broken into three segments, one presented each of the first three weeks of employment. This allows the analyst to digest the information and integrate it into the on-the-job instruction they are receiving from their Section Supervisor. A lesson plan for the 3 hour QA training is presented in Table 1.

All employees are required to receive the complete introductory training regardless of job area. At the next level of training, the classes are more directed toward job function. Field service personnel take an OSHA and hazardous waste field sampling course, while all laboratory analysts participate in a 40 hour Analyst course. Georgia, as does a number of states, requires laboratory analyst licensing for persons performing drinking water or wastewater analysis. The licenses are obtained through written examination. The Analyst class is oriented toward helping employees pass the certification exams. A large number of references are used to develop and supplement the information presented. These are listed in Table 2. The topics of the Analyst class are chosen to present a wide variety of general chemistry knowledge (Table 3) that encompasses the subject range of the certification exams. The class is presented in one hour segments, with two classes a week during the lunch hour. The participants eat lunch and listen to the lecture. The whole course takes 20 weeks and at the end of the schedule, the class presentation cycles back to hour #1 and is repeated. The presentations are largely independent and analysts can join at any point of the schedule. Problem sets (homework) are frequently handed out and the answers discussed at the next meeting of the class.

Obviously, one hour of semivolatile organics class is not going to make an analyst proficient in the analysis of organic target analyses using a gas chromatograph or any other instrument or involved technique. For these job positions, the analyst will receive specialized training by either the manufacturer of the instrument or other person certified to present the training. Although it is sometimes advantageous to hold the training in-house, for the most part these courses require the analyst to travel to the manufacturer's site, particularly when extensive instrument hands-on instruction is involved. Examples of these courses include, basic and advanced Gas Chromatograph Operation and Maintenance, Gas Chromatograph-Mass Spectrometer Operation and Maintenance, Mass Spectral Interpretation, ICP-AES Operation and Maintenance, Atomic Absorption Spectrometer Operation and Maintenance, Microbiological Species Identification, Laboratory Data Evaluation, *etc.*

During the development training, and continuing on through their career, formal evaluations of the analyst are performed. Two key evaluations in Georgia are the State Certification examinations for drinking water laboratory analyst and wastewater laboratory analyst. The exams are administered under the authority of the Georgia State Board of Examiners for Certification of Water & Wastewater Treatment Plant Operators and Laboratory Analysts by LGR Examinations (Pennsylvania). The examinations that are used are drawn from the test bank of questions prepared and maintained by the Associated Boards of Certification (ABC). We require that all analysts pass at least one of the certification exams by the end of their first year of employment, with the second examination passed not later than the end of the second year.

A number of other states (California, Connecticut, Idaho, Kansas, Kentucky, Louisiana, Nevada, Ohio, and Pennsylvania) have voluntary or mandatory analyst certification that is performed through testing, and most use the ABC exams. For states and areas that are subject to limited or no state-sponsored testing, ABC currently offers administration of analyst exams to individuals through designated proctors. Both drinking water and wastewater laboratory exams are available. The wastewater analyst exams have four levels of difficulty:

Class I - Plant operators who perform process control tests: alkalinity, BOD, CBOD, chlorine, coliforms, color, DO, odor, oxygen uptake, pH, SDI, solids, turbidity, *etc.*

Class II - Intermediate level treatment plant laboratory analysts who perform regulatory monitoring and process control: Class I plus COD, conductivity, nitrogen, oil & grease, phosphorus, *etc.*

Class III - Advanced laboratory analysts in larger municipal or commercial labs: Class II plus bioassay, cyanide, inorganics, metals, organics, phenols, *etc.*

Class IV - Expert laboratory analysts/laboratory managers Class III plus detailed instrumental analysis - AA, ICP, GC, GC-MS, etc., and management skills

The Georgia certification exams are drawn from the Class II question bank. These serve as an excellent starting point for analyst evaluation. The higher classification exams can be used to measure analyst progress through later stages in their career. More information about the ABC exams can be obtained from the Executive Director of ABC[4].

There are no written examinations available that measure analyst skills outside of the drinking water or wastewater arenas[5]. Our experience has been, however, that the wastewater exams are an accurate measure of the analyst's general success in other areas of environmental analysis, with the single exception of knowledge of specific regulations. Part of the reason, I believe, lies in the compliance monitoring analytical requirements under the water and wastewater permitting programs are much more stringent than the requirements under other regulatory programs. It's easier to move from a very strict regimen of testing to a less stringent protocol, rather than *vice versa.*

Evaluations of the analyst's hands-on technical capability are separate from evaluations of the analyst's general knowledge,. but no less important. Initial demonstrations of ability (IDA) are method-specific evaluations of the ability of the analyst to perform a particular test, prior to any analysis of real-word samples. Many EPA test methods contain a detailed description of a required IDA. Normally it consists of analysis of 4 to 7 repetitions of a spiked reagent water sample, with the accuracy and precision of the replicate analysis compared to performance standards. Successful completion of a Method Detection Limit Study as described in 40 CFR 136, Appendix B, is an evaluation that is performed at least once a year for each test analyte for which the analyst is responsible.

Other important evaluations include performance audits of analyst success in following test procedures. A performance evaluation (PE) sample is a blind test of the analyst's ability to obtain an acceptable result on samples containing unknown concentrations of target analyses. The two most common PE Studies are the Water Supply (WS) and Water Pollution (WP) series administered by EPA. Both of these studies are conducted twice a year and cover metals, pesticide/PCB, volatile organics, and general chemistry parameters. Several commercial firms also provide PE samples that cover the entire range of environmental analyses and in a variety of matrices. PE samples serve as an excellent test of analyst capability and are frequently the first indicator that there are egregious problems in the way the analyst is following a test procedure.

Another form of performance audit is performed in conjunction with preparing and updating performance expectations (data quality objectives) for detection/reporting limits, accuracy, and precision. This evaluation reviews quality control results over a period of time and compares the results with either historical laboratory performance or with method specified performance.

Periodic system audits are valuable evaluations. System audits take many forms and may be conducted by either in-house Quality Assurance personnel or by visitors to the laboratory. Most state certification programs and many federal government programs require an on-site visit and audit as part of the certification or validation process. The visit may be conducted by a state or federal government employee, or the audit may be contracted out to a third-party accreditation organization. These audits from persons outside the laboratory are extremely valuable as an independent source of evaluation. Often we who work in the lab get so involved with day-to-day operations that we can't see the forest for the trees. Our objectiveness is further clouded by the personal relationships that exist in the lab, frequently leading to the decision that, "It's not really that big a deal and I don't want to hurt her feelings." Regardless of the feelings of the analyst, failure to follow prescribed procedures hurts the laboratory. Outside auditors are free from these personal relationships and can give a more objective evaluation.

System audits compare in detail what the analyst is doing on the bench with what is prescribed in the official approved method, the lab's Quality Assurance Manual and the appropriate standard operating procedure (SOP). An annual system review of the SOP by the analyst and the laboratory's most knowledgeable chemist is an excellent procedure. A system audit should always be triggered by an unacceptable result on a performance audit.

TRAINING DOCUMENTATION

As was discussed in the Introduction to this article, the training of an analyst is a necessary part of foundation evidence to support scientific evidence in court cases. Proof of the training is best supported through documentation to give credence to any testimony claiming proper training. This suggests that individual training records need to be maintained for each employee.

The file should contain a resume of the analyst that summarizes any technical formal training or experience that they had prior to being employed at your laboratory. A one page resume is often more than adequate and an example is illustrated in Figure I . If the analyst has attended or graduated from a university, a copy of the transcript is frequently useful.

It is necessary to document each class or course that the analyst attends while they are at your laboratory. If the course consists of more than one session, having a sign-in sheet is useful for keeping up with who has attended which session. Once a course of study is completed, the Training Manager issues a signed certificate. An example is illustrated in Figure 2. Necessary information on the certificate is the name, date and reference source for the course, the name of the student, and the name and dated signature of the instructor. For in-house courses, it is frequently beneficial to attach a copy of the lesson plan to the certificate in the file, especially if the record is to be admitted in a court case. For courses taken outside the laboratory, a copy of the training completion certificate should be placed in the file.

Evaluations also need to be documented. Passage of the certification exam is accompanied by issuance of a Certificate by the state certification board. A copy should be kept in the file. A copy of the license that goes along with the certification, and any subsequent renewals, should be kept in the training file.

Copies of completed IDA and MDL studies should be available in the training records. Acceptable results on PE samples should also be documented. We use the form illustrated in Figure 3 It has been suggested that a copy of the official report from the organization responsible for the PE sample be attached to the certificate in the training record file. This may or may not be useful.

Written reports of audits, regardless of whether internal or external, should be included in the training file. They should indicate by whom and when the audit was conducted, the findings of the audit, and recommendations to correct deficiencies. Most audits require a written response, and a copy of the response should be attached to the audit report. Any documentation that is produced as a corrective action to deficiencies should be copied and included.

There are a number of ways to keep these records. In some laboratories the personnel, technical training and safety training records may be kept together in a single folder. In other labs, where the personnel/finance, training, and chemical hygiene/safety functions are managed by different people at different locations, the three sets of records may be maintained separately. Regardless of where the records are stored, it is important to give the employee a copy of the record and to keep at least one copy for filing. When the training records are required to be produced in court, frequently it is a period of 3-6 years or more after the event of the analysis and often the employee is now working elsewhere. The necessity to prove that the analyst was trained and capable of doing the text procedure at the time the test was done still exists. Training record files are invaluable in this situation.

It is beneficial to the Training Manager to maintain tabular training summaries. These allow one to tell at a glance who has had what training. There are computer programs available that will accomplish this function. An example is "PC Compliance Training Tracker" available from J.J. Keller & Assoc. Other companies who produce comparable software include Achieve Technology, Eclipse, Envirowin Software, and Software Resources & Marketing. Hardcopy printouts of these training summaries are also useful in marketing efforts by the laboratory. Project proposals can be enhanced through inclusion of lists of employees who hold particular certifications such as OSHA field sampling or drinking water licensed analyst.

CONCLUSION

No one is born an expert analyst. Training is absolutely necessary to produce a knowledgeable, competent laboratory worker. I have described the program we have been using at Analytical Services for a number of years with some degree of success. Hopefully, with some situation specific modifications, this program will work equally well in your facility.

1. Berger, W., H. McCarty, and R.-K. Smith. Environmental Laboratory Data Evaluation. Genium Publishing, Schenectady, NY, 1996.
2. Imwinkelried, E.J. The Methods of Attacking Scientific Evidence, Second Edition. The Michie Company, Charlottesville, VA, 1992.
3. Industrial user inspection and sampling mutual for POTW's, EPA 831-B-94-001, 1994.
4 Dr. Stephen Ballou, ABC, 208 5th Street, Ames, Iowa 50010-6259, telephone number 515-232-3623.
5 ABC used to offer an Environmental Laboratory Analyst exam but it is no longer available.

Table 1. Introduction to Quality Assurance lesson plan

Subject	Informational Objective and Method
Definitions of QA & QC	Quality assurance and quality control are defined.
Analytical validity and legal defensibility	Definitions and how ASI accomplishes the two requirements of environmental regulatory analysis are described. The legal accountability of each analyst for their work is described. Personal responsibility is stressed.
ASI QA Manual	The purpose, use and frequency of updates of the QA Manual are described.
SOPs	How SOPs are written and updated are described. The format and authority of the QP is described. The frequency of update is described.
Approved methods	The 4 types of regulatory analysis performed at ASI (Drinking water, wastewater, RCRA and USACE) and location of the approved methods are discussed along with role of CFR and other regulatory documents.
Holding times	Definition of holding time, how to calculate and location of holding time lists in the ASI QA Manual and other regulatory sources.
Preservatives	Definition of preservatives and location of preservative lists in the ASI QA Manual and other regulatory sources.
Containers	Location of container lists in the ASI QA Manual and other regulatory sources.
Accuracy and Precision	Terms are defined, target analogy and mathematical methods of quantitation are presented.
Batch QC	The idea behind batch QC is described and the requirements for it's implementation is illustrated.
Control charts	The company policy and daily up-dating of control charts is described. How limits are established and the frequency of adjustment is described.
MDL	Mean and standard deviation are defined and illustrated along with normal distribution. MDL is defined and EPA method of determination is presented.
Significant figures	DIscussion of implied ±1 error in last place, ASI standard of no more than 3 significant figure reporting, how measurement with least significant figures affects final reporting significant figures quantitation limit effect.
Error correction	Demonstration of approved method for correcting errors in analytical records such as benchsheets by drawing a single line through the error, annotation with initials and date and addition of corrected data.
Unit conversions	ppt, ppb, ppm and % defined and related to µg/L, mg/L, µg/kg and mg/kg. Interconversions are presented. Air reporting units.
Volumetric glassware	Definition of Class A volumetric glassware and recognition of what is not volumetric glassware such as Erlenmeyer flasks and beakers.
Volumetric pipets	Definition and demonstration of correct use of TD and TC volumetric pipets.
Volumetric calibration	Discussion of method of calibration of non-Class A volumetric devices with water and inclusion of temperature correction for water density. Required documentation and frequency of procedure is discussed.
Representative samples	Discussion and demonstration of methods for obtaining a representative sample from a container. Separation of layers and mathematical combination of results is described.
Dilution factors	Discussion of dilution equation, C1xV1 = C2xV2.
Percent moisture	Percent moisture and percent solids are defined, method of determination explained and example of dry weight reporting worked through.
PE samples	Importance of PE sample success is discussed along with internal records and reports.

Analyst Certification	Reasons, requirements and forms are discussed.
Organizational Chart	Chain of command and laboratory management structure.
Client Contracts	Role of Project Managers.
Flow of work	How samples are received, logged-in and processed. How data is entered into LIMS and turned into a final report.
Record Keeping	Retaining and storage of records. Need for authentication of records.
Bar-code system	Need and use of internal chain-of-custody, recording supplyroom withdraws.
Building security	Custody and security of samples and building, wearing name badges, escorting visitors.

Table 2. References and Study Materials used in the Analyst Class

1	Laboratory Procedures and Chemistry, Chapter 16, *Operation of Wastewater Treatment Plants,* Volume 2, 1991. California State University, Office of Water Programs.
2	*Standard Methods for the Examination Water and Wastewater,* current edition, WEF, AWWA, and APHA.
3	Smith, R.-K., 1997. *Handbook of Environmental Analysis,* 3rd Edition, Genium Publishing, Schenectady, NY.
4	*Methods for Chemical Analysis of Water and Wastes,* USEPA 1983.
5	Title 40, *Code of Federal Regulations,* Parts 100-149, US Government Printing Office, current year's edition.
6	Smith, R.-K., 1995. *Water and Wastewater Laboratory Techniques,* WEF, Alexandria VA.
7	*Handbook for Analytical Quality Control in Water and Wastewater Laboratories,* USEPA 1979.
8	*Manual for the Certification of Laboratories Analyzing Drinking Water,* USEPA, current edition.
9	Laboratory Procedures, Chapter 11, and Advanced Laboratory Procedures, Chapter 21, *Water Treatment Plant Operation,* California State University, Office of Water Programs, 1993.
10	Berger, W., H. McCarty, and R.-K. Smith, 1996. *Environmental Laboratoy Data Evaluation,* Genium Publishing, Schenectady, NY.
11	Any first year college general chemistry textbook.

Table 3. Analyst Class Schedule

Hour	Topic
1	Molecular formulas and names of chemicals, Part 1
2	Molecular formulas and names of chemicals, Part 2
3	Molarity, solutions and dilutions
4	Stoichiometry and calculations, Part 1
5	Stoichiometry and calculations, Part 2
6	Chlorine chemistry and analysis, Part 1
7	Chlorine chemistry and analysis, Part 2
8	Chloride and Fluoride analysis
9	Nitrate, nitrite, TKN and ammonia analysis, Part 1
10	Nitrate, nitrite, TKN and ammonia analysis, Part 2
11	DO, BOD and COD, Part 1
12	DO, BOD and COD, Part 2
13	Fecal and total Coliform, Part 1
14	Fecal and total Coliform, Part 2
15	Regulatory programs
16	Sample receipt, Chain-of-Custody and LIMS
17	Sampling, holding times, containers and preservatives
18	Accuracy, precision and MDLs (DQO)
19	Regulatory reporting levels (NPDES and SDWA)
20	Reagents standards and lab water (Specific gravity)
21	Calibrations
22	Glassware and volumetric ware
23	Temperature measurement and conductivity
24	Solids, Part 1
25	Solids, Part 2
26	Phosphorus
27	Sulfate, sulfite and sulfide
28	Metals
29	Volatile organics
30	Semivolatile organics
31	Turbidity and colorimetric measurement
32	Color
33	Odor and taste
34	Oil and grease and TPH
35	Surfactants
36	Cyanide
37	pH, alkalinity and hardness, Part 1
38	pH, alkalinity and hardness, Part 2
39	pH, alkalinity and hardness, Part 3
40	Jar test

Name: Roy-Keith Smith, PhD	
Position: Anlalytical Methods Manager Quality Assurance Manager	Date Began: 1 March, 1992
Education:	
High School: East Greenwich HS, East Greenwich RI	
College. Georgia Institute of Technology Degree: BS Chemistry, 1976	
College: Colorado State University Degree. Ph. D. Chemistry, 1981	
College: California Institute of Technology Research Faculty in Chemistry 1981-1982	
Technical Schools:	
Year: 1987	Course: Finnegan OWA 1020 GC-MS Operation, MS Interpretation
Year: 1990	Course: GA Right to Know Hazardous Chemical Supervisor
Year: 1992	Course: H-P MS-DOS GC/MS, UNIX, and Target analysis
Year: 1992	Course: all H-P GC and Cap. Column courses
Year: 1992	Course: TJA ICP-AES Operation
Seminars Attended: EPA Annual Technical Conference 1992, 1993, 1994, 1995, 1996; EPA WTQA 1992, 1993, 1994, 1995, 1996; PittCon 1991, 1995, 1997; and many others	
Work Experience:	
Last Position: Assistant Professor of Environmental Chemistry	Company: Southern College of Technology Dates: Jan 1990 - Jun 1992
Position: Laboratory Manager	Company: Southeast Laboratories Dates: Oct 1989 - Dec 1989
Position: Senior Scientist	Company: GA Dept. Agriculture Dates: Mar, 1985 to Oct 1989
Current Job Skills: Thorough knowledge of QA/QC and EPA, NIOSH and misc. analytical methods for analysis of pollutants in air, water, and solids by LC, GC, GC-MS, AA, Furnace AA, ICP, spectroscopic methods and wet chemistry. Responsible for laboratory certifications, regulatory agency contact, QA program development and management, and Analyst Training	
Certifications: State of Georgia Licensed Water Laboratory Analyst and State of Georgia Licensed Wastewater Laboratory Analyst	
Courses Presented: Environmental Analysis (Southern Institute of Technology), 5890 GC Operation and Maintenance (H-P), Environmental Laboratory Data Evaluation (ASI), and many others	
Publications. 43 articles and books in peer-reviewed and trade publications including: *Handbook Environmental Analysis,* ISBN 0-931690-55-2, Genium Publishing, Schenectady NY, 1993: *Handbook of Environmental Analysis,* Second Edition, ISBN 0-931690-77-3, Genium Publishing, Schenectady NY, 1995: *Water and Wastewater Laboratory Techniques,* ISBN 1-57278-014-2, Water Environment Federation, Alexandria VA, 1995: *Environmental Laboratory Data Evaluation,* ISBN 0-931690-91-9, Genium Publishing, Schenectady, NY 1996	
Other Information: Listed in *Who's Who Environmental Registry.* Consultant for chemistry and GC courses to the Analytical Education Center, Hewlett-Packard, Inc., Part Coordinator for Part 4000, *Standard Methods for the Examination of Water and Wastewater;* educational consultant and instructor for Georgia Water and Wastewater Institute; recipient of WEF/GWPCA Laboratory Analyst Excellence Award 1994; Chair, Education and Training Subcommittee, Lab Practices Committee, WEF	

Figure 1. Example of a Technical Training/Experience resume.

ASI

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ENVIRONMENTAL MONITORING & LABORATORY ANALYSIS
110 TECHNOLOGY PARKWAY • NORCROSS, GA 30092
(770) 734-4200 • FAX (770) 734-4201

RECORD OF TRAINING

Name:	Homer Simpson
Date(s):	8 July, 1996
Training Subject:	Introduction to Quality Assurance Procedures, Part I
Reference:	*Handbook of Environmental Analysis*, 2nd Edition
Number of Hours:	1.0
Instructor(s):	Roy-Keith Smith, Ph.D.
Instructor's Signature:	
Date:	15 July 1996

Figure 2. Example of an in-house certificate of training.

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RECORD OF PE SAMPLE SUCCESS

Name:	Jean Zheng
Date(s):	December, 1996
PE Sample:	USACE validation check sample
Analytes:	Explosives in soil and water (8330m)
QA Manager:	Dr. Roy-Keith Smith
Signature:	
Date:	22 January, 1997
Comment:	

Figure 3. Record of Acceptable Results on PE samples.

INVESTIGATION VERSUS REMEDIATION: PERCEPTION AND REALITY

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OHM Remediation Services Corp., 5731 West Las Positas, Pleasanton, California 94588
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Tetra Tech, Inc., 670 North Rosemead Blvd., Pasadena, California 91107-2190, telephone (818) 351-4664

ABSTRACT

Investigative strategies, not based on project Data Quality Objectives (DQO) and/or not statistically justified, have a high risk of producing non-representative analytical data. The problem is further aggravated by a data validation process that is often devoid of professional judgment. As a result, many site investigation (SI) studies do not provide sufficient or representative chemical data necessary to make solid decisions related to the selection and implementation of remedial actions. Case studies often demonstrate the discrepancy between the commonly grossly underestimated extent, type and magnitude of contamination reported in the SI and the reality that is uncovered during the actual remediation work. Causes for inadequate site investigation work are discussed, and remedies are proposed.

INTRODUCTION

Planning of remedial actions is frequently based upon existing chemical data generated during site investigative studies that usually include such elements as:

- record search
- planning documents preparation
- sampling
- analysis
- data validation and interpretation
- reporting and review by regulatory agencies

One may assume that this kind of effort would produce reliable information of sufficient volume to form the foundation for a remedial action plan. Remedial action case histories have, in fact, proved the opposite - the perception of site conditions based upon site investigation findings does not reflect reality. Use of site investigation data invariably leads to underestimating or overestimating of the extent of contamination, sometimes, on an alarming scale. In either case, ramifications may be substantial with respect to remediation budgets and public perception of the environmental industry.

STATEMENT OF THE PROBLEM

During evaluation of environmental data quality by application of the PARCC parameters, *i.e.* precision, accuracy, representativeness, completeness and comparability, the criterion of *representativeness* is often overlooked or misunderstood. According to the U.S. Environmental Protection Agency (EPA), representativeness is "the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition".[1] Representativeness is a qualitative parameter that depends on proper design of the sampling program.[2,3] The planners of remedial investigations/feasibility studies (RI/FS) often understood this criterion as narrowly relating only to parameter variation at a sampling point, and placed more emphasis on accuracy, precision and completeness of chemical data.

The data may be accurate, precise and complete, but if they are not representative of site conditions, they become useless or even financially damaging. Principal reasons for underestimating or overestimating the extent of contamination that usually originate from improper sampling and analysis design are as follows:

- non-representative samples analyzed for the correct contaminants
- representative samples analyzed for the incorrect contaminants
- non-representative samples analyzed for the incorrect contaminants

All three situations present a distorted view of the site under investigation and are equally useless for planning remediation activities.

In spite of the fact that over the years the environmental industry has accumulated significant experience in RI/FS, a review of the RI/FS reports shows that in the past environmental consultants had a poor understanding of, or ignored, the Data Quality Objective (DQO) process.[4,5] In their work plans, RI/FS firms adhered to strict analytical protocols and data validation to achieve the goals for the data quality indicators instead of focusing on the overall project objectives and the means to fulfill them, such as:

- understanding the intended use of the data
- using screening techniques
- developing representative sampling designs
- statistically evaluating the collected data

During contract negotiations they were forced to reduce the number of samples and sampling locations, while substituting the required-analyses with less expensive and thoroughly irrelevant tests. In one instance in 1996, the previous SI studies had indicated that the site was contaminated with selected semivolatile organic contaminants as determined using EPA Method SW8270 [Gas Chromatography/Mass Spectrometry (GC/MS)]. During Phase II of the same investigation, budget cuts reduced the number of samples from a projected 200 to 39, and substituted the non-selective Diesel Range Organics (SW 8015 Modified) for EPA Method SW 8270.

During budget negotiations Quality Assurance/Quality Control (QA/QC) was the preferred target of "reduction in scope" cutbacks by the project managers and contracting personnel of the negotiating parties. It is obvious that many of the sampling and analyses plans were prepared by engineers and geologists without chemist's participation. Chemists who validated the data did not take part in project planning or execution and did not assist in the interpretation of the data for project decisions.

During review of the project work plans, regulatory agencies often compromised to get at least some work done in a "better than nothing" attitude. Reductions in the comprehensiveness of the field investigation, based on budgetary considerations, schedule-driven approval of incomplete plans, superficial or protocol-oriented reviews by technically unqualified agency personnel, all come back to haunt the stakeholders at remediation time.

CASE STUDIES

The following case studies clearly illustrate the need for more effective site characterization sampling and analysis approach that will generate representative and usable chemical data.

Case Study 1. Pesticide Shop at a Former US Military Installation

Investigation

A small building has been used to store, mix and dispense pesticides for mosquito control. During site investigation, the RI contractor collected four judgment surface samples for Contract Laboratory Program (CLP) organochlorine pesticides and polychlorinated biphenyl (PCB) analysis. The pesticides detected in the soil were *DDT* and *DDE* at concentrations ranging from *0.07 mg/kg to 2.6 mg/kg. Aroclor 1260* was also detected in one of the samples at a concentration of *1.7 mg/kg.* Based on these data, the RI contractor recommended removal and incineration of approximately *75 cubic yards* of contaminated surface soil. Site-specific cleanup levels were established as follows: *DDT* and *DDE* at a concentration of *1 mg/kg,* and *PCBs* at concentrations of *1 mg/kg* for the upper 4 feet of the subsurface and *25 mg/kg* for the soil at 4 feet below ground surface (bgs).

Remediation

In order to better define excavation boundaries, the remedial contractor conducted a thorough surface delineation at the site prior to excavation. A mobile laboratory operated by the remedial contractor developed and validated a screening analytical method for DDT and its metabolites. This screening method which was based on EPA Method

SW 8080 with relaxed QC acceptability criteria, produced quantitative data of known quality. The PCB screening was conducted with immunoassay kits with the detection limits of 1 mg/kg and 25 mg/kg.
Due to the low mobility of the contaminants of concern in the subsurface and based on the history of site use, the remedial contractor selected the judgment sampling strategy. Sample locations were initially placed in the areas where the RI contractor detected elevated concentrations of contaminants. Further delineation proceeded laterally to the depth of 4 feet. A total of 60 samples were collected and screened for DDT and DDE. Table 1 summarizes the results of the DDT screening.

Table 1. Summary of DDT screening

DDT Concentrations	Number of samples collected at different depths			
	0.25 feet	2 feet	3 feet	4 feet
Below 1 mg/kg	14	11	4	4
Between 1 mg/kg and 10 mg/kg	12	4	None	None
Greater than 10 mg/kg	3	2	None	None
Maximum DDT concentrations at different depths, mg/kg				
	790	>60	0.2	0.73

The remedial contractor also screened for PCBs a total of 11 surface samples, that were collected from the area of previous PCB detection by the RI contractor. Five out of eleven surface samples had the *PCB concentrations above 1 mg/kg, and the concentrations of PCBs in three of these samples exceeded 25 mg/kg.* Four samples collected at the depth of 4 feet bgs did not contain PCB contamination above the concentration of 1 mg/kg.

Excavation of contaminated soil was guided by the results of screening analyses, with contaminated soil selectively removed from the "hot spot" areas until the cleanup levels had been reached. Confirmation analysis of 136 samples was conducted by an off-site laboratory that used the CLP analytical protocol. *Based on results of field screening, a total of 668 cubic yards of DDT and PCB contaminated soil were removed from the site, compared to 75 cubic yards originally estimated by the RI contractor.*

There were 10 sites at this military installation that were identified by the RI contractor as having limited surface contamination with organochlorine pesticides and PCBs. The RI contractor projected that a total of 735 cubic yards of contaminated soil would be removed from all sites and incinerated. Based on accurate contaminant delineation, the remedial contractor removed a total of 2,300 cubic yards of contaminated soil. The client reviewed the project budget and ruled out incineration as a disposal option due to prohibitively high costs for transportation and disposal. Instead, after conducting a treatability study, the remedial contractor carried out a more cost effective on-site stabilization treatment, followed by disposal at a local landfill.

Case Study 2. A Former Landfill

Investigation

Drums with hazardous waste were buried in a landfill. No records were kept to document the nature of the hazardous waste or the number of drums. In 1985, during Stage 1 site investigation, the RI contractor did not find any significant levels of contaminants at the site, and recommended additional investigation. In 1988 during Stage 2 investigation, another RI contractor conducted magnetic, electromagnetic and electrical resistivity surveys, a soil gas survey and placed 5 soil borings and one monitoring well at the site. Three soil boring samples contained *Total Petroleum Hydrocarbons* (TPH) concentrations of up to *6,700 mg/kg* and various concentrations of benzene, toluene, ethyl benzene and xylenes (BTEX). Shallow buried drums were also uncovered.

In 1993, another RI contractor conducted a Stage 3 site investigation which included the placement of 5 borings to 50 feet bgs, 1 boring to 100 feet bgs, with a total of 12 soil samples collected at various depths. Eight surface soil samples were also collected. All samples were analyzed for Volatile Organic Compounds (VOCs), pesticides, herbicides, Polynuclear Aromatic Hydrocarbons (PAH) and metals, and the data were validated. The only contaminants found in surface soil samples were *PCBs,* with the highest concentration of *54 mg/kg.* The RI contractor unearthed five drums with hazardous waste that contained trichloroethane (TCA) and PCBs. Results of soil boring samples analyses did not show elevated target analyte concentrations and were consistent with the background concentrations at the site.

Based on Stage 1, 2 and 3 site investigation reports, the RI contractor came to the following conclusions:

1. The number of drums remaining in the subsurface was estimated as 10-20. Later, after a second drum burial area was identified, this number was revised upward to 40-50.
2. The size of the drum burial pit was predicted to be 40 feet wide, 40 feet long and 10 feet deep.
3. The drums contained products with PCBs, and were the source of surface soil contamination.
4. The volume of PCB-contaminated soil to be excavated was estimated at 300 cubic yards.

Remediation

A non-time-critical removal action was planned for the site. Site-specific cleanup criteria were set up for PCBs and TCA, and the EPA Region IX Preliminary Remediation Goals (PRGs) for industrial soil served as the cleanup goals for an extensive list of target analyses.

In 1995, a remedial contractor conducted a trenching drum removal action at the site, during which *177 drums were removed.* Drum contents were composited and analyzed for disposal profiling. The *highest PCB* concentration found in the drum samples was *0.91 mg/kg.* The only other target analyses detected at elevated concentrations were the BTEX compounds. Thirty cubic yards of excavated soil were not contaminated with PCBs.

In 1996 another remedial contractor continued drum removal activities at the site. A total of *469 decomposed, leaking drums were removed from a pit which measured 100 feet in length, 55 feet in width and up to 14 feet in depth.* The contents of the drums were composited and characterized for disposal profiling. The major components of the drum contents were diesel fuel and waste oil. One out of eight composite samples had a concentration of *PCB at 2.3 mg/kg,* and five had *TCA* detected at concentrations ranging from *1 mg/kg to 1300 mg/kg.* Soil in some areas of the burial pit was grossly contaminated with diesel fuel and waste oil.

The last remedial contractor extensively characterized surface soil next to the drum pit by collecting 127 surface samples on a 20 foot square grid and screening them for PCBs with immunoassay kits. *As delineated by the site investigation data, the characterized area should have covered 13,200 square feet east of the excavation pit. The actual extent of surface area contamination to the north, east and south of the pit as determined by field screening was 51,000 square feet.* The vertical extent of PCB contamination was limited to the upper two feet of the subsurface. Contaminated soil was selectively removed, and a total of 520 cubic yards of PCB-contaminated soil were disposed of at a Toxic Substances Control Act (TSCA)-permitted facility.

DISCUSSION

Why did these situations happen? In our opinion, they took place because of an incorrect focus of the RI contractor on the accuracy and precision of data, instead of data representativeness.

Comparison of on-site screening results for the pesticide shop in Case Study 1 to the RI results showed a dramatic discrepancy in DDT concentrations. The R:1 contractor disputed the findings of the remedial contractor using the following arguments:

- The RI data were acquired according to the CLP protocols, followed by data validation, therefore, they must be correct.

- The on-site laboratory screening results were too high. Since they were not obtained by the CLP protocol, it was claimed-that they were likely to be incorrect.

To resolve the argument, homogenized split samples were analyzed by the on-site laboratory and an off-site laboratory. The obtained results were comparable, and the concentrations of DDT were in the range of 300 mg/kg.

Data sets obtained by the RI contractor and the remedial contractor were precise, accurate and legally defensible. However, due to inadequate sampling design, the data collected by the RI contractor, were not representative of the site conditions. In our experience, at DDT handling facilities one can expect sporadic distribution of DDT at shallow depths in the subsurface. Surface soil contamination is affected by wind, rain and human activities, and often does

not reflect the true site conditions. This project would have benefited if more samples had been collected and screened during the RI phase. *Placing emphasis on expensive analytical protocols and data validation instead of focusing on the sampling design and the project DQOs lead to misleading conclusions on the site conditions and in the selection of remedial options.*

It was apparent that the sampling plans for the landfill project (Case Study 2) were prepared by geologists because the RI/FS report was more detailed in its geology than its chemistry, and the focus of the investigations was on vertical, instead of lateral site delineation. The three RI contractors, who were probably constrained by project budgets, collected a very limited number of samples from the site. No field screening for soil was conducted; instead, emphasis was on placement of expensive deep soil borings and data validation.

Discovery of shallow buried drums during Stage 2 investigation should have alerted the RI contractor to the fact that surface contamination from drum spillage and handling was a distinct possibility, and that more surface characterization would be beneficial. The presence of BTEX and TPH in the subsurface was an indicator that the drums most likely contained petroleum products. Nevertheless, the TPH analyses were not conducted during Stage 3 site investigation. Instead, the RI contractor used a more expensive PAH analysis to delineate the site, without considering the fact that only trace levels of selected PAH are present in refined petroleum products such as diesel fuel and waste oil.

The three site investigations did not provide nearly enough information for estimating the magnitude of the cleanup effort. Inadequate numbers of samples, improper sampling design and analyses provided an unrepresentative picture of the true site conditions. That is why the number of buried drums and the extent of surface soil contamination with PCBs came as a major surprise during removal actions. *The inability of the magnetic, electromagnetic and electrical resistivity surveys to distinguish between 10 and 500-600 steel drums buried at shallow depths makes one wonder if these techniques were properly applied or results were misinterpreted.*

SUMMARY

Remediation plans and projected costs of the remediation contractor are only as good as the conclusions of the latest RI/FS report at hand. Inadequate RI/FS work of the past resulted in a loss of time and money, and caused loss of confidence in the accuracy of future RI/FS projects. Preoccupation of RI/FS contractors with data validation and fear of screening and sample compositing to obtain more representative data are apparent. The prevalent problems as we see them are as follows:

1. In the past, RI/FS work has been driven by the protocol, and not the DQO process.

2. Many RI/FS firms use chemists only for the preparation of the contract-specific Quality Assurance Project Plans and data validation. Professional judgment of chemists has neither been valued nor solicited for data interpretation and preparation of sampling plans.

3. Budgetary considerations often put constraints on the numbers of samples and types of analyses, and therefore adversely affect the sampling design and sampling representativeness.

4. The use of "low bidder" laboratories, procured without the project chemist's recommendations, has been a damaging practice, and in the past it has produced a mountain of questionable data. The problem has been compounded by the management of subcontractor laboratories by non-chemist project personnel who were not knowledgeable in the areas of laboratory procedures and QA/QC protocols.

As an industry, we need to develop a better understanding of the DQO process and the intended use of the data. We can, perhaps, then convince the regulatory community that if the tenets of the old "CLP approach" are dropped, site investigations can be conducted in a more meaningful, productive and cost-effective manner.

New tools for RI/FS are available today, such as numerous EPA-approved field screening methods for a wide range of contaminants, new and innovative techniques, and performance-based analytical methods. Participation of experienced chemists in the development of the DQOs, in the preparation of the sampling and analysis plans, laboratory selection and oversight, and in the interpretation of data for the final report, all of these are paramount ingredients for a successful RI/FS project.

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A CASE STUDY ON THE USE OF FIELD IMMUNOASSAY TESTS FOR PCBS TO EXPEDITE A SUPERFUND CLEANUP

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ABSTRACT

Immunoassay testing methods are a cost-effective and time-saving tool used for guiding contaminated soil removal. These methods, in combination with a confirmatory analysis program, are also used to successfully demonstrate cleanup compliance. This study evaluates use of immunoassay test methods for polychlorinated biphenyls (PCBs) in soil and sediment samples applied during a removal action at a Superfund Site.

The Strandley/Manning Superfund site consists of approximately 35 acres of lowland located in Kitsap County, Washington. A spring-fed stream flows through the property and discharges into a salt marsh at Burley Lagoon near Purdy, Washington. From 1972 through 1983, transformer salvage operations at the Strandley/Manning site included scrapping and salvaging of transformers and other electrical equipment received from utilities and other sources. A 1984 US Environmental Protection Agency (EPA) site investigation discovered contaminated soils and sediment with elevated concentrations of PCBs and transformer oil. Subsequent activities at the site included an initial removal of contaminated soils, construction of a containment basin to collect contaminated stream sediments, monitoring of groundwater and sediments, and additional contaminant source characterization. The final phase of site cleanup and restoration, conducted from July through October 1996, included soil excavation and removal. More than 9,000 cubic yards of contaminated soil and stream and pond sediment were excavated. Field testing using immunoassay methodology was performed to guide daily excavation decisions and identify locations where the 1 mg/Kg PCB site action level criteria was met. Field testing for total petroleum hydrocarbons (TPH) was also conducted, using a spectrophotometric method, to confirm soil or sediment removal to an action level of 200 mg/kg. Once field screening indicated that excavation was complete in a work area, confirmatory samples were collected to verify field screening results prior to backfilling with clean soil. Confirmatory samples were analyzed by a contract laboratory employing standard methods for PCBs and TPH.

Over 750 PCB immunoassay tests were performed on soil and sediment samples. Confirmatory analytical testing was performed on 21 percent of the samples. The immunoassay methods had an acceptable 93 percent level of agreement between the Ohmicron RaPID Assay™ PCB Kit and the confirmatory laboratory. Of the twelve disagreements, nine involved immunoassay results higher than indicated by the standard analytical method, as expected. Of the three disagreements that involved a negative bias, two were attributed to experimental error and one was attributed to a highly heterogeneous soil sample.

INTRODUCTION

The Strandley/Manning Superfund site, a former scrap metal/salvage facility, consists of approximately 35 acres of lowland located in Kitsap County, Washington. A small, spring-fed stream flows through the property and discharges into a salt marsh at the head of Burley Lagoon, a tidal inlet connected to Henderson Bay near Purdy, Washington. From 1972 through 1983, transformer salvage operations at the Strandley/Manning site included the scrapping and salvaging of transformers and other electrical equipment received from utilities and other sources. A 1984 EPA site investigation discovered contaminated soils and sediment with elevated concentrations of PCBs and transformer oil.

Under an Administrative Order of Consent, the *Voluntary Group,* a group of eight utilities represented by Seattle City Light has conducted site investigation and cleanup activities since the mid-1980s. The final phase of cleanup activities, which included soil and sediment removal, was conducted at Strandley/Manning from July through October 1996. During these activities, field testing methods for PCBs and TPH were used to monitor compliance with cleanup criteria and to make daily excavation decisions. Confirmatory samples were analyzed by a fixed laboratory to ensure that cleanup criteria had been achieved.

This study evaluates use of immunoassay test methods for PCBs and TPH in soil and sediment samples at the Strandley/Manning Superfund Site.

INVESTIGATIVE METHODS

Several analytical methods for PCB testing were reviewed prior to field activities. Immunoassay methodology for PCB field testing was selected because it met the data quality objectives, was cost-effective, and could be performed quickly. A colorimetric field test method for screening TPH concentrations (Petroflag™ - Dexsil) was also selected because tests could be performed quickly and inexpensively with minimal personnel training.

To determine the effectiveness of the proposed field testing using PCB and TPH methods, samples collected from the site prior to the removal action, were split and submitted to both the field testing and confirmatory laboratory(s).

In general, PCB immunoassay field testing and confirmatory laboratory concentrations correlated fairly well in most areas tested. Results for samples collected from the stream bed did not correlate well. This was likely due to the highly variable matrix of decomposing organic matter, the sand, and the high moisture content. Based on results from this comparison, field testing was not performed in certain areas, and preparations were made to correct and in some cases modify the PCB testing method for samples with high moisture content.

A review of proposed TPH field screening by colorimetric analysis (Petroflag™ - Dexsil) indicated that test kit results were consistently higher than the confirmatory laboratory results. After review of the preliminary screening results and previous site characterization results that indicated minimal TPH contamination, it was decided that field screening for TPH would not be performed.

During the removal action, however, TPH was detected at concentrations exceeding cleanup criteria in some source areas and field testing became essential. TPH concentrations, rather than PCB concentrations, guided soil removal in these areas. TPH from soil and sediment samples was extracted and analyzed using a modified WTPH-418.1 (IR spectrophotometric) procedure in the field laboratory.

SAMPLING APPROACH AND METHODOLOGY

Site cleanup goals required that contaminated soils exceeding 1 mg/kg (dry weight) for PCBs, and 200 mg/kg for TPH, be removed and disposed of during site restoration. During site remediation more than 9,000 cubic yards of soils and sediments (Parametrix, March 1997) were removed and disposed of.

The Ohmicron RaPID Assay™ PCB test yields semi-quantitative and quantitative results. At the start of the removal action, results exceeding the cleanup criterion of 1 mg/kg were reported as "greater than 1 mg/kg PCBs," and results below the cleanup criterion were reported as "less than 1 mg/kg PCBs." This reporting system was later optimized to support the needs of the removal in certain site areas. Additionally, since the working range of the

standard curve was 0.9 to 10 mg/kg, quantitative results within this range were reported. The flexibility of the Ohmicron RaPID Assay™ PCB test also allowed field testing for soils with elevated PCB concentrations (300 mg/kg) to help facilitate removal of soils from "hotspot" areas. The required quantitation limits were achieved by both laboratories, as shown in Table 1.

Table 1. Required Cleanup Levels and Quantitation Limits

Parameter	EPA Cleanup Goals (mg/kg, dry wt.)	Field Testing Laboratory (mg/kg, dry wt.)	Confirmatory Laboratory (mg/kg, dry wt.)
TPH	200	10	10
Total PCBs	1.0	0.9[a]	045[b] to .090[c]

[a] Ohmicron RaPID Assay™ PCB test reports that PCBs can be detected down to 0.5 mg/kg. Their detection limit study indicates a positive bias in the range of 0.5 to 0.9 mg/kg (based on Environmental Users Guide, 1994). In this study, 0.9 mg/kg has been selected as a lower cutoff value for reporting quantitative data.
[b] For Aroclors 1016, 1232, 1242, 1248, 1254, and 1260.
[c] For Aroclor 1221.

Soil sampling points were specified at the grid intersections (nodes) of an evenly spaced (15-foot square) grid pattern. After excavation was completed, soil and sediment samples were collected, with few exceptions, from the surface of the open excavation at each grid node.

Samples were submitted to the field testing laboratory for PCB analysis. Other samples, collected from certain areas of the site, particularly from suspected source areas, were also submitted to the field testing laboratory for TPH testing. If field testing laboratory results exceeded the cleanup criteria at a sample location, an additional 1-foot layer was collected around that location and removed for appropriate disposal. The re-excavated area was re-sampled until field screening results indicated that cleanup criteria had been met. A minimum of 20 percent of all field samples testing below cleanup criteria, using field-screening techniques, were submitted to the laboratory for confirmatory TPH and PCBs testing.

Field analytical testing for PCBs was performed on over 750 samples and testing for TPH was performed on 180 soil samples from excavated areas at the site. To confirm field testing results, 167 samples (approximately 21 percent) were submitted to a contract laboratory for analysis of PCBs, and 38 samples (approximately 22 percent) of the 180 submitted for laboratory TPH analysis. Additionally, 111 PCB and 276 TPH samples were analyzed by the fixed laboratory that were not field tested.

ANALYTICAL METHODS AND QC SAMPLES

PCB Field Testing

PCBs were extracted and analyzed using Ohmicron's RaPID Prep™ Sample Extraction and RaPID Assay™ Kits. This sensitive enzyme immunoassay (ELISA) determines PCBs in soils and sediments; it was selected for its ease of use, as well as its ability to meet data quality, time of analysis, and cost objectives.

The minimum detection limit for the PCB test kit is 0.5 mg/kg (Aroclor 1260). Methodologies for the PCB field testing followed Ohmicron's RaPID Prep™ PCB Sample Extraction Kit and PCB RaPID Assay™ Kit instructions.

The target PCB analyte at the site was Aroclor 1260. Kit antibodies exhibit a strong binding affinity for Aroclor 1260, although the kit is also sensitive to Aroclors 1016, 1232, 1242, 1248, 1254, 1260, 1262, and 1268. The test kit is only moderately sensitive to Aroclor 1221. Based on Ohmicron's studies, a specific reactivity factor for Aroclor 1260 was multiplied by the required action level (1 mg/kg), the estimated extraction recovery factor (0.85), and the analytical confidence factor (0.7) to obtain a site-specific cutoff concentration. This cutoff concentration was calculated to be 0.90 mg/kg (RaPID Assay™ Environmental User's Guide).

Over the course of the remedial action, several method modifications to the Ohmicron RaPID Prep™ and RaPID Assay™ PCB test kits were necessary. They are discussed briefly below:

1. **Issue:** Scratching on the outside of the plastic tubes was observed after repeated insertions and removals from the separation rack. Based on preliminary analytical results, it was believed that the scratches interfered with the (RPA-1™ RaPID Photometric Analyzer) optical readings.

   Modification: The Assay Protocol required vortexing each round plastic RaPID Assay™ reaction tube to ensure adequate mixing of reagents. Rather than vortexing each individual tube, the entire rack of tubes was vortexed by carefully placing the upper corner on the vortex and mixing.

2. **Issue:** Occasionally, proficiency and/or control samples had elevated or diminished absorbance readings and were consequently outside Ohmicron's control limit criteria.

   Modification: Potentially contributing factors were considered and corrective actions taken. As the immunoassay test is fairly temperature-sensitive, care was taken to remove the reagents from the refrigerator just prior to implementing the assay protocol rather than prior to sample extraction. Additionally, the temperature fluctuations inside of the laboratory were minimized.

   Error can be introduced by not performing the method consistently and precisely. To reduce variability in results and minimize deviation from the expected standard curve, it was critical to be consistent with the analytical technique (i.e., length of time when performing such tasks as agitating the samples during the extraction interval and vortexing the tubes, and ensuring that magnetic particles were suspended by mixing the container prior to pipetting the solution into tubes).

TPH Field Testing

TPH from soil and sediment samples was extracted and analyzed using a modified WTPH-418.1 procedure. This procedure uses an IR spectrophotometer to analyze for TPH concentrations. Principally, C-H bonds (aliphatic component of "hydrocarbons") exhibit absorption of IR light at 2930 reciprocal centimeters. The solvent Freon™ 113 was used to extract the TPH from the samples because it does not absorb IR light at wavelengths characteristic of the bonds present. Unknown TPH concentrations in soil samples can be calculated by comparing the absorbance of the unknown with absorbencies of a known set of standards.

Field Quality Control Samples

Quality control checks assessed and documented data quality. The collection and analyses of field duplicates, laboratory duplicates, replicate samples, and method blanks were used as quality control checks on the representativeness of the environmental samples and the precision of the sample collection, handling, and field screening procedures. Field (blind) and laboratory duplicates were collected and analyzed as follows: one duplicate for every batch of 20 samples, or one duplicate per sampling event, whichever occurred first during routine testing. Method preparation blanks were analyzed with each batch of samples to evaluate the effect of solvents, diluents, and reagents. A blank sample was analyzed for each sample batch. Post-extraction duplicates (multiple analyses of the same sample extract) were run with each batch to assess precision in pipetting and/or dilution. These sample duplicates were analyzed at the rate of one sample replicate for every 20 samples, depending on daily batching. Finally, calibration standards (proficiency samples, and control checks) were analyzed with each sample batch to adequately quantify the PCB concentration levels in each sample. A calibration check sample was analyzed along with each batch of samples.

Analytical Laboratory Confirmatory Samples

Confirmatory soil samples were submitted to Analytical Resources, Inc. (ARI) of Seattle, Washington, for PCB and TPH analyses by the following methods:

TPH: Using WTPH-DE (a Washington State TPH GC-FID Method quantified against both diesel and transformer oil)
PCBs: Using a Modified EPA Method 3550 to extract the samples and EPA Method 8081 to analyze the extracts. Additionally, cleanup methods EPA 3650, or EPA 3665 were performed.

RESULTS

The results of field and confirmatory laboratory testing are discussed below as is the precision and accuracy of the methods used.

A verification level validation was performed on copies of the original RPA-1™ RaPID Analyzer paper printouts, Sample Immunological Reaction/Analysis Logs, Sample Log-In Sheets, and the Sample Percent Moisture (%M) Log. Verification for transposition errors between database and Sample Log-In Sheets was performed to verify that transposition errors had not occurred. Approximately fifteen percent of the data were verified for transposition errors and data quality. Overall, data were considered acceptable.

Percent moisture content for each sample was estimated by drying wet soil samples in a oven until the "dry weight" had stabilized. Percent moisture was calculated by subtracting the sample's dry weight from the wet weight, dividing by the wet weight, and multiplying the value by 100. These estimated percent-moisture correction factors were used to calculate and interpret final PCB and TPH concentrations in soils and sediments.

PCB Results

For this project, results above 1.0 part per million (ppm), the action level at the site, were considered a positive result. Of this data set, 155 out of the 167 samples (93 percent) had detection results that predicted achievement of cleanup criteria. Of the twelve detection disagreements, the immunoassay screening methodology detected three false-negative results. These disagreements are evaluated further in the Discussion.

An acceptable level of agreement (less than 2 percent false-negatives), predictive of cleanup criteria achievement, was reached between the RaPID Assay™ immunoassay field testing results and ARI confirmatory laboratory analytical testing.

TPH Results

Results above the 200 ppm, action level at the site were considered a positive result. Of this data set, only 1 of the 38 samples showed disagreement in detection results. This false-positive detection disagreement is evaluated in the Discussion.

An acceptable level of agreement (having fewer than 2 percent false-negatives) on TPH detections was achieved between the TPH field screening results and confirmatory laboratory testing.

DISCUSSION

Polychlorinated Biphenyls

Over 750 samples (including reanalysis of extracts or dilutions) were field-tested for PCBs to confirm that cleanup criteria had been met at the Strandley/Manning Site. The immunoassay field testing, to demonstrate that PCB cleanup concentrations had been met, greatly expedited the removal action.

Only twelve PCB sample results (7.1 percent) were not predictive of cleanup criteria. These consisted of three false-negative and nine false-positive results. False-positives are expected when using the immunoassay test and are conservatively protective of cleanup goal achievement. A false-negative result indicates that the PCB concentration was assessed at less than the 1 mg/Kg criterion by the immunoassay technique, but was measured at greater than that level in the confirmatory analysis. In the paragraphs that follow, false-negatives are discussed.

Two field testing results for PCBs were reported as 0.87 and 0.7 mg/kg. Associated confirmatory laboratory results for these field tests were 1.3 and 1.9 mg/kg, respectively. Although falling on opposite sides of the action level, these results show acceptable precision and are within normally expected sampling and analytical variability for split samples. The percent moisture content for one sample varied greatly between the field testing laboratory (13 percent) and the confirmatory laboratory tests (48.8 percent). This difference in percent moisture is a potential source of variability between the split-sample results.

The PCB field-testing result for one of the samples was 0.68 mg/kg, while the associated confirmatory laboratory result for this sample was 11 mg/kg. Sample heterogeneity is the most likely explanation for this false-negative result. This sample had a moisture content of 35 percent (field test result). Variability is expected for sample splits of soils with such high percent moisture. Of the 64 samples collected from the stream bed area, ARI analyzed 34 samples and 30 were field-tested. All other results showed agreement relative to the cleanup levels. Percent moisture concentrations in this area ranged from 12 to 35 percent.

Total Petroleum Hydrocarbons

For TPH, the field and confirmatory laboratory methods are distinctly different. The WTPH-D extended method performed by the confirmatory laboratory uses a gas chromatograph (GC) with a flame ionization detector (FID) to provide both qualitative and quantitative data. The modified WTPH-418.1 method provides only quantitative data, because it uses the spectrophotometer to measure total C-H bonds, regardless of their source, in a given extract. Since the modified WTPH-418.1 method is considered a screening tool, field-testing for TPH was used conservatively to provide guidance during excavation. TPH results between the confirmatory and the field-testing laboratories compared very well. TPH results were predictive of cleanup levels. No false-negatives and only one false-positive, discussed below, were found.

One of the sample field-testing results for TPH was 3,000 mg/kg. The associated confirmatory laboratory result for this field sample was 71 mg/kg. This result cannot be explained and likely is due to experimental error.

COST AND SCHEDULE COMPARISON

A review of the field testing performance and a comparison with conventional analytical methods indicated that the project time would have doubled if field-testing methods had not been used. The schedule, using fixed laboratory conventional analytical methods for PCBs, was calculated assuming that the laboratory could analyze and report results in approximately two to four days. Samples were collected and analyzed over a four-month period (approximately 50 sample batches were analyzed by the field testing laboratory for PCBs during the removal action). Calculations indicate that the removal action would have been extended by at least 50 days (2 to 2.5 months). The actual confirmatory analytical costs for the project were approximately $90,000. Field testing, including test kits, labor, and supplies totaled $90,000 for a total project analytical cost of approximately $180,000. Estimated costs using conventional analysis for all samples would have exceeded $125,000. Far greater would be the impact on construction labor, equipment standby, and construction oversight for ten or more additional weeks of construction. Given the unanticipated extent of source area contamination discovered during site cleanup, it is doubtful that the project could have been completed in the 1996 construction season without the rapid turnaround of field screening results.

CONCLUSIONS

The Ohmicron RaPID Assay™ PCB test kit was selected for its ease of use as well as its ability to meet data quality, time of analysis, and cost objectives. Based on the field-testing results, the data quality objectives were satisfied. False-negative field-testing results for PCB tests were very infrequent. The field-testing results indicated that immunoassay results had a slight positive bias and that, in some cases, some over-excavation may have occurred. However, this bias provided a margin of confidence that confirmatory analysis would verify that cleanup goals were achieved and backfilling could proceed without further excavation and testing. From the perspective(s) of involved parties, however, it was better to over-excavate soils at the site rather than risk the chance of leaving contaminated materials behind. Quick turnaround requirements were satisfied, and rough estimates of cost savings indicate that it was cost-effective to perform PCB field testing at the site.

Although the TPH testing also met data quality objectives and provided screening support in the field, the method required the use of Freon™, an expensive chlorofluorocarbon that is currently being phased out by regulatory agencies. Different methods capable of satisfying specific project data quality objectives are currently under review.

Based on this evaluation, it is important to ensure that data quality objectives will be met by performing preliminary analyses with the proposed test kit on representative site samples. Additionally, all analytical testing must be performed with an adequate quality assurance and quality control program to establish data quality.

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SELECTING APPROPRIATE QUALITY ASSURANCE CRITERIA FOR BROWNFIELDS INVESTIGATIONS

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During a Brownfields investigation, matrices of unknown composition, such as potentially contaminated soils and ground water, are sampled to determine if remedial actions are required. This type of sampling is used to protect human health by accurately identifying hazardous waste and contaminated aquifers.

Brownfields data quality requirements are less stringent than CERCLA data quality requirements. For example, CERCLA RI/FS investigations require independent data validation of comprehensive analytical deliverables to improve the legal defensibility of data. Independent data validation of comprehensive analytical deliverables is very expensive and time consuming. Brownfields data quality requirements would not include independent data validation of comprehensive analytical deliverables. However, appropriate quality assurance procedures must be followed when sampling potentially contaminated matrices. The data quality objective (DQO) process is used to ascertain appropriate data quality requirements.

DQOs are qualitative and quantitative statements which specify the quality of data required to make a decision. These DQO statements describe the level of uncertainty a decision maker is willing to accept when the results are going to be used in a regulatory decision.

Whenever EPA partially or fully funds a Brownfields project, 40CFR31.45 requires environmental related measurements to incorporate appropriate quality assurance procedures to produce data adequate to meet project objectives. To comply with 40CFR31.45, a Brownfields grantee must have a quality assurance management plan (QAMP), and a site specific quality assurance project plan (QAPP). The QAMP defines an organization's quality assurance (QA) related objectives, policies, criteria, responsibilities, authorities, and explains how those QA objectives will be attained for all activities which generate or evaluate data. The QAPP describes project objectives, DQOs, and QA procedures for a specific site.

QAPPs are reviewed by regulatory agencies to ascertain if proposed sampling and analytical methodologies are consistent with project and data quality objectives. QAPPs are approved if the collected data will be: scientifically valid, of known precision and accuracy, of acceptable completeness, representativeness, and comparability.

PERFORMANCE-BASED EVALUATION OF LABORATORY QUALITY SYSTEMS
An Objective Tool to Identify QA Program Elements that Actually Impact Data Quality

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ABSTRACT

On-site laboratory evaluations, a key element of the laboratory approval process, encourage the proper implementation of analytical methods and provide supporting documentation to demonstrate method performance. These evaluations, regardless of their complexity, usually do not focus on identifying the key, explicit QA program activities that may *in fact* adversely affect the production of acceptable level data quality. They emphasize secondary elements of a QA system or program, such as, the organization, facilities, equipment, good laboratory practices, record keeping habits, and performance in the external intercomparison studies.

This paper proposes a non-conventional, performance-based evaluation to *effectively* assess the technical ability of an analytical laboratory to perform acceptably over the lifetime of an extended project. It focuses on the assessment of (1) current, valid method proficiency data in terms of empirical method detection limits, (2) related quantitative measures of precision and accuracy, and (3) on-going demonstration of precision and accuracy through the analysis of laboratory control samples using statistical techniques. Effective, comprehensive laboratory QA programs comprise of, but are not limited to, internal audit and non-conformance/corrective action reports, training and analytical proficiency files, properly maintained instrument logbooks and laboratory bench sheets, etc. The evaluator's review of these documents can detect trends and systematic deficiencies, thus providing a more sweeping technical evaluation of the laboratory's potential to perform.

INTRODUCTION

Selecting the analytical laboratory that will provide the best complement of services for an environmental project is of utmost importance. Each year, analytical laboratories are subjected to numerous on-site systems audits by various regulatory authorities and by prime contractors as part of pre-award and post-award evaluations. These, a key element of the laboratory selection and approval process, encourage the proper implementation of analytical methods and provide supporting documentation to demonstrate method performance. The objective is to select laboratories that are capable, technically qualified, and credible so that a laboratory performs adequately during a data collection process. Systems evaluations typically range from one-day surveillances to five-day or more intensive compliance audits conducted by a team of two or more auditors. Although sometimes seemingly complex, these evaluations do not necessarily focus on identifying the key, explicit QA program activities that may *in fact* adversely affect the production of acceptable level data quality.

SCOPE OF AUDITS

On-site audits are typically associated with large Federal programs, namely Department of Defense (DoD), Department of Energy (DOE), U.S. Environmental Protection Agency (EPA), etc. There are no universally recognized guidelines or unified checklists for laboratory audits.[1,2,3] Different segments of the same Federal entity may conduct the evaluations based on historical precedence, experience (or lack thereof) of the evaluators, and requirements of special Quality Assurance Project Plans (QAPP) and data quality objectives (DQOs). Unless it is a health risk assessment investigation, most commercial clients are notably less demanding, hence their audits are usually less rigorous.

The vast majority of the audits annually experienced by a laboratory fall in the category of CLP-like evidentiary or "paper-trail" audits, or those focusing on the identification of common deficiencies, such as:

- inconsistencies in laboratory support equipment monitoring, such as:
  - temperature excursions
  - reagent water
  - balance calibrations
  - pipette calibrations
- determination of precision and accuracy of containers
- incomplete training files (e.g., resumes);
- adequacy of bench space, facilities, or instrumentation;
- whether or not the laboratory has a procedure for cleaning glassware;
- improper error corrections;
- labeling of reagent containers;
- inadequacy of logbook reviews, etc.;
- and whether or not logbooks are permanently bound.

Most self-respecting laboratories have a system ensuring that these types of quality control (QC) checks are implemented routinely. Identification of occasional incidents of inefficiencies in the laboratory's QA system does not necessarily constitute a major breakdown of the system that would result in the production of unacceptable quality data. In parallel, a laboratory that may seem to have in place an adequate system of minimizing these common deficiencies mentioned above does not guarantee the generation of high-quality data. All phases of laboratory operations should be designed with the objective of preventing problems and improving quality on a continuous bases.

The US Air Force for Environmental Excellence (AFCEE)[4] and the US Army Corps of Engineers[5] provide a more useful type of guidance for "validation of analytical chemistry laboratories." Here the emphasis is more on actual day-to-day compliance with the QAPPs and the analytical methods.

USING KEY ELEMENTS OF THE LABORATORY'S OWN QA SYSTEM

There are specific, key elements of a QA system that must be assessed to determine whether the laboratory's quality system is capable of meeting the DQOs needed to generate analytical data of sufficient quality. Assurance of data quality can only be achieved through understanding the client's needs and expectations and developing effective means to communicate these requirements to all personnel involved in a data collection project.

An effective QA system is one that emphasizes prevention rather than detection. To accomplish this, laboratories conduct routine internal surveillances to determine the extent of conformance to established, internal procedures and policies covering all critical functions affecting data quality.

Attention to quality begins by ensuring that all technical staff are thoroughly trained in their assigned responsibilities. An auditor, through observation and interviews, can determine the evidence of deviations from laboratory's own internal procedures and project-specific requirements and poor documentation which may indicate a lack of understanding of the procedures, a lack of training, and a lack of QA oversight of staff and procedures.

An evaluator with a working knowledge of laboratory operations and specific analytical procedures can determine the presence and effectiveness of an internal QA system by reviewing:

1. Documents that indicate that the QAPPs, *Request for Proposals (RFPs)/Requestfor Qualifications (RFQs),* or other pertinent contractual documents are routinely reviewed by key operational and project management and QA personnel;
2. The laboratory's manual or electronic mechanism that enables the effective and timely dissemination of project-specific requirements,
3. The laboratory's internal technical systems audit and data validation reports: these provide a more realistic, candid illustration of on-going nonconformities and the management's commitment to resolving them.
4. A full set of method SOPs, followed by analyst interviews; and
5. Method performance data generated by the analysts using internal and/or external blind performance evaluation (PE) samples, *e.g.* method detection limits (MDLs), laboratory control samples (LCSs), EPA Water Pollution/Water Supply PE samples, etc.

ELEMENTS OF PERFORMANCE-BASED EVALUATIONS

The performance-based evaluation must focus on the assessment of on-going method performance in terms of:

1. Current, valid method proficiency data in terms of empirical MDLs;
2. Related quantitative measures of precision and accuracy; and
3. On-going demonstration of precision and accuracy through the analysis of LCSs using statistical techniques.

The sample receiving area is generally the starting point for most audits, when tracing the route of a sample. A laboratory must have a well-documented system of ensuring the traceability of environmental samples from receipt to disposal via maintaining unique identification throughout the life of a sample. An evaluator must be able to determine that sample integrity is maintained through adequate custody of samples from the time samples are collected until disposal or until they may be introduced as evidence in legal proceedings.[6]

Reviewing the results of the laboratory's *internal system audit* reports usually provides the auditor with a plethora of quality issues to help focus his/her attention on the critically deficient areas of operation. Similarly, reports delineating *independent validation* of data reports performed by QA personnel provide a wealth of information about the systematic nonconformities in the data production system.

Coupled with external PE sample data, *internal blind PE samples* can establish the analysts' proficiency in preparing and analyzing multi-media samples and prove acceptable method performance.

The review of *instrument logbooks and laboratory bench sheets* yields information on the prescribed analytical sequence of the correct number, types, and frequencies of method-required QC samples.

The system in place for *technical data review* at various steps during the data production process can illustrate the level of commitment to the early detection and correction of those anomalies that adversely affect data quality. An observation related to reporting of out-of-control data may be an indication of poor review procedures as well as poor techniques in the laboratory.

Nonconformance/corrective action documentation should be reviewed to assess the degree of the systematic deficiencies, and whether adequate corrective measures were implemented in time to eliminate the root cause of such deficiencies. This review can also confirm management's commitment to addressing such nonconformities that lead to insufficient data quality.

Follow-up reviews of nonconformance/corrective action reports indicate the effectiveness of the corrective action program in identifying and correcting *systematic* deficiencies before data quality is further impacted.

Regardless of the advancements in the analytical technologies, competence and expertise of the technical staff are essential to quality measurements. Reviews of *training files* should then emphasize documentation demonstrating analysts' proficiency in performing the assigned tasks. These files should also document the required procedures for training as appropriate for each laboratory staff member.

Reviews of *software validation* documentation can help determine whether a laboratory has a policy and a procedure in place to ensure that Laboratory Information Management System (LIMS), internally developed or modified software configurations (e.g., spreadsheets), and instrument software provided by instrument manufacturers produce accurate and precise data.[7] It is also critical for laboratories to thoroughly document procedures for control of software configuration and process for controlling the release and change of configuration items through the system life cycle and data security. In recent years, software QA has become a central issue for many of the projects governed by DoD, DOE, and EPA organizations. Lack of software QA system has resulted in the generation of questionable data which has cost the government multimillion dollars in resampling and reanalysis costs. For example, an instrument data system not adequately verified can easily process quantitative results that are biased high or low resulting in false positives or false negative. This would result in the generation of erroneous data leading to costly, incorrect clean-up decisions.

Chemical measurements almost always involve the comparison of an unknown with a standard. Laboratories without exception must use standards with documented uncertainties.[8] For reference materials, integrity and traceability to a

known, certified source are prerequisites to accurate and precise chemical measurements. Standard labeling with dates of preparation and expiration will aid in avoiding use of reference materials past their normal shelf life. Routine purity verification on a lot-by-lot basis can establish the quality of the material. Unique identifiers for standards must be documented on bench sheets and in the standard preparation logs to document traceability. Integrity of the standard materials must be ensured through proper storage facilities. A review of traceability documentation can reveal information regarding a laboratory's process in ensuring all of the required elements mentioned above.

Another key element of the QA system is to assess the degree of deficiencies and the corrective actions so that similar deficiencies will not recur. Too often the symptoms of individual deficiencies get corrected, not the fundamental cause, and, when the evaluator performs a follow-up evaluation, he generally uncovers the same type of deficiencies.[8] A detailed review of nonconformance/corrective action reports provides a tool to evaluate a laboratory's ability in correcting data deficiencies early in the process before they impact data quality. It is vital that key laboratory personnel (analyst, supervisor, and QA) take part in the problem solving and identifying the most effective measures that will correct the root cause of the nonconformity.

An active, effective QA Program is vital to the success of a laboratory in the environmental arena. However, to conform to any given requirements demands that an organization has the desire and direction from top management to perform and enforce the discipline necessary to maintain a quality system.[9] Without this, no Quality system can be effective.

CONCLUSION

The effectiveness of the QA Program is measured by the quality of data generated by the laboratory. The analytical laboratory already functions with an effective, comprehensive QA program that implements the critical QA/QC elements discussed above. The performance-related documentation of the laboratory itself provides the evaluator with a vast array of critical issues to focus on. The initial as well as the on-going qualifications of an environmental laboratory should be undertaken using primarily these tools. Technical systems evaluations are most effective when they are tailored to examining the critical methods of interest for a specific environmental project. To accomplish this, a good procedure is to trace the path of a group of project samples through all vital areas of the laboratory operations. Another focus of laboratory evaluations should be to identify noteworthy practices or procedures that help maximize data quality. The on-site laboratory audits should not be intended as a policing function. Rather, these audits should serve as a basis to nurture a successful partnership between the laboratory community, prime contractors, and the regulators. These tools can ultimately be used to select competent laboratories and ensure successful and sustained performance of an environmental project.

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SALVAGING QUALITATIVE GEOTECHNICAL DATA: OBTAINING EPA's PROVISIONAL APPROVAL TO INITIATE CONSTRUCTION OF A NATURAL GAS COGENERATION FACILITY AT A RCRA SITE ON SCHEDULE

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ABSTRACT

EPA Region II and representatives of a proposed natural gas cogeneration facility creatively salvaged qualitative geotechnical data to allow construction to commence on schedule. Postponing construction for additional sample collection, analyses, validation, and assessment would have increased project costs by more than $20,000 per day, seriously jeopardizing the viability of the project. Chemical data previously generated as part of a geotechnical investigation of the site were accepted by EPA for use in the site characterization with the provision that pre-construction activities would include additional sample collections and analyses performed according to an EPA-approved Quality Assurance Project Plan (QAPP) with the submission of validated analytical data. Further construction at the site will be subject to EPA approval based on the environmental conditions of the site materials indicated by the results of these pre-construction analyses. Construction of the natural gas cogeneration facility is of great importance to the regional economy, making the efforts to minimize delays and avoid additional costs crucial to the success of the project.

INTRODUCTION

When the EPA's review of the Environmental Site Assessment performed in late 1995 yielded the response that insufficient samples had been collected to adequately characterize the site, chemical analysis results generated in conjunction with a geotechnical survey performed in early 1994 were offered as supplemental information. These samples, however, had not been collected under an approved QAPP or Work Plan, analyses had been performed on a "rush" turnaround time basis, and no data package documentation had been requested; EPA agreed to consider these results IF they were first validated according to Contract Laboratory Program (CLP) guidelines.

The subsequent validation effort required that the laboratory generate full, "CLP-like" raw data packages "after the fact." In some cases, associated laboratory quality control (QC) sample results could not be located, in other instances, some calibration standard results were found to be outside established acceptance limits for individual target analyses. Evaluation of these data required efforts well beyond the normal scope of data validation, focusing entirely on technical validity and data usability, rather than on contractual compliance. As a result, data that might otherwise have been summarily rejected as non-compliant (and, therefore, unusable) by EPA, were deemed acceptable, as a whole, for the purposes of gaining provisional approval to continue with construction plans.

SUMMARY

Seven weeks of labor-intensive efforts by representatives of the EPA, the field personnel, the laboratory, the client, and the data validation contractor were successfully concluded with a conditional EPA approval to continue with facility construction plans. Based on a careful, technically oriented evaluation, analytical data previously generated for a different purpose were determined to be usable for site characterization purposes, thereby avoiding the need for additional sample collection and analysis activities and the associated costs and delays.

THE METHOD DETECTION LIMIT: FACT OR FANTASY?

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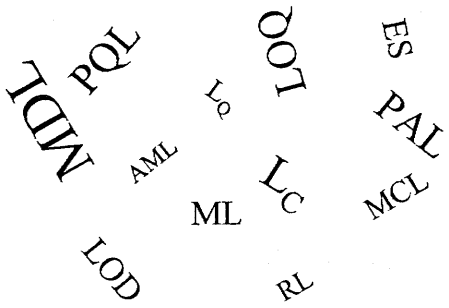

2

MDL

- The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

3

MDL

- If the true concentration is zero, then a false positive at or above the MDL level should be obtained in 1% of determinations
- If the true concentration is at the MDL, then a concentration greater than the MDL should be determined 50% of the time and a concentration less than the MDL 50% of the time. (Assuming 100% recovery)

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DRIVERS TOWARDS LOW MDLs

- Regulatory limits
- Used to judge "quality" of lab
- Method and QAP MDLs

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RESULTS OF DRIVERS

- Labs committing to unrealistic reporting limits.
- Databases contaminated with false positives and negatives
- Estimated values(J) and None Detects(ND) have lost meaning on real world samples

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PURPOSE OF MDLs

- Definitely not to create the Drivers
- Ascertain the reproducible level of detection of the method
- Evaluate the various matrices for the level of detection

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WHY FANTASYLAND?

- Data users (Risk Assessors) are causing the Drivers
- Desire for more Confidence in the MDL
- Purpose of MDLs being ignored
- Instead of changing the Methods to get better MDLs we select unrealistic items to achieve a lower MDL.

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MDL DETERMINATIONS AND ROUTINE ANALYSIS

Instrument specific MDL	*Routine sample analysis*
Analyst knows which analytes are present and what the concentrations are expected.	*Analyst does not know which analytes/ concentrations may be present*
Reagent water or a solid matrix that generates no interferences is used.	*Matrix generates varied and unpredictable interferences*

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MDL DETERMINATIONS AND ROUTINE ANALYSIS

Instrument specific MDL	Routine sample analysis
Test is generally performed on an instrument in pristine condition.	Test is performed on an instrument that meets routine calibration criteria, and may have been affected by previous samples.
Test is performed on a single instrument	Tests are performed on multiple instruments.
Test is repeated if analyte is not detected or has poor recovery or excessive variability.	Test is not repeated if QC criteria are met.

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INCREASING CONFIDENCE IN MDLs?

- Analyst specific MDLs?
- Instrument specific MDLs?
- Multiple iterations?
-

Generally reduce variability and therefore the MDL

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INSTRUMENT SPECIFIC MDLs

- Shows that each instrument can meet a certain detectability level?
- Increases confidence that the lab is not "hiding" a poor instrument?
- Minimize variation, MDLs

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POSSIBLE MDL COMBINATIONS

- BTEX Compounds = 5
- Number of dual column GCs = 6
- Number of MDLs = 5 * 6 * 2 = 60
- Number of possible MDL combinations = 12^5 = 248,832

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POSSIBLE MDL COMBINATIONS

- 8270 Compounds = 85
- Number of GC/MS = 4
- Number of MDLs = 85 * 4 = 340
- Number of possible MDL combinations = 4^{85} = 1.49E+51

Since the complexity is too great for data management systems, generally the "worst case" MDL is used

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INSTRUMENT AND ANALYST SPECIFIC MDLs

- If the SOP is followed, MDL should be analyst independent
- MDL is a snapshot - different analysts and instruments will have different MDLs on different days.
- Ongoing QC should demonstrate that instrument can meet required level of detection

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REAL VS. FANTASY MDLs

1,1,1-Trichloroethane			
	Published MDL	Interlab MDL	Mult.
502.2	0.03, 0.01	8.96	299, 896
524.2	0.08	6.35	79

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REAL VS. FANTASY MDLs

Aroclor 1016 / 1242			
	Published MDL	Interlab MDL	Mult.
608	0.065	0.98	15

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REAL VS. FANTASY MDLs

1,1,1-Trichloroethane			
	Published MDL	Quanterra MDLs	Quanterra WS-037 MDL
524.2	0.08	0.05-0.10	2.68

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OPTION 1 - USE LOW LEVEL CALIBRATION STANDARDS

- Collect seven replicate low level standard results for each instrument
- Calculate IDLs for each instrument
- Perform the MDL study on the worst case instrument

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USE LOW LEVEL CALIBRATION STANDARDS

- Pros
  - Uses existing data that demonstrates instrument performance over extended period of time
  - Demonstrates that each instrument can meet the MDL
- Cons
  - Still a "fantasy " MDL

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OPTION 2 - PERFORM THE MDL REPLICATES ACROSS ALL INSTRUMENTS

- Pros
  - Demonstrates that all instruments detect the analyte at the MDL spike level
  - Increases variability, thereby increasing MDL, bringing MDL closer to real world situation
- Cons
  - Still far removed from routine sample analysis experiment

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OPTION 3 - USE MULTI LAB PERFORMANCE EVALUATION DATA

- Pros
  - Much closer to real world routine analysis experiment
- Cons
  - MDLs will be higher than many regulatory compliance levels

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SUMMARY

- Current procedures for determining MDLs do not reflect the routine sample analysis experiment and result in MDLs that are much too low.
- Efforts to increase confidence in MDLs by making them analyst or instrument specific only exacerbate the situation, since the MDLs will be even lower.

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SUMMARY

- Let's travel back to reality and concentrate on the purpose of MDLs
  - Encourage industry to improve on the methods to lower MDLs
  - Run MDLS on site specific matrix samples
  - Educate all on the risk of the Fantasy approach to MDLS

ACKNOWLEDGMENTS AND REFERENCES

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ACCEPTANCE OF ISO 14000 IN THE USA

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INTRODUCTION

Quietly, without fanfare or broad proclamations, U.S. organizations both in the private and public sectors have been moving steadily to implement the ISO 14001 environmental management system. This quiet approach is somewhat uncharacteristic for American enterprises but one that is readily understandable when we consider the realities surrounding ISO 14000 at this time. It is still unclear, for starters, how regulatory compliance and enforcement of environmental laws will be changed in the U.S. to accommodate ISO 14001. And, while evidence of commercial advantage is growing, it is not yet a foregone conclusion that meeting the requirements of ISO 14001 will ever become a necessity for trade. Also, American firms already have well-established regulatory compliance systems and are unsure what benefits they will get from an additional layer of systems for environmental management. Finally, they hesitate to take on additional costs for what some (erroneously) perceive to be a bureaucratic exercise that requires more paperwork and red-tape without real payback. Given these hurdles and doubts, it is a tribute to many organizations that they have embarked on the ISO 14001 voyage. There are some very good reasons for them doing so, but first we need to review briefly what ISO 14000 consists of.

ISO 14000

ISO 14000 is an evolving series of generic standards being developed under the auspices of the International Organization for Standardization (ISO) to provide organizations with the tools and systems for managing environmental impacts. The series addresses six distinct but related subjects:

- environmental management system (EMS)
- environmental auditing (EA)
- environmental performance evaluation (EPE)
- environmental labeling (EL)
- life-cycle assessment (LCA)
- environmental aspects in product standards (EAPS)

In all, some 18 separate documents are being drafted, only one of which (ISO 14001) is necessary to implement a management system. The other 17 documents are guidelines that support either the implementation of a management system or the evaluation of product characteristics. The EA and EPE guidelines are designed specifically to support the implementation of an ISO 14001 management system.

Very much like ISO 9000 in the Quality Management area, ISO 14001 specifies the framework for the management system that allows an organization to meet its environmental obligations reliably and consistently. The approach used is straightforward and pragmatic. The organization first takes an inventory of all the environmental "aspects" associated with its activities, products, and services. It determines which of these are significant and then proceeds to define and implement a management system that includes a policy, objectives and targets, resources, responsibilities, controls, maintenance, corrective action, education and training, management reviews, and audits. In addition, the organization is required to make three fundamental commitments:

1. To comply with applicable laws and regulations and establish procedures to evaluate compliance,
2. To make continual improvements in the management system so as to keep it vital, effective and significant in the operational life of the organization and,
3. To prevent pollution as a preemptive strategy when it is technically and economically possible to do so.

The most significant challenge in fulfilling these requirements is to integrate environmental protection into all the activities of the enterprise; to bring employees into the picture as committed, knowledgeable and enthusiastic agents for constant vigilance and improvement. ISO 14001 also calls for top management involvement in setting the organization's aspirational goals and guiding principles. Such involvement is key to the success of the EMS. By doing all these things, the organization will gradually develop an environmental ethic to sustain a culture of heightened awareness for environmental care. That cultural orientation will inevitably lead to improved performance vis-à-vis the environment. An ISO 14001 management system can easily propel organizations beyond regulatory requirements. It will improve their effectiveness and their public image. Importantly, it will also improve the quality of the environment.

REASONS TO IMPLEMENT ISO 14000

There are four major reasons for implementing ISO 14001 in the U.S. at this time.

1. TO IMPROVE ENVIRONMENTAL PERFORMANCE

While it is true that considerable effort and resources are expended by U.S. industry in complying with regulatory requirements, there is a growing realization that compliance alone will neither fully protect the environment nor lead to efficiencies and cost savings. Though US regulatory requirements are extensive, major aspects of industrial operations are in fact not regulated. So, for example, there are virtually no restrictions on how much water and energy can be used, nor on the amount of carbon dioxide and other global warming gases that can be emitted, nor on how products should be better designed to minimize their environmental impact. There are also no limitations on how employees travel to their work which has led to a situation where virtually each employee drives his or her own automobile with no other passengers. With the focus on legal compliance, there is almost no recognition that better management of environmental aspects will inevitably lead to more efficient and less expensive operations. Traditionally, there has been little effort to avoid waste of materials and resources. Not only is this costly, but it accelerates the depletion of the earth's stocks unnecessarily. That same exclusive focus on compliance has often led to passivity by organizations so that they would wait for governmental edicts rather than proactively seek opportunities to increase efficiencies and avoid waste. This is all changing now and ISO 14001 is seen to comport with a new attitude in U.S. industry to become more efficient, more competitive and more proactive in all dimensions including environmental protection. ISO 14001 puts the onus for environmental protection on organizational initiatives not on directives from government, it spreads responsibility to all employees not just those in environmental engineering and it builds the organizational ethic and discipline that lead to efficiencies and better utilization of materials and resources.

2. TO BE READY FOR GLOBAL DEMANDS

These is still no clear evidence that ISO 14000 will become a significant factor in international trade. There are only a few examples of organizations from Europe declaring that they expect their suppliers to have environmental management systems. Some governments (e.g. Canada, Holland, and China) have declared ISO 14000 requirements for their own government agencies but not yet for governmental procurement. Despite the lack of movement in this area, many organizations in the U.S. have concluded that it is only a matter of time before ISO 14000 will be universally recognized as the benchmark for environmental acceptability. As the world population continues to increase inexorably towards the twelve billion mark that's expected by the year 2050,

environmental performance and commitment will become increasingly more important. Organizations will be expected to commit to and employ environmental management systems to be accepted as world citizens and suitable trading partners. Major corporations in the U.S. have basically concluded that ISO 14000 is a visible, authoritative statement on environmental care from the international community that cannot be lightly flouted without consequences. They deem it wise to position themselves for what may inevitably be required - a passport for global environmental citizenship.

3. TO ACQUIRE REGULATORY BENEFITS

Neither the U.S. Environmental Protection Agency (USEPA) nor the U.S. Department of Justice (DOJ) have yet made declarations relative to ISO 14000. However, based on existing policies many US organizations have concluded that having an ISO 14001 system will be favorably considered by those agencies in cases where the organization is found to he out of compliance with U.S. law. For example, the USEPA will consider penalty mitigation for companies that discover, promptly disclose and correct noncompliance they find through voluntary audits as long as the company has exercised "due diligence" in addressing its environmental obligations The expectation is that having an ISO 14001 management system equates to "due diligence" for purposes of the USEPA audit policy. In 1991, DOJ issued a policy titled, "Factors in Decisions on Criminal Policy Prosecutions for Environmental Violations in the Context of Significant Voluntary Compliance or Disclosure Efforts by the Violator." The DOJ policy views self-auditing, self-policing and voluntary disclosure of environmental violations as "mitigating factors" when deciding between civil or criminal enforcement. ISO 14001 is again seen as satisfying these criteria that would earn an organization consideration under DOJ's policy. Furthermore, the Organizational Sentencing Guidelines issued by the U.S. Sentencing Commission provide for substantial reductions of criminal penalties for organizations that implement a compliance assurance program that encourages employees to comply with the laws. Here too, ISO 14001 is deemed to satisfy these requirements and thereby bring benefits to organizations. So, while no specific statements have been issued by USEPA and DOJ, many organizations have concluded that conforming to ISO 14001 will satisfy a number of enforcement and penalty mitigation policies that are already in place. This is clearly a strong motivator for many organizations to implement ISO 14001.

4. TO ADD TO EXISTING SYSTEMS AT INCREMENTAL COST

Many companies have discovered that adding an ISO 14001 environmental management system to their existing quality management system (ISO 9000) is relatively easy and inexpensive. ISO 14001 includes a number of system requirements that are similar to ISO 9000 and can therefore be used for both purposes. It has also been found that organizations which already have implemented ISO 9000 are familiar with the systems' approach and need not go through a long learning process. Some organizations estimate that the incremental cost of implementing ISO 14001 on top of ISO 900 may only be 10 to 20 percent of the original cost for ISO 9000. As word spreads that ISO 14001 implementation can cost significantly less than the original cost of ISO 9000, many organizations are deciding this is a cost effective move irrespective of the trade and regulatory implications.

CONCERNS ABOUT ISO 14001

While many organizations are proceeding to implement ISO 14001 for the reasons given above, some stakeholder groups in the U.S. still harbor concerns over possible costs and impacts. Some of these are as follows:

1. CONCERNS OF SMALL AND MEDIUM SIZED ENTERPRISES

There are several concerns related to small and medium sized enterprises (SME). Many SMEs are not yet familiar with the 14001 standard; they dismiss it as being an issue of big business, or they see the certification process as being too complicated and expensive. The 14000 standards were developed so they could be tailored to the size and needs of any organization; therefore, a smaller enterprise will have proportionately less cost and complication than a large enterprise. The 14000 standards will benefit organizations of all sizes, and could in fact have a greater beneficial impact on SMEs because they have the greatest amount to lose from costly and inefficient systems. SMEs will have much more to gain than larger organizations if certification to the standard is a factor in insurance and banking applications. And all organizations, whether large or small, have the potential to be impacted by the trade implications of the standards as products are exported to Europe where the standards may very well be a de-facto condition of doing business.

2. CONCERNS OF SOME REGULATORS

A few regulators are concerned that emphasis on the management approach to environmental protection will de-emphasize command and control regulation. They believe that environmental performance can only be achieved through coercive measures and detailed legal requirements. Such attitudes show a failure to appreciate the fact that environmental protection can only be guaranteed over the long term by behavioral change and institutional acceptance and integration. While holding a gun to someone's head will usually make that person behave as you want, you have not necessarily changed his views or attitude. This is the untenable situation we have today with environmental compliance and it is regrettable that some regulators want to see this mode perpetuated. It seems reasonable that as these regulators begin to understand the significance of the ISO 14001 approach, they will embrace its use in alternative compliance schemes to create win-win situations for all parties.

3. CONCERNS OF ENVIRONMENTAL GROUPS

Like regulators, environmentalists worry that ISO 14001 may lead to relaxation of the command and control approach. They worry that ISO 14001 registration will be mix-used to incorrectly denote environmental excellence of the organization or environmental superiority of the organization's products. As we know, conformance to ISO 14001 does not necessarily equate to environmental excellence. It only reflects that the organization has a management system that satisfies the elements of ISO 14001. It would be a misuse of registration, as well, to imply that the organization's products are environmentally preferable. This would confuse ISO 14001 registration with environmental labeling of products. These are valid concerns that are now being addressed by the leadership of Technical Committee 207 and specifically by Subcommittee 3 of that Committee.

EVOLUTION OF PUBLIC POLICY

Public policy related to ISO 14000 is evolving gradually in a number of fora in the USA. The USEPA has formed an intra-agency working group that is trying to formulate federal USEPA compliance and enforcement policies around ISO 14000. This work is proceeding very slowly within the agency as there are many divergent views and factions that pull in different directions. A separate inter-agency group is trying to develop federal policy among the various agencies of the US government including the Department of Defense, Department of Energy, Commerce Department, State Department and USEPA. This is also going very slowly since each agency is still trying to develop its own policy. The best progress is being made by individual states as well as by a coalition of states which is crafting a common approach to incorporating ISO 14000 into their regulatory schemes. It remains to be seen whether USEPA will allow states to use ISO 14000 in creative approaches or whether it will exert its power to invalidate state initiates. This is a somewhat tricky issue in the U.S. as there has been a strong movement in recent times towards more state power and less federal power. ISO 14000 could become one more item of contention in that greater struggle over how much federalism Americans want in their government.

A number of academic institutions have taken an interest in ISO 14000 but have not yet had much influence on its development, its implementation or the evolution of public policy. Some that readily come to mind include: The Massachusetts Institute of Technology (MIT), Tulane University, Purdue University, Rice University, University of Houston and Carnegie Mellon University. It is expected that some analysis on the implications of ISO 14000 will emerge from one of these at some point.

CONCLUSION

ISO 14000 offers many intriguing possibilities for U.S. companies and for environmental public policy. There are many good reasons for moving forward but there are still some significant concerns and institutional roadblocks to overcome. All in all, progress is being made and it looks like ISO 14000 will be successful in the U.S. We need only to be patient and to work diligently to continue to explain the many benefits and advantages of environmental management systems. Some of us are working hard to do just that.

A CASE STUDY USING A COMPARATIVE TIERED VALIDATION SCHEME

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ABSTRACT

While data validation is an important step in ensuring data quality and usability, many project managers are reluctant to include validation due to the perceived cost and time requirements. When validation is not performed, the issue is sometimes forced by the regulatory oversight agencies, or by potential litigation. The 'after-the fact' validation effort is often more expensive and time consuming, as the laboratory has moved on to other samples, and the validator must gather and understand all project requirements prior to validating the data. This can have a significant impact on project budgets and deadlines, especially for large projects.

This paper describes such a situation, and details the tiered validation scheme used to quickly review all of the data, while the most intense efforts were focused on data with potential quality or usability issues. The tiered approach was a combination of limited and full review, using both electronic and manual validation. The tiered validation satisfied the regulatory requirements, while providing the client with a rapid turnaround at a reduced cost. An additional benefit was that the electronic validation process created a database of validated data that was used for trend analysis, risk assessment calculations, and to identify data gaps for the Phase II investigation.

INTRODUCTION

Working on a base realignment and closure (BRAC) investigation, a project manager inherited a large site that had already undergone several years of investigation using the US Army Environmental Center's (USAEC, formerly the US Army Toxic and Hazardous Materials Agency, or USATHAMA) quality assurance program. All analytical data were generated using USAEC methods. Oversight responsibility for the project had passed from the USAEC to state and federal agencies, including the US Environmental Protection Agency (USEPA). The next step of the project was a risk assessment, however, since the data were not produced using USEPA recognized analytical methods or reporting procedures, the oversight regulatory agencies required that prior to acceptance of the risk assessment, a full validation be performed on 100 percent of the data, demonstrating data quality and comparability to data produced using USEPA protocols.

The potential cost implications to the project were significant—there was a large volume of data (over 300 data packages), some of which were several years old. Many of the data packages were archived, and there was very limited backup documentation (or technical assistance) available from the laboratory. The validation was also made difficult by the different approach used by the USAEC quality assurance program. The USAEC methods use a statistical approach to quality control (QC) that monitors quality on a laboratory specific basis (one set of methods for each laboratory if a laboratory passes certification and meets certain general QC requirements, all sample results are assumed acceptable), rather than the USEPA methods which control quality on a more global, program basis (one set of methods for all laboratories sample quality monitored through various sample or batch specific QC elements). Finally, the data packages (in the USAEC format) did not include any summary forms, such as surrogate recoveries, spike recoveries, blank association, etc. Most of the data were presented 'as is' from the instruments.

DATA COMPARABILITY

The first step was to determine the comparability of the data produced by the two different quality assurance systems. Methods from both systems (USAEC and USEPA) were broken down into QC elements, such as calibration, precision, accuracy, contamination, etc. A table listing the QC elements (and the organization responsible for determining the accuracy of the reported information) was created, and is presented as Appendix A. Using methods from both systems, cross reference tables were created that indicated how the methods addressed each QC element, producing data of known and defensible quality. An example cross reference table is included as Appendix B to this report.

As can be seen by the tables, a comparison of several USEPA methods to the USAEC methods indicated that the same QC elements were addressed by each method. The same fundamental building blocks were used by both programs, and both programs set up a framework that is used to produce data of known quality. The

differences were in the initial approach, the reporting style, and some of the specific acceptance criteria. To fully assess the quality of the data, it was decided to validate the data against the requirements of each program, and then compare the data quality (as determined by volume of qualified or non-useable data). The final determination of data quality was based on whichever program used a more conservative approach for a given QC element.

The findings of this review were submitted to the regulatory oversight agencies, both as a technical memorandum and as an oral presentation. The agencies agreed to wave the requirement for 100 percent full validation in favor of the tiered validation approach proposed for this project.

TIERED DATA VALIDATION APPROACH

To mitigate the cost and time impacts on the project, a two tiered validation scheme was developed. Tier 1 was a combination of electronic and manual review, which produced a validation level of effort equivalent to a USEPA Level 3 review. The electronic review utilized the electronic data deliverable (EDD) required by the USAEC for all analyses, and a Data Quality Screening Tool (DQST) program. One hundred percent of the data were evaluated (electronically and manually) for these quantitative QC elements (when appropriate for a method):

- Sample index
- Holding times
- Blank contamination
- Reporting limit verification
- Blank spike percent recovery
- Surrogate percent recovery
- MS/MSD percent recovery
- MS/MSD RPD values
- Field duplicate RPD values
- Laboratory duplicate RPD values
- Target analyte list verification

Initial and continuing calibration results, instrument tuning (GCMS) and internal standard areas (GCMS) were not provided on the EDD from the laboratory therefore, these QC elements were evaluated manually, using the hard-copy data package. The Tier 1 provided a rapid review of all of the data to identify any potential problem areas.

Tier 2 was defined as a full validation, equivalent to an USEPA full data validation, as defined by National Functional Guidelines. The Tier 2 validation included all of the Tier 1 elements and a complete evaluation of all raw data, including:

- Completeness of laboratory documentation for sample receipt, sample analysis, and sample result reporting.
- Overall documentation practices.
- Presence and completeness of chain-of-custody documentation.
- Instrument performance, and tuning.
- Compound identification and quantification.
- Review of calculations
- Transcription check (from raw data to final results)

The Tier 2 review also included a verification of the electronic results (raw data was compared to results generated by the DQST, and to a percentage of the reported sample results in the database).

Several criteria determined which data packages were subjected to a Tier 2 review. The first criterion was the projected end-use of the data. The second criterion was that a sufficient percentage of all data packages, representative of the entire project, were selected for Tier 2. The third criterion was that any data package identified as 'critical' by the Tier 1 process was included in the Tier 2 review. A 'critical' package was defined as any data package that had more than 5 percent of the QC elements (such as surrogate/spike recoveries, relative percent difference [RPD] values, blank contamination, etc.) outside the control limits. This ensured that any package that would potentially result in a large number of qualified (or rejected) data points was subjected to the most thorough scrutiny by the validation chemists.

DATA QUALITY SCREENING TOOL (DQST)

The DQST is an electronic validation tool developed by EcoChem, Inc., and is similar to other data evaluation programs (such as CADRE). Translation modules were developed to accept EDD specific to the USAEC IRDMIS (Installation Restoration Data Management Information System) format. The DQST performed a validation level-of effort similar to an EPA Level III validation, with the exception that instrument calibration and internal standard areas are not reviewed by the DQST because this information was not specified in the IRDMIS EDD (transfer file). The DQST compared the data to both the USAEC and USEPA acceptance criteria, and identified data points that are non-compliant. Modules containing criteria from additional project or agency QA programs can also be run.

The DQST accepted information downloaded from IRDMIS or from the IRDMIS transfer files, and converts the data into a form usable by the DQST. The data were then sorted according to QC elements, and each QC element is run through a subroutine that compared the reported data points to lists of previously input criteria. The DQST created a sample index and holding times table, tabulated all blank contamination, and reported obvious transcription errors (incorrect analyte names, a reported concentration with a 'less than' designation, etc.). The DQST calculated and tabulated surrogate and spike recoveries, and also duplicate analysis RPD values. The DQST used QC codes to identify duplicates and differentiated between field duplicates and other duplicates.

Once the DQST completed all the subroutines, the results were printed out as a series of tables and suggested qualifiers were listed on an Electronic Qualifier Action Table. A flow chart of the DQST process is included as Appendix C. The DQST results, qualifiers, and additional manual validation elements were reviewed by a qualified chemist to complete the Tier 1 review. The chemist then determined if the data set required an additional tier of review.

After all validation was complete, quality assessment reports were generated by each chemist. The final data qualifiers were added to the database, and all work was peer-reviewed. Deliverables to the client included the final database, validation reports specific to each study area at the site, and tables of qualified data sorted by method and study area.

CLIENT BENEFITS

The tiered validation scheme provided the following benefits to the client:

- Rapid review of a large volume of data
- Reduced project costs
- Focused review of each method to determine if systematic errors existed
- Focused review of data with potential usability or quality issues
- Comparison of two quality assurance systems

There were also additional benefits that became apparent as the project progressed beyond the data validation. During the electronic validation, the DQST created a database of all sample results. This database was updated after completion of the validation, providing the client with a fully validated, qualified set of all site data. This database was used to perform in-depth analysis of any data trends (both site-wide or specific to a certain study area), a comparison of positive results to risk based levels, and also to perform some of the calculations required for the risk assessment. Since the risk assessment identified several potential data gaps, a Phase 2 investigation was begun by the client. The tiered validation approach was included in the Phase 2 Quality Assurance Project Plan.

SUMMARY

The use of a tiered validation approach can allow for a rapid review of all data, with a focus on any data or areas of concern, while controlling project costs. The use of electronic data validation is integral to this effort, and can provide additional benefits due to increased access and control of the analytical data.

APPENDIX A

CONTENT AND FORMAT FOR TYPICAL DATA QUALITY ASSESSMENT REPORT (QC ELEMENTS)

Criteria Reference	Element (From USAEC QA or Method)	Reviewed or Verified
PAM 11-41[a] Sec. 10.5	Data package completeness & document control	Lab/Validator
PAM 11-41 Sec. 7.5	Chain-of-Custody—Transcription of Field ID and Audit Trail	Lab/Validator
PAM 11-41, Sec. 11.5.1 & Method	Holding Time Verification	Lab/Validator
NFG[b] & QAPP	Field QC Sample Evaluation • Field Duplicate • Rinsate (Decon) Blanks • Field Blanks • Trip Blanks	Validator
Method	Mass Calibration/Tuning Evaluation	Lab/Validator
PAM 11-41, pp. 71 & 77-79	Initial Calibration and Calibration Checking Standards	Lab/Validator
PAM 11-41, pp 76-77	Daily Calibration	Lab/Validator
NFG	Internal Standards (if appropriate)	Lab/Validator
NFG & Method	Method Blank Evaluation	Lab/Validator
NFG & Method	System Monitoring Compounds (surrogate spikes if appropriate)	Lab/Validator
PAM 11-41, Sec. 11.5	Evaluation of Precision and Accuracy and Subsequent Non-Conformances • Control Charts	Lab/USAEC/Validator
NFG & Method	Matrix Effects Evaluation (MS/MSD)	Validator
NFG	Compound Identification	Validator
PAM 11-41 & Method	Compound Quantitation and Certified Reporting Limits (CRL)	Lab/Validator
NFG & Method	Tentatively Identified Compounds (TIC) Evaluation	Lab/Validator
PAM 11-41, Sec. 10.8	Transcription—10% within each lot • Worksheets/Notebooks to Instrument Printouts • Standard & Sample preparation & injection records to inst. output to ensure that each output is associated with correct sample • Worksheets/notebook pages must be initiated, dated and explanation for changes • Transfer File (Level I results) to record and group check results to analysis results	 Lab/Validator Lab/Validator Lab/Validator Lab
PAM 11-41, Sec. 10.8	Calculation Verification • Field sample and QG sample results (10% unless problem noted, then 100% until resolved) • Spike recovery and %RSD calculations	Lab/Validator
QAPP	Evaluation of System Process Control (control charts) and relation of "lot" control to site DQO (Data Quality Objectives). NOTE: USAEC/CLIENT/Lab look for "valid" data points (data entry) on a lot by lot basis.	Validator

Note: Not all of the above QC elements will be appropriate to every type of analysis.

[a] *US Army Toxic and Hazardous Material Agency Quality Assurance Program* (1/90)
[b] *USEPA National Functional Guidelines* (2/94)

APPENDIX B

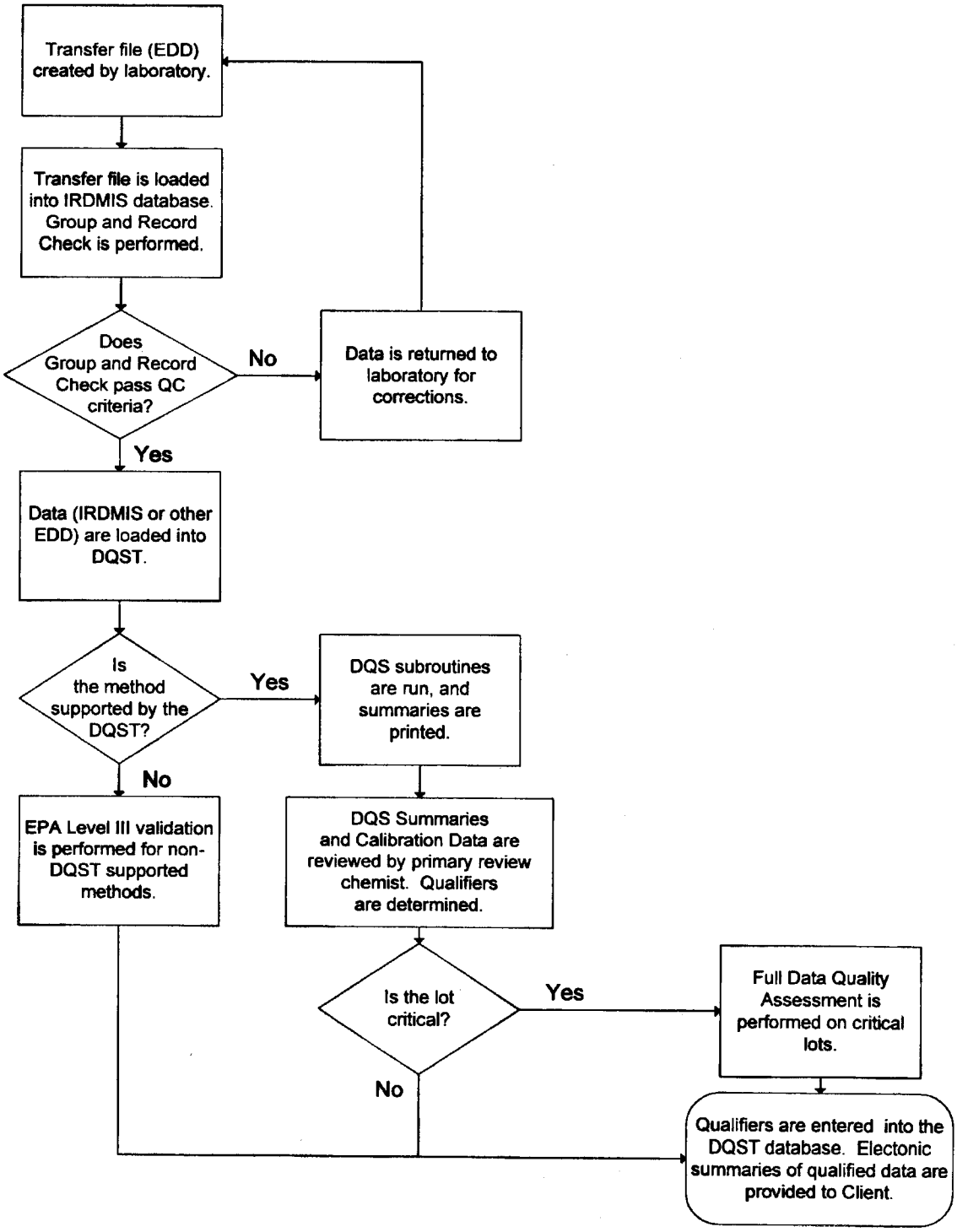
METHOD CROSS REFERENCE COMPARISON TABLES
VOLATILE ORGANIC ANALYSIS METHODS

PROCEDURE	METHOD 524	METHOD 624	METHOD 8240/8260	EPA CLP SOW 3/90 OLM01.0	WATER: METHOD UM21 12/22/92 VERSION 4A	SOIL: METHOD LM23 12/22/91 VERSION 3A	METHODS UM 21 AND LM 23 (ADDITIONAL LAB PROCEDURES)
Holding Time	14 days (Preserved)	14 days	14 days (Preserved) 7 days (Unpreserved)	10 days from VTSR	14 days (Preserved) 7 days (Unpreserved)	7 days from sampling Analysis hold time 14 days from sampling	
Tuning							
• Requirement	50 ng BFB	50 ng BFB	50 ng BFB	50 ng BFB	50 ng BFB	50 ng BFB	
• Frequency	8 hours	Daily	12 hours	12 hours	12 hours	12 hours	
• Criteria	Table 3	Table 3	Table 3	Table 3	same as EPA 624	same as EPA 8240	
Initial Calibration (IC)							
• Requirement	All target analytes	All PP analytes	All target analytes	All TCL analytes	Target analytes and surrogates	Target analytes and surrogates	
• Levels	3-5: near DL-upper end	5: near DL-upper end	5: near DL-upper end	5: 10, 20, 50, 100, 200 µ/L	5: 10.0, 20.0, 50.0, 100.0, 150.0 µg/L	5: 10.0, 20.0, 50.0, 100.0, 150.0 µg/L	
• Frequency	Initially, or when CC fails	Initially	Initially, or when CC fails	Initally, after major instrument maintenance, or when CC fails	Initally (berfore certification or analysis of field samples), or Instrument startup, or different analytes, or daily calibration fails	Initally (berfore certification or analysis of field samples), or Instrument startup, or different analytes, or daily calibration fails	
• Criteria RRF	NS	NS	5 SPCC > 0.300; Bromoform > 0.250	All > 0.01; Most > Min Value	NS	NS	
%RSD	All < 35%	All <35%	6 CCC < 30%	Most < 20.5%	NS	NS	
	or generate second or third order linear regression curve	or plot a calibration curve			Curve linearity determined by lack-of-fit; zero intercept tests, and least squares linear regression, 2/3 analytes must pass calibration	Curve linearity determined by lack-of-fit; zero intercept tests, and least squares linear regression, 2/3 analytes must pass calibration	
Continuing Calibration (CC)							
• Requirement	Mid-level standard	20 µg/L QC Check	Midpoint standard	50 µg/L standard	50.0 µg/L	50.0 µg/L	
• Includes	All target analytes	All PP analytes	All target analytes	All TCL analytes	Target analytes and surrogates	Target analytes and surrogates	
• Frequency	8 hours	Daily (usually 12 hours)	12 hours	12 hours	Before and after 12-hr. sample analyses	Before and after 12-hr. sample analyses	
• Criteria RRF	NS	NS	5 SPCC > 0.300; Bromoform > 0.25	All > 0.01; Most > Min Value	NS	NS	
%D	< ± 30%	Method QC limits	6 CCC < ± 25%	Most < ± 25.0%	2/3 analytes < ± 25% of IC 50.0 µg/L std.	2/3 analytes < ± 25% of IC 50.0 µg/L std.	
IS area	± 30% of last CC or ± 50% of IC	NS	-50% to +100% of last CC	-50% to +100% of last CC	NS	NS	
IS RT	NS	NS	± 30 sec of last CC	± 30 sec of last CC	NS	NS	
Method Blank					Standard matrix (ASTM Type I) method blank	Standard matrix (site background soil) method blank	
• Frequency	Daily	Daily	12 hours	12 hours	1 per lot (20 samples/lot)	1 per lot (20 samples/lot)	
• Criteria	Analytes < MDL	Interference free	Interference free	CH_2Cl_2, acetone, MEK < 5x CRQL; All others < CRQL	Interference free < CRL	Interence free < CRL	
Spike	Blank spike--All target compounds and surrogates	Matrix spike using EPA QC check solution	Matrix spike--5 compounds plus surrogates	Matrix spike--5 compounds plus surrogates	Standard matrix (ASTM Type I) method blank/spike--all surrogates spiked	Standard matrix (site background soil) method blank/spike--all surrogates spiked	Additionally, lab performs standard EPA SOW MS/MSD for Army work

• Frequency	Daily or 5% samples	5% samples	5% samples	5% samples or once per SDG	1 per lot (20 samples/lot)	1 per lot (20 samples/lot)	NS
• Concentration	0.2-5 µg/L	20 µg/L or 1-5 x MDL	20 µg/L or 1-5 x MDL or 10 x PQL	50 µg/L for 5 analytes	Approx. 10 x CRL (surr. cmpds. only)	Approx. 10 x CRL (surr. cmpds. only)	EPA CLP SOW levels
• Criteria	80-120% recovery	Method % Rec limits	Method % Rec limits	Method % Rec limits	Accuracy is control chart dependent using Dixon's outlier test	Accuracy is control chart dependent using Dixon's outlier test	EPA CLP SOW criteria
Duplicate	Blank spike dup	Not required	Matrix spike dup	Matrix spike dup			Matrix spike dup
• Frequency	Quarterly	Not required	5% samples	5% samples or once per SDG	Not required	Not required	NS
• Criteria	% Rec 80-120%; RSD < 20%	Not required	Method QC limits	Method % Rec and RPD limits	NS	NS	EPA CLP SOW criteria
Sample Analysis							
• Qualitative ID	RT within ± 30 sec of standard RT	RT within ± 30 sec of standard RT	RRT within ± 0.06 RRT units of standard RRT	RRT within ± 0.06 RRT units of standard RRT	RRT within RT windows (± 3 x standard deviation of average RRT in calibration standards)	RRT within RT windows (± 3 x standard deviation of average RRT in calibration standards)	
•	3 characteristic ions in std. Present in sample within ± 20% relative intensity	3 characteristic ions in std. Present in sample within ± 20% relative intensity	Ions > 10% in std. Present in sample within ± 20% of ion abundance in std.	Ions > 10% in std. Present in sample within ± 20% of ion abundance in std.	Characteristic ion	Characteristic ion	Lab uses EPA CLP SOW identification criteria
• IS area	NS	NS	NS	-50 to +100% of CC area	NS	NS	-50 to +100% of CC area (no action for outliers for Army)
• IS RRT	NS	NS	NS	± 30 sec of CC RT	RRT within RT windows (± 3 x std. dev. of average RRT in calibration standards)	RRT within RT windows (± 3 x std. dev. of average RRT in calibration standards)	
• Surrogate Criteria	80-120% recovery	Statistically generated from laboratory results	Method % Rec limits	Method % Rec limits	Accuracy is control chart dependent using Dixon's outlier test	Accuracy is control chart dependent using Dixon's outlier test	Method % Rec limits (no action for outliers for Army)
• Quantitative	Within calibration range	Within calibration range	Within calibration range	Within calibration range	Within calibration range. Upper limits in Sec. II.C.	Within calibration range. Upper limits in Sec. II.C.	
QC Check Sample	External source	20 µg/L check standard	Laboratory control sample	Performance evaluation sample	None (other than blank/spike)	None (other than blank/spike)	
• Frequency	Quarterly	5% sample	Each sample batch	Each sample delivery group	(1 per lot)	(1 per lot)	
• Criteria	Specified QC limits	Method QC limits	Specified QC limits	EPA QC limits	(Accuracy is control chart dependent using Dixon's outlier test)	(Accuracy is control chart dependent using Dixon's outlier test)	
Initial Demonstration of Competency							
• Requirement	4-7 replicate spikes at 0.2-5 µg/L	4 replicate spikes at 20 µg/L	4 replicate spikes at 20 µg/L	Performance evaluation samples	Certification	Certification	
• Frequency	Initial, one-time	Initial, one-time	Initial, one-time	Pre-award	Initial, one-time	Initial, one-time	
• Criteria	% Rec 80-120%, RSD < 20%	Method % Rec and SD limits	Method % Rec and SD limits	EPA QC limits	Certification, performance sample, and QA/QC plan results acceptable (PAM Fig. 5-1)	Certification, performance sample, and QA/QC plan results acceptable (PAM Fig. 5-1)	
Method Detection Limit Determination	Required	Required	May be required for specific matrices	Not Required	Determined during certification	Determined during certification	
Other QC	Field blanks	Field duplicates	Equipment blanks, trip blanks, field duplicates	Trip blanks, storage blanks, field duplicates	Field blanks, trip blanks, rinse blanks, field duplicates as per Project Workplan. 1 per 20 or 1 per lot (whichever is greater).	Field blanks, trip blanks, rinse blanks, field duplicates as per Project Workplan. 1 per 20 or 1 per lot (whichever is greater).	

APPENDIX C

DATA QUALITY SCREENING TOOL PROCESS FLOW



GENERAL

THE ENHANCED ETTRINGITE FORMATION PROCESS (EEFP) FOR THE TREATMENT OF HAZARDOUS LIQUID WASTE CONTAINING OXYANIONIC CONTAMINANTS SUCH AS BORON AND SELENIUM

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ABSTRACT

A recently patented waste treatment technology called the Enhanced Ettringite Formation Process (EEFP) is a process for the treatment of hazardous liquid wastes containing oxyanionic contaminants such as arsenic, boron, chromium, molybdenum, selenium, and vanadium. In this process, the mineral ettringite $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ is formed in solution and can result in a 99 % reduction in contaminant concentration through incorporation of the analyte of interest into the ettringite structure. Although the process is currently optimized for the elements boron and selenium, there are numerous additional applications including the trace elements listed above. The process, unlike other treatment technologies such as iron precipitation, is not redox state-sensitive and is extremely efficient at removing either selenite or selenate. The process utilizes relatively inexpensive reagent chemicals and simple unit processes for successful application. In addition to the use of the EEFP in the treatment of hazardous liquid wastes, there are numerous applications for this technology in solidification/stabilization, especially in portland cement and/or coal fly ash systems where ettringite formation might be utilized to enhance immobilization of trace constituents through chemical fixation. The economics of this process have been evaluated, and the costs are comparable to other waste treatment technologies. This represents a mature technology ready for field application. The author is currently seeking an industrial partner for commercialization of this unique treatment technology.

Coal ash also appears to have potential in waste stabilization applications based on ettringite formation. Previous research performed at the Energy & Environmental Research Center (EERC) identified an important stabilization mechanism for oxyanionic species of elements including selenium, boron, chromium, and vanadium. This mechanism is the formation of the secondary hydrated mineral ettringite which has been shown to incorporate oxyanionic species into its structure during the formation process. This mineral has been identified in commingled by-products from coal combustion and gasification and many high-calcium coal combustion by-products (CCBs) during hydration. Ettringite formation in hydrated CCBs has also been associated with a reduction in mobility of several trace elements present in these materials such as boron and selenium. Ettringite formation in CCBs is also of interest because of its significance in cementitious reactions that are key to the utilization of CCBs in many engineering and construction applications including waste stabilization. In recent years, CCBs have been used successfully in waste stabilization demonstrations and field projects.

RECYCLED PLASTIC, A POTENTIAL CONSTRUCTION MATERIALS AT WATERFRONT

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The material traditionally used for the construction of piers, docks, and bulkheads is either preservative-treated or creosoted wood, which do not have long-term resistance to marine boring organisms, and leach potentially toxic materials into the marine environment. In 1994-95 the New York City Department of General Services designed and managed construction of a 11,390 ft^2 pier to replace a decaying wooden recreational pier in the East River at the foot of Tiffany Street, the South Bronx. The new pier was constructed almost entirely of post-consumer recycled plastic (PCRP). We report here an environmental assessment of the impact of the pier on water quality in the East River. A chemical baseline was obtained prior to construction of the pier by assaying the East River water at the site for dissolved organic and inorganic species. A leaching study was carried out using simulated East River water to leach organic and inorganic species from the plastic used in the construction, and compared with similar leaching of CCA wood. The organic and metallic compounds in the leachates were characterized quantitatively. In addition, the odor from the constructing recycled plastic was trapped by headspace device and analyzed qualitatively. From the data

collected, we conclude that the recycled plastic will not add appreciably to the pollutant load of the East River. Plastic timber seems to have significant environmental advantages in addition to its aesthetic and functional qualities.

INNOVATIVE TECHNOLOGIES FOR LEACHATE TREATMENT PART 1: APPLICATION OF MICROBIAL MATS

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Two innovative technologies, Microbial Mats and Zero Valent Iron, are evaluated for leachate treatment. Part 1 of the presentation will discuss the application of Zero Valent Iron technology. The leachate used in this study was collected from a closed site that had accepted municipal, commercial, and industrial wastes for treatment and disposal. Samples were collected from several wells located in the perimeter of each landfill. The leachate contains elevated levels of volatile organics--Benzene, 1,1-DCE, cDCE, Toluene, TCE, Vinyl Chloride, Xylene, Cadmium, Chromium, and Ammonia.

Microbial mats utilize a fixed film comprised of blue green algae and bacteria. The microorganisms form a durable mat held together by the slimy secretions produced by the blue green algae. The surface slime of the mats effectively immobilizes the ecosystem on a variety of substrates, thereby stabilizing the most efficient internal microbial structure. Since mats are both nitrogen-fixing and photosynthetic, they are self sufficient, solar-driven ecosystems with few growth requirements.

The microbial mats' technology has the potential for the bioremediation of a broad class of contaminants, including metals, organic compounds and nutrients. Metals removal occurs by adsorption or by precipitation with the microorganisms. Organic and nutrient removal or destruction is facilitated by the diverse population of microorganisms present in the microbial mat.

The primary advantages and limitations of Microbial Mats technology including the results obtained from the treatability study will be discussed in this part of the presentation. The second part will summarize the results obtained from Zero Valent Iron technology for leachate treatment.

INNOVATIVE TECHNOLOGIES FOR LEACHATE TREATMENT PART 2: APPLICATION OF ZERO VALENT IRON

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Two innovative technologies, Microbial Mats and Zero Valent Iron, are evaluated for leachate treatment. Part 2 of the presentation will discuss the application of Zero Valent Iron technology. The leachate used in this study was collected from a closed site that had accepted municipal, commercial, and industrial wastes for treatment and disposal. Samples were collected from several wells located in the perimeter of each landfill. The leachate contains elevated levels of volatile organics--Benzene, 1,1-DCE, cDCE, Toluene, TCE, Vinyl Chloride, Xylene, Cadmium, Chromium, and Ammonia.

The zero valent iron treatment technology involves the use of granular iron filings to remove metals and enhance the dehalogenatation of dissolved chlorinated organic compounds. Metals are precipitated as a result of locally reducing conditions and high pH that promote the precipitation of metallic oxides and hydroxides and carbonates. VOCs are effectively degraded by an electrochemical process involving the oxidation of iron and the reductive dechlorination of the organic compounds.

Laboratory batch and flow through column studies have been used to assess the effectiveness of the technology for reducing concentrations of chlorinated volatile organics. The primary advantages and limitations of Zero Valent Iron technology including the results obtained from the treatability study will be discussed in this part of the presentation. Part 1 of the presentation will summarize the results obtained from Microbial Mats technology for leachate treatment.

ENVIRONMENTAL CHEMICAL IMPACT OF SLUDGE PRODUCTS AS LAND FERTILIZER

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The long-term sludge management program of New York City involves processing of sewage sludge into locally-useful land-applicable products: fertilizers, soil conditioners, and landfill cover material. Among the limiting factors in the safe commercial utilization of sludge products is the presence of potentially toxic levels of certain organic compounds. If these sludge products are to be applied to land, it is important to determine whether the toxic components can be leached by rainwater into the subsoil, making them available to plants and to soil microorganisms, or potentially into groundwater. In this study, we simulated the sludge leaching process by amending a sandy soil and a garden soil with three sludge products, dewatered sludge, composted sludge and thermally dried sludge pellets. Simulated acid precipitation (sulfuric/nitric acid, mole ratio 3/2, pH 4.0) was used to leach the sludge/soil columns. A set of organic standards was added to the sludge product to monitor the migration of different kinds of organics. The leachates were collected at regular interval and extracted with methylene chloride. Polynuclear aromatic hydrocarbons (PAHs) and phthalate esters were analyzed by HPLC. The characterization of other organic compounds was done by GC-MS. Sludge products and soils were characterized by ultrasonic extraction and capillary gas chromatography coupled with a mass spectrometer (GC-MS). Quantitation was performed by spiking the leachates with deuterated standards before the extraction. The migration of organics in the sludges through the soils and the potential contamination to environment were evaluated.

FLUORESCENT LAMP TCLP TESTING - PROTOCOL DEVELOPMENT

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ABSTRACT

Within the past 6 years considerable study has ensued to address the variability that can occur between environmental laboratory TCLP testing of fluorescent lamps. Considerable effort to determine the sources of variability through round robin testing of fluorescent lamp samples was performed by the National Electrical Manufacturers Association, NEMA, as well as the Scientific Applications International Laboratory, the latter organization commissioned by the EPA in 1992. While the studies of both groups identified several key variables related to fluorescent lamp testing that can affect leachable mercury values, variable leachable mercury values were still found between external laboratory testing conducted in 1994-1995. To address some the issues related to TCLP

testing of fluorescent lamps that have not been identified in past, a detailed and controlled study has been performed at General Electric's Corporate Research and Development Center. The result of the effort is improved knowledge and continued development of a NEMA protocol for fluorescent lamp testing that addresses issues related to lamp sample preparation, extraction, filtration, storage, and vessel preparation that if not specified, can lead to variable leachable mercury values.

INTRODUCTION

The United States Environmental Protection Agency has established a method for the determination of the hazardous status for non-listed wastes. That method is the Toxicity Characteristic Leaching Procedure (TCLP). Samples are examined to determine the amount of regulated materials that can be solubilized. Certain metals are regulated; these metals include arsenic, barium, cadmium, chromium, lead, mercury, silver, and selenium. Table 1 shows the threshold limits for these metals. Fluorescent lamps contain a number of regulated metals including barium, lead, and mercury. It is the mercury that can be leached from a fluorescent lamp that has been the topic of numerous studies.

Table 1. Toxicity Characteristic Leaching Procedure Threshold Limits for Regulated Metals

Metal	Concentration (mg/L)
Arsenic	5
Barium	100
Cadmium	1
Chromium	5
Lead	5
Mercury	0.2
Selenium	1
Silver	5

Fluorescent lamps which are disposed of in landfills are a concern since they are the second largest identified point source of mercury entering landfills (Figure 1)[1]. Of late, the amount of mercury entering landfills has been decreasing. While the amount of mercury in fluorescent lamps has been steadily decreasing[2], the use of fluorescent lamps has been increasing. In addition, it has been estimated that the amount of mercury entering landfills from the other major point sources is decreasing faster than that from fluorescent lamps. The result is that the percentage of mercury entering landfills from fluorescent sources has probably increased since 1989.

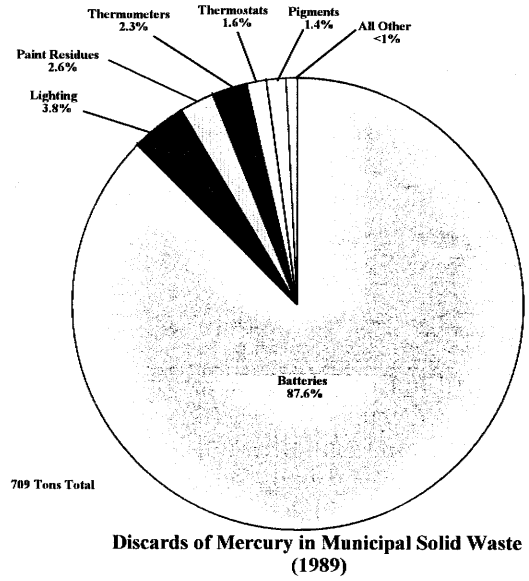


Figure 1.

The TCLP test is performed by first determining which of two aqueous extraction fluids (#1 a mixture of sodium hydroxide and acetic acid or #2 acetic acid only) will be used. At least 100 g of a representative sample of the material to be tested is reduced in size such that it could pass through a 3/8 inch screen. Twenty times the weight of the sample in extraction fluid is added and the mixture rotated end-over-end at 30±2 rpm for 18±2 hours at 23±2.5°C. The vessel may be opened to relieve generated gases during extraction. The mixture is filtered through a 0.7 µm filter and the filtrate analyzed for the contaminant of interest. The filtrate may be stored at 4.5°C until analysis. All materials used must be such that they neither add nor remove a contaminate to the test.

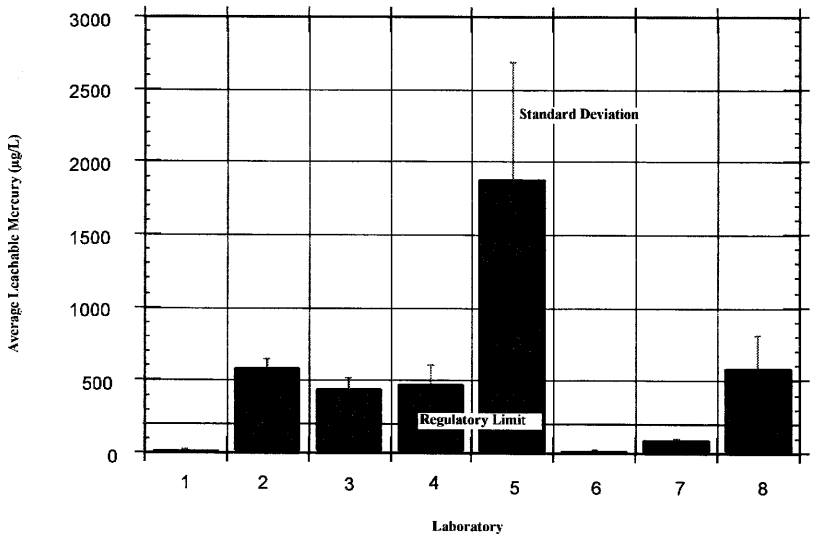


Figure 2. Variability in NEMA TCLP Results for Fluorescent Lamps

A study commissioned by the National Electronic Manufacturers Association (NEMA) and reported in 1992 found wide variability in the concentration of leachable mercury derived from fluorescent lamps[2]. Figure 2 shows over 3 orders of magnitude difference in the average leachable mercury values were reported among eight participating laboratories. The source of variability was sought. Three screening tests were performed to determine if the variability was in the analysis of the solutions resulting from the extraction procedure, the extraction procedure itself, or the preparation of the lamp prior to the extraction procedure. It was found that the analysis of the solutions was not the source of error. The extraction procedure had more variability and the total procedure including lamp breakup produced the most variability.

Leachability studies performed on mercury-containing soils have shown little correlation between total mercury in the sample and the amount of mercury solubilized during extraction[3-4]. A lack of correlation between total silver content and leachable silver in the TCLP test has also been reported[4]. The form of mercury in the soil greatly affected the leachability of mercury. Oxides of mercury were the most soluble while elemental mercury and mercuric sulfide were the least soluble[6]. Soils with 1000 mg/kg of HgO or Hg_2O have leachable mercury values in the TCLP test greater than the regulatory limit of 200 µg/L while the TCLP leachable mercury values for soils contaminated with 10,000 mg/kg elemental mercury or HgS are less than 200 µg/L.

Science Applications International Corporation (SAIC) undertook a study to reduce the variability in leachability mercury from fluorescent lamps documented in the NEMA report[7]. A better procedure to reduce particle size was proposed. The lamp was crushed inside plastic-lined laboratory bench paper and the pieces transferred to an extraction vessel. A correlation between liquid-to-solid ratio and leachable mercury was postulated. Whole lamp testing was also recommended. Differences in filtration techniques of the mixture following extraction were not found to be variables in the leachable mercury values. Results from their procedure on new four foot linear T12 lamps with an average mercury dose of 21.9±10.3 mg were an aver- age leachable mercury value of 1167±230 µg/L, and all eight lamps tested having leachable mercury values greater than 200 µg/L.

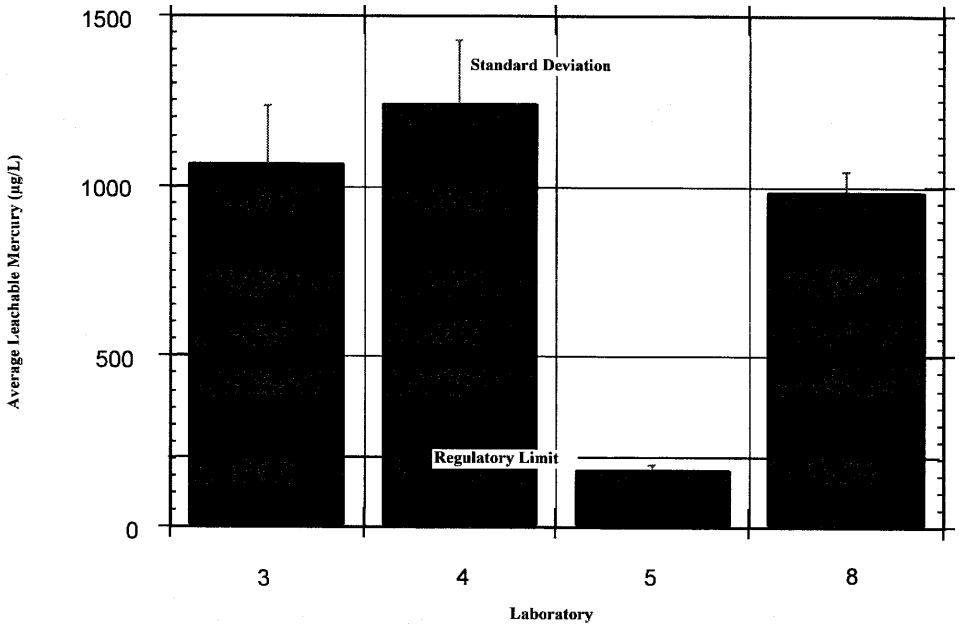


Figure 3. NEMA TCLP Results Using SAIC Procedure

In 1994, NEMA initiated another round of fluorescent lamp testing, this time using the recommendations from SAIC. The results in Figure 3 show that the source of variability had

still not be found. While three of the four participating laboratories produced results comparable to those of SAIC, the fourth differed by an order of magnitude. A study directed by the Ontario Hydro Technologies in April of 1995 examined the leachability of mercury from fluorescent lamps[8]. This testing was directed toward Canadian regulations, and thus is not directly applicable to the United States' TCLP test. Several points of interest, however, came from this study. First of all, loss of material during lamp preparation was deemed to be a critical variable. Whole lamp testing was performed by breaking the lamp inside a specially designed extraction vessel. A method of cleaning and reusing extraction vessels was devised and successfully tested. Finally, all lamps tested exceeded the toxicity criterion.

Another report in 1995, this from the Palm Beach County, Florida, Solid Waste Authority examined the leachability of mercury from fluorescent lamps[9]. Again, the focus was on lamp preparation. The SAIC protocol was also examined versus a method which used a polycarbonate lamp shield to breakup the lamp. Whole lamp samples as well as lamp pieces from a drum containing crushed lamps were examined. Six of seven whole lamp samples had leachable mercury values of 200 µg/L or greater and two of four drum crush samples had leachable mercury values of 200 µg/L or greater.

At the United States Department of Energy complex in Oak Ridge, TN the leachable mercury from fluorescent lamps was recently examined via TCLP[10]. Considerable variability was again observed. Four of ten whole lamps tested at the Oak Ridge National Laboratory failed the TCLP criterion for leachable mercury. At the Y-12 site, seven of thirteen crushed lamps failed the test. At the K-25 site, none of the seven crushed lamps tested had a leachable mercury value of 200 µg/L or greater. It is the purpose to of this study to define the variables associated with the testing of fluorescent lamps for leachable mercury.

EXPERIMENTAL

Four foot linear T12 lamps from General Electric's Bucyrus manufacturing facility were used in this study. These lamps contained no mercury. Elemental mercury was manually added to the lamp in the laboratory in order to definitively ascertain the amount of mercury contained within the extraction vessel. TCLP extraction fluid #1 was used for the study. Lamps were reduced in size, and samples were mixed with 20 times their weight in TCLP solution. The extraction vessels were tumbled end-over-end at 30 rpm for 18 hours at 25°C. The solutions were filtered through 0.7 µm glass-fiber filter paper. The pH of the filtrate was adjusted to <2 with concentrated nitric acid and the solution stored at 4°C until analysis. Mercury content was determined by cold vapor atomic absorbance analysis. The process is depicted in Figure 4.

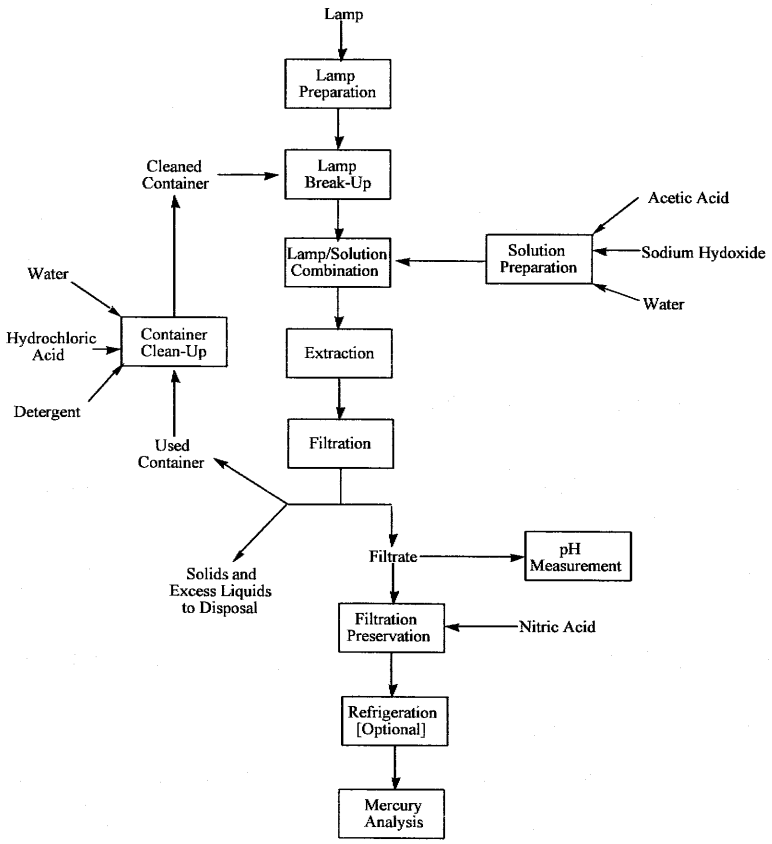


Figure 4. Flow Chart for TCLP Process

RESULTS AND DISCUSSION

Materials of Construction

A variety of materials were examined to determine if they would alter the mercury content of a standard solution. A number of metals are known to absorb onto glass at low concentrations over time[11]. Trace levels of mercury have been reported to absorb onto plastics[12]. Therefore, a known amount of mercuric oxide was dissolved in TCLP fluid #1

and its mercury content measured. The solution was then allowed to tumble in vessels made of a variety of materials. Vessels made of glass and/or plastic had no effect upon soluble mercuric oxide. Elemental mercury is known to amalgamate with a wide variety of metals including zinc and copper[13]. It was therefore deemed that no metal containing materials should be used in the procedure. Polypropylene vessels were therefore chosen as extractor vessels and for filtration units. Liquid samples were stored in glass bottles with Teflon-lined caps.

Lamp Sizing

The breakup of the lamp was for the most part performed within the extraction vessel. Initially, a modification of the SAIC procedure was employed in which a lamp was wrapped with Teflon-coated paper (By-Tac) and smashed with a hammer. The pieces were placed within the appropriate extraction vessels. Three concerns lead toward a different approach. First, there was considerable dust left behind on the Teflon surface. Second, the paper would often be pierced by the shards of resulting glass, causing the package to leak powder. This was also a safety risk to the researcher. Finally, the By-Tac was quite expensive and was not being reused. An alternate procedure was found to be much more effective. A diamond-tipped tool was used to scribe a line around the circumference of the lamp once the vacuum was relieved. Next, a hot wire was brought in contact with the scribed line, resulting in a clean break of the glass. The lamp was cut into appropriate lengths and the aluminum end cap sized. All of the pieces were placed within the extraction vessel, minimizing the loss of solids. The lid was secured to the vessel, and the contents shaken. A number of variables were examined in this process including the material of the vessel, the amount of lamp placed within the vessel, the time of shaking, the method of shaking, and the type of lamp. Results indicate that polypropylene and glass vessel gave similar size distributions for the glass particles following shaking. The time of shaking influenced the size of the resulting particle; longer shaking times resulted in smaller particles. A shake time of at least eight minutes was required to reduce the particle size such that the particles would pass through a 3/8 inch screen. The type of agitation also affected the particle size. Manual shaking was much more effective than agitation in a paint shaker. The more free space in the vessel the greater the breakup of the particles.

While shaking time affected particle size, there was not an effect on leachable mercury. The data in Table 2 show that samples of lamps containing 10 mg mercury that were shaken for various times, and thus contained various size distributions of glass, had essentially the same leachable mercury values.

Table 2. Effect of Shaking Time on Leachable Mercury

	Leachable Mercury (µg/L)	
Shaking Time (sec)	Trial 1	Trial 2
15	114	-
30	98	159
120	92	145
240	109	-
480	-	144

• Samples were manually shaken for 30 seconds inside the extraction vessel.

Lamp Components

Fluorescent lamps contain elemental mercury. Little elemental mercury leaches in TCLP solution. As seen in Table 3, no detectable leachable mercury was found when 40 mg of elemental mercury was tumbled in 2.8 L of TCLP solution. The amount of leachable mercury was dependent on the form of mercury.

A fluorescent lamp contains a variety of materials. The data in Table 4 show the break-down of materials in a lamp. Glass is by far the material in greatest abundance in a fluorescent lamp. The EPA protocol for TCLP calls for a 100 g (minimum) representative sample of the material being tested. To obtain representative data either the 100 g sample must include the proper proportions of metal components, or the entire lamp must be tested.

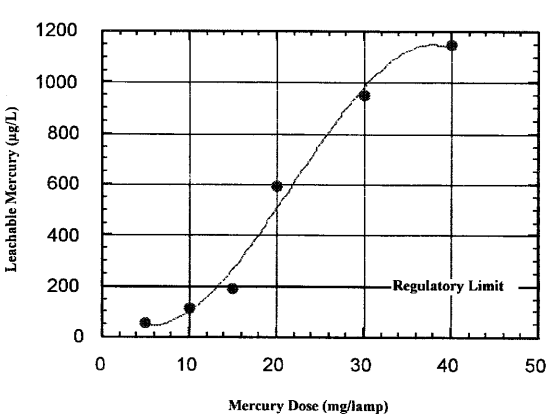
Table 3. Leachability of Various Mercury Compounds

Form of Mercury	% Solubilized
Hg	<0.4
Hg_2O	100
HgO	100
HgS	<0.3
$Hg_3(PO_4)_2$	32

Table 4. Component Make-Up of 4 Foot Linear T12 Cool White/Watt Miser

		Metal Content (mg)		
Component	Weight (g)	Mercury	Iron	Copper
Soda Lime Glass	258.45	1.18 **(7%)**	13.2 **(3%)**	2.42
Leaded Glass	7.37	1.31 **(8%)**	1.44	0.59
Phosphor and Coatings	4.95	14.03 **(85%)**	0.04	<0.01
Basing Cement	3.63	<0.01	5.045 **(1%)**	0.083
Aluminum End Cap	2.25	<0.004	10.4 **(2%)**	4.92 **(1%)**
Fiber Filler	0.76	<0.01	0.98	0.032
Brass Pins	0.74	<0.002	4.50 **(1%)**	545 **(91%)**
Inner Lead	0.28	<0.002	303 **(71%)**	7.05 **(1%)**
Outer Lead	0.12	<0.005	85.0 **(20%)**	39.6 **(7%)**
Filament	0.04	0.004	<0.002	<0.005
Total	278.59	16.5	424	600

- Since a small fraction of the lamp affects the TCLP result and a 100 g representative sample could not be easily taken from a lamp, it is recommended that the entire lamp be used for TCLP testing.



Elemental mercury is contained with a fluorescent lamp. Increasing the amount of elemental meroury within the lamp increases the leachable mercury derived from that lamp. As seen in Figure 13, the relationship between total mercury and leachable mercury (dose/response curve) is not linear. In addition, the mercury found within a lamp is not evenly distributed among the components of the lamp (Table 4) and is not evenly distributed end-to-end along the lamp (Table 5).

Figure 5. Relationship Between Total Mercury and Leachable Mercury in a 4 Foot T12 Cool White/Watt Miser (Dose/Response Curve)

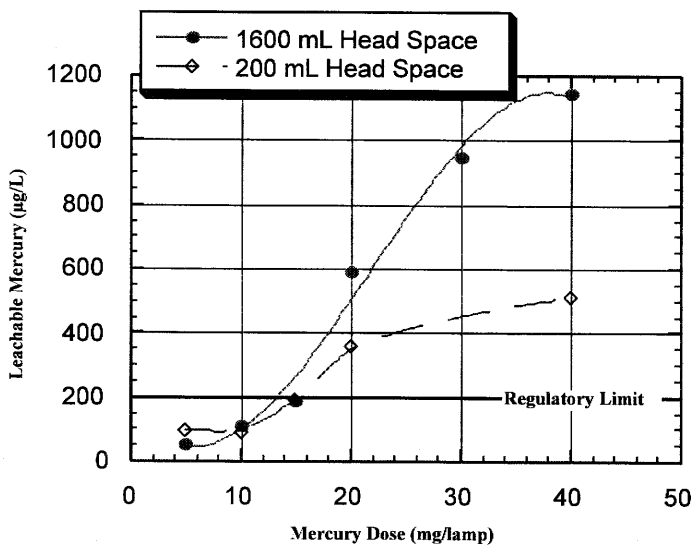
- Fluorescent lamps were tested whole, in a single extraction vessel.

Table 5. Distribution of Mercury Within Selected Fluorescent Lamps

	Mercury Content (mg/end)	
Lamp #	Labeled End	Non-Labeled End
1	<1.7	13
2	<3.0	28.8
3	<3.0	23.1
4	17.8	5.0
5	<3.0	18.0

TCLP Solution

Fluid #1 (sodium hydroxide/acetic acid in water) is used for the extraction of fluorescent lamps. Since a 5 g representative subsample could not be obtained from a lamp, one half of a four foot linear T12 Cool White/Watt Miser was used. This sample weighed 140 g. All manipulations of this sample were scaled upward by a factor of 28. The glass was crushed to pass through a 1 mm screen. The metal components were cut so as to pass through a 1 mm screen. Addition of water to the sample followed by vigorous mixing produced a solution with a pH greater than 5. The required amount of hydrochloric acid was added to the mixture. Following heating, stirring, and cooling the mixture had a pH less than 5. Based on this test, fluid # 1 is prescribed.



Head Space

The results in Figure 6 show that altering the amount of head space changes the leachable mercury values for the dose/response curve for a four foot linear T12 Cool White/WattMiser lamp.

Figure 6. Effect of Amount of Head Space on the Dose/Response Curve for T12 Cool White/Watt Miser

The leachable mercury values could be altered by varying the amount of oxygen in the system. The TCLP test allows for the venting of the extraction vessel during tumbling to alleviate the build-up of gases within the vessel. Two types of venting were examined The first was cracking open the lid to permit trapped gases to exit; the other was to remove the lid completely from the container for thirty seconds, then return it. Venting was performed every 30 minutes for the first five hours of the extraction. For the data presented in Table 6, venting did not affect the leachable mercury values.

Table 6. Effect of Venting on Leachable Mercury

Condition	Leachable Mercury (µg/L)
Closed Container	777
Lid Cracked	760
Lid Opened	675

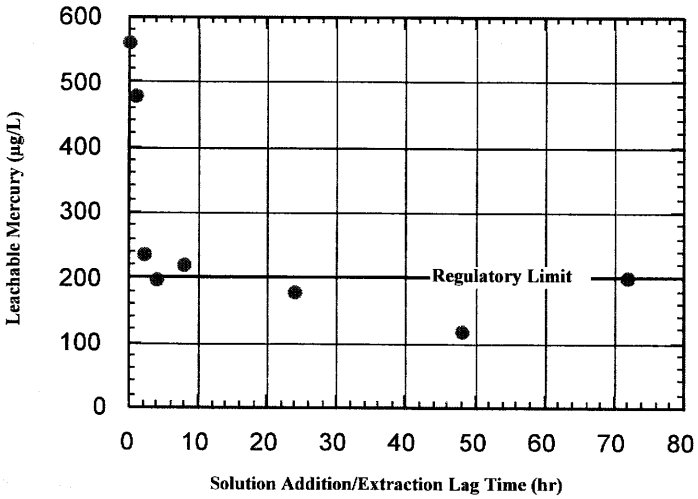
- Head space is a key uncontrolled variable in the TCLP test. To minimize variability, head space should be at least 1 liter. Size determination for the extraction vessel therefore must be made to accommodate the entire volume of the lamp, twenty times its weight in extraction fluid, and 1 L of head space.

Time Between Lamp Preparation and Extraction

In order to assess the effect of the time period between lamp breakup in the extraction vessel and extraction of the lamp with the TCLP solution, a series of 4 foot T12 Cool White/Watt Miser lamps containing 15 mg mercury each were prepared. Each was shaken in an extraction vessel and the time period prior to extraction was varied The data in Table 7 show that retaining the prepared lamps for extended periods of time prior to testing increases the amount of leachable mercury.

Table 7. Effect of Time Between Lamp Preparation and Lamp Extraction

Time Between Lamp Preparation and Lamp Extraction (days)	Leachable Mercury (µg/L)
0	187
3	269
7	243
41	232



Effect of Extraction Fluid Addition/Extraction Lag Time

A series of four foot linear T12 Cool White/Watt Miser lamps were dosed at 20 mg/lamp. The lamps were placed in the extraction vessels, shaken, and 20 times the weight of the lamp in extraction fluid was added. The vessels were sealed, mixed for 5 seconds and were placed in a dark area for various lengths of time. The data represented in Figure 7 show that this lag time has a dramatic effect on leachable mercury.

Figure 7. Effect of Extraction Fluid Addition/ Extraction Lag Time on Leachable Mercury

- After addition of the extraction fluid to the prepared lamp in the extraction vessel, the sample should be immediately (<1 hour) tumbled.

Extraction

Time has a pronounced effect on the leachable mercury values observed for fluorescent lamps. After 18 hours of extraction, the system is not yet at equilibrium. Leachable mercury values increase with time up to about 40 hours, then decrease. This phenomena has been observed for a variety of levels of mercury closings. Long extraction times has a

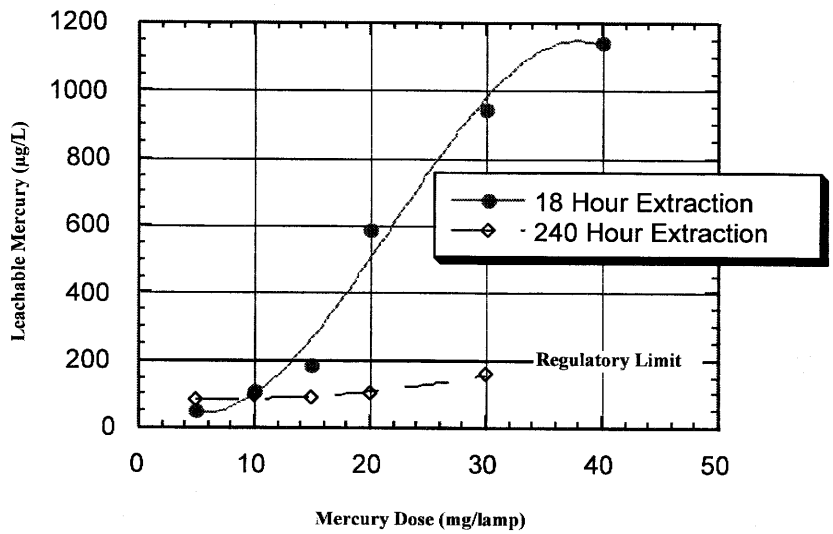


Figure 8. Effect of Extraction Time on Dose/Response Curve

dramatic effect on the dose/response curve for four foot T12 Cool White/Watt Miser lamps (Figure 8).

- While time is specified in the TCLP protocol, clearly the extraction of mercury from fluorescent lamps has not yet reached equilibrium at 18 hours.

- A number of factors associated with the extraction process including the rate of agitation, time, and temperature affect the leachability of mercury from fluorescent lamps.

Extraction Vessel Re-Use

Extraction vessels were re-used after the completion of experiments. Methods of ensuring no mercury carry-over from one experiment to another were explored. Examining the mercury mass balance from a typical experiment reveals that the majority of mercury resides with the solids at the end of an extraction. Therefore, removal of the solids would be critical to re-use of the extraction vessels. The liquid and solid contents from used extraction vessels were first properly discarded and the vessels rinsed with deionized water. A variety of clean-up procedures were then tested. In order to avoid the use of hazardous acids, a detergent scrub was chosen. Following 10 re-usages, a blank was run on the vessel. The blank contained 17 µg/L mercury. It was also noted that the vessels had begun to take on a yellow hue, a color similar to that of the filtrates obtained prior to sample preservation. A rinse with concentrated hydrochloric acid removed the discoloration from the vessel. Following over 50 re-usages in which a detergent scrub was followed by a hydrochloric acid rinse and a thorough water rinse, blanks on the extraction vessels contained 1 µg/L or less soluble mercury.

- Extraction vessels were cleaned for re-use by emptying their contents, rinsing with de-ionized water, scrubbing with detergent, rinsing with hydrochloric acid, and finally rinsing with de-ionized water.

SUMMARY

TCLP testing of fluorescent lamps is a complicated process. The lamp must be considered as part of a system. Table 8 is a summary of the potential variables examined in this work (not all variables examined are discussed in detail in this report due to limitations in length). They are classified as either non-variables (did not influence leachable mercury), prescribed (specified in EPA TCLP protocol), controlled (specified in protocol), or uncontrolled.

ACKNOWLEDGMENTS

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Table 8. Summary of Variables

Potential Variable	Type of Variable	Result of Variable
Mercury Dose	Uncontrolled	• Leachable mercury increases non-linearly • Standard deviation is not constant • Dose is not homogeneously distributed in lamp
Lamp Usage	Uncontrolled	• Leachable mercury can increase with lamp usuage
Metal Components	Controlled	• Can influence leachable mercury • Attachment of components to each other can affect leachable mercury
Head Space	Controlled	• Increased head space leads to increased leachable mercury
Venting	Non-variable	-
Materials	Controlled	• Plastics and glass are inert to soluble mercury; metals should be avoided
Type of Agitation	Non-variable	-
Rate of Agitation	Specified	• Leachable mercury decreases with decreasing agitation rate
Extraction Temperature	Specified	• Leachable mercury increases with increasing temperature
Extraction Time	Specified	• Leachable mercury increases, then decreases with increasing extraction time
pH of Extractant	Specified	• Leachable mercury decreases with increasing pH
Liquid/Solid Ratio	Specified	• Leachable mercury decreases with increasing amounts of solids
Ionic Strength	Specified	• Decreasing ionic strength leads to increased pH and decreased leachable mercury
Sodium Ion Content	Specified	• Decreased sodium ion content leads to decreased leachable mercury
Container Clean-up	Controlled	• Improper clean-ups lead to high blanks
Post Lamp Preparation Lag Time	Controlled	• Longer lag times result in increased leachable mercury
Post Extractant Addition Lag Time	Controlled	• Longer lag times lead to decreased leachable mercury
Sample Preservation	Non-variable	-
Post Extraction Lag Time	Non-variable	-
Sample Break-Up	Non-variable	-

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