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WESTERN PROCESSING: SURFACE AND GROUND WATER MONITORING DURING A SUPERFUND REMEDIATION

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ABSTRACT

Collecting high quality, defensible samples from the environment can be a controversial and difficult task. This paper describes an operating ground water and surface water sampling program that is monitoring the progress of a long-term superfund remediation.

In 1983, Western Processing was listed under CERCLA as one of the fifty most contaminated sites in the nation. Written into the consent decree are requirements for both surface and ground water monitoring. The stream that runs adjacent to the site has intensive monitoring requirements during remediation with clearly defined water quality objectives. Ground water monitoring is required during remediation and for 30 years thereafter.

The monitoring approach includes comprehensive quality assurance/ quality control (QA/QC) and sampler training programs. Dedicated ground water monitoring equipment is utilized to minimize introduction of contamination by sample collection. The surface stream that runs adjacent to the site is sampled with non-dedicated equipment. A rigorous QA/QC program has been implemented to track any possible contamination introduced during sample collection and to ensure the integrity of every sample obtained.

The monitoring equipment and the methods employed on this project as of 1987 are discussed including presampling activities, sampling procedures, field records handling, sample parameters (which include priority pollutant listed compounds, sampling schedule, and analytical parameters and procedures, and QA/QC objectives. The health and safety approach for the environmental monitoring program at Western Processing is discussed, and a brief description of the environmental cleanup is given.

I INTRODUCTION

History

The Western Processing superfund site is located in Kent, Washington, approximately 20 miles south of Seattle. The site is presently surrounded by warehouse and manufacturing facilities that were built over the last decade.

From 1952 through 1961 the site was operated by the U.S. Army as an anti-aircraft battery. The Western Processing Company purchased the 13 acre location and began operations in 1961 as an animal by-products and brewers yeast processor. Operations were expanded to include the reprocessing of pickle liquor, recovery of heavy metals and waste solvents, neutralization of acids and caustics , electrolytic destruction of cyanide, chemical recombination to produce zinc chloride and lead chromate, reclamation of flue dust, metal finishing by-products, and ferrous sulfide in fertilizer production. In 1983, due to environmental problems associated with the site, the U.S. Environmental Protection Agency initiated closure of the facility and an emergency response cleanup action. Following surface remediation and establishment of surface water control measures, an intensive shallow soil contamination study was conducted to determine the extent of hazardous chemical contamination and provide a baseline for remedial activities. Sampling investigations conducted between 1982 and 1986 have identified over 70 contaminants in soils and 46 contaminants in ground water samples. From this initial data ground water and surface water indicator chemicals were selected for long term environmental monitoring, (Tables 1 and 2).

Geology

Western Processing is located in the Duwamish/Green River Valley flood plain and is bounded to the west by Mill Creek and to the east by a shallow drainage ditch (Figure 1). Ground water is shallow, ranging from 3 to 15 feet below the ground surface. Underlying soils are comprised of fill and laterally discontinuous and unconfined lenses of sands, silts, and clays. A discontinuous sandy and clayey silt layer is present at about 35 feet below the ground surface. This aquitard is about 5 feet thick. Below 40 feet the soil is generally unconfined sands and constitutes the regional aquifer. The regional ground water flow is generally to the northwest resulting in an upgradient direction to the east and southeast of the site. Shallow ground water flow is influenced by discharge to Mill Creek at depths of 30 to 40 feet during normal to low flow periods. Regional ground water flow is about 100 feet per year.

TABLE 1

ANALYTICAL SUITE FOR GROUND WATER
(Indicator Chemicals)

Volatile Organics - All volatile organic priority pollutants

Metals (total)
- Cadmium
- Chromium
- Copper
- Nickel
- Lead
- Zinc
- Iron
- Manganese
- Sodium
- Calcium

Base Neutral/Acid Extractibles
- Bis (2-ethylhexyl) phthalate
- 2,4 Dichlorophenol
- 2,4 Dimethylphenol
- Isopherone
- Phenol

Other
- Cyanide
- 3-(2-Hydroxypropyl)-5-Methyl-2-Oxazolidinone

Conventional Parameters
- Total Hardness
- Temperature (field)
- pH (field)
- Specific Conductance (field)
- Total Chlorides
- Sulfates
- Bicarbonate
- Carbonate

TABLE 2

ANALYTICAL SUITE FOR SURFACE WATER
(Indicator Chemicals)

Volatile Organics
- Chloroform
- 1,1-Dichloroethane
- 1,1-Dichloroethene
- Ethylbenzene
- Methylene Chloride
- Tetrachloroethene
- Trans-1,2-Dichloroethene
- Cis-1,2-Dichloroethene
- 1,1,1-Trichloroethane
- Trichloroethene
- Toluene

Conventional Parameters
- Temperature (field)
- pH (field)
- Specific Conductance (field)
- Dissolved Oxygen (field)
- Hardness
- Chloride
- Ammonia
- Turbidity
- Nitrate
- Phosphorous
- Total Suspended Solids

Metals (Total & Dissolved)
- Cadmium
- Chromium
- Copper
- Nickel
- Lead
- Zinc
- Iron
- Manganese
- Sodium
- Calcium

Base Neutral/Acid Extractibles
- Bis (2-ethylhexyl) phthalate
- 2,4 Dichlorophenol
- 2,4 Dimethylphenol
- Isopherone
- Phenol

Other
- Cyanide
- 3-(2-Hydroxypropyl)-5-Methyl-2-Oxazolidinone

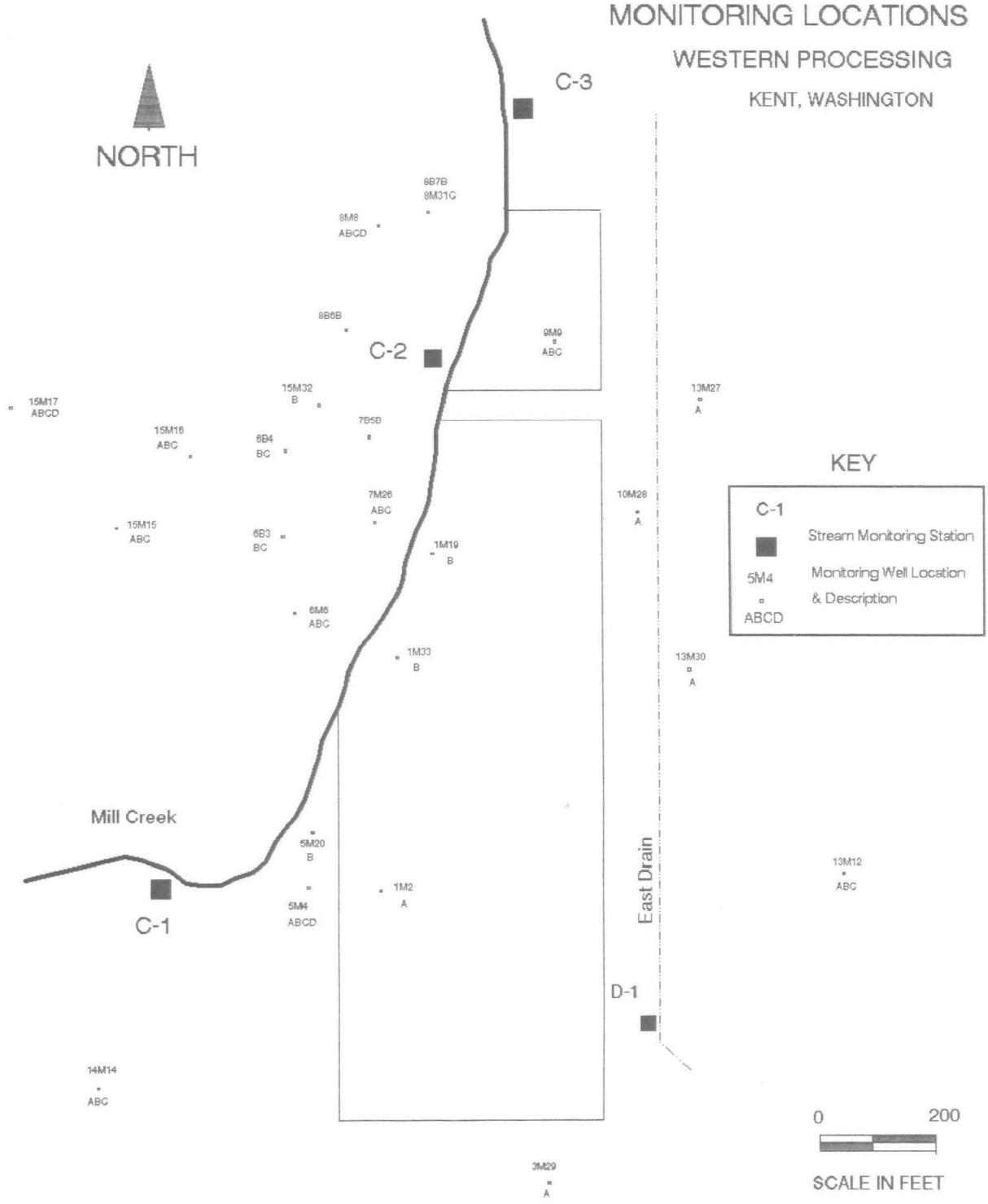
MONITORING LOCATIONS
WESTERN PROCESSING
KENT, WASHINGTON
NORTH
C-3
C-2
C-1
D-1
Mill Creek
East Drain
8B7B
8M31C
8M8
ABCD
8B6B
9M9
ABC
15M32
B
15M17
ABCD
15M16
ABC
6B4
BC
7B5B
7M26
ABC
15M15
ABC
6B3
BC
1M19
B
6M6
ABC
1M33
B
5M20
B
5M4
ABCD
1M2
A
10M28
A
13M27
A
13M30
A
13M12
ABC
3M29
A
14M14
ABC
13M13
ABCD
KEY
C-1
Stream Monitoring Station
5M4
ABCD
Monitoring Well Location
& Description
0
200
SCALE IN FEET

FIGURE 1

Contractor/Client/Government Interaction

The Western Processing superfund project may be unique with its proactive approach to overall site management. Informal weekly meetings are held to inform the Trust overseeing the cleanup, the governments (U.S. Environmental Protection Agency, Washington State Department of Ecology, and the City of Kent) and other regulatory parties of the status of site operations. Regulatory interaction and cooperation to resolve project issues is very high.

II REMEDIATION

Subsurface remediation included the removal of highly contaminated soils and non-leachable materials, installation of ground water extraction, infiltration and water treatment systems and a ground water monitoring network. A site-dedicated laboratory was constructed to analyze both process and environmental samples generated by the project.

Twenty-two thousand cubic yards of highly contaminated and low permeability materials were excavated, and the pits backfilled with clean, high permeability fill. The site was then graded and bermed, and a shallow (30 feet deep) extraction well system was installed. Organics and metals contaminated ground water is pumped from these wells by vacuum extraction and transferred to a water treatment facility where metals are removed by precipitation/clarification and organics are removed by air stripping and carbon adsorption. The dedicated laboratory performs analysis on water and soils for organic and inorganic parameters. Laboratory instruments include three gas chromatograph/mass spectrometers for volatile and semi-volatile analyses, an inductively coupled plasma-arc furnace and two atomic absorption furnaces for metals analyses, a gas chromatograph for pesticide analysis, an ion chromatograph for anion analysis, and a UV vis spectrometer for phenol and cyanide.

A slurry wall was constructed to minimize lateral ground water movement into or away from the site during ground water extraction. This wall encircles the site and is composed of a soil and bentonite mixture with a hydraulic conductivity of about $1X10^{-7}$ cm/sec. Its depth ranges from 40 to 45 feet so it junctions with the aquitard zone which is present at 35 feet. The Western Processing Consent Decree stipulates that an inward gradient to the site must be maintained during ground water remediation. Twenty-two pair of shallow and deep piezometers were installed inside and outside the slurry wall to monitor the horizontal and vertical gradient relative to the site and to aid in management of the extraction and infiltration systems.

III MONITORING PROGRAM

The monitoring program at Western Processing is divided into two parts: process monitoring, which includes discharge compliance monitoring and environmental monitoring. Process sampling and analysis monitors remediation progress of the extraction field and treatment efficiency through the various treatment processes. Environmental monitoring at Western Processing tracks relatively low levels of contaminants in the ground water that originally migrated off-site. Immediately adjacent and down-gradient from the site is Mill Creek. Performance standards for Mill Creek water quality are specified in the Western Processing Consent Decree. These standards were achieved by reducing the contaminant concentrations at the downstream sampling locations (Figure 1) below the applicable ambient water quality criteria (AWQC). The applicable AWQC are those that were published in the Federal Register at the time of entry of the Consent Decree (April 1987). Relevant AWQC are for cadmium, chromium (hexavalent and total), copper, lead, mercury, nickel, silver, zinc and cyanide. This performance standard was achieved within its three year compliance period. Sampling protocol is extremely important for collection of representative samples and elimination of potential contamination from sample collecting activities. Mill Creek water is sampled monthly for ground water source contamination at one upstream location and at two downstream locations. In addition, Mill Creek sediments are sampled semiannually at one upstream location and three downstream locations.

Monitoring wells have been installed up-gradient of Western Processing for background data and down-gradient of the site to track site-related contaminant migration. Presently the monitoring network includes 54 wells, 11 of which were pre-existing. The monitoring installations are individual shallow wells and clusters, consisting of three or four wells with individual wells in each cluster, each screened in a different zone. All newer installations are single completion wells with 10 foot screen lengths placed in depth zones of 10 to 30 feet, 40 to 60 feet, 80 to 100 feet, or 120 to 140 feet. The actual screen interval was determined during well installation by both sieve analysis of the soils in the proposed screen zone and observations of the hydrogeologist that logged the boring. All monitoring wells were installed using cable tool drilling equipment. Long-term ground water monitoring is conducted on a quarterly basis with special interest wells being monitored monthly. Water levels are being monitored monthly during the operation of the ground water extraction system. The duration for long-term ground water monitoring is thirty years after the governments have determined that an acceptable level of remediation has been achieved by ground water extraction and treatment.

Monitoring Approach

Since environmental monitoring for Western Processing will be conducted for thirty years after completion of remedial activities, a comprehensive and defensible program had to be developed. To assure that the sampling was consistent, especially due to project duration and the long term potential for litigation concerning the analytical data, a comprehensive Quality Assurance/Quality Control (QA/QC) program was established. QA/QC for the monitoring program includes:

- o Rigorous sampling methodologies;
- o Defensible documentation of all calibrations, chain-of-custody, maintenance, training and sampling procedures;
- o Sample contamination evaluation to determine if technique or equipment is introducing contamination to the sample;
- o Duplicate sampling and analyses to assess analytical precision;
- o Round robin analyses to measure field analytical performance;
- o Instrument calibration and performance checks to assess whether the field instruments are performing within acceptable parameters and;
- o Frequent sampling audits.

Position requirements for sampling personnel at Western Processing are high. Physical requirements are demanding as the sampler must perform sampling tasks in protective clothing in a variety of weather conditions. The sampler must possess adequate academic training to comprehend the concepts and goals of the work. Sampler training is essential to assure the competency of the sampling team in performing their tasks and maintaining consistency of protocol and technique throughout the duration of the program. Training is required a minimum of once a year for all samplers. Training includes a thorough review of all relevant work plans, discussion of the sampling theory and it's application, and supervised demonstration of sample collection. A sampler proficiency test is administered annually by comparing analytical results of the trainee to the trainer. All sampler training is documented and archived with project records.

Monitoring Equipment

The monitoring program is operated out of a 10 X 40 foot trailer that has been modified for field operations. The monitoring laboratory contains both domestic and deionized water sources for decontaminating equipment, a lab hood for application of solvent and acid rinses, flammable storage, equipment and supply storage, work counters for instrument calibration and maintenance, and a waste

water tank to collect all decontamination water for treatment. Equipment common to both the ground water monitoring program and the surface water monitoring program are pH meters, specific conductivity meters and a dedicated sampling van. The van is the platform from which all field activities are conducted. This includes field pH and specific conductivity analyses, field data entry and sampling equipment and supply storage.

Monitoring Wells

Presently, 54 monitoring wells are being sampled for Western Processing. To eliminate the possibility of cross contamination, the sampling equipment that comes in direct contact with ground water is dedicated to each well. The type of sampling pump utilized for all monitoring wells on the project are submersible mechanical pumps. The pump is a double check valve, positive displacement, piston pump. Actuation of the pump is accomplished from the well head with a portable pneumatic motor. The mechanical connection to the submersible pump is by a small diameter stainless steel pushrod. Only the pump, pushrod, and discharge pipe contact ground water down the well. Materials of construction of the sampling pump are teflon and stainless steel, which provide good chemical resistance while maintaining reliability. Discharge pipe is 3/4 inch schedule 80 PVC, which provides an adequate discharge rate while providing enough room between the discharge pipe and the well casing to allow the use of a water level probe. The well head discharge is a 3/4 inch PVC tee with a hose-fitting connection. The advantage of this system is that the well can be purged at a reasonable pumping rate (5 gal/min) and sampled (as low as 120 ml/min) with the same pump. The compressed air source for the pneumatic motors is a trailer-mounted air compressor. The compressor produces sufficient volume to purge three wells concurrently to minimize total sampling time. A 1000 gallon purge water collection tank is also mounted on this trailer.

Surface Water Monitoring

Unlike the ground water monitoring program, the surface water and sediment sampling program does not employ dedicated sampling equipment. To assure high quality surface water and sediment samples, rigorous QC procedures have been incorporated to detect sample contamination. These procedures are described in QA/QC objectives.

Non-dedicated equipment includes mechanical current meters for flow measurement, a subsurface grab-type sampler for collecting stream samples, an Ekman-type dredge

for collecting stream sediments, a 2.4 liter pressure filter for filtering stream samples, and stainless steel mixing bowls and trowels for compositing sediment samples.

During sample collection, current meters are used to determine stream flow by taking velocity measurements at different points in the stream's cross section. Two types of current meters are used- selection depends on the water depth. A current meter consists of a vertical axis rotor with cups that is attached to a wading rod. Sediment samples are collected from Mill Creek with a pole-mounted Ekman dredge. This sediment sampler is a stainless steel box with spring loaded jaws that are tripped after the box has been driven into the sediment. The pressure filter is an acrylic pressure filtration unit designed for field filtration of water samples. The filter unit is pressurized with nitrogen and is used for collecting samples for dissolved metals analysis. A one liter grab-type water sampler is utilized for collecting all water samples. Water is transferred directly from the grab sampler to individual sample bottles. In-situ oxygen measurements are observed with a dissolved oxygen meter.

Monitoring Methods

Pre-Sampling Activities

Before entering the field and initiating field activities, available background information on the monitoring station is reviewed. This information includes the condition of the well or stream station and range of historical field test data (pH, specific conductivity, dissolved oxygen, temperature, purge volume, etc.). Field equipment is checked for proper operation (i.e., the air compressor is run, pneumatic motors are operated, current meters are assembled, the dredge is tested, etc.). The field instruments are calibrated and results recorded in a laboratory logbook. Part of the calibration procedure is an instrument performance check (IPC/QC). Results of this IPC/QC must be within two standard deviations or the instrument is recalibrated. A closing calibration check is conducted at the end of the sampling day with the results recorded in the laboratory logbook. All calibration logbooks are reviewed and initialed monthly by the site QA officer.

Pre-cleaned and quality controlled bottles are utilized for sample collection. To minimize contamination introduced from the field, preservatives, if required, are added by the laboratory with the exception of volatile samples. Volatile samples are preserved in the field immediately after sample collection. Proper labels, chain of custody forms, and custody seals are assembled.

Field Records

Field sampling records consist of the chain of custody, field parameter form, and field logbook. The chain of custody (COC) accompanies and tracks the sample from acquisition through analysis to final disposition. The form is designed to summarize the contents of the shipment, dates and times of custody transfer, and signatures of all individuals relinquishing and receiving the samples. It includes the following information:

- o Project name
- o Sampler's name
- o Analysis parameters
- o Remarks
- o Date/time
- o Sample number
- o Date/time
- o Number of containers
- o Relinquished by
- o Received by

The Western Processing COC form closely resembles the NEIC form with the addition of analytical parameters and project name printed on the basic form for efficiency.

The field parameter form contains information about sampling procedures, equipment, conditions, and field measurements. All field information is recorded via a laptop computer and downloaded at the end of the day into the laboratory database. A hard copy is printed at that time for review, date and signature by the field sampler. The signed hard copy is archived for future reference. The field parameter form contains the following information:

- o Sample point - the complete sample number which includes the sample location plus the laboratory ID number.
- o Purging information - date, time, volume.
- o Sample depth, water depth, flow.
- o Sampling equipment information.
- o Field measurements - pH, temperature, conductivity, dissolved oxygen, and ground water elevation.
- o Field comments - weather conditions, well and dedicated equipment condition, sample appearance and preservatives added in the field, if any.

The field logbook is a numbered controlled document that contains hand written field notes and data that compliment the information provided on the field parameter form and COC. Each page is numbered, initialed, and dated by the

sampler. The field log book provides the additional information necessary to respond in detail to inquiries about a sampling event, especially when conditions require deviation from the procedures specified in the workplan.

Sample Storage and Transfer

Immediately after sample collection, the bottles are placed in an insulated shuttle with ice packs and transported to the laboratory for analysis. Samples are transferred to the laboratory usually within 4 hours of collection, minimizing any temperature changes that might result from shipping to an off-site laboratory. Transfer of samples to the laboratory requires a properly prepared chain of custody form. An incomplete or improperly prepared chain of custody could invalidate any resulting data.

Analytical Procedures

Laboratory analysis is accomplished using USEPA Methods, SW-846, Standard Methods for the Analysis of Water and Wastewater, and CLP Methods. Table 3 presents these methods.

TABLE 3
Analytical Laboratory Methods

Parameter	Method Reference	Matrix
Acidity	305.1	Water
Alkalinity	310.1	Water
Ammonia	350.3	Water
Anion Chromatography, Chloride, Nitrate, Sulphate	300.0	Water
Cyanide	335.2	Water
Hardness	130.2	Water
Metals (ICP)	200.7	W/S
Arsenic (GFAA)	206.2	W/S
Antimony (GFAA)	204.1	W/S
Lead (GFAA)	239.2	W/S
Mercury (CVAA)	245.1	W
Mercury (CVAA)	245.5	S
Selenium (GFAA)	270.2	W/S

TABLE 3 - Analytical Laboratory Methods (cont'd)

Thallium (GFAA)	279.2	W/S
Phosphorous	365.2	Water
Total Suspended Solids	160.2	Water
Turbidity	170.1	Water
Volatile Organics	8260	W/S
Semi-Volatile Organics	8270	W/S
Pesticides/PCB	8080	W/S

Quality Assurance and Quality Control Objectives

A strong quality assurance/quality control (QA/QC) program for sampling and analysis is incorporated to determine actual environmental contamination. QA/QC is used to assess the sample's ability to represent its sampling location. A minimum of 10% of the total number of samples collected are quality control samples. These include both sample duplicates and method blanks.

Duplicate samples are collected in the same manner as the actual environmental samples. The duplicate is not a split sample, but, is collected immediately after the original environmental sample. Over the duration of the project each station is being included in this process.

For ground water sampling, a field method blank consists of the appropriate sampling containers filled by the laboratory with deionized water and sent into the field with other containers to check the quality of the sampling environment. These blanks are opened at the sampling station and poured into sample containers during the sampling event and transported to the laboratory for analysis. Volatile blanks are not opened in the field and serve as a trip, or transport blank to test container quality. If contamination is present after analysis of the volatile blank, container banks are collected and analyzed on the specific lot(s) of samples bottles used during that event. The well would then be resampled.

For surface water sampling, field method blanks are collected to check equipment decontamination procedures, quality of the sampling environment, and sample container quality. The method blank consists of pouring laboratory deionized water into the grab sampler and then transferring it to sample containers to be analyzed as a regular sample. For filtered samples, the water is poured into the pressure filter and filtered as a normal investigative sample. Volatile sample bottles are filled in the laboratory and travel to the field and back without being opened.

For sediment sampling, the Ekman dredge, and mixing equipment interact with the sample. Acid washed sand is placed in the dredge, emptied into the bowl and then transferred to the jar as an actual sample would be handled.

Monitoring Wells

Sampling Procedures

After arrival at the well location, the conditions of the well and the immediate surroundings are observed and recorded. This includes weather conditions, well integrity, evidence of tampering or contamination, and conditions in the area that could effect the quality of the sample (airborne contaminants, etc). All wells are photographed annually to document the condition of each well. Prior to sampling, the ground water elevation is measured and the monitoring well purged. The well is purged so that the ground water sample collected is representative of the formation water at that point in time. The ground water surface elevation is measured with an electric tape from the top of the well casing to the water level in the casing. Water levels are measured to the nearest hundredth of a foot with precision at $\pm$ two hundredths of a foot. After the ground water surface elevation has been determined, the volume of ground water in the well casing can be calculated and the total purge volume determined. The industry standard and the approved purge amount for this project is three casing volumes. Purge volumes are measured in the field with in-line flow meters calibrated in gallons and tenths of gallons. Once a year pH, temperature and conductivity are measured continuously during the purge process to verify that purging three casing volumes of ground water is adequate to provide a representative sample. All the wells monitored to date are stable with respect to these parameters before complete removal of the third casing volume.

The pneumatic motor and purge water discharge line are attached to the well head assembly and the well pumped until the required volume has been evacuated. The purge water discharge lines are not dedicated to each well, so the end contacting the well head assembly is decontaminated before and after each use. A backflow preventer assures that purge water cannot drain back into the well during the pumping process. After completion of purging, the well is allowed a reasonable period to recharge (usually five to thirty minutes, depending on the recharge rate) prior to sampling. During this recharge period the dedicated small diameter 3/8 inch sample hose is attached and the motor adjusted for minimum flow operation. Ground water samples are collected immediately after well purging and recovery. Samples are collected over a bucket to minimize the possibility of contaminating the

immediate vicinity of the well. A one liter bulk sample is collected and split into four discrete samples from which temperature, conductivity and pH are measured.

Collection of volatile organic samples involves filling the appropriate vial very slowly with as little air contact as possible. Because the analysis requires that volatile samples be headspace free, the vial is allowed to overflow at least 1.5 volumes. The appropriate amount of preservative (concentrated HCl) is added and the cap is gently replaced. All other sample bottles are filled with a minimal amount of air contact. These bottles are filled as full as possible without any overflow.

Sample Parameters and Schedule

The long term ground water monitoring network is sampled on a quarterly basis for the constituents listed in Table 1. Monitoring wells are sampled in the same sequence each quarter to insure that the individual sampling frequency remains one quarter apart. During the summer quarter, a complete priority pollutant scan is conducted on a sample from each monitoring well in addition to those parameters not on the priority pollutant list.

Surface Water Monitoring

The stream that lies adjacent to the site is continuously monitored for flow using a pressure transducer located behind a weir. Resulting information is recorded by a data logger. Comparative flow measurement data is manually collected at each stream sampling station immediately following sample collection. Velocity measurements and stream flow are determined using U.S. Geological Survey methods.

Sampling Procedures

Prior to sampling, weather conditions and stream height are evaluated to determine if storm conditions (abnormally heavy rain and high stream conditions) exist. Monitoring will occur if conditions are within the norm for that time of year. This is to develop data representative for that period and not storm data. The sampling station is evaluated for any physical changes or conditions that could impact flow measurement or sample collection. These are noted on the field parameter form.

Field measurements are conducted using the same protocol as for ground water monitoring. A one liter bulk sample is collected with the grab sampler and the contents split into four discrete samples from which temperature, conductivity and

pH are measured. Dissolved oxygen calibration and measurements are conducted in-situ. Collection of volatile organic samples involves filling the appropriate vial from the grab sampler with as little air contact as possible. As with ground water samples, the analysis requires that volatile samples be headspace free. When filling, the vial is allowed to overflow at least 1.5 volumes. The appropriate amount of preservative (concentrated HCl) is added and the cap is gently replaced. All other sample bottles are filled with a minimal amount of air contact. These bottles are filled as full as possible without any overflow. For total and dissolved metals analysis, the sample is split into two aliquots. One aliquot is filtered in the field and the other is left unfiltered. This insures that laboratory analyses are performed on one sample of water.

Sediment Sampling Procedures

Mill Creek sediment within the reach of Western Processing is generally silty with some sand. The ekman dredge was selected for sediment sampling because it can collect an adequate volume of reasonably undisturbed sample from this sediment type. The number of individual samples collected at each station ranges from one to three, and is dependent upon the stream width at each location. Multiple samples are mixed to obtain one composite sample for each station. Volatile samples are collected by taking approximately equal aliquots from beneath the undisturbed surface of the individual samples immediately after sample collection and before compositing.

Sample Parameters and Schedule

Mill Creek water is sampled monthly until the completion of remediation. Parameters for analyses are listed in Table 2. During the summer quarter, a complete priority pollutant scan is conducted on each surface water sample in addition to those parameters not on the priority pollutant list.

IV HEALTH & SAFETY

The environmental monitoring program is carried out in accordance with the approved health & safety plan for the project. Enough historical data has been accumulated on both the monitoring wells and surface water sampling to allow protective clothing requirements to be addressed on a well-by-well and station-by-station basis. Minimum requirements include a working uniform with safety glasses and disposable latex or PVC gloves.

V SUMMARY

The Environmental Monitoring Program at Western Processing has been refined with input and constructive criticism by both government and private industry from the first workplan drafts in June 1987 until government approval of the workplans in the summer of 1990. The result is a monitoring program that provides defensible and reproducible data that may well be tested by the courts in the future. A specific monitoring history can be pulled from archives and a specific sampling event can be recreated without reliance on the sampler's memory.

VI ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Dennis Steeves and Paul Anderson of Chemical Waste Management for their input. The authors would also like to acknowledge the Western Processing Trust Fund, the U.S. EPA, Region X, and the Washington State Department of Ecology for their proactive approach to resolving both technical and regulatory issues during the Western Processing remediation.

VII REFERENCES

U.S. EPA Region 10, Investigation of Soil and Water Contamination at Western Processing, King County, Washington, May 1983

Landau Associates, Extraction/Infiltration Systems Management Manual, Western Processing, July, 1990

Chemical Waste Management, Inc., Ground Water Monitoring Program Workplan, Part B, July, 1990, Revision 1

Chemical Waste Management, Inc., Mill Creek & East Drain Monitoring Plan, August, 1990, Revision 1

Chemical Waste Management, Inc., Laboratory Quality Assurance Quality Control Project Plan, July 1, 1990

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A QUALITY ASSURANCE PROGRAM FOR REMEDIAL ACTIONS WITHIN THE USEPA ARCS PROGRAM

by

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ABSTRACT

The Superfund Program has continually evolved over the past decade and many of the NPL sites have advanced to varying stages where clean-up activities are to commence. The USEPA has established an alternative Remedial Contracting Strategy (ARCS) whereby contractors provide support for remedial activities (response action contracts). Quality Assurance (QA) activities are an integral component of the technical support provided. These QA activities are inculcated into the RI/FS and RD/RA phases, as well as in PRP oversight tasks. Although general QA activities are relatively defined including development of sampling plans and QA project plans, the management and technical details remain to be implemented.

As an ARCS contractor, we have implemented a practical QA management system with multiple geographic locations. This system is built around a QA Program Plan, a unique quality assurance manual and SOPs, our laboratory and equipment facility, an audit system and a technical director - quality management review process with review teams. Applying this system, we have conducted audits of field events and of other contractors. This paper will present details of the organization of the QA program, key components and past experience in implementing and managing the process.

INTRODUCTION

The Superfund Program has steadily grown in size and complexity over the past decade and the number of hazardous waste sites placed on the National Priority List (NPL) has grown accordingly. The Superfund Program and its legal and technical components have influenced or affected numerous Federal and State programs and industrial practices. During the past decade, EPA used the services of Contractors to fulfill specific tasks and objectives. Hazardous waste sites were and continue to be evaluated through contracts

termed Field Investigation Team (FIT) Contracts. Services provided survey and assess sites, "score" for hazard ranking, and if warranted place the site on the NPL list.

The Superfund Program Contract strategy has undergone internal program management reviews and has been changed at times to achieve EPA's goals and objectives. Consequently acronyms for Programs, Contracts, tasks, etc., have arisen and in some cases, dropped from use. In 1990, the EPA established a long-term contracting strategy for Superfund(1). The Agency's objectives in developing the strategy were to analyze the long term contracting needs of the program, and to design a portfolio of Superfund contracts to meet those needs over the next ten years. Contract support was to be implemented for enforcement support, regional management support, removal contract support, analytical support, preremedial and remedial contract support. The preremedial activities include site preliminary assessments, inspections and "scoring" of sites for NPL consideration. Remedial activities include a variety of activities necessary to actually remediate a site such as the remedial investigations/feasibility study phase (RI/FS) and the remedial design/remedial action phase (RD/RA). To conduct preremedial and remedial activities, the Agency established contracts termed Alternative Remedial Contracting Strategy (ARCS) contracts. As an additional task under ARCS, some contractors may be assigned oversight and review tasks of PRP (Potentially Responsible Party) sponsored cleanups.

A key component of ARCS in the implementation of a Quality Assurance Program which is a requirement within all EPA programs(2). There are numerous technical guidance documents (3-11) and manuals which must be integrated into a Superfund ARCS QA program. The components include establishment of standard operating procedures (SOP's), field sampling plans (FSP), quality assurance program plan (QAPP), quality assurance project plan (QAPjP), use of the CLP program, data validation, conducting audits of the processes (eg. field audits, data quality audits, management systems or program audits, file audits, lab audits, etc), adherence to other "applicable and relevant agency regulations" (ARAR's), and quality control and quality assurance activities for remedial design and action phases.

QA PROGRAM

As a new EPA Region II ARCS Contractor, Malcolm Pirnie, Inc. (MPI) has developed a quality assurance program for administering and monitoring requisite Superfund Quality Assurance (QA) activities within ARCS remedial work and site assignments. Traditionally quality assurance at Malcolm Pirnie was a project specific activity and the responsibility of individual project officers. The focus was on the quality of technical work products and did not require extensive documentation. The ARCS program activities covered include all phases of RI/FS and RD/RA work and includes multiple MPI Offices and the subcontractor, CH2M Hill, Inc., and functions (eg. ARCS equipment and storage, lab, program management, site management). A unique aspect of the ARCS and MPI approach is the staff structure. Unlike other EPA contracts where staff were "dedicated" to the Contract,

MPI's staff is not dedicated. Personnel are drawn from MPI Offices throughout Region II and assigned to ARCS Projects on an as-need basis. This allows a cost-effective application of appropriate skills and talents to ARCS projects on a timely basis. This program is now expanding to include preremedial work assignments and subcontractors.

With the initiation of the ARCS contract, a Quality Assurance Program Plan (QAPP) was established which identified the administrative structure, oversite functions, and responsibilities and process of technical and QA reviews. A Quality Assurance Project Plan (QAPjP) was also established defining how QA functions, activities, and duties were to be implemented. The QAPP documents the structure. The Program Management Office (PMO) receives work assignments and administers the Program. Within PMO, the PMO Quality Assurance Manager oversees the ARCS QA program. Site Managers are located in different Offices in New York or New Jersey, depending on site location and available resources. The site manager is responsible for all activities concerning a site. These activities include establishment of a site specific QAPjP and Field Sampling Plan (FSP) plus additional documents, when needed, for the site Work Plan. The site manager is responsible for arranging adequate technical input including technical reviews. Each site is also assigned a Quality Assurance Officer (QAO) whose duties are to assist the site manager on QA issues, and review and forward the site QAPjP and FSP to the PMO QA Office for review. The PMO QA Office reviews the QAPjP and FSP and may return the documents with written review comments to the site manager. Figure 1 illustrates the process of review of FSP and QAPjPs. When these comments have been addressed or resolved, the documents are returned to PMO QA for forwarding to EPA for approval. A PMO QA office provides coordination, QA reviews, QA training, and conducts and oversees audits. Within the MPI QA program, each site QAO is responsible for conducting field audits of FSPs and QAPjPs. The PMO provides oversite audits of QAO's, field audits, and management system and file audits of the ARCS Program, subcontractors, and components within the program (i.e. ARCS equipment storage and staging facility, non CLP lab activities). The PMO QA also oversees data validation services for project data and may audit laboratories when non CLP laboratories are used in projects.

To manage effectively QA activities within the ARCS program, an MPI ARCS Quality Assurance Procedures manual was established. This QA Manual specifies how QA is to be administered in the Program, the duties and responsibilities of the PMO QA and site QAO personnel. and QA standard operating procedures (SOPs) for carrying out QA functions for the PMO QA Manager and the site QAO's. Table 1 is The Table of Contents of the QA Manual and lists of the QA SOP's currently in use. QA and technical details are derived from EPA technical documents(3) whenever possible. A training session was conducted for site QAO's and site managers, when the MPI ARCS QA manual was implemented.

Technical memoranda, reviews and audits from EPA are distributed to all site managers and QAO's and those affecting QA are to be included in the QA manual in a Technical Memoranda section. In addition, MPI has now initiated a new phase, whereby site

managers convene to discuss status, trends, problems and resolutions of QA and technical issues within the ARCS program.

The MPI QA Program to date, has been relatively successful. Problems noted have usually been the result of short time leads, new personnel (EPA and MPI), normal project problems, technical complexity of each site, changing objectives and DQOs. The ARCS Program has continued to expand to include more sites, PRP oversite assignments and preremedial work. These tasks will require more audits and an extension of MPI's QA Program.

MPI's audits have observed how difficult it has become to incorporate the growing number of technical advisories, procedures, memoranda, etc, into a manageable Work Plan for a site. In addition, the extensive paper trail necessary for all operations, field sampling and sample booking into the CLP, and the long lead term for booking SAS and RAS presents real challenges for all involved. As MPI work assignments shift into RD/RA implementation and preremedial work, so will the focus of QA activities to assure that quality data and quality work are attained.

CONCLUSION

In conclusion, the MPI ARCS QA Program has provided a workable, cost effective program for administering QA activities in the ARCS Program. The key components in the process are the site QAO, the PMO QA manager and establishment and use of an MPI ARCS QA Manual. Use of the Manual, in addition to reviews and audits, provide an effective QA Program.

REFERENCES

1. U.S.E.P.A., 1990. Long-term Contracting Study for Superfund. Public. No. 9242.6-07FS.

2. U.S. E.P.A., 1984. "Policy and Program Requirements to Implement the Mandatory Quality Assurance Program," EPA Order 5360.1., Office of Research and Development.

3. CERCLA Quality Assurance Procedures Manual, Region II, U.S.E.P.A.

4. U.S.E.P.A. 1990. Quality Assurance/Quality Control Guidance for Removal Activities. EPA Public. No. EPA/540/G-90/004.

5. U.S.E.P.A. 1991. Preparation Aids for the development of Category I Quality Assurance Project Plans. EPA Public. No. EPA/600/8-91/004.

6. U.S.E.P.A. 1991. Preparation Aids for the development of Category II Quality Assurance Project Plans. EPA Public. No. EPA/600/8-91-/004.

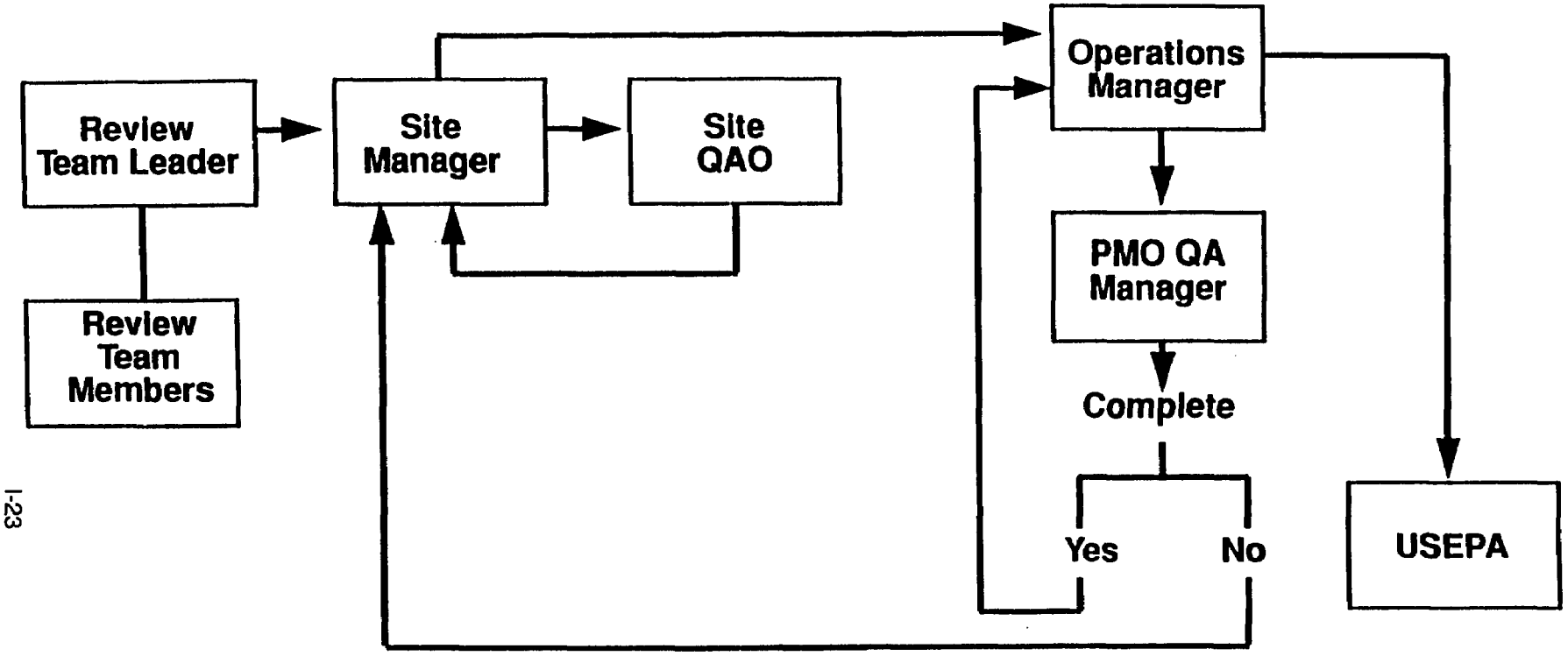
7. U.S.E.P.A. 1991. Preparation Aids for the Development of Category II Quality Assurance Project Plans. EPA Public. No. EPA/600/8-91/005.

8. U.S.E.P.A. 1987. Data Quality Objectives for Remedial response activities. EPA Public No. EPA/540/G-87/003.

9. U.S.E.P.A. 1988. User's Guide to Contract Laboratory Program. EPA Public No. EPA/540/8-89/012.

10. U.S.E.P.A. 1988. Guidance for Conducting remedial Investigations and Feasibility Studies Under CERLLA. EPA Public. No. EPA/540/G-89/004.

11. U.S.E.P.A. 1990. Guidance for Expediting Remedial Design and Remedial Action. EPA Public. No. EPA/540/G-90/006.



ARCS II Quality Assurance Document Review System

Figure 1

TABLE 1. MALCOLM PIRNIE QA PROCEDURES MANUAL - ARCS II

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TABLE 1. MALCOLM PIRNIE QA PROCEDURES MANUAL - ARCS II

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A NATIONAL QA STANDARD FOR ENVIRONMENTAL PROGRAMS FOR HAZARDOUS WASTE MANAGEMENT ACTIVITIES

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ABSTRACT

The clean-up of Federally-owned facilities contaminated by mixtures of hazardous chemical and radioactive wastes involves critical decisions based on environmental data. The Federal Government is currently using several different standards or sets of requirements, including U.S. Environmental Protection Agency (EPA) guidance for establishing the quality assurance and quality control (QA/QC) procedures for these sites. These standards defined the criteria for the QA activities and documentation required, the content and format of the documentation, and who was responsible for them. Shortcomings in these standards or requirements have led to efforts by several Federal groups to develop a uniform, consistent standard that produces the needed type and quality of environmental data in a more cost-effective manner. These efforts are being conducted under the auspices of the American Society for Quality Control (ASQC) and involve participation by EPA, the Department of Energy (DOE), Department of Defense (DOD), Nuclear Regulatory Commission (NRC), and others in the contractor and regulated communities.

This paper describes the progress which has been made toward establishing a consensus standard and associated requirements for use by DOE, EPA, and others for hazardous waste management activities. The standard proposes two distinct but related levels for management and technical activities, which include, respectively, the organizational structure, policies and procedures, and roles and responsibilities needed to conduct effective site operations, and the project-specific Quality Assurance Program activities necessary to produce the desired data quality. It is expected that the "harmonization" of QA/QC requirements will significantly improve the cost-effectiveness of hazardous waste management activities involving environmental data operations, as well as provide the basis for a needed revision and expansion of EPA guidance.

INTRODUCTION

The emergence of hazardous waste remediation as one of the principal environmental issues of the 1980s has resulted in large-scale environmental sampling and analysis programs to characterize the waste sites and to select and implement appropriate remedies. Quality assurance (QA) programs developed in support of the environmental programs have varied widely in content and in application. As the responsible authority for implementing environmental regulations, the U.S. Environmental Protection Agency (EPA) has mandated a QA program for its environmental programs in EPA Order 5360.1,[1] issued in 1984. This Order directed that all

environmental data operations conducted by or for EPA in support of Agency decision-making develop and implement an acceptable QA program. Prior to the Order, Agency requirements were manifested in two documents developed by the Quality Assurance Management Staff (QAMS): QAMS-004/80,[2] which discussed QA Program Plans, and QAMS-005/80,[3] which defined QA Project Plan requirements for individual data collection activities. Both of these documents were issued in 1980 and became the *de facto* standard for EPA QA requirements for all environmental programs.

While the EPA Order establishes specific authorities and responsibilities for QA, it does so almost entirely within the context of EPA organizations. Externalization of EPA QA requirements was accomplished largely through the contracts regulations, found in 48CFR15,[4] and the financial assistance regulations for grants, cooperative agreements, etc., given by 40CFR30[5] and 40CFR31[6]. Both sets of regulations limited the requirements for QA essentially to QA Project Plans for individual environmental data collection activities. The full scope of the EPA Order has not been extended to the regulated community, and EPA guidance to implement the Order was not officially distributed outside the Agency.

Moreover, until recently, QA was not generally included in specific rulemaking by the agency. Air quality regulations have included QA and quality control (QC) specifications since the 1970s, but the ongoing rulemaking to incorporate Chapter One into SW-846[7] represents the first explicit inclusion of QA requirements in a regulation. Since neither QAMS-004/80 nor QAMS-005/80 has been revised or updated since their initial issue, the public was not aware of the changes to the EPA QA program as it has grown and expanded. Consequently, interpretations of EPA QA requirements became varied as EPA programs, such as RCRA and Superfund, developed their own expanded requirements based on specific program needs and the ten EPA Regional Offices responsible for implementing the hazardous waste programs under RCRA and CERCLA developed their own interpretations of QAMS QA Program Plan and Project Plan guidance and program office guidance. In the meantime, the general public continued to use QAMS-004/80 and QAMS-005/80, and to interact individually with Regional Offices on their interpretation. Consequently, ten years after issuing QAMS-004/80 and QAMS-005/80, EPA was faced with multiple interpretations of QA requirements documents which do not reflect the current vision of QA in the Agency. The need for new QA guidance from QAMS provided impetus for EPA to examine the experiences of the past ten years and to develop focused criteria upon which such guidance could be based for use in the next ten years.

The situation in other Federal agencies was not dramatically different from that of EPA. The U.S. Department of Energy (DOE) uses NQA-1[8] as its standard for QA requirements. The Nuclear Regulatory Commission bases its QA program on 10CFR50, Appendix B, which is identical to NQA-1. The U.S. Department of Defense has used various MIL Standards as well as NQA-1 in its Installation Restoration Programs. NQA-1 was developed for nuclear facilities and its application to environmental programs has been difficult to accomplish effectively. Moreover, different field offices in DOE, for example, like their EPA Regional counterparts, have taken differing interpretations of what in NQA-1 is applicable to environmental programs.

Currently, DOE, DOD, and other Federal facilities are generally responding to multiple sets of QA requirements while trying to satisfy CERCLA and RCRA regulations. Often this has meant preparing two sets of QA documentation, one to satisfy the EPA Region (usually QAMS-005/80 requirements and format) and one to satisfy the "owner" agency (DOE, DOD, etc.), which has often meant NQA-1 requirements and format. At the least, it has meant having to prepare one document which satisfactorily addresses the expectations of the EPA Region and the "owner" agency. This has resulted in costly and time-consuming duplication of effort. In addition, the perception of inconsistent and often conflicting QA requirements has created confusion and frustration in the regulated community. It became increasingly clear that action was needed to bring some order to the process. The staggering cost of clean-up at Federal facilities has focused considerable public pressure on all agencies involved, including EPA, to plan and carry out cost effective clean-ups.

THE HARMONIZATION PROJECT

In the fall of 1989, an initiative was begun which would, as a minimum, attempt to "harmonize" the varied QA requirements into a single, uniform, consistent set for application to environmental programs. This effort was conducted under the auspices of the American Society for Quality Control (ASQC) and included active participation by EPA, DOE, DOD, NRC, and representatives of the contractor community. A Work Group and a Policy Group were formed in the spring of 1990 to pursue the harmonization effort. The Work Group was composed of experienced QA professionals representing EPA, DOE, and Federal contractors, who would make the initial efforts of harmonizing current QA requirements. The Policy Group included senior officials at EPA, DOE, DOD, and NRC, and senior QA consultants, who would guide the efforts of the Work Group.

It became apparent very quickly that a new, national consensus standard would be the most effective way to harmonize the existing QA requirements. Moreover, those engaged in the harmonization effort were committed to producing a standard which could encompass the broad scope of environmental programs without being overly prescriptive. Emphasis was placed on defining WHAT the requirements should be, not the HOW TO or BY WHOM. This recognized that a detailed, omnibus standard could not meet the needs of all Federal agencies. Their missions are too diverse. The Work Group and Policy Group decided early to retain as much flexibility as possible in the standard and not try to prescribe format or detailed specifications. The differing missions and personalities of the organizations would be served best by allowing them to define detailed requirements for their QA programs based on the general requirements of this standard. For example, the standard would require the use of QA Project Plans, but it would not prescribe the content and format of the plans. This decision would be left to the implementing organization.

The outline for this proposed standard was presented in September 1990 at the ASQC Energy Division National Conference in Tucson.[9] Subsequently, a standard was drafted and is currently undergoing public review and comment as part of the ASQC standard-setting process. As part of this process, EPA will develop new guidance to implement the standard across

Agency programs. Included among the new guidance documents planned are replacements for QAMS-004/80 and QAMS-005/80. This guidance is expected to be available shortly after acceptance of the formal standard by EPA.

PROPOSED NATIONAL QA STANDARD FOR ENVIRONMENTAL PROGRAMS

Environmental data have an important role in decisions involving the protection of the public and the environment from the adverse effects of a variety of pollutants from waste operations and discharges. To assure that these data are of the appropriate type and quality to support their intended use, a proposed standard has been developed for environmental programs.

The proposed standard includes the basic requirements for a Quality Assurance Program to plan, implement, and assess the effectiveness of multimedia data operations to characterize environmental processes and conditions and to design, construct, and operate environmental engineering systems. Included in this Quality Assurance Program are the necessary QA and QC activities to assure that technical and quality specifications are satisfied.

As noted earlier, NQA-1 has been utilized extensively for environmental programs by several Federal agencies. Many of the fundamental concepts found in NQA-1 have been incorporated into this standard and, in several cases, improved. The standard also reflects the current vision of EPA's Quality Assurance Program as well as numerous Total Quality Management-based concepts which have gained wide-spread acceptance.

The proposed standard provides for two distinct levels of requirements to be addressed:

- the organization (or institutional) level, and
- the technical/project level

In each distinct level, there are specific QA elements or functions which must be addressed.

The elements at the organization level include defining the organizational structure, policies and procedures, and roles and responsibilities for the activities to be performed. These elements define what must be addressed in order to establish and manage an effective Quality Assurance Program for planning, implementing, and assessing effective environmental data operations. The organization level elements provide a framework or infrastructure to enable consistent quality procedures across similar environmental projects. The organizational level also defines the requirements for necessary management functions to support multiple technical activities or projects. These include procurement of services and items, documents and records, use of computer hardware and software, and operation of analytical facilities and laboratories. The basic requirements for these functions are assembled into **Management Systems, Part A**, and may be viewed as an umbrella under which technical projects

are performed.

The technical or project level consists of two parallel parts within the framework defined by the organization level requirements. Each part describes the project-specific Quality Assurance Program activities necessary to produce the desired type and quality of data -- one part relates to process or site characterization and the other part relates to environmental engineering systems. Dividing technical/project operations into two parts reflects the differences between requirements for characterizing an environmental process or condition (Part B) and requirements for designing, constructing, and operating environmental engineering systems (Part C).

Characterization of Environmental Processes and Conditions, Part B, contains the basic requirements for planning, implementing, and assessing operations to collect, analyze, and evaluate chemical, biological, ecological, or physical data in the environment. This also includes compiling, modeling, and analyzing environmental processes and conditions by mathematical or computerized methods. The emphasis here is on planning and the approach is based largely on EPA's Data Quality Objectives process.[10] The study design completes the planning phase and the standard requires that the data operations be implemented as planned and documented. There is a focus on performance-based objectives for the study so that a measure of success may be readily determined. During assessment of the results obtained, it is recognized that results from environmental data operations may not completely satisfy the performance objectives. However, the assessment of data usability may enable the data or part of the data to be used provided that the data user is willing to accept lees confidence in the results and a greater risk in making the decision for which the data were needed.

Environmental Engineering Systems, Part C, provides the basic requirements to ensure effective design, construction, and operation of physical engineering systems, and their components, which remediate environmental contamination or remove pollutants from multimedia discharges. While these requirements were not originally within the scope of the proposed standard, it was recognized that environmental engineering systems may require rigorous QA activities to assure their safe and effective operation. EPA guidance on QA for engineering systems is sparse and has limited application to hazardous waste remediation technologies being developed today. The requirements for Part C were drawn largely from NQA-1, since the principal concern driving NQA-1 was the protection of public health and safety from the operation of nuclear facilities. While the magnitude of the potential threat is not as great, it is reasonable to suggest that the inadequate design, construction, or operation of some remedial technologies could pose health and environmental concerns. Consequently, the need to include Part C in the proposed standard became evident.

The Basic Requirements contained in the current draft of the proposed standard are listed in Table I.

NEXT STEPS AND SUMMARY

The standard-setting process is under way within the ASQC. Public comment on the proposed standard has been invited. While it is not possible to estimate a completion date for the standard at this time, the outlook is optimistic.

The "proof" of the value of this proposed standard lies largely in its acceptance and implementation by Federal agencies. Here again, the outlook is promising. By involving key senior QA officials from the major agencies in the development of the proposed standard, many issues have already been addressed which otherwise would have posed serious barriers to acceptance of the standard.

The value of this standard to future hazardous waste management activities is severalfold. First, the QA requirements of Federal agencies would be the same. Some programmatic differences may still occur between RCRA and CERCLA, for example, but essentially the QA "playing field" would be level. The consistency of a national consensus standard also opens new opportunities for increased standardization in other areas, such as, field methods, analytical procedures, and data validation and verification processes. The standard provides a basis for increased cooperation among the Federal agencies conducting waste remediation activities and for the sharing of ideas and experiences. Given the finite resources available and the magnitude of the clean-up job ahead, no one can afford to re-invent the wheel. The cost savings that will result from this proposed standard are difficult to estimate, but they could be substantial.

EPA assumes that an acceptable national consensus standard for QA will emerge from ASQC. Preparations for adopting and implementing the standard across EPA programs are under way, including the development of a comprehensive set of new QA guidance documents. The transition to a new standard probably will not happen quickly. In time, some programs will likely recognize the added value and benefits of revising their QA programs to reflect the standard and the new guidance. Not all programs will have to be revised or even have new QA Management Plans (QAMP) prepared, while some others may need more extensive changes.

This standard will help to forge new partnerships among Federal agencies engaged in hazardous waste management activities and to foster greater efficiency and effectiveness in future work.

REFERENCES

(1) EPA Order 5360.1, Program and Policy Requirements to Implement the Mandatory Quality Assurance Program. U.S. Environmental Protection Agency, 1984.

(2) Interim Guidelines and Specifications for Preparing Quality Assurance Program Documentation. U.S. Environmental Protection Agency, QAMS-004/80, 1980.

(3) Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. U.S. Environmental Protection Agency, QAMS-005/80, 1980.

(4) EPA Acquisition Regulations. U.S. Environmental Protection Agency, 48 CFR 15, 1984.

(5) Financial Assistance Requirements. U.S. Environmental Protection Agency, 40 CFR 30, 1983.

(6) Financial Assistance Requirements. U.S. Environmental Protection Agency, 40 CFR 31, 1988.

(7) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (3rd Ed.), SW-846. U.S. Environmental Protection Agency, Federal Register 55(27), February 8, 1990.

(8) ASME NQA-1, Quality Assurance Program Requirements for Nuclear Facilities, 1989 Edition. ASME, September 1989.

(9) Blacker, Stanley M. Harmonization of Quality Assurance First Focus: NQA-1 and QAMS. Proceedings, 17th Annual National Energy Division Conference, Tucson, September 1990.

(10) Draft Information Guide on Data Quality Objectives. U.S. Environmental Protection Agency, 1986.

TABLE I

QUALITY ASSURANCE PROGRAM
REQUIREMENTS FOR
ENVIRONMENTAL PROGRAMS

Part A. Management Systems

1	Management Commitment and Organization
2	Quality Assurance Program
3	Personnel Training and Qualification
4	Management Assessment
5	Procurement of Services and Items
6	Documents and Records
7	Use of Computer Hardware and Software
8	Work Processes and Operations
9	Quality Improvement

Part B. Characterization of Environmental Processes and Conditions

1	Planning and Scoping
2	Design of Data Collection Operations
3	Implementation of Planned Operations
4	Quality Assessment and Response
5	Assessment of Data Usability

Part C. Design, Construction, and Operation of Environmental Engineering Systems

1	Planning
2	Design of Environmental Engineering Systems
3	Implementation of Engineering Systems Design
4	Inspection and Acceptance Testing
5	Operation of Environmental Engineering Systems
6	Quality Assessment and Response

4

THE IMPACT OF CALIBRATION ON DATA QUALITY

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ABSTRACT

The basic functional elements of the typical Quality Control (QC) program are the QC samples used to evaluate control of the analytical process. The ability to meet acceptance criteria associated with QC samples, as well as the acceptance criteria themselves, are directly influenced by the calibration process. Despite the critical role that calibration plays in the generation of accurate data, it is the aspect of environmental analysis that is controlled the least, based on a comparison of the calibration process established in the common regulatory programs.

As the requirements for litigation quality data become more restrictive, the calibration process will need to be re-evaluated, and subject to more rigorous controlling measures. This paper discusses the key aspects of the calibration process, and the strengths and weaknesses associated with each. Without more control, it will be difficult to achieve data comparability between laboratories using the same referenced methods.

INTRODUCTION

The calibration process represents the initial controlling mechanism for the generation of quality data, yet there is a general lack of guidance regarding specific evaluation techniques for this process. One of the drawbacks of providing such little guidance is the potential loss of data comparability, one of the chief Data Quality Objectives identified by the EPA.

This paper examines several critical aspects of the calibration process, and identifies those features that, if overlooked, can significantly impact the quality of the data generated. Initially, a comparison of calibration processes, as outlined in the various regulatory programs, is presented. In order to provide a more focused scope for this paper, the discussion is limited to the impact on methods for the analysis of Volatile Organics, Pesticide/PCBs, and Semi-volatile Organics. The concepts presented, however, can be extended to other organic and inorganic analytical methods as well.

It is important to note that some of the issues raised in this paper have been addressed in regulatory programs that were not evaluated specifically for this paper. The USATHAMA[5] program, in particular, has incorporated a requirement that calibration data be subject to statistical tests for both Zero Intercept and Lack of Fit, which serve to resolve some of the problems associated with non-linear data and calibration intercepts. These problems are discussed in detail in this paper.

COMPARISON OF REGULATORY APPROACHES TO CALIBRATION

There exists a great deal of difference in the calibration protocols and requirements of the key regulatory programs, including the 500[1] and 600[2] series of EPA methods, those published in SW-846[3], and the Contract Laboratory Program[4]. A summary of calibration requirements of the various regulatory methodologies is presented in Table 1.

In general, the 600 series of methods offers the least amount of guidance, and thus is the most open to individual interpretation. More recent revisions to the 500 series of methods for analyses conducted under the SDWA program introduce several new requirements that provide greater control over the accuracy of the resultant calibration. As Table 1 indicates, wide variation exists in the number of calibration standards required both within and across the series of regulatory protocols. One particularly important assumption that the 500, 600, and 8000[3] series all share in common relates to curve linearity. In each of these methods, if the %RSD of response factors associated with calibration standards is within certain criteria (10-35%), "then linearity through the origin can be assumed." Clearly, there are widely ranging views regarding when the intercept of a calibration curve deviates significantly from the origin. In keeping with the goal to establish data comparability, there is a need to consider the incorporation of a statistical technique to provide an objective means of determining whether a particular set of data essentially has a zero intercept.

In the event that %RSD criteria cannot be achieved, 3 of the 4 programs allow the user to simply prepare a calibration "curve" from concentration vs. instrument response. Unfortunately, there are no requirements for the type of curve algorithm (linear regression, polynomial fit, etc.) allowed.

As cleanup criteria continue to evolve, this variability between the different regulatory protocols can have significant, adverse impact on the comparability of data generated by laboratories. Due to either regional or site specific preferences, analytical programs can be based on methodologies from any of these programs. While each of the programs is considered to be designed to produce quality analytical data, the differences between the calibration protocols will result in significantly different data quality.

In order to provide more control over the calibration process, each element of the process must be considered so that the most appropriate combination of elements is employed. The basic "parts" of the calibration are shown below:

- number of calibration levels
- calibration algorithm
- calibration levels
- calibration acceptance criteria
- effect of "curve-smoothing" routines

The remainder of this paper focuses of detailed analysis of each of these sections. In particular, those aspects that potentially lead to inaccurate or biased data are discussed. In addition, the areas of the methods that are open to interpretation, or require further guidance are identified.

NUMBER OF CALIBRATION LEVELS

Essentially, as the number of calibration levels increases, the relative risk is reduced, as a better picture of the analyte's performance is obtained. The analytical run-time is also an important consideration in determining the number of levels to employ. For analyses with a relatively short analysis time, such as the majority of inorganic parameters, additional calibration levels do not represent a burden to production. This is not the case, however, for most organic analyses, with routine run times of 40 to 60 minutes. Laboratories are engaged in a constant struggle between quality and production. While an increased number of calibration levels would certainly improve the quality of the data, this is not always possible. The implications of establishing calibration "curves" with a minimum of data points are brought to light in the next few sections.

CALIBRATION ALGORITHM

While most laboratories default to the standard (least squares) method of linear regression analysis to develop a calibration algorithm, a wide array of non-linear calibration technique options are available. These options including, polynomial fits, exponential and power curves, segmented fits, and even specific manufacturer options, are routinely provided as part of the software bundled with instrument data stations.

The most common approaches to quantitation use an average response factor (e.g., in GC/MS), single point quantitation (multi-component analytes such as PCBs), and multiple point calibration "curves". Of these approaches, single point quantitation has the greatest potential for inaccuracy because the response from the single standard analyzed is deemed to be representative of the linearity of the analyte in question. There are two sources of error in single

point quantitation. First, any error in the preparation or concentration of the standard will directly affect quantitation. In addition, if the level chosen actually represents a significantly non-linear portion of the relationship between response and concentration, substantial bias will be introduced.

The use of an average response factor is designed to normalize differences in response factors over the calibration range. The drawback to this approach is if only a single response factor deviates significantly from the others, the bias is normalized by distributing an equivalent degree of bias in the opposite direction over the other standards.

Non-linear data require more advanced statistical treatment. Typically, regressions of a higher order, quadratic equations, or polynomial fits of the data are employed. The main precaution associated with these techniques is the minimum number of data points required. As the minimum number of points required to form a line is two, then a linear regression (1st order polynomial fit) actually requires a minimum of 3 data points to be significant. Similarly, with each higher order equation, one more data point is required. As with a simple linear regression, the correlation coefficient must not be used as a measure of linearity. The correlation coefficient only provides a measure of how well the data points fit the equation generated. Finally, as the degree of non-linearity increases, the curve of a 2nd or 3rd order polynomial becomes parabolic (Figures 1B, 2B). This results, at the upper end of the curve, in two solutions for a given data point. Unless the actual curve is carefully evaluated, the analyst may not even be aware that multiple solutions are possible for a given response. The consequence associated with this type of situation is that significantly inaccurate data could be reported.

Essentially, a linear regression results in the equation for a straight line, whereas polynomial fits above the 1st order will result in the equation for a curve. The most recent versions of the 524.1, 524.2, and 525, GC/MS methods for the analysis of volatile and semi-volatile organics, specifically allow the use of 2nd or 3rd order regression equations if the response factor criteria cannot be met. Figure 3 shows the curves that are associated with a linear fit as well as polynomial fits of orders 2 through 5 for Sample Data Set #1. Note, in particular, the significant differences in the curve fit to the data in the region between points D and E. If these higher level curves are used for the Sample Data Set, serious inaccuracies would result at the upper range of the curve-- the recommended range for sample quantitation.

While, in specific cases, each of these statistical manipulations of calibration data can provide a "better fit" of the calibration equation to the data, they can also have significant impact on the quality of the data generated. Essentially, with the number of statistical programs readily available, an equation can be found that will provide a mathematical solution (i.e. "fit") to **any** set of data. Consequently, without a complete understanding of the actual effect on the raw data, none of these statistical techniques should be used in the generation of data for regulatory compliance.

CALIBRATION LEVELS

The specific levels that are selected for calibration can have a significant impact on the validity of the calibration equation. Calibration levels should be established based on consideration of (1) the range of the levels, (2) the reportable detection limit, and (3) the linear range of the analyte(s). The majority of the regulatory programs reviewed provide little guidance with respect to the range of calibration levels. A generic statement is provided that indicates that the levels selected should be based on the expected range of sample results. In some cases, the "expected" sample concentrations exceed the working linear range of the detector. In the interest of obtaining accurate results, it is more important to define the linear range of the analyte and/or instrument, and dilute sample concentrations that exceed this range.

A wide calibration range, based on only a few calibration levels, will nearly always result in a correlation coefficient greater than 0.995, which is frequently used as the sole calibration evaluation criterion. In the example of Sample Data Set #2, the linear regression calculated from all 5 data points yields a correlation coefficient of 0.963. If only the first two and the uppermost data points are used (10, 20, and 200) however, the correlation coefficient is increased to 0.999. This is a consequence of the derivation of the correlation coefficient.

The relative difference between the concentration of the low level standard and the reportable detection limit is critical to providing confidence in the accuracy of low level measurements. Bias is more pronounced as the calibration curve approaches the detection limit for a particular analyte. Consequently, if the low level standard is significantly greater than the detection limit, then accuracy in the proximity of the detection limit is compromised, because linearity of response has not been evaluated in this region. Ultimately, the detection limit itself may come into question. While the majority of the regulatory methods specify that the low level standard must be prepared at a concentration "near, but above, the detection limit", methods 524.1 and 524.2 allow the low level standard concentration to be as much as 10 times higher than the detection limit[1].

Finally, analytes have detector-specific linear ranges. In order to accurately evaluate non-linear regions of the curve, there must not be a significant difference between the uppermost standard (X) and the (X-1) concentration level. The consequence of not considering this in a calibration, is the user may fail to identify a parabolic curve. This is one of the consequences that can result from establishing calibration levels based solely on the expected concentration range of the samples.

Recent revisions to the 500 series of methods represent the first attempt (other than the CLP program, where calibration levels are contractually defined) to provide stronger guidance regarding the calibration range. Methods 524.1 and 524.2 require at least 3 calibration levels to encompass a factor of 20 calibration range (i.e. 1 to 20, 10 to 200). In addition, at least 4 standards are required to cover a range of a factor of 50, and at least 5 standards are required for a range factor of 100.

CALIBRATION ACCEPTANCE CRITERIA

Once a calibration has been performed, there must be a set of criteria to determine if the curve is acceptable for use in generating analytical results. This is one of the key weaknesses in the published regulatory methodology. With the exception of the CLP program, the referenced regulatory methods have only established acceptance criteria if the mean response factor is to be used for quantitation. The alternative, if %RSD criteria (relative standard deviation of response factors from the calibration curve) cannot be achieved, is to simply generate a plot of concentration vs. response or response factor. This allows the generation of data without control of data quality until the analysis of the first continuing calibration standard, where a limited measure of control is obtained. In addition to %RSD criteria, the CLP program has established minimum response factor criteria for most analytes. This requirement is associated with confidence in the ability to detect the analyte, however, rather than in quantitation of the analyte.

As indicated in Table 1, even the acceptance criteria associated with continuing calibration verification (CCV) offer little assurance of accurate quantitation. The most stringent CCV acceptance criteria are found in method 502.2, which requires the analysis of a midpoint standard to yield a response within $\pm$ 20% of that obtained for the same standard in the initial calibration. In addition, this method requires the analysis of a laboratory fortified blank (LFB) per batch of 20 or fewer samples, fortified at a concentration of 20 ug/L.

For a set of data which is essentially linear, the mathematical basis of a linear regression attempts to establish the midpoint of the curve as the point which deviates least from the linear equation. The extent of the deviation then increases at the extremes. The deviation is absolute rather than

relative to concentration, which creates the greatest impact at the lower end of the curve. Due to the magnitude of response associated with the highest calibration level, the relative effect is minimal. In the case of strongly non-linear data, such as that in Sample Data Set #2, the point at which the curve becomes non-linear (in this case, the upper calibration level) is central in the minimization of deviation from the curve. This effect is evident in Table 4, which indicates that relatively minimal bias occurs in the upper calibration level, even considering such non-linear data.

The relationship between bias and concentration has its greatest impact on the continuing calibration verification process (CCV). The concentration of the CCV is typically equal to the midpoint concentration of the initial multi-point calibration. With linear calibrations (typically the norm), the midpoint level is associated with the least degree of bias from the plot of the calibration equation. Consequently, if the overall accuracy of the analysis is less than 20%, there is a significant probability that the acceptance criteria for the CCV and the fortified laboratory blanks can be met.

The correlation coefficient ("r") is the most commonly used statistical measure of calibration acceptability. One longstanding misconception is that this parameter also provides a measure of linearity. The correlation coefficient is a measure of the "goodness of fit" of a series of data points. Basically, the correlation coefficient can be viewed as a mathematical process which determines the tightest ellipse that defines a set of data. The more the ellipse resembles a straight line, the higher the "r" value (to a maximum of 1.00). The more the data appear to be randomly distributed, or the ellipse appears more as a circle, the lower the "r" value (to a minimum of 0). This effect is illustrated in Figure 4. Consequently, even a particular random set of data can result in a high "r" value if the data range is such that the data can be described by a tight ellipse.

Calibration acceptance criteria should be designed to evaluate the relationship between the intercept of the calibration equation and the reportable detection limit (RDL). The data in Tables 2A and 2B, for Sample Data Sets 1 and 2 show significant negative bias at the low end of the calibration. If, as required by most of the regulatory methods, the low level standard is just slightly greater than the actual RDL, then the RDL would clearly not be valid for these calibration sets. One requirement that should be imposed on calibration data is that the x-intercept (expressed as concentration) should be no greater than 50% of the RDL. This will serve to minimize the reporting of low level false positive results.

One final consideration regarding the evaluation of calibration data, is to consider the bias at each calibration level that results from obtaining a concentration from the calibration equation using the actual raw calibration data. The software in use today provides graphic representations of the calibration data, but the plots are typically too small and the resolution too poor to be used to accurately evaluate point-specific bias.

Each of the generally accepted calibration evaluation mechanisms should be considered no more than a single data assessment tool, rather than an absolute indicator of calibration acceptability. For example, the correlation coefficient, used frequently in the inorganic arena, can provide misleading information if there is a significant range between the uppermost and lower calibration levels.

EFFECT OF CURVE "SMOOTHING" ROUTINES

With the advent of powerful software routines and instrument data stations, the analyst is now provided with a series of tools that can be used to "smooth" the fit of any curve. While these techniques certainly are not an element of the calibration process, their use is rapidly becoming routine. High-powered calibration algorithms are most often used without understanding the mathematical functions behind them as well as the limitations to their use and impact on a particular data set. For this reason, these techniques are discussed here.

One of the most routine software options available is that of "forcing" the curve through the origin. Theoretically, a blank should yield no response for a particular analyte. Due to signal-to-noise considerations, however, this is rarely the case. Many analysts, however, have been trained that a curve should pass through the origin, and thus this option is selected. There are two ways in which curves can be forced through the origin. The first, is a simple mathematical formula designed to result in a slope and zero-intercept. The other option is a manual one, which is based on the repetitive inclusion of (0,0) data points until the curve is eventually forced through the origin.

Curve "weighting" techniques are often used to obtain a better fit of the data points at either extreme of the calibration range. Typically, the low end of the curve is susceptible to poor fit of the calibration equation. The most common weighting routine employed to improve the fit is a 1/X manipulation of the data. Basically, each data point is weighted by a factor of the inverse of the associated concentration. The result of this weighting, for the entire set of data, is a 91 point curve vs. the original 5 point curve. The results of this weighting are summarized in Table 3. The table indicates that a significantly better fit is achieved at the low end of the curve while affecting the midpoint and upper range only minimally.

While each of these techniques results in a better fit of the data points to the calibration equation, they remain little more than data manipulation techniques. In the generation of environmental data, analysts must be trained to understand that the use of these techniques can result in mis-interpretation of the data.

SUMMARY

In a regulatory climate that is increasingly concerned with Quality Assurance, most data quality assessments remain reactive in that they rely on quality control information generated during the course of analysis, rather than prior to the analysis of environmental samples. The calibration process should be viewed as the initial opportunity to assess the quality of data to be generated. Consequently, there is a need for more structure and guidance in the evaluation process in order to provide analytical methods which ensure data comparability.

REFERENCES

1. U.S. EPA, 1988. Methods for the Determination of Organic Compounds in Drinking Water. EPA/600/4-88/039. December, 1988.

2. U.S. EPA, 1985. Methods for the Organic Chemical Analysis of Municipal and Industrial Wastewater. 40 CFR Part 136, Appendix A. July, 1985.

3. U.S. EPA, 1990. Test Methods for Evaluating Solid Waste. Volume IB: Laboratory Manual, Physical/Chemical Methods. SW-846. 3rd ed., Revision 1. November, 1990.

4. U.S. EPA, 1990. Contract Laboratory Program, SOW 390. Statement of Work for Organic Analyses, Multi-Media, Multi-Concentration. March, 1990.

5. USATHAMA, 1990. United States Army Toxic and Hazardous Materials Agency. Quality Assurance Program. USATHAMA PAM 11-41, rev. 0. January, 1990.

Table 1: Comparison of regulatory method requirements for various aspects of the calibration process.

	500	600	8000	CLP
No. Standards	• 3 to 5 • 5 recommended • 1 point allowable with criteria. • 6 pre-set: 525	3 minimum	5 minimum	5: general GC/MS 4: 8 Semivolatiles 3: Pesticides 1: Multicomponents
Low standard	• Near, but above EDLs, to • 2-10x MDL	Each analyte: near, but above MDL.	Each analyte: near, but above MDL.	Contractual requirements
Calibration Range	Range factor: 20: 3 minimum 50: 4 minimum 100: 5 minimum	• Expected range of samples. • Detector range.	• Expected range of samples. • Detector range.	Contractual requirements
Initial Calibration: Requirement to use mean RF	RSD <10% (502) <20% (508,524) <30% (525)	RSD <10% 602,608 <35% 624,625	RSD <20%	• Generally: RSD... <20.5% [GC/MS] <10-15% [GC] • No RSD criteria: - 20 Semivolatiles - 10 Volatiles
Initial Calibration: Alternative to RF	• Generate a plot of peak height or area response vs. concentration. • No acceptance criteria.	• Generate a plot of peak height or area response vs. concentration. • No acceptance criteria.	• Generate a plot of peak height or area response vs. concentration. • No acceptance criteria.	Use mean RRF.
Cont. Calibration Frequency	• Daily (502, 508) • every 8 hours: (524, 525)	Once daily	• Once daily • More frequently for ECD methods.	Every 12 hours
Cont. Calibration Acceptance Criteria	• % of initial standard response: ±30%: 525,524 ±20%: 502, 508	• % of initial standard response: 15%: 608 20%: 625 • QC Check standard analyte specific: 601, 602, 624	Standard response within ± 15% of initial response.	Generally: Maximum %D = 25% (for most)

Table 2A: Sample Data Set #1

X	Y	RF
1	65,000	65000
2	140,000	70000
5	365,000	73000
10	680,000	68000
50	2,250,000	45000

RSD of RFs = 17.3%
LSR= Y= 43320X + 110840
2nd Order= Y = -599.1X^2 + 75069X - 5816.7

Table 2B: Sample Data Set #2

X	Y	RF
10	650,000	65000
20	1,400,000	70000
50	3,650,000	73000
100	6,800,000	68000
200	9,000,000	45000

RSD of RFs = 17.3 %
LSR= Y= 44071X + 950580
2nd Order= Y= -238.2X^2 + 94494X - 356730

Table 3: Calculated X values for Sample Data Set #1 using both Linear regression (LSR) and LSR weighted 1/X.

X	LSR	LSR (1/X)
1	-1.1	0.4
2	0.7	2.0
5	5.9	6.7
10	13	13
50	49	46

Table 4: Summary of the biased observed in Sample Data Set #1 data using different quantitation techniques.

				<--- Single Point --->		
X	LSR	PF 2	$\overline{RF}$	Mid	Low	High
1	-191%	6%	1%	-4%	0%	44%
2	-60%	-2%	9%	3%	8%	56%
5	19%	-1%	14%	7%	12%	62%
10	31%	0%	6%	0%	5%	51%
50	-2%	0%	-30%	-34%	-31%	0%

$\overline{RF}$= Average Response Factor
LSR= Least Squares Linear Regression
PF 2= 2nd order Polynomial Fit

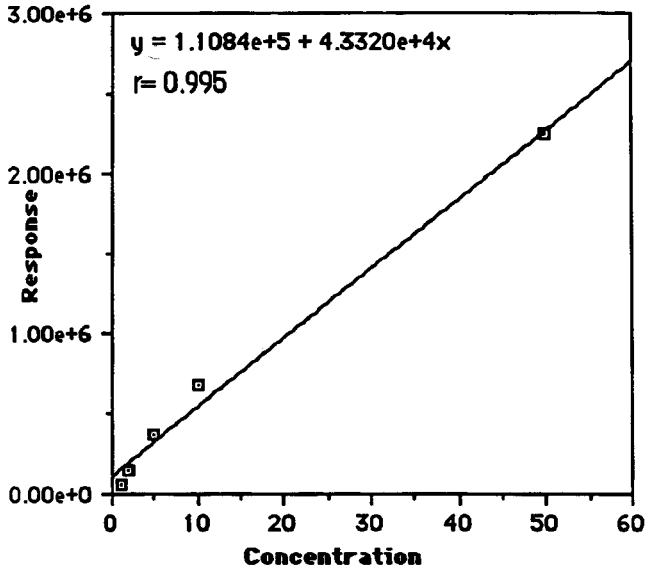

Figure 1A: Sample Data Set #1, Linear Regression Plot.

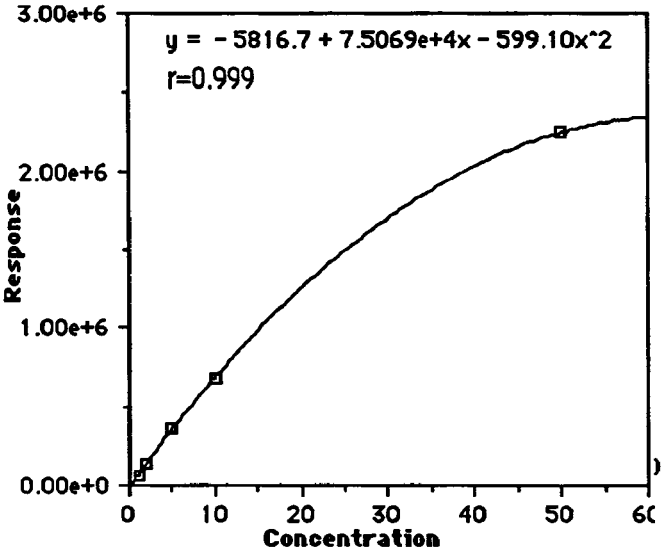

Figure 1B: Sample Data Set #1, 2nd Order Polynomial Fit.

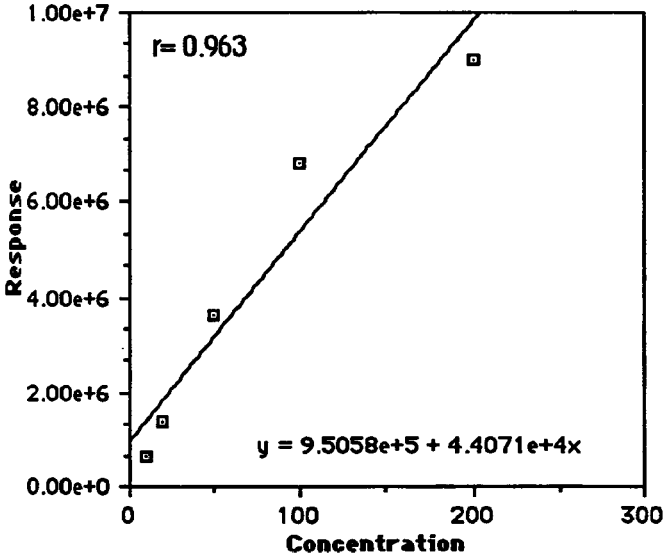

Figure 2A: Sample Data Set #1, Linear Regression Plot.

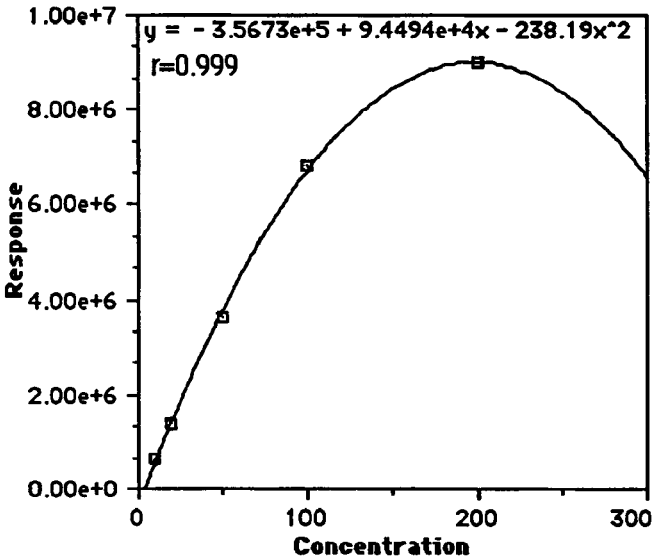

Figure 2B: Sample Data Set #2, 2nd Order Polynomial Fit.

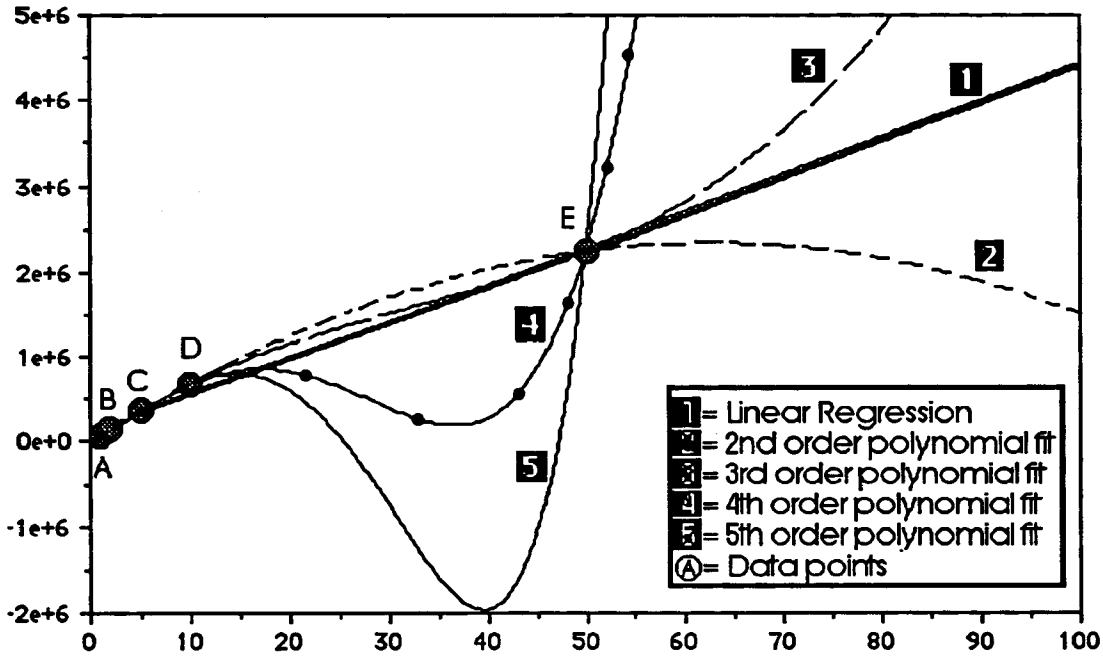

Figure 3: Plot of Calibration curves generated from various algorithms using data from Sample Data Set #1.

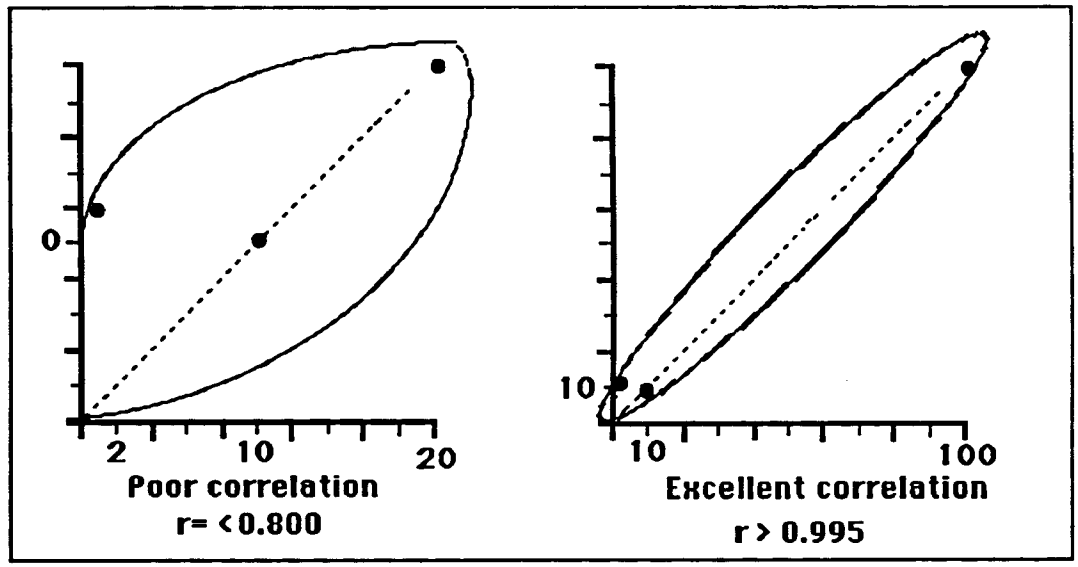

Figure 4: Illustration of the relationship between the range of data points and the correlation coefficient (r).

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PROFICIENCY EVALUATION SAMPLE PROGRAM FOR SOLID WASTE ANALYSIS: A PILOT PROJECT

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ABSTRACT

The use of Proficiency Evaluation (PE) samples for laboratory evaluation is an accepted practice for clinical, industrial hygiene, and drinking water chemistry laboratories. It has not been systematically applied to the analysis of solid waste by environmental laboratories. This paper discusses the theoretical and practical considerations involved in preparing a pilot PE sample program. The project was designed to assess the types and frequency of laboratory error, completeness of data packages, and to identify logistical and tracking problems that might occur in an ongoing PE program.

Two sets of PE samples were distributed among 319 environmental laboratories accredited by the Environmental Laboratory Accreditation Program (ELAP) for either PCB or elemental analysis. One set consisted of five soils spiked with Aroclor 1260, and the other set of five soils spiked with arsenic, cadmium, molybdenum, selenium, and thallium.

This project is an attempt to evaluate the competence of the environmental laboratory industry providing services in the state of California. The data and statistical analysis for this study are presented here.

6

TECHNICAL DATA REVIEW - THINKING BEYOND QUALITY CONTROL

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ABSTRACT

Considerable attention has been given to the concept of quality assurance (QA) during sampling, laboratory testing, and data reduction; however, few aspects of quality assurance have been incorporated into the technical review of data that will be used to make critical project decisions. This paper focuses on the QA aspects of technical review and presents an alternative to the traditional multi-tiered data review process. In addition, techniques and methods used to perform overall data assessment are described. The process includes:

1. Quality assurance in data processing
2. Technical review of data
3. Evaluation of trends and anomalies
4. Comparison of historical project information

The use of computer tools and relational databases can streamline the overall process.

INTRODUCTION

Most laboratories have implemented a multi-tier data review process as part of their internal Quality Assurance/Quality Control (QA/QC) program. Typically, the review moves up the management chain, beginning with activities such as simple math checks, passing into verification of QC sample frequency and acceptance criteria (which are usually well defined) and then, perhaps, some limited "technical" review of the data.

As environmental testing moves into the next phase of quality assurance, it is becoming evident that analyzing increasing numbers and types of QC samples does not, in and of itself, ensure that quality data are being reported. QC samples are routinely subject to more intense scrutiny due to their very nature, and the implications that they present to managers, clients, and the end users of the data. Simply put, errors are not being made on the QC sample themselves, because these samples are subjected to very specific acceptance criteria. Unfortunately, routine environmental samples rarely receive this level of effort.

With errors come legal liability. The analytical data generated by laboratories are used to determine regulatory compliance of industry. The implications of not providing quality data that can withstand the challenge of a court of law are forcing the analytical laboratory industry to improve its data review process. Even data validation done under the Contract Laboratory Program does not sufficiently provide for review of data in the technical sense; it merely contractually provides for review of specific criteria.

This paper presents an alternative to the traditional approach to data review. Described are specific techniques and examples that can be used to focus on the technical aspects of the data review process, and the deductive rationale that must be applied in order to understand the "big picture" needed for sound project decisions.

THE TECHNICAL REVIEW PROCESS

Laboratory analyses are critical in determining project direction, therefore the reliability of the analytical data is essential. The financial implications of such decisions have prompted Warzyn to develop an effective review of our results from a project and regulatory viewpoint.

In this alternative approach, QA is an integral part of laboratory operations, rather than an isolated entity. QA is an interactive element in each phase of the analytical process including technical review of data and reports. Figure 1 illustrates this approach to QA.

Technical review is an interpretive process designed to evaluate the overall ability of the data to satisfy the project objectives. Initially, analytical results must be reviewed in relationship to the other analytes reported. The purpose of this type of review is to attempt to identify trends, anomalies, or interferences which can bias the overall usefulness of the data. The technical review process begins at the onset of any project. Recommendations for testing programs and data quality objectives (DQO) are examples of project support services offered. This strategy moves the laboratory from a "black box" to a highly visible, integral part of the project team where technical expertise is critical to:

- The selection of testing programs
- Regulatory assistance
- Development of project DQO's

The technical review process incorporates an initial review of the testing program upon receipt of the samples. The reviewer evaluates analyses requested to ensure project DQOs are being met.

As analytical results are generated, initial math check, QC review and supervisors' technical release of data are performed within the operations unit of the laboratory. Reviewers consider the relative accuracy and precision of each analyte when interpreting the analytical results. This may assist in establishing the reliability of the results before proceeding with the overall project interpretation.

The data entry process is a unique function which requires double key protocols for data entry. An internal computer error-checking routine is employed to compare both data entries and generate an exceptions report. The double key entry greatly reduces the transcription error rates and cuts down on the time required for non-technical review and the errors associated with report preparation.

Once reports have been generated, the next phase of the technical review begins. This review is performed from a technical perspective and based on a wealth of environmental experience. Laboratory performance verification (precision and assurance) is designed to determine the quality of individual analyses. The interpretive technical review ties all parameters together to obtain an overall picture of the data quality.

A number of computer generated reports assist as individual parameter relationships are evaluated. One of the "red herrings" that typically appear in Quality Assurance Program Plans (QAPPs) or Quality Assurance Project Plans (QAPjPs), is the discussion of historical data comparison as part of the review process. While this technique is quite valuable in long term monitoring situations, it is most often performed from memory rather than actual comparison to previous data. Current technology allows the opportunity to store monitoring data for future comparison. Advances in relational database software also provide the capability for statistical and trend analysis, modeling, and evaluation of regulatory compliance.

Figure 2 shows a historical comparison report which clearly presents data at a sampling location for the past four quarters. With this information the technical reviewer can trace anomalies or request laboratory confirmation of any analyte in question. The development of this historical report format has greatly increased trend analysis capabilities. With real historical information available, anomalies are easily identified.

Figures 3A and 3B illustrate a two stage process which shows how detailed historical reports can be used to identify anomalous data and provide information to ascertain which specific parameters are in question. Initially, the technical reviewer reviews the summary data (Figure 3A) and

observes that the hardness value is significantly lower than recent historical data indicate for this sampling point. The alkalinity value, which closely correlates to hardness, does not exhibit a similar trend. The next step in this process is to compare these two results to the conductivity value (Figure 3B). The technical reviewer can now evaluate all parameters given as a whole. In this case, the TDS and sodium values provide clues to assist in pinpointing the problem analyte, i.e., hardness. The laboratory benchsheet for hardness is then reviewed to determine if a mathematical error was made. In this case, all the parameters indicate that the source of the anomaly is in the hardness value alone, which was indeed confirmed in an audit of the raw data.

Figure 3C represents a different scenario. In this case, there is a significant reduction in the hardness value from the previous quarter, and the sodium result is significantly higher than in the previous quarter. The conductivity results, however, are not significantly different. The field log notes would then be reviewed to determine if the sampling location might shed some light on the hardness anomaly, such as water sampled downstream from a water softener. In this example, the field observations confirmed that a water softener had recently been installed upstream of the sampling point.

If no apparent error is found, the technical review section has authority to schedule an immediate confirmation of the analyte(s) in question. Other routine data relationships which are considered during the review process include:

- Anion-cation balances and relationships to EC
- Comparison of theoretical and measured EC/TDS
- Demand parameter relationships (BOD/COD/TOC ratios)
- Evaluate trace element data in terms of potential interelement interferences
- "Logical" VOC degradation patterns (landfill age vs. solvent breakdown product appearances).
- Confirm the presence/absence of common laboratory contaminants such as: solvents, phthalates, methylene chloride.
- Interpretation of data relative to detection limits and dilutions.
- Close scrutiny of "rarely" detected analytes.
- Relationship of detected analytes to potential source contamination (e.g., elevated lead and cadmium near highways).

Some projects require detailed comparison of analytes. Figure 4 shows a detailed program which calculates the ion balance for a monitoring well. Upon further examination, the sum of the parameters exceeds the measured TDS; the TDS value appears biased low. Also, by reviewing historical data, it was determined that prior alkalinity values were approximately 250 mg/L. With this correction, an ion balance is achieved.

Another example of a computer database report which assists the technical review process is an Exceedance Summary. In Wisconsin, the DNR has "NR 140" Preventive Action Limits (PALs) for groundwater standards. The Exceedance Summary report assimilates all historical data for a site and compares the found values to that of the PAL and presents the comparison in a summary table. Figure 5 is an example of this report. In this example, the client is provided with the actual sample results and any regulatory criteria. Any value which exceeds a regulatory criterion level is flagged appropriately on the report.

One of the most powerful tools for a technical reviewer is a database of compiled technical information to help further their environmental knowledge. Common organic contaminants, trace elements in natural soils, and common inorganic interferences are a few examples of the type of support this gives to the technical review group. A central library is maintained, and pertinent articles are routed throughout the QA and management staff.

TECHNICAL REVIEW - THE NEXT GENERATION

Quality is an evolutionary process. The next step in the ever-expanding quality assurance "tool-box" is the development of an interactive database. Rather than relying solely on practical experience, Warzyn is currently experimenting with a user-friendly, menu-driven, software program that integrates text and graphics in a relational database format. The information being electronically cataloged and cross-referenced includes the following:

- common analyte names and "aliases"
- sources of the analytes
- environmental fate
- chemical structures
- available analytical method summaries
- information regarding inclusion on various regulatory lists
- regulated levels for compliance

Figure 6 shows two "snapshots" of the computer screens which are available with the current program. These screens provide a wealth of information that can be assimilated by the technical reviewer. The information on sources and environmental fate can be used to evaluate whether or not a site is likely to be contaminated with these analytes, and which long-term breakdown products might be expected. Our long range goal is to offer strong technical support to all locations within our firm.

We envision this program as an excellent tool for staff training as well. Our colleges and universities simply do not prepare graduates adequately for work in the environmental field. However, with modifications to this program detailed information regarding analytical techniques can be presented in an intriguing, informative format. The net effect would be to provide hands-on, visual training in critical interpretation of peak overlap, mass spectral identification, and the impact of method interferences. Each training module can be designed to include an interactive "test" to help assess trainees' comprehension of technical information and concepts.

SUMMARY

Environmental decisions depend on the quality of the data used to make those decisions. There is a growing need to look beyond quality control data and ask if the data "make sense". The aim of the review process described in this paper is to improve the quality of data generated by incorporating QA as an integral part of laboratory operations. Only with this type of holistic approach to data review can the "black box" aspect of environmental analysis be eliminated and attention be focused on technical advancement with full support to project and client needs.

REFERENCES

"Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans", QAMS-005-80, United States Environmental Protection Agency, EPA Document 600/4-83-004, 1983.

U.S. EPA, 1988 Methods for the Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039, December 1988.

U.S. EPA, 1979 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019 March 1979.

U.S. EPA, 1986 Test Methods for Evaluating Solid Waste. SW846 3rd Edition November 1986.

U.S. EPA Office of Solid Waste and Emergency Response. Hazardous Waste Land Treatment. SW-874, April 1983, pp. 273.

Quality Commitment

Warzyn's Quality Assurance Program serves as a critical link to laboratory operation, rather than as an ancillary function.

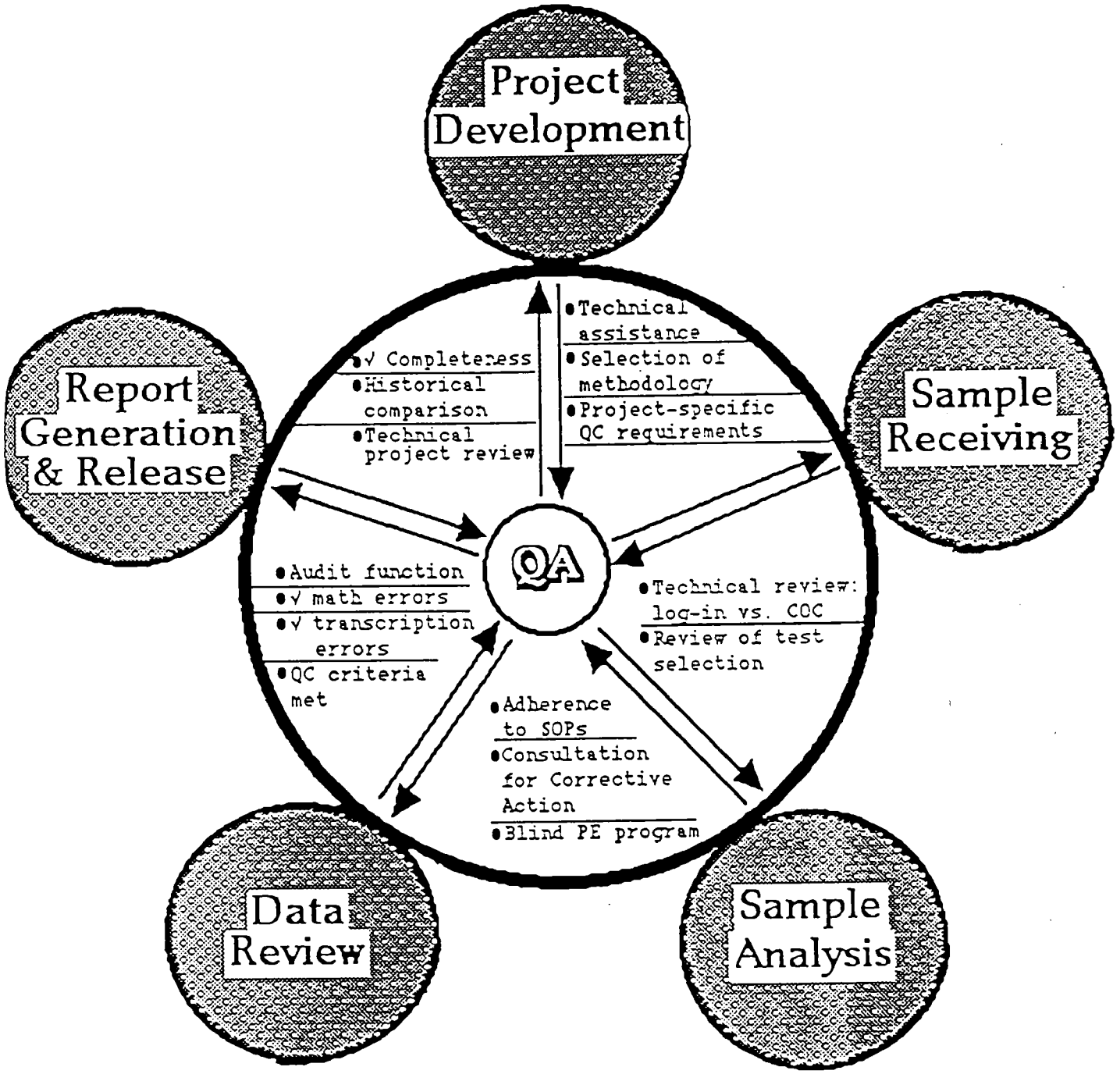

Figure 1

PROJECT NO: 30205 00RL
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DATE ISSUED:
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WARZYN ANALYTICAL LABORATORY RESULTS

LOCATION: MADISON, WISCONSIN

		06/07/90	09/18/90	12/11/90	03/04/91
Leach MH2	pH	6.49	6.26	6.68	5.63
	Conductivity @ 25 Deg C	5270	7950	9020	10000
	Alkalinity, Total	3610	3300	4950	5200
	Biochemical Oxygen Demand	3190	4700	5370	6030
	Carbonaceous BOD	2690	3600	5490	4840
	Chemical Oxygen Demand	4060	6940	6960	7760
	Chloride	537	728	965	1040
	Cyanide, Total	0.007	0.006	0.006	<0.025
	Hardness, Total	2400	3560	4160	4260
	Nitrogen, Total Kjeldahl	89.8	166	159	158
	Total Suspended Solids	198	520	128	350

Results in mg/L except elev(ft), pH (S.U.), conductivity (umhos/cm).

Figure 2

PROJECT NO: 30205 00RY
CK'D: APP'D:
DATE ISSUED:
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HISTORICAL REPORT EXAMPLE

WARZYN ANALYTICAL LABORATORY RESULTS
LOCATION: MADISON, WISCONSIN

		09/18/90	12/11/90	
Lysimeter 3	pH	6.46	6.22	
	Conductivity @ 25 Deg C	1510	1470	
	Alkalinity, Total	804	817	
	Chemical Oxygen Demand	64	48	
	Chloride	37	28	
	Hardness, Total	955	535	←
	Nitrogen, Ammonia	3.06	0.37	
	Nitrogen, Nitrate + Nitrite	0.09	<0.02	
	Nitrogen, Total Kjeldahl	4.1	1.64	
	Phenolics, Total	0.066	0.036	
	Sulfate	38	78	
	Iron	7.58	20.4	
	Manganese	0.83	1.02	
	Sodium	20.7	14.6	
	Solids, Total Dissolved	1020	1100	

Historical Hardness Data indicates a low bias.

Results in mg/L except elev(ft), pH (S.U.), conductivity (umhos/cm).

Figure 3A

PROJECT NO: 30205 00RY
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HISTORICAL REPORT EXAMPLE

WARZYN ANALYTICAL LABORATORY RESULTS
LOCATION: MADISON, WISCONSIN

		09/18/90	12/11/90
Lysimeter 3	pH	6.46	6.22
	Conductivity @ 25 Deg C	1510	1470
	Alkalinity, Total	804	817
	Chemical Oxygen Demand	64	48
	Chloride	37	28
	Hardness, Total	955	535
	Nitrogen, Ammonia	3.06	0.37
	Nitrogen, Nitrate + Nitrite	0.09	<0.02
	Nitrogen, Total Kjeldahl	4.1	1.64
	Phenolics, Total	0.066	0.036
	Sulfate	38	78
	Iron	7.58	20.4
	Manganese	0.83	1.02
	Sodium	20.7	14.6
	Solids, Total Dissolved	1020	1100

Alkalinity, conductivity and TDS results further indicate low bias on Hardness.

Results in mg/L except elev(ft), pH (S.U.), conductivity (umhos/cm).

Benchsheets reviewed; math error was identified. Confirmation of the Hardness value was performed.

Figure 3B

PROJECT NO: 30205 00RY
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PAGE: 1

HISTORICAL REPORT EXAMPLE

WARZYN ANALYTICAL LABORATORY RESULTS
LOCATION: MADISON, WISCONSIN

		09/18/90	12/11/90	
Lysimeter 3	pH	6.46	6.22	
	Conductivity @ 25 Deg C	1510	1470	
	Alkalinity, Total	804	817	
	Chemical Oxygen Demand	64	48	
	Chloride	37	28	
	Hardness, Total	955	12	Hardness and sodium values out of line with Historical.
	Nitrogen, Ammonia	3.06	0.37	
	Nitrogen, Nitrate + Nitrite	0.09	<0.02	
	Nitrogen, Total Kjeldahl	4.1	1.64	
	Phenolics, Total	0.066	0.036	
	Sulfate	38	78	
	Iron	7.58	20.4	
	Manganese	0.83	1.02	
	Sodium	20.7	233	

Results in mg/L except elev(ft), pH (S.U.), conductivity (umhos/cm).

Indicative of softened water. Field notes confirmed this conclusion.

Figure 3C

Sample Monitoring Well Data

Based on theoretical EC, field EC is biased high.

NOTE: Since the sum of the parameters exceeds measured TDS, the TDS value is biased low.

	Measured	Theoretical	%D
pH	7.35		
EC	2597	1404	-46%
TDS	435	628	44%
TDS/ECm	0.17	0.24	
TDS/ECt	0.31	0.45	

NOTE: By reviewing historical data, it could be determined that prior values were in the range of 250 mg/L.

This would result in an ion balance.

Parameter	mg/L	EC [µmho]	"+" meq/L	"-" meq/L
Alkalinity	120	203.0		2.40
HCO3-	*121*	*as CaCO3*		
CO3=	*0.3*	*as CaCO3*		
Chloride	181	387.3		5.11
Nitrate	0	0.0		0.00
Sulfate	120	184.8		2.50
Calcium	70	182.0	3.49	
Magnesium	32	122.2	2.63	
Sodium	150	319.5	6.53	
Potassium	2.7	5.0	0.07	
Σ=	**628**	**1404**	**12.72**	**10.00**
Discrepancy=				**2.72**

Ion Balance

%Diff. = 12.0% Acceptance criteria= ± **2.0%**

Anions too low Anion Σmeq/L x100 should = EC

Cations OK

Affected Parameter (assumed discrepancy source)

Subsequent impact on:

	mg/L	Theoretical TDS	Theoretical EC	TDS/EC	Prior Year Data
Alkalinity	256	709	1634	0.43	249
Chloride	277	724	1610	0.45	175
Nitrate	168	796	1598	0.50	<0.1
Sulfate	250	758	1605	0.47	109
Calcium					81
Magnesium					26
Sodium					139
Potessium					7

Figure 4

Summary of Chapter NR 140 PAL

Concentration Attainments and Exceedances

Parameter	PAL	ES	SWLS 06/08/90	SWLS 09/14/90	SWLS 12/14/90
Chloride (mg/L)	125.	250.	*397.	221.	
Iron (mg/L)	0.15	0.3	*2.72	*5.46	*7.05

Notes:

(1) PAL = Preventive Action Limit (Chapter NR 140, Wisconsin Administrative Code).

ES = Enforcement Standard (Chapter NR 140, Wisconsin Administrative Code).

* = Concentration attains or exceeds Enforcement Standard Concentration.

(2) The concentration listed may not be actual PAL or ES exceedances depending on the location of the facility's Design Management Zone, Site Specific PAL's, etc. What constitutes an NR 140 exceedance is defined on a site-by-site basis.

(3) Does not include NR 140 Welfare parameters color and odor or organic health parameters.

Figure 5

Acrolein

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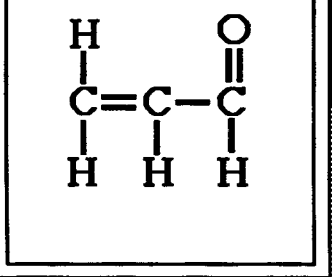
Structure



Other Names
- Allylaldehyde
- Acrylaldehyde
- 2-Propenal
- Aqualin

Regulatory Lists
- RCRA App. VIII
- AB1803 (CA)

Sources/Fate

1. Byproduct of tobacco smoke.
2. Thermal decomposition of fats/greases, i.e. restaraunt kitchens.

•••••••• ENVIRONMENTAL FATE ••••••••

Undergoes addition of halogens easily.
Unstable-polymerizes rapidly in light or strong acid.

MCL info

Use

- Polyurethane foams
- Polyester resins
- Intermediate for syn. glycerol
- Military- poison gas mixtures
- Aquatic herbicide
- Warming agent (Chloromethane refrigerant)

Analytical Methods

---------- SOIL ----------

SW-846: 8030: purge & trap GC/FID
SW-846: 8240: purge & trap packed col. GC/MS

---------- NOTES ----------

GC/MS method 624 is only approved as a screen for this compound. If quantitation is critical or low level detection is required, the GC method is the method of choice.

1,2-Dibromoethane

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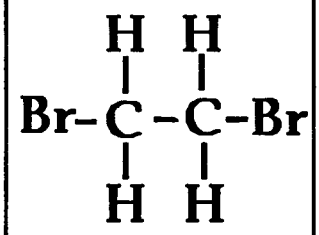
Structure



Other Names
- Dowfume W85
- EDB
- Ethylene dibromide

Regulatory Lists
- SDWA List 2
- RCRA Appendix VIII

Sources/Fate

•••••••• ENVIRONMENTAL FATE ••••••••

- Biodegradation occurs in 30-120 days at levels of 15-18 ppm
- Degrades to Bromoethane

MCL info

Use

- Scavenger for lead in gas. Occurs at levels up to 0.025% (w/v)
- Grain and tree crop fumigant
- Waterproofing preparations

Analytical Methods

---------- WATER ----------

EPA 504: microextraction GC/ECD
EPA 502.1: packed P&T GC/HECD
EPA 502.2: capillary P&T GC/HECD
EPA 524.2: capillary P&T GC/MS

---------- SOLID/WASTE ----------

SW-846 8011: microextraction GC/ECD
SW-846 8021
SW-846 8240

Figure 6

TABLE 1

COMMON LABORATORY CONTAMINANTS

Substance	Use in Analytical Laboratory
1,1,2-Trichloro-2,2,1-Trifluoroethane	Solvent for oil & grease/TPH extractions
1,2,4-Trichlorobenzene	Calibration compound, matrix spike
1,4-Dichlorobenzene	Calibration compound, matrix spike
2,4,6-Trichlorophenol	Calibration check compound
2,4-Dichlorophenol	Calibration check compound
2-Chlorophenol	Matrix spike compound
4-Bromofluorobenzene	Surrogate compound for VOA
4-Nitrophenol	Matrix spike compound
Acenaphthene	Calibration compound, matrix spike
Acetone	Extraction solvent
Aluminum	Matrix spike (high concentration)
Arsenic	Matrix spike (high concentration)
Benzene	Matrix spike compound
Benzo(a)pyrene	Calibration check compound
Boron	Glassware
Carbon Disulfide	GC thermal desorp work (air)
Chlorobenzene	Matrix spike compound
Chloroform	Extraction solvent, sample preservation
Chromium	Cleaning solution/digestion reagent (COD)
Copper	Sample preservation (phenols)
Diethyl Ether	Extraction solvent
Fluoranthene	Calibration check compound
Freons (CCl_3F, CCl_2F_2)	Refrigerants (A/C, freezers) fire extinguishers
Iron	Matrix spike (high concentration)
Mercury	Gas displacement/digestion reagent (COD &TKN)
Methylene Chloride	Extraction solvent
MTBE	Solvent for many new 500 series
Naphthalene	Petroleum distillate (pesticide spraying)
Pentachlorophenol	Calibration compound, matrix spike
Phenol	Calibration compound, matrix spike
Pyrene	Matrix spike compound
Selenium	Shampoo
Silver	Digestion reagent (COD)
THMs	Water supply system chlorination by-product
Toluene	Carpet glue, paints, extraction solvent, matrix spike, electrical tape
Trichloroethene	Matrix spike compound
Various Phthalates	Inks, plasticizers, plastics
Xylenes	General solvent, slide cleaning
Zinc	Sample preservation, hand cream

TABLE 2

TRACE CHEMICAL ELEMENT CONTENT OF NATURAL SOILS

Element	Symbol	Common Range (ppm)	Average (ppm)
Aluminum	Al	10,000-300,000	71,000
Antimony	Sb	2-10	--
Arsenic	As	1-50	5
Barium	Ba	100-3,000	430
Beryllium	Be	0.1-40	6
Boron	B	2-100	10
Bromine	Br	1-10	5
Cadmium	Cd	0.01-0.7	0.06
Cesium	Cs	0.3-25	6
Chlorine	Cl	20-900	100
Chromium	Cr	1-1,000	100
Cobalt	Co	1-40	8
Copper	Cu	2-100	30
Fluorine	F	10-4,000	200
Gallium	Ga	0.4-300	30
Gold	Au	--	1
Iodine	I	0.1-40	5
Lanthanum	La	1-5,000	30
Lead	Pb	2-200	10
Lithium	Li	5-200	20
Magnesium	Mg	600-6,000	5,000
Manganese	Mn	20-3,000	600
Mercury	Hg	0.01-0.3	0.03
Molybdenum	Mo	0.2-5	2
Nickel	Ni	5-500	40
Radium	Ra	8×10^{-5}	--
Rubidium	Rb	5-500	10
Selenium	Se	0.1-2	0.3
Silver	Ag	0.01-5	0.05
Strontium	Sr	50-1,000	200
Thallium	Tl	--	5
Tin	Sn	2-200	10
Tungsten	W	--	1
Uranium	U	0.9-9	1
Vanadium	V	20-500	100
Yttrium	Y	25-250	50
Zinc	Zn	100-300	50
Zirconium	Zr	60-2,000	300

Ref: USEPA Office of Solid Waste and Emergency Response.
Hazardous Waste Land Treatment. SW-874 (April, 1983) page 273.

7 QUALITY ASSURANCE STRATEGIES TO IMPROVE PROJECT MANAGEMENT

by
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Guy F. Simes, U.S. EPA, Risk Reduction Engineering Laboratory

In these times of ever-shrinking budgets, the primary objective in effective project management becomes one of how to accomplish as much as possible for minimal cost. There is no longer any margin for repeating work which was done incorrectly the first time, or for extraneous investigations which are not directly related to the objectives of the project. Quality assurance, applied before, during, and after the inception of a project, can vastly decrease misdirected efforts and needless expenditures.

Some of the key aspects in the conceptual stages of any project are those involving identification of the types of decisions to be answered by or made as a result of the outcome of the project, specification of the project objectives, and identification of the uses for and quality of the resulting data. These are the types of questions which need to be answered before a quality assurance plan can be written. These concepts are inherent in the strategy embodied by the Data Quality Objectives (DQO) process, which, though originally developed for application to the array of problems associated with Superfund sites, may be applied with equal success to aspects of the RCRA program.

Once a Quality Assurance Project Plan (QAPjP) has been written, a QAPjP review by an independent third party is often able to identify experimental design flaws, inappropriate experimental methods, or insufficient QA measures for either sampling or analytical procedures. The SITE Program has documented several examples of substantial monetary savings to projects which were accomplished by employing QAPjP reviews prior to the initiation of any sampling or analytical efforts.

After the project is underway, an audit is the primary means to ensure that the data meet the established project-specific QA criteria or that the project has not deviated from the quality assurance plan, and that overall technical systems are all in proper working order. Two types of audits achieve these purposes: audits of data quality (ADQs) and technical systems audits (TSAs), respectively. These audits may be conducted by an independent third party, or by in-house personnel. Regardless of who conducts the audit, however, management must place a high degree of commitment in responding to the findings of the audit and in rectifying any problems noted.

With the incorporation of such quality assurance measures, it is possible to meet project goals within pre-established budgetary constraints. Without including appropriate QA procedures in a project, not only will redundancy of work and cost overruns be likely, but overall project goals may be compromised.

8

BIAS CORRECTION: EVALUATION OF EFFECTS ON ENVIRONMENTAL SAMPLES

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ABSTRACT

September 25, 1990 began a new era in data evaluation. Under the new Toxicity Characteristic (TC) rule, as well as the Land Disposal Restrictions (LDR) program, a requirement for the bias correction of TCLP data was implemented. Since that deadline, Wadsworth/ALERT Laboratories has analyzed hundreds of samples for which bias correction factors were generated and applied. The spike data and the corresponding correction factors associated with those samples have been collated and evaluated. For the population of samples studied, the number of samples having hazardous levels of contaminants and those which became hazardous after applying the bias correction factor was small compared to those samples which were non-hazardous.

This paper evaluates the magnitude of the corresponding bias correction factor for each analyte on the TC list, the variability of the factor for each analyte, and the likelihood it will change a sample's hazard classification. A comparison of the individual correction factors to the recoveries of the respective analytes in control samples is presented to demonstrate the possibility of using the control sample recoveries for bias determination. And finally, analytical anomalies, especially for the organic compounds, are addressed.

From these discussions, proposals are suggested to aid in making decisions for future sample analyses. An estimate of the benefits and expenses of these options will be discussed.

INTRODUCTION

On March 29, 1990, the long expected Toxicity Characteristic Leaching Procedure (TCLP) was finally promulgated in the Federal Register(1). The short phrase "A matrix spike shall be performed for each waste and the average percent recovery applied to the waste characterization" (Section 10.3) sent shockwaves throughout the environmental laboratory industry. A flurry of comments and questions prompted the EPA to issue corrections to the TCLP on June 29, 1990(2). The above statement was replaced by another clarifying statement, "The bias determined from the matrix spike determination shall be used to correct the measured values." (Section 8.2). Also included was the formula (Equation 1) for calculating this corrected value (Section 8.2.4).

Equation 1

$$X_c = 100\ (X_u/\%R)$$

Where:

X_c = *Corrected value*
X_u = *Measured value of unspiked sample*
$\%R$ = *Percent recovery of matrix spiked amount*

The Toxicity Characteristic (TC) for which the TCLP is to be used, became effective for large-quantity generators of hazardous waste September 25, 1990. Since that date, thousands of samples have been extracted using this procedure and subsequently analyzed and the appropriate correction factors calculated and applied.

Wadsworth/ALERT Laboratories analyzed a portion of those samples. The data for nearly 6000 determinations for the toxicity characteristic have been compiled to evaluate the effect this requirement has had on the types of samples this laboratory has encountered. This paper will present data on the magnitude and variability of the bias correction factors calculated for these samples and compare it to data collected from control samples run in the same TCLP extraction fluids. It will also evaluate the probable effect on future samples, suggest changes in protocols, propose the use of control sample recoveries for bias determination, and present some interesting anomalies.

The data base for this study consisted of sample matrices from industrial wastes, soils, oils, sludges, and waters. All samples studied had undergone TCLP extraction (filtration in the case of waters), had been spiked with the analytes on the TC list, and a correction factor calculated following the analysis. Correction factors (CF) as used in this paper are the decimal equivalents to the percent recovery used in Equation 1. Table 1 indicates the number of analyses performed for each analyte and the number of samples having a specific analyte concentration in excess of the regulatory limit. Of the 5871 determinations, only 0.9% of the uncorrected results exceeded the regulatory levels. And it can be readily seen that the majority of those samples exhibiting a toxicity characteristic are the result of metals contamination. Not seen in this table are another 8.3% of the results that exceeded the laboratory established method detection limits yet remained below regulatory levels. (Many of those values were likely due to trace levels of metals in the TCLP extraction fluid as demonstrated by the blank analysis.) The remaining 90.8% of the sample results were less than the method detection limit.

To determine whether an individual correction factor will have an impact on a given population of samples a new term was coined, the Critical Correction Factor (CCF). It is defined in Equation 2. The CCF allows one to evaluate the potential impact of bias correction on each individual

Equation 2

$$CCF = \frac{\text{Method Detection Limit}}{\text{Regulatory Limit}}$$

analyte within a population of samples with no detectable contaminants. It is simply the value at which a "non-detect" would be bias corrected and thus exceeds the regulatory limit. As the method detection limit approaches the regulatory limit, the CCF approaches 1. The smaller the CCF, the less likely that a component will exceed the regulatory limit even if very poor recoveries are measured. The right-hand column of Table 2 presents the value of the CCF for each analyte as calculated for this laboratory. Since detection limits vary among laboratories, the CCF will change proportionally and must be calculated for each location.

The use of the CCF to predict whether samples within a data set will exceed regulatory levels can be demonstrated by comparing it to the magnitude and variability of measured correction factors (Table 2). A frequency distribution of the CFs for each analyte was plotted to evaluate its statistical behavior since a broad spectrum of matrices were included. A normal distribution occurred in most cases. Figures 1 - 6 show the distributions for representative constituents from each analyte group.

For the metals, the mean for the correction factors varied from 0.86 to 1.04. Mercury (Figure 1) had the widest range within the data and was the only metal where a CF was found to be less than the critical correction factor.

The variation in the averages of the pesticide correction factors was very similar to the metals, 0.86 to 1.04. However, the standard deviations are somewhat larger, indicating the greater variability within the measurements expected for these analyses. On the other hand, the value for the lowest calculated correction factor in this group (endrin - Figure 2) was nearly twenty times larger than the CCF for the compound.

The two herbicide residues had average correction factors which were very similar, and the standard deviations were comparable to the pesticides. The range within the silvex data (Figure 3) was wider than the previous constituents. However, the CCF for both herbicides is so small (<0.001) none of the results approached this level.

All of the volatile organic constituents showed consistent average correction factors, 1.01 - 1.06, except for methyl ethyl ketone (MEK). For several samples, the correction factors for MEK (Figure 4) were in the range of 4 - 8. This variability caused the standard deviation to exceed 0.8. Vinyl chloride (Figure 5) also exhibited a large standard deviation (0.47). However, none of the calculated correction factors approached its respective CCF since most of the recoveries were biased high.

Finally, the semivolatile organic compounds had the lowest average correction factors (0.53 - 0.74). And the standard deviation for many of the compounds were larger, which seems to be the case for the analysis of most semivolatile compounds. Two of the compounds, 2,4-dinitrotoluene and hexachlorobenzene (Figure 6), had CCFs much larger than any of the other compounds. (This is due to the fact that the regulatory limit is only a factor of three greater than the detection limit [CCF = 0.308]). In spite of that, only six instances out of the combined total of 249 determinations where no contaminants were detected exceeded the regulatory limit when the correction factor was applied.

In all of the above discussions, it has been assumed that the detection limit would be bias corrected in the same manner as any measurable quantities. Since it is unlikely that a detection limit study would be performed for each matrix analyzed, this is a necessary assumption. Therefore from the above discussions, it can be concluded that for the majority of matrix types encountered in this laboratory the corrected detection limits will not exceed regulatory limits. But it must also be recognized that a few constituents exhibit recovery characteristics that warrant more careful review. Of the 288 mercury analyses, only one sample (0.3%) had a corrected detection limit greater than the regulatory limit. There were four such occurrences in the 116 analyses for 2,4-dinitrotoluene (3.4%). And the 133 hexachlorobenzene analyses showed two occurrences (1.5%). None of these percetages suggest a serious problem. Several other semivolatile compounds have relatively low biases, but the CCF in each case is small and is unlikely to be a problem compound. One might expect the MEK results to be similarly affected, but the bias is toward recoveries greater than 100% which tend not to be a regulatory concern. Vinyl chloride results do not approach the CCF (0.05) even though its very large standard deviation accentuates the spread in the recovery data and makes it suspect.

Although it has been documented that some type of sample matrix effect may exist, the argument for the need for bias correction must also consider the effect of the TCLP buffer solution itself on the ability to recover each of the spiked compounds. To evaluate this effect, the recovery data for control samples run with each batch of samples was collated. These control samples were prepared by spiking an aliquot of the TCLP buffer blank in the same manner as the matrix spikes were prepared. These control samples then underwent the same extraction or preparative procedures and analyses as the actual samples. Table 3 summarizes the number of control samples analyzed, the average recovery, standard deviation, and measured recovery range for each analyte. It should immediately be noted that for both 2,4-dinitrotoluene and hexachlorobenzene, the control sample recoveries in at least one case were less than the respective CCFs.

To compare this data to the recoveries of the matrix spikes (CFs), a graph was prepared plotting the pairs of mean correction factors and mean control sample recoveries for each analyte (Figures 7 - 10). For each mean the range of two standard deviations is indicated (a 95% confidence

interval). A quick survey of the graphs shows the remarkable similarity of the two sets of data. Interestingly, the spike recoveries and control sample recoveries for several of the compounds previously discussed do not stand out as being significantly different when compared in this manner. The CCF for each analyte has also been included for comparison purposes.

Before formulating any conclusions, there are still a couple of significant anomalies that should be discussed. Methyl ethyl ketone had recoveries that frequently exceeded 100% compared to a standard purged from deionized water. This was true in the control samples and was even more pronounced in the matrix spiked samples. It is felt that this can be explained by the decreased solubility of the MEK in the higher ionic strengths routinely present in the buffer. This would then be even more exaggerated in the extracts of many of the samples which contained soluble salts. Similar effects have been noted in this laboratory during the routine analysis of other water-soluble ketones and alcohols under similar conditions.

Another important anomaly was found for four of the compounds from the semivolatile fractions. The cresols, 2,4-dinitrotoluene, nitrobenzene, and pyridine showed no detectable spike recovery in a small number of samples. These data were not included in the tables since a bias correction factor could not be calculated. In such cases the recovery data could not be used to support or reject the analytical results. Instead, results had to be evaluated based on the generator's knowledge of the process producing the waste sample, not on recovery factors. Ideally, another method should be developed that is capable of quantitating these compounds in the more difficult matrices.

CONCLUSIONS

Now, what can we now imply from this data? Can we just disregard spike recovery data as being insignificant? Though it might appear so on first review, the opposite is really true. For many of the analytes, the information presented indicates there are potential problem areas that need to be addressed.

For example, if the sample in question is being characterized for the first time or comes from a process where the characteristics are continually changing, the data presented suggests that the matrix needs to be evaluated to determine the extent to which it may affect the recovery of the designated analytes. However, if it has been demonstrated that no unusual sample matrix effects are biasing the data, there seems to be no need to apply any correction factors. The method bias can be represented by the mean of the control sample recoveries. If a sample contains concentrations of contaminants that approach a regulatory level, and it is felt that the bias suggested by the control sample recoveries do not represent this particular matrix, a more extensive matrix spike study for those analytes may be considered.

It must be emphasized that only 0.9% of all constituents tested initially exceeded the hazardous classification limits. When the calculated correction factor was applied to the remaining data, an additional 0.2% exceeded regulatory levels, including the seven samples where the corrected detection limit was elevated above those limits. Therefore, nearly 99% of all the analyses completed by this laboratory were still classified as non-hazardous following bias correction. It can be argued that there may be a large number of matrix types which are regulated but are not included in this sample population. This may be true and each of these matrices needs to be evaluated on its own merit. But as the data base expands, it is predicted that it will become apparent that the need to evaluate bias will be based more on the TCLP extraction fluid's effect than on any sample matrix effects.

If the bias correction requirements are to remain, it is proposed that control sample recoveries established from a statistically significant database be used. Figures 7 - 10 graphically showed the differences between the average correction factor and the average control sample recovery value. In all but six cases, this difference is less than 0.05. Four of the cases involve pesticides where the CCF is very small because of very good detection limits. These larger differences (0.08 - 0.23) are not statistically significant and would seem to have no effect. MEK's spike recovery is larger than the control sample recovery so the difference is actually negative. But both averages are well above 100% and any bias correction would only cause the result to be adjusted downward. Nitrobenzene (a difference of 0.11) is the only remaining compound where the control sample recoveries might be seen as adversely affecting the data from an enforcement standpoint. Yet the CCF for this compound is still very small (0.02) and the actual measured value (or an elevated detection limit) would have to approach forty times the normal detection limit before it would be significant. As suggested before, any concentration approaching a regulatory limit should be evaluated on an individual basis.

What then are the options and any potential detrimental effects? From the data used in this study, it seems there is very little opportunity for significant abuse. By evaluating the bias for a specific component based on the recoveries from control samples as described in this paper, the cost of analysis can be significantly reduced with minimal environmental impact. Another option for determining bias, which has been suggested by many, is to use isotope dilution techniques, thus reducing the need for the extra matrix spike. Though reducing the cost and supposedly any duplicate sample preparation problems, this technique is only useful for GC/MS methods. But if the control sample can give similar information, then the same result can be achieved with even less expense than isotope dilution and can also be used with all the methods. If there is a requirement that first time or uncharacterized samples undergo some type of matrix spike recovery evaluation, very few samples which may have seriously biased data will be overlooked and potentially harm the environment.

SUMMARY

To approach all samples that may be regulated by the Toxicity Characteristic rule using the same bias correction requirement seems to be impractical and definitely unnecessary. Though many argue that the process is statistically unsound, with which I agree, the fact that bias may exist should be recognized. If the data being generated is to be compared to a regulatory level that has been set based on absolute recoveries, the bias for a given analyte will need to be considered. But from the data presented, the bias for many matrix types can be represented by the recoveries of laboratory control samples without the added expense of another spiked sample analysis.

REFERENCES

1) U. S. Environmental Protection Agency, March 29, 1990. Hazardous Waste Management System; Identification and Listing of Hazardous Waste; Toxicity Characteristics Revisions; Final Rule. 40 CFR Parts 261, et al. Federal Register 55: 11798 - 11877.

2) U. S. Environmental Protection Agency, June 29, 1990. Hazardous Waste Management System; Identification and Listing of Hazardous Waste; Toxicity Characteristics Revisions; Final Rule. 40 CFR Parts 261, 264, 265, 268, 271, and 302. Federal Register 55: 26986 - 26998.

TABLE 1 SUMMARY OF BIAS CORRECTION SAMPLES

Constituent	Number of Spiked Samples	No. of Analytes Exceeding Regulatory Levels
Arsenic	289	1
Barium	290	2
Cadmium	300	16
Chromium	313	5
Lead	320	19
Mercury	288	3
Selenium	286	4
Silver	291	0
Chlordane	64	0
Endrin	64	0
Heptachlor (& its epoxide)	64	0
Lindane	64	0
Methoxychlor	64	0
Toxaphene	64	0
2,4-D	74	2
2,4,5-TP (Silvex)	65	0
Benzene	159	1
Carbon tetrachloride	158	0
Chlorobenzene	158	0
Chloroform	158	0
1,2-Dichloroethane	157	0
1,1-Dichloroethene	158	0
Methyl ethyl ketone	157	0
Tetrachloroethene	158	0
Trichloroethene	159	1
Vinyl chloride	159	0
Cresols	118	0
1,4-Dichlorobenzene	132	0
2,4-Dinitrotoluene	116	0
Hexachlorobenzene	133	0
Hexachlorobutadiene	132	0
Hexachloroethane	132	0
Nitrobenzene	119	0
Pentachlorophenol	125	0
Pyridine	128	0
2,4,5-Trichlorophenol	128	0
2,4,6-Trichlorophenol	127	0

TABLE 2 SUMMARY OF CORRECTION FACTOR DATA

Constituent	Average Correction Factor (%R)	Standard Deviation of Corr. Factor	Range	Critical Correction Factor
Arsenic	0.95	0.093	0.5 - 1.3	0.100
Barium	0.87	0.117	0.5 - 1.4	0.001
Cadmium	0.88	0.072	0.6 - 1.4	0.100
Chromium	0.88	0.070	0.55 - 1.4	0.020
Lead	0.89	0.103	0.3 - 1.5	0.020
Mercury	1.04	0.212	0.08 - 1.5	0.100
Selenium	0.92	0.192	0.4 - 1.5	0.300
Silver	0.86	0.069	0.45 - 1.3	0.020
Chlordane	0.86	0.193	0.5 - 1.38	0.017
Endrin	1.04	0.202	0.45 - 1.38	0.025
Heptachlor (& its expoxide)	1.02	0.162	0.65 - 1.4	0.013
Lindane	0.90	0.250	0.36 - 1.3	<0.001
Methoxychlor	0.89	0.208	0.49 - 1.25	<0.001
Toxaphene	1.00	0.198	0.54 - 1.42	0.010
2,4-D	0.80	0.166	0.43 - 1.23	<0.001
2,4,5-TP (Silvex)	0.78	0.213	0.15 - 1.5	<0.001
Benzene	1.04	0.134	0.8 - 2.0	0.010
Carbon tetrachloride	1.02	0.091	0.7 - 1.4	0.010
Chlorobenzene	1.02	0.071	0.8 - 1.2	<0.001
Chloroform	1.03	0.086	0.8 - 1.3	0.001
1,2-Dichloroethane	1.05	0.110	0.8 - 1.4	0.010
1,1-Dichloroethene	1.01	0.156	0.3 - 1.8	0.007
Methyl ethyl ketone	1.32	0.823	0.4 - 8.2	<0.001
Tetrachloroethene	1.01	0.104	0.8 - 1.8	0.007
Trichloroethene	1.06	0.185	0.2 - 2.0	0.010
Vinyl chloride	1.01	0.474	0.4 - 5.0	0.050
Cresols	0.57	0.213	0.06 - 1.14	<0.001
1,4-Dichlorobenzene	0.62	0.120	0.1 - 1.11	0.005
2,4-Dinitrotoluene	0.53	0.158	0.05 - 1.1	0.308
Hexachlorobenzene	0.66	0.172	0.11 - 1.22	0.308
Hexachlorobutadiene	0.62	0.114	0.18 - 0.93	0.080
Hexachloroethane	0.56	0.163	0.06 - 1.08	0.013
Nitrobenzene	0.74	0.221	0.09 - 1.36	0.020
Pentachlorophenol	0.58	0.275	0.08 - 1.54	0.002
Pyridine	0.59	0.185	0.08 - 1.06	0.008
2,4,5-Trichlorophenol	0.54	0.169	0.015 - 0.89	<0.001
2,4,6-Trichlorophenol	0.62	0.205	0.03 - 1.1	0.020

TABLE 3 SUMMARY OF CONTROL SAMPLE RECOVERIES

Constituent	Number of Control Samples[1]	Average Recovery	Standard Deviations of Control Sample Recoveries	Range
Arsenic	94[2]	0.93	0.113	0.10 - 1.19
Barium	92	0.91	0.066	0.73 - 1.21
Cadmium	92	0.92	0.045	0.77 - 1.06
Chromium	92	0.92	0.045	0.73 - 1.00
Lead	92	0.93	0.057	0.74 - 1.30
Mercury	89	1.09	0.113	0.80 - 1.41
Selenium	97[2]	0.98	0.162	0.60 - 1.42
Silver	92	0.89	0.056	0.56 - 1.02
Chlordane	49	0.9C	0.206	0.24 - 1.32
Endrin	49	1.12	0.157	0.74 - 1.42
Heptachlor (& its epoxide)	49	1.07	0.147	0.63 - 1.45
Lindane	49	1.13	0.153	0.75 - 1.40
Methoxychlor	49	1.04	0.148	0.60 - 1.35
Toxaphene	49	1.07	0.224	0.53 - 1.63
2,4-D	55	0.83	0.171	0.44 - 1.34
2,4,5-TP (Silvex)	55	0.73	0.218	0.30 - 1.29
Benzene	62	1.00	0.081	0.81 - 1.22
Carbon tetrachloride	62	0.98	0.088	0.68 - 1.19
Chlorobenzene	62	1.01	0.079	0.72 - 1.19
Chloroform	62	1.01	0.084	0.79 - 1.18
1,2-Dichloroethane	62	1.03	0.097	0.83 - 1.29
1,1-Dichloroethene	62	0.99	0.178	0.30 - 2.07
Methyl ethyl ketone	62	1.18	0.323	0.10 - 2.17
Tetrachloroethene	62	0.99	0.082	0.78 - 1.24
Trichloroethene	62	1.02	0.094	0.81 - 1.72
Vinyl chloride	62	0.96	0.202	0.47 - 1.43
Cresols	95	0.62	0.123	0.33 - 0.99
1,4-Dichlorobenzene	95	0.61	0.097	0.37 - 0.92
2,4-Dinitrotoluene	95	0.48	0.171	0.06 - 1.12
Hexachlorobenzene	95	0.69	0.170	0.20 - 1.12
Hexachlorobutadiene	95	0.60	0.105	0.32 - 0.91
Hexachloroethane	95	0.59	0.125	0.28 - 0.91
Nitrobenzene	95	0.85	0.234	0.48 - 1.72
Pentachlorophenol	95	0.52	0.219	0.07 - 1.25
Pyridine	95	0.62	0.245	0.18 - 1.82
2,4,5-Trichlorophenol	95	0.57	0.120	0.28 - 1.05
2,4,6-Trichlorophenol	95	0.68	0.124	0.42 - 1.29

[1]Represents duplicate analyses
[2]Includes both ICP and AA furnace results

Figure 1

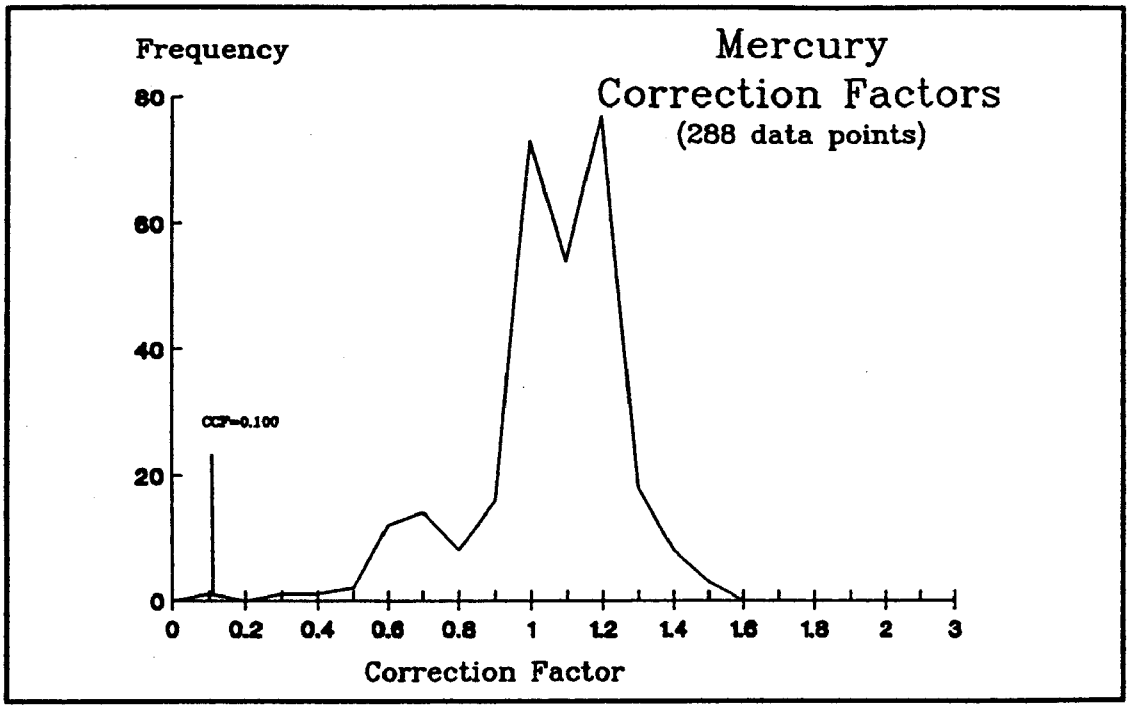
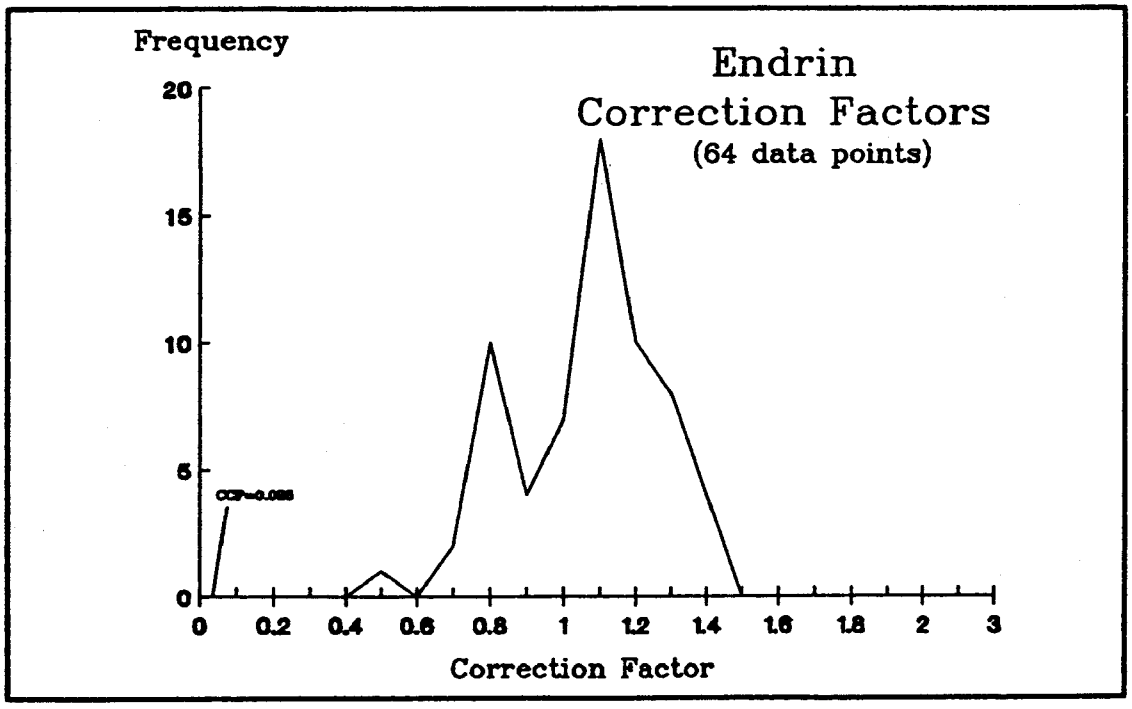


Figure 2



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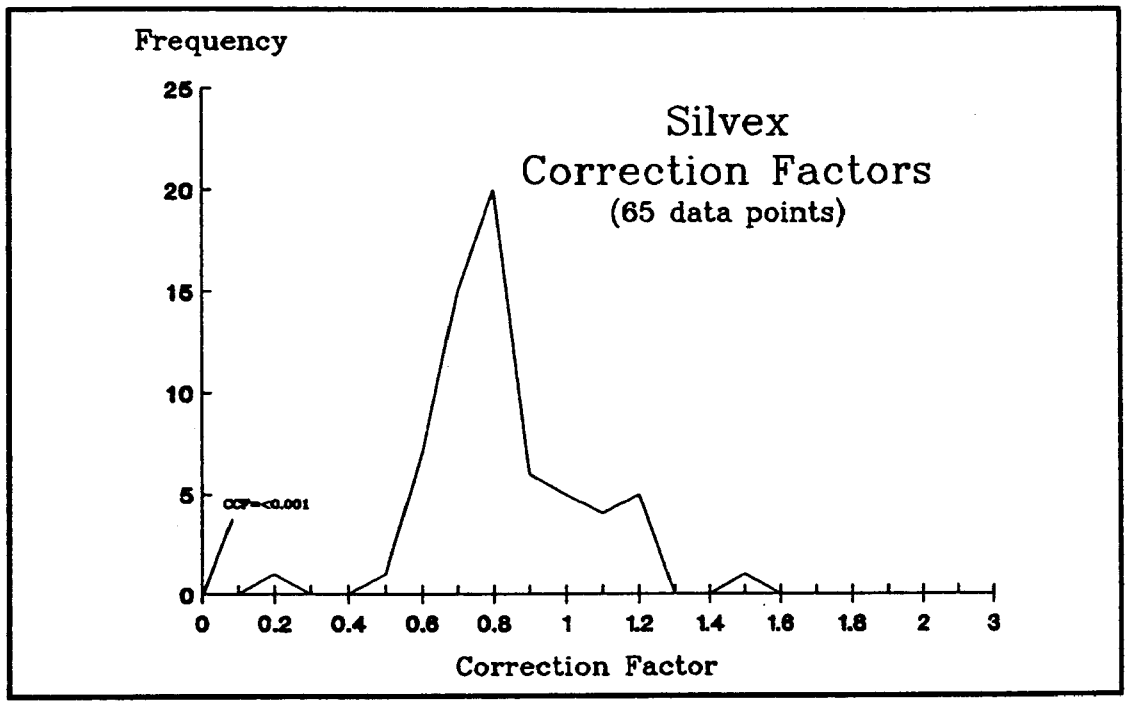
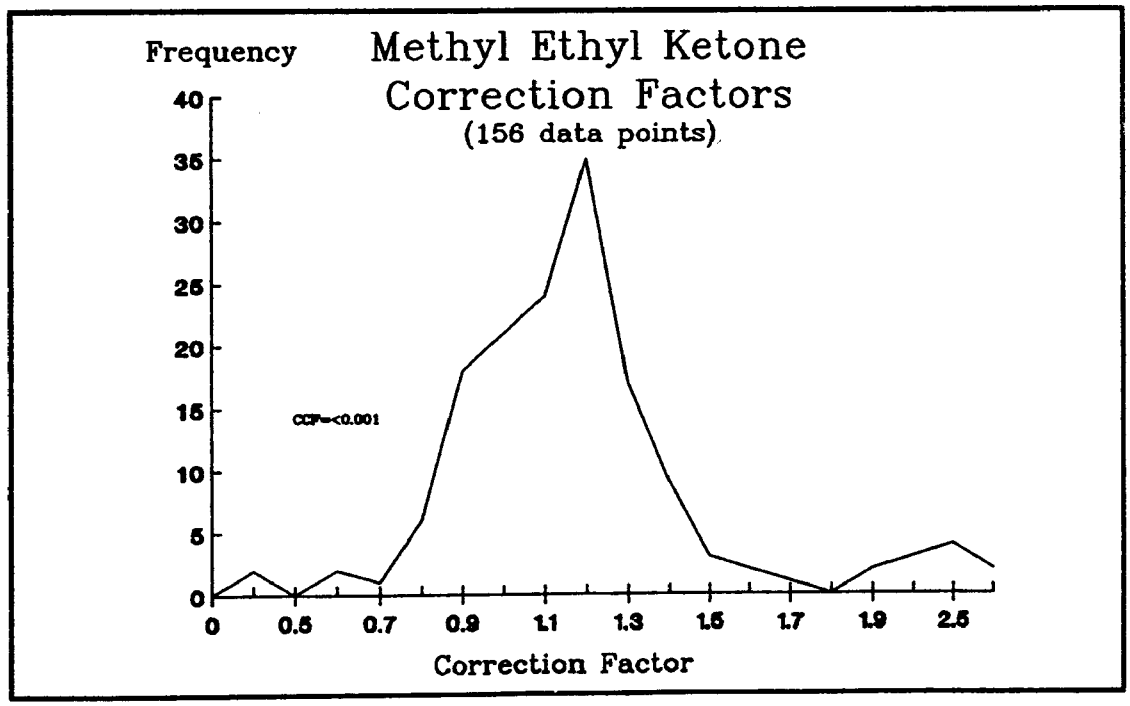


Figure 4



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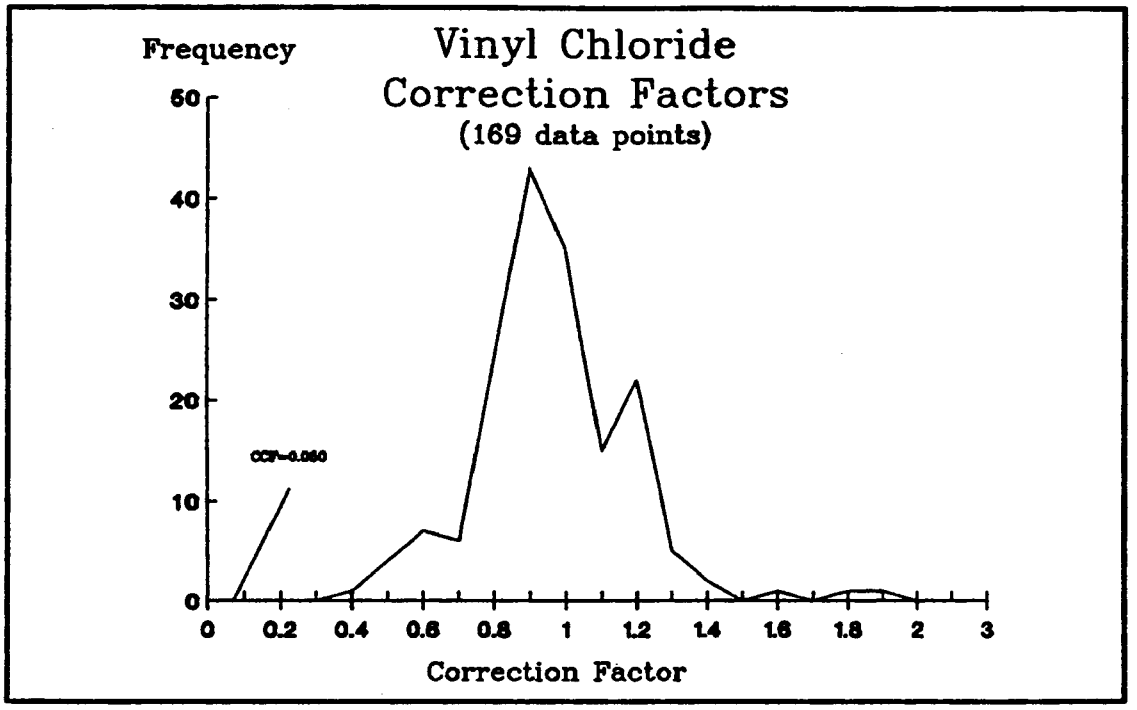


Figure 6

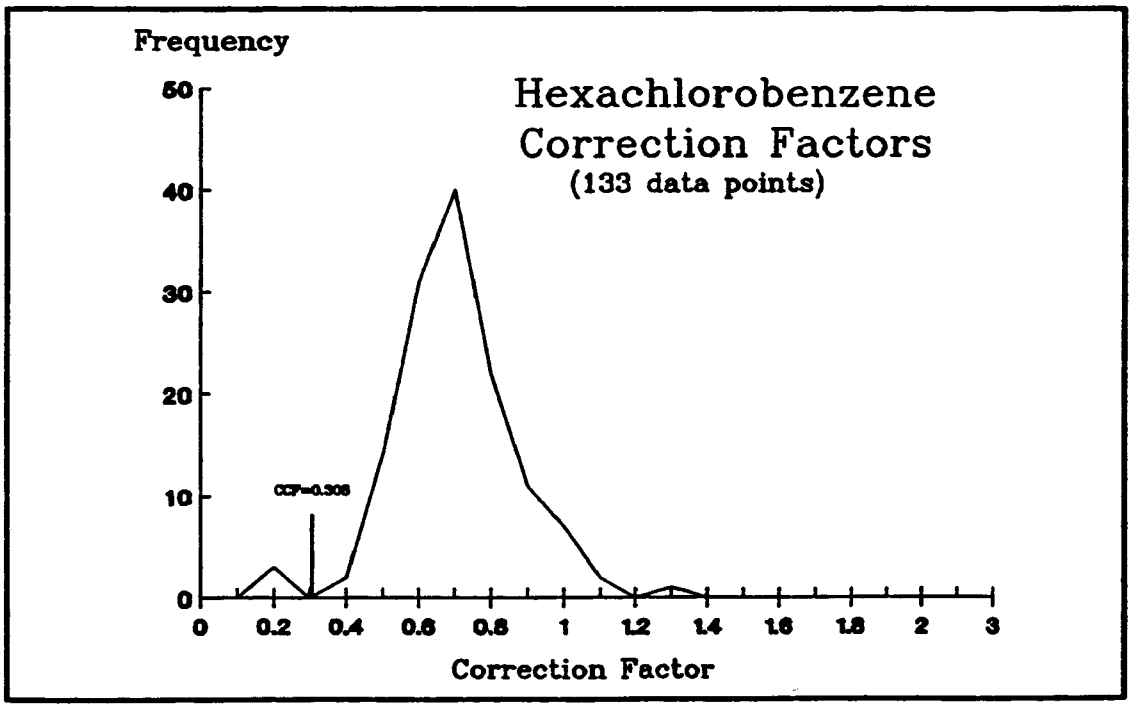


Figure 7 Comparison of correction factor and control sample recovery for metals.

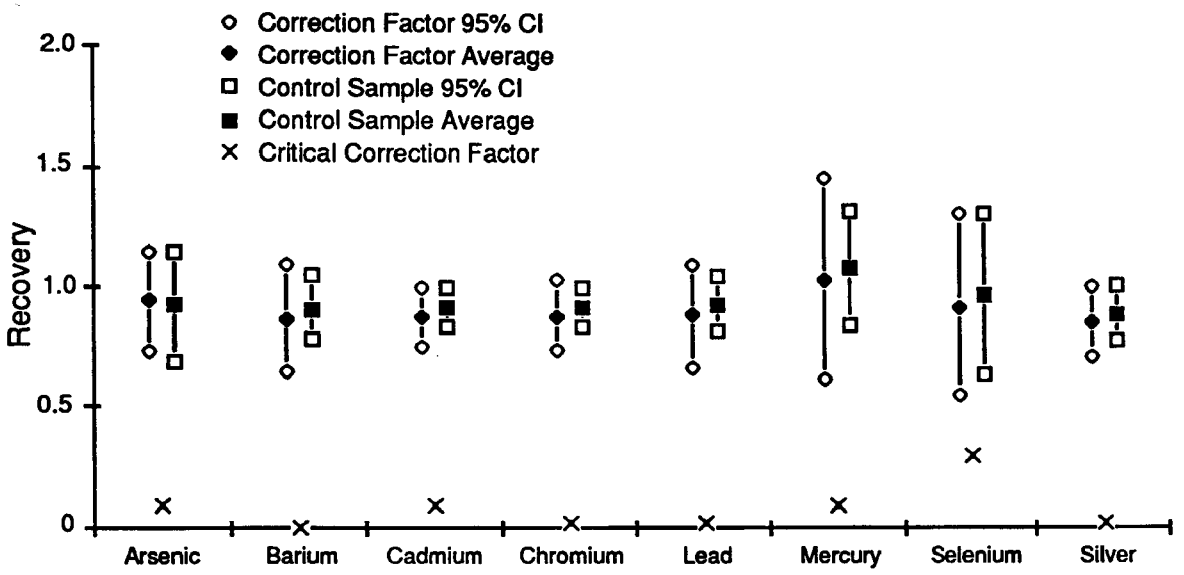


Figure 8 Comparison of correction factor and control sample recovery for pesticides and herbicides.

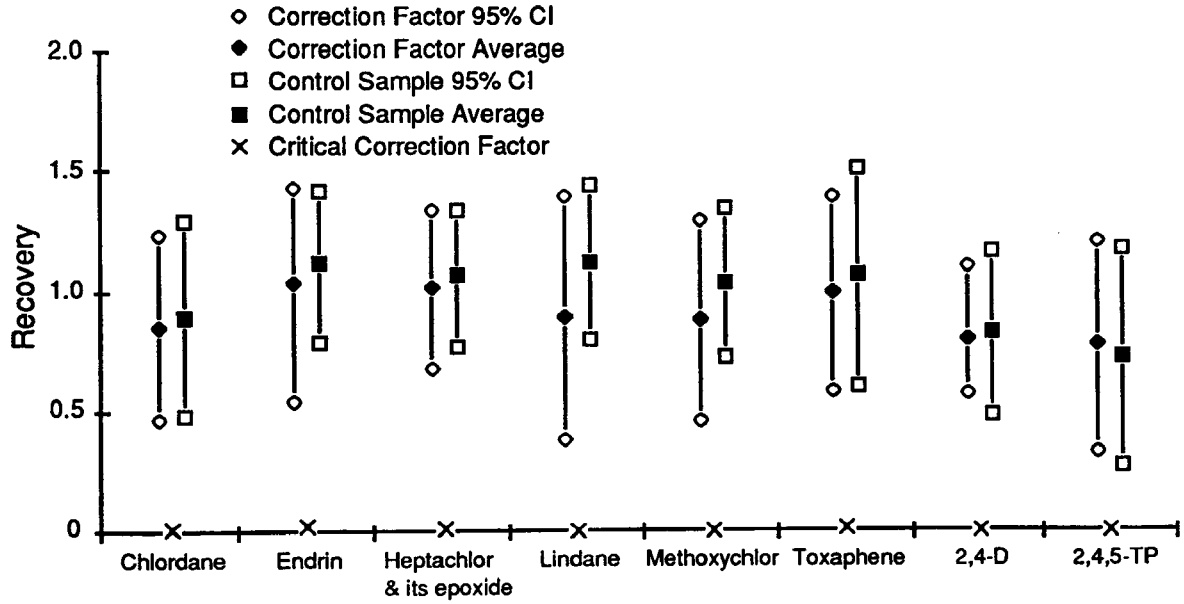


Figure 9 Comparison of correction factor and control sample recovery for volatile organic compounds (VOC).

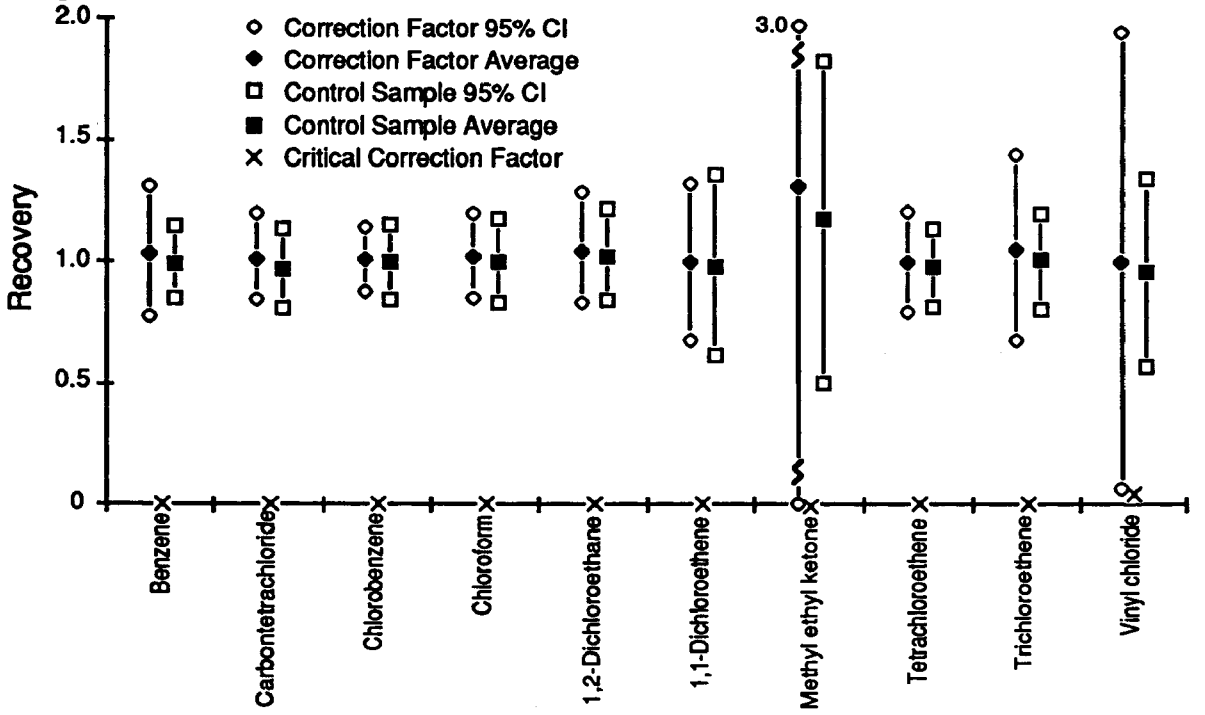
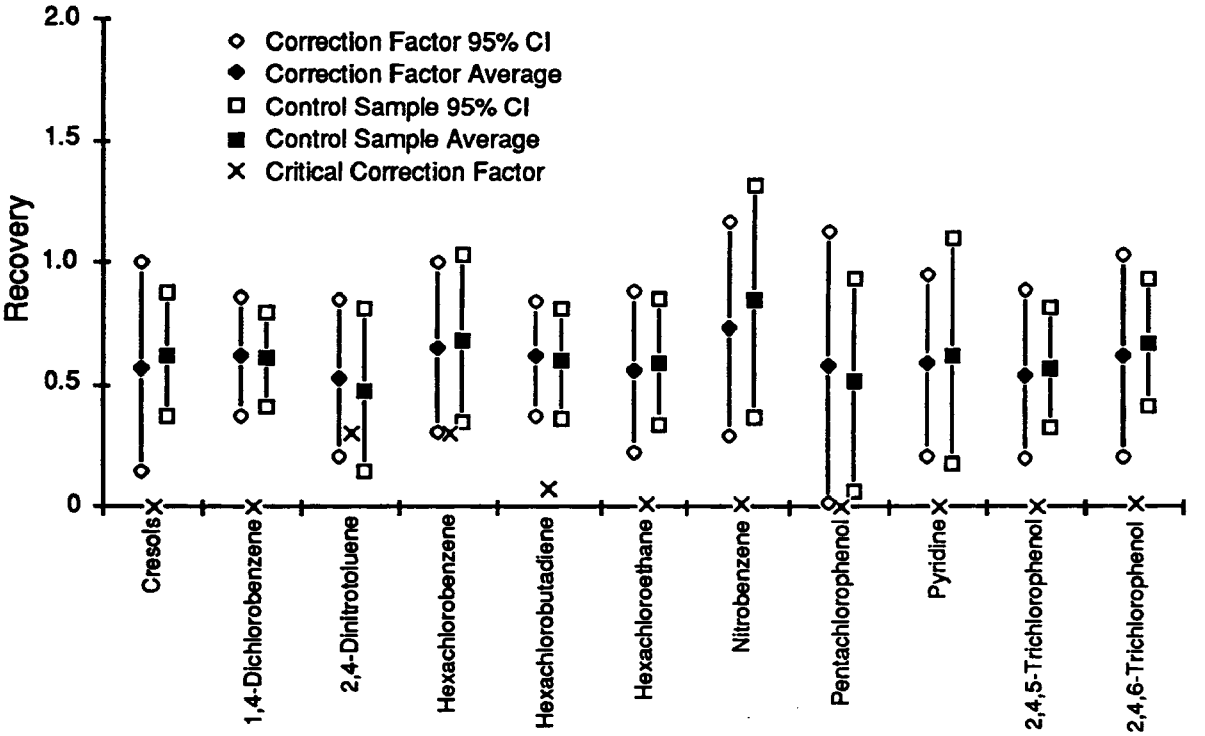


Figure 10 Comparison of correction factor and control sample recovery for base/neutral/acid compounds (BNA).



9

ABSTRACT

Ensuring Data Authenticity in Environmental Laboratories

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Data delivered to both government and public clients by environmental laboratories is no longer reviewed only for contract compliance and acceptability of quality assurance techniques, data users are concerned that the data be "authentic".

Investigations into data authenticity by government agencies have sparked organized efforts by data users to ensure that the data delivered is exactly what it is purported to be. Laboratory personnel should seize the initiative and embrace concerns for data authenticity as a normal part of conducting business.

Laboratories and other generators of environmental data need to develop policies and procedures to ensure the authenticity of their own data. These procedures should include authenticity monitoring as a function of both laboratory management and quality assurance staff.

The authors present a summary of the practices that have resulted in the delivery of data that is not authentic and a plan for developing policies and procedures for data authenticity including:

- Education and training,
- Internal audits,
- Laboratory documentation procedures, and
- Automated laboratory practices.

10

ESTABLISHMENT OF LABORATORY DATA DELIVERABLE REQUIREMENTS FOR DATA VALIDATION OF ENVIRONMENTAL RADIOLOGICAL DATA

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ABSTRACT

In the world of environmental sampling and analysis, the importance of obtaining accurate, valid data has become increasingly important. Much attention has been placed on the review and validation of sample data from CLP organic and inorganic analyses (U.S. EPA Functional Guidelines for Review of Inorganic and Organic Data). In the field of nuclear waste management, we are seeing a significant increase in the analysis of mixed-waste samples from waste sites containing potential radiological contamination. In light of this fact, a need has been identified for the establishment of a protocol for data quality assessment and validation of sample data from radiological analyses. The EPA CLP program protocol provides a means for obtaining consistent data deliverables from different analytical laboratories performing organic and inorganic analyses. This allows for a reasonably equal assessment of sample data regardless of the laboratory doing the analyses. The same type of protocol is necessary to adequately address the need for data of known precision, accuracy, representativeness, comparability and completeness when radiological analysis of environmental samples is performed.

Establishment of a consistent set of radiological deliverables provides a method of obtaining useable, accurate data even when using more than one laboratory for sample analysis. A data assessment and validation program for radiological data can then be designed from the data deliverable requirements.

At EG&G Idaho a set of forms have been designed to provide a master template for the laboratory to format their data deliverables. Use of these templates insures consistency in the data received from different laboratories. Sample results from these forms may be transmitted to EG&G on computer diskette or electronically transferred directly into a database. An initial evaluation of sample results data and quality control data can be performed by a computer analysis of selected data fields in the forms against an established set of criteria. Initial flagging of quality control and sample results data can also be computer generated. This system provides for a substantial savings in time and money for both data entry functions and the data validation process.

11

AN ASSESSMENT OF QUALITY CONTROL REQUIREMENTS FOR THE ANALYSIS OF CHLORINATED PESTICIDES USING WIDE BORE CAPILLARY COLUMNS-- A MULTI-LABORATORY STUDY

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Wide bore (> 0.5 mm) capillary columns are frequently used for the analysis of chlorinated pesticides by gas chromatography/electron capture detection (GC/ECD). In March 1990, the U.S. EPA Contract Laboratory Program (CLP) included the use of wide-bore capillary columns in its protocols for pesticide analysis. In August 1990, as part of the contracting process, single blind samples were distributed to 43 laboratories for pesticide analysis.

The CLP protocols allow variability in the analytical columns and conditions used for pesticide analysis, but the protocols require stringent quality control (QC) to enable the use of the results for a wide variety of purposes. The QC requirements include chromatographic resolution, compound breakdown, compound retention time stability, and detector linearity.

The laboratories participating in the blind study demonstrated a wide range of proficiency in the use of GC/ECD. An examination of the results of the blind study thus gives insight into the ruggedness of the chromatographic procedures under variable conditions. This assessment presents results of a study of the QC data and its impact on the analytical quality. Recommended QC modifications that were derived from the study will be discussed.

Notice: Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through contract number 68-C0-0049 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

12 ANALYSIS-SPECIFIC TECHNIQUES FOR ESTIMATING PRECISION AND ACCURACY USING SURROGATE RECOVERY

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Statistical techniques are presented for estimating the precision and accuracy of gas chromatography / mass spectroscopy (GC/MS) analytical determinations by using associated surrogate recoveries.

The statistical techniques employed involve variations on the so-called "using the regression line in reverse" common in linear calibration. An appropriate regression model is first identified using prior data. In the simple case, where the means and variances of analyte and surrogate recoveries are constant with respect to true concentration, prediction intervals for recovery are inverted to provide confidence intervals for analyte concentration. Otherwise (if means and/or variances are functions of concentration), variance stabilizing transformations are first performed as needed, and then computations similar to those used in conditional multivariate calibration provide confidence intervals for analyte concentration. In either case, the resulting confidence intervals provide the desired information regarding precision and accuracy.

Examples of the use of the techniques are given, using data sets based on quarterly blind performance evaluation studies conducted by the U.S. EPA Contract Laboratory Program and other sources. For these data sets, intra-analysis estimates of precision and accuracy obtained by the techniques presented here are

compared and contrasted with inter-analysis estimates available from, for example, matrix spike studies. The relationship of the improvement in intra-analysis over inter-analysis estimates to the variability and correlation in analyte and surrogate recoveries is explored with these examples.

Finally, we discuss the implications of these results regarding the usefulness of surrogate and/or matrix spike recoveries in "correcting" analytical determinations, and suggest statistical procedures that might be employed when such "corrections" are warranted.

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13

USE OF ORGANIC DATA AUDITS IN QUALITY ASSURANCE OVERSIGHT OF SUPERFUND CONTRACT LABORATORIES

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ABSTRACT:

Organic data audits are performed to assess the technical quality of analytical data and to evaluate overall laboratory performance. The technical data quality is assessed on the basis of the total number of problems observed in the case. The processes used to identify problems in organic analytical data range from a check of the quality control to a thorough investigation of the raw data submitted with the case will be presented. Besides providing the basis for determining the technical quality, the number and type of problems provide a mechanism to track data quality for the Contract Laboratory Program (CLP), or for an individual laboratory, over time. Long-term tracking is accomplished by the use of an audit comment data base that contains standardized comments explaining common problems found within the data submitted by CLP laboratories. Each comment represents an individual problem, and the frequency of use for the comments is tabulated by the data base. Common problems observed during the past year in CLP data packages such as calibration errors, failure to submit deliverables, instrument contamination, and use of incorrect quality control solutions will be presented.

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14 **USE OF INORGANIC DATA AUDITS IN QUALITY ASSURANCE OVERSIGHT OF SUPERFUND CONTRACT LABORATORIES**

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William R. Newberry, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada

ABSTRACT:

Inorganic data audits are performed to assess the technical quality of analytical data and to evaluate overall laboratory performance. The technical data quality is assessed on the basis of the total number of problems observed in the case. The processes used to identify problems in inorganic analytical data range from a check of the quality control to a thorough investigation of the raw data submitted with the case. Besides providing the basis for determining the technical quality, the number and type of problems provide a mechanism to track data quality for the Contract Laboratory Program (CLP), or for an individual laboratory, over time. Long-term tracking is accomplished by the use of an audit comment data base that contains standardized comments explaining common problems found within the data submitted by CLP laboratories. Each comment represents an individual problem, and the frequency of use for the comments is tabulated by the data base. Common problems observed during the past year in CLP data packages include calibration errors, failure to submit deliverables, instrument contamination, and use of incorrect quality control solutions.

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15

Improved Evaluation of Environmental Radiochemical Inorganic Solid Matrix Replicate Precision:

Normalized Range Analysis Revisited

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ABSTRACT: The Normalized Range Statistic, as defined in EPA-600/4-81, provides the radiological laboratory analyst with a generally robust index of analytical precision in unknown replicate analyses. Inorganic solids, however, present a statistical assessment problem; replicate analyses of low level environmental samples with these necessarily small (usually <20 g.) aliquots frequently return spurious QC "outliers" owing to the relative magnitudes of the calculated and "expected" sigmas, the "expected" value being based on a 1 kg. aliquot and the factor employed by the traditional Range Analysis method. This paper examines the mathematical nature of the statistical deficiency and proposes alternative solutions for improvement in the evaluation of environmental radiochemical inorganic solid matrix replicate precision.

The monitoring of laboratory accuracy and precision at the IT Oak Ridge Laboratory is guided by the statistical procedures detailed in EPA-600/4-81-004, methods which provide generally practical empirical point estimators of analytical performance. Accuracy evaluation is accomplished through the use of the "Normalized Deviation" statistic, in which the analytical result of a spiked sample test is "normalized" to the "known" value and "expected laboratory 1-sigma" precision; in traditional statistical parlance, a "Z-transformation." Normalized Deviation statistics (NDEVs) are computed and plotted on control charts with a mean of zero, warning limits at +/-2.0s and control limits of +/- 3.0s.

Similarly, the analytical precision of unknown replicates (i.e., samples where a "known" value from a reference standard is not present) is assessed via the Normalized Range (NRANGE) estimator, in which the numerical difference between replicate results is evaluated in the context of both an "expected 1-sigma" precision level and an "expected range" factor. NRANGE statistics are computed and plotted on control charts containing an X-Y origin of zero, an "expected range" of 1.0s, and warning and control limits at +3.0s and +4.0s respectively (i.e., mean, or "expected" range plus 2 and 3 sigma). NRANGE points lying above the +4.0s Control Limit mandate an investigation of the analytical data for the replicates in question to ascertain the causes of the excessive divergence.

These statistical tools assume the presence of a liter or kilogram sample aliquot, the latter necessitated by the EPA food matrix crosscheck. Analytical results are adjusted to their respective activities at a liter or kilogram before the statistics are computed. Where the samples are constituted of low-level, low-volume inorganic solid matrices, the generation of spurious "outlier" statistics is a recurring phenomenon, owing principally to the relative magnitudes of the analytically determined 1-sigma and the "expected 1-sigma" used by the NRANGE computation. This a-priori 1-sigma, while empirically appropriate for 1 kg. samples, imposes an unrealistic constraint on small aliquot inorganic replicates. Clearly, in such cases a method of incorporating the analytically determined 1-sigmas must be employed to make the NRANGE statistic reflect the true precision level of the replicates; to the extent that these "outliers" are invalid they con-

tribute to a misleading impression of laboratory precision capabilities and result in unwarranted technical review of the replicate sample data, an examination required of all "out-of-control" QC results.

Since every quantitative sample result is essentially a point-estimate of a "mean" value which approximates a "true" activity or concentration level, it would be tempting to dismiss any "expected sigma" constraints on replicate results, particularly of the types under discussion here, and apply a sort of "t-test" on our experimental "means" incorporating only the analytical 1-sigmas in determining the acceptability of the range between replicate values. Support for such a method derives from the fact that the relative standard deviation (i.e., the "percent sigma," or coefficient of variation) accompanying each production analysis is not routinely evaluated against an "expected" sigma; it is generally accepted that, as activities and/or aliquots are lesser, sigmas will tend to be proportionally greater, frequently approaching or even exceeding the magnitudes of the quantified activities themselves. An expected sigma," while serviceable in the main as an objective standard of analytical variability, is frequently inappropriate in light of the component measurement particulars of individual cases such as those under review in this presentation.

$$Z_{alt1} = \frac{|R_1 - R_2|}{\frac{\sigma_1+\sigma_2}{2}} \quad [1]$$

$$Z_{alt2} = \frac{|R_1 - R_2|}{\sqrt{\sigma_1^2+\sigma_2^2}} \quad [2]$$

$$NR_{adj} = NR_{epa} \times \frac{\sigma_{epa}}{\frac{\sigma_1+\sigma_2}{2}} \quad [3]$$

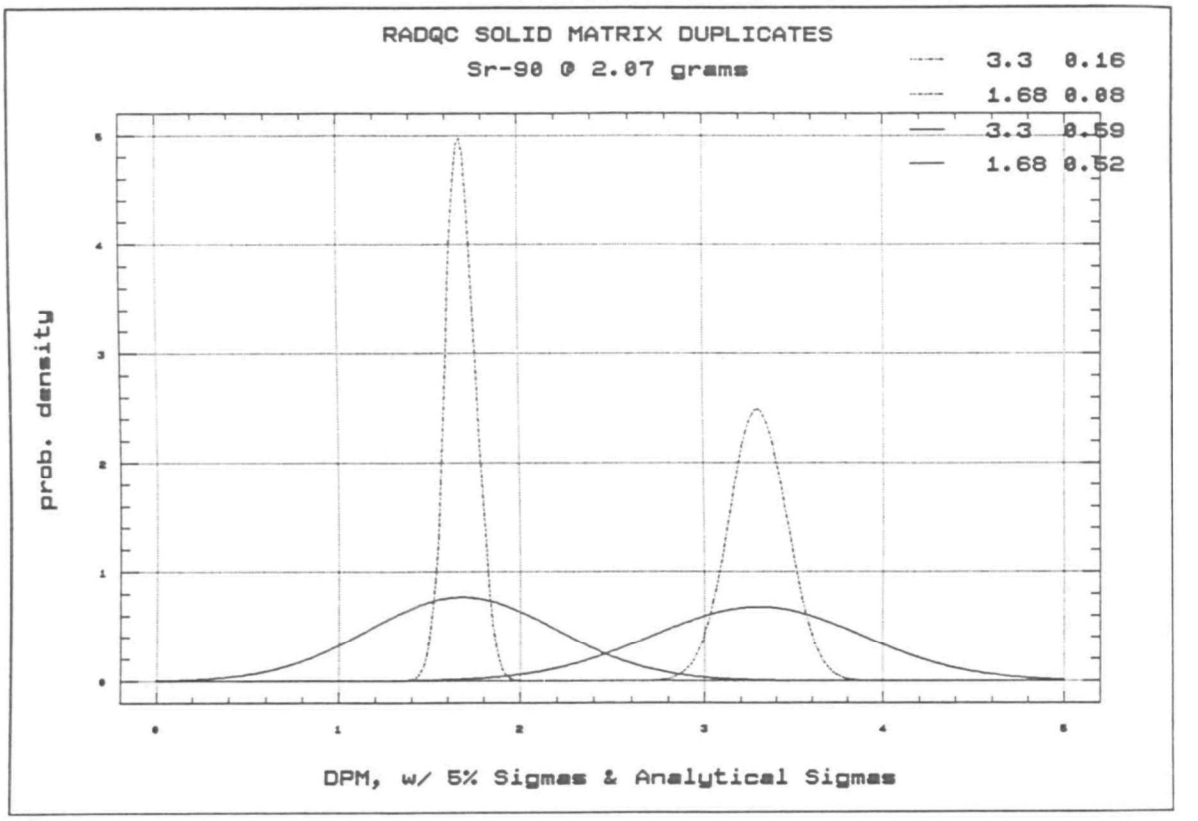
The conventional t-test cannot be directly applied to replicate radioanalytical results owing to the fact that "N=1" for each sample dataset, leaving us without "degrees of freedom" to employ in the derivation of t-values. Given this problem, should we wish to retain the mathematical simplicity of the NRANGE statistic, we could simply replace the "expected" sigma in the formula with the mean of the analytical percent sigmas. Such a replacement would yield NRANGE statistics derived totally in the context of the error terms of the lab results themselves, removing any empirically objective" variability standard in favor of the case-specific uncertainty estimates. The virtue of such an approach would be to remove any potential argument over whether an "NRANGE>4" calculated in such a fashion in fact represented an "out-of-control replicate set. Replicate results so divergent as to normalize out to "NRANGE > 4" even after taking their own individual error terms into account would indisputably be indicative of unacceptable precision and would indeed merit technical review to determine the causes of the disparity.

Alternatively, eschewing the NRANGE formula entirely, we might statistically examine our replicates via one of two variations on a "Z-test" formulation, employing either the mean of the analytical sigmas or the square root of the sum of the variances as divisors of the replicate range, as shown in the box below.

Under either "z-score" approach (Eq. 1 & 2 in box) our "outliers" would be those resulting in a z-statistic > 3.0 absolute. This approach makes intuitive sense, but is a bit bothersome in that any utilization of a reference value such as the "expected sigma" is again precluded, a tactic that contravenes an implicit assessment principle of the EPA-600 method: the application of empirical guideposts to laboratory precision capability accounting. A simple adjustment to the NRANGE statistic is therefore proposed, one that incorporates both the EPA sigma factor *and* the mean of the analytical sigmas into the NRANGE calculation, as shown by Eq. 3 above: a ratio of "expected" over "found."

It should be readily apparent that where the mean lab sigma nearly equals the "expected" sigma the NRANGE statistic will be quite close to the value returned by the standard method. Where the lab error coefficient is greater than the expected, the NRANGE will be attenuated by the ratio of the two. Further, where the mean lab sigma coefficient is *smaller* than the expected, the adjustment factor wil be > 1.0, thereby *expanding* the NRANGE value. In this manner the sigma-ratio adjustment factor is a double-edged sword; if individual error terms are better than the expected, the results had better be minimally divergent to avoid being pushed into "out-of-control" status. Such a condition makes methodological sense; analytical sigmas are mathematical expressions of our confidence in our quantitative estimates. Replicates returning better-than-expected error terms *and* grossly disparate "means" are indicative of a condition warranting quality control review.

A graphical example effectively illustrates the problem posed by the application of an expected sigma to a low-level small aliquot solid matrix duplicate result set. Two Sr-90 results, at 3.30 and 1.68 dpm respectively, are graphed as normal distributions (see box, below right), first with an assumption of a 5% CV, then overlaid using sigmas derived in the analyses (0.59 and 0.52 1-sigmas, respectively). While the results are displayed as narrow, peaked distributions whose tails are quite far apart under a 5% CV assumption, when viewed in the distributional context of the analytically derived sigmas, quite another picture emerges; the tails of the distributions overlap substantially. The traditional NRANGE statistic for this set came in at NR=14.73, while the "corrected" NR=3.01, and this adjusted Normalized Range value seems appropriate; our replicates diverge, perhaps more than we would prefer, but certainly not to the extent indicated by a Normalized Range of 14.73. Were these replicate results those of a full kilogram vegetation matrix emanating hundreds of dpm, we would perhaps have cause for concern at the disparate replicate values returned by the lab. In the instance of 2.07 gram inorganic aliquots evincing a few dpm, however, the range between R1 and R2 is not all that severe, certainly not to the point implied by an NRANGE statistic of 14.73. The relative standard deviations (the CVs) for R1 and R2 were, respectively, 17.86% and 30.91%.



EPA-600 expected 1-sigma % precision guidelines are grouped by type of analysis into four levels: 5%, 10%, 15%, and 25%. An examination of 116 inorganic solid matrix replicate results from our RADQC™ laboratory QC database is revealing. As might be expected, most of the NRANGE difficulty lies with the analyses classified in the "5% precision" group, as the following table illustrates:

N	EPA 1-sigma	LAB 1-sigma
68	0.05	0.125
4	0.10	0.121
38	0.15	0.159
6	0.25	0.232

The column on the right tabulates the average CVs found in actual practice, grouped by the EPA sigma classifications. It is evident that a 5% sigma represents an unrealistic level of precision where small aliquot solids are concerned. The application of the NRANGE sigma ratio adjustment factor factor to the 116 samples investigated for this research effort reduced the "NR>4.0" outliers by 75%, and the attenuated "adjusted NR" statistics were overwhelming of a magnitude consistent with the type of graphical evidence obtained by plotting the gaussian distributions in the manner of the above example.

Further statistical support for the use of the NR adjustment is seen by a correlation matrix comprised of the values obtained for this QC data under the formulas displayed in Eqs. 1, 2, and 3:

	NR_adj	Z_alt1	Z_alt2
NR_adj	1.000	0.903	0.925
Z_alt1	0.903	1.000	0.956
Z_alt2	0.925	0.956	1.000

The high Pearson-R correlations among the three methods indicate a significant agreement between the two Z-score variations and the adjusted NRANGE method; we are measuring the same phenomenon, irrespective of algebraic method. Any of these formulations serve to reduce the quantity of spurious QC outliers, improving the assessment of inorganic solid matrix precision.

A second graphic plot example is provided below to further demonstrate the utility of the NRANGE adjustment method. This replicate set consisted of Gross Beta analyses performed on aliquot weights of 264 and 258 mg. The dpm results were calculated to be 112 +/- 23 and 134 +/- 28 (2-sigmas). The unadjusted NR=4.38, just slightly over into the outlier realm. The "corrected" NR=2.11, and again, the distribution plots seem to provide visual agreement with the numerical statistic. The mean CV was 10.36%.

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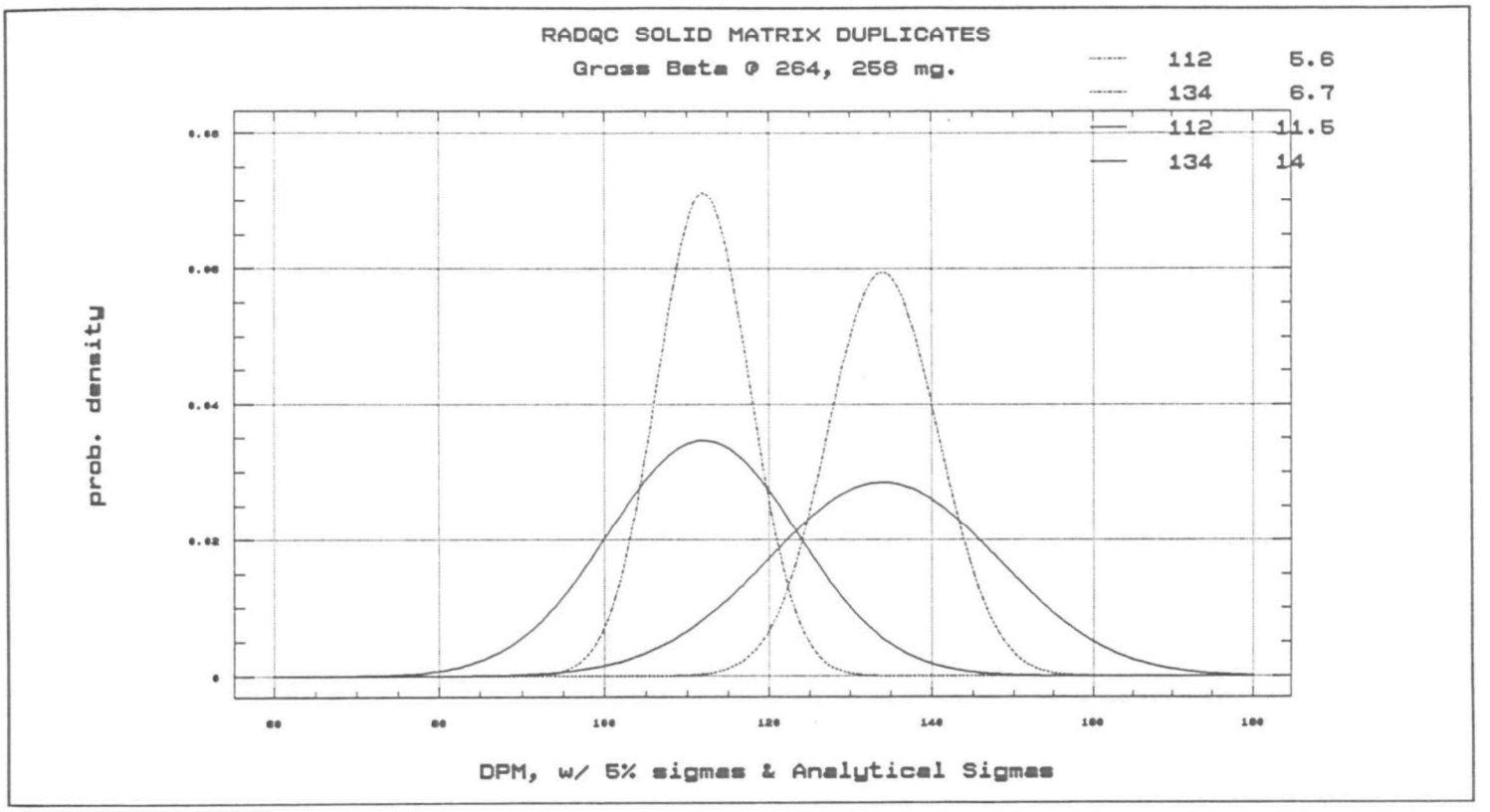

A quick look at some of the aggregate univariate and correlation statistics for the dataset of solid matrix replicates used in this effort is useful. The median uncorrected NRANGE was 2.14, with a mean of 3.74, while the median adjusted NRANGE was 1.48, with a mean of 2.02. The smallest aliquot was 4.8 mg., and the largest was 841.9 grams, with a median of 2.07 grams and mean of approximately 69 grams. The lab sigma precision was, as we might expect, inversely correlated with aliquot (R=-.25, statistically "significant" with p=.007) The median lab sigma precision was 12.17% with a mean of 14.04%. One lesson flowing from these data is that perhaps those types of QC analyses currently classified as requiring "5% expected 1-sigma precision" be instead calculated using a 15% expected precision statistic where the samples are those of inorganic solid matrices. The NRANGE sigma ratio adjustment factor employed here is essentially performing roughly that very sort of task in attenuating the Normalized Range where the sigmas are closer to 15% in the laboratory production environment.

REFERENCES

Kanipe, Larry G. (1977), *Handbook for Analytical Quality Control in Radioanalytical Laboratories,* TVA/USEPA Interagency Energy-Environment Research & Development Program (EPA 600/7-77-088)

Walpole, Ronald E. & Myers, Raymond H. (1989), *Probability and Statistics for Engineers and Scientists, Fourth Edition,* New York, MacMillan

EPA 600/4-81-004, USEPA, EMSL Office of Research & Development, Las Vegas, NV.

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Laboratory On-site Evaluations as a Tool for Assuring Data Quality

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In its role of providing quality assurance support to the Superfund Office, the Environmental Protection Agency's Environmental Monitoring Systems Laboratory-Las Vegas has developed a program for conducting laboratory on-site evaluations ("on-sites"). Although developed principally for use with Superfund's national Contract Laboratory Program (CLP), "on-sites" have been incorporated as an integral element in an overall scheme of laboratory performance evaluation for activities supporting the Resource Conservation and Recovery Act and the Department of Energy.

The purposes of the laboratory on-site evaluation, together with the complementary performance evaluation sample program, are (1) to determine whether a given laboratory can effectively perform required analyses and (2) to identify laboratory problems that negatively impact performance. As a part of the "on-site," the following elements are reviewed: the laboratory's quality assurance plan; its standard operating procedures; its utilization of available space; adequacy of personnel; instrumentation capacity; sources of possible contamination; and the ability to perform the required analyses.

This presentation will describe those good laboratory practices examined in the "on-site," and highlight the types of problems encountered and their potential impact upon data quality.

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APPLICATION OF BIAS CORRECTION

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ABSTRACT

EPA has required bias correction of analytical data generated under the Toxicity Characteristic Leaching Procedure (TCLP, SW-846, Method 1311) since September of 1990. In order to determine the validity of correcting data based on recoveries of matrix spikes, two Standard Reference Materials (SRMs) were created from real environmetal samples. These SRM's were spiked with stable isotopically labeled compounds. Results were corrected for bias by three different methods: 1) on an individual sample basis per individual compound; 2) on an individual compound per batch of ten basis; and 3) on a class of compounds per individual sample basis. Results of uncorrected and corrected recoveries were compared to known or "true" concentrations and conclusions drawn about the effect bias correction has on data quality.

INTRODUCTION

The 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA) directed the EPA to re-examine the Toxicity Characteristic (TC) portion of the Extraction Procedure Toxicity test [1] and make changes necessary to better address the leaching of wastes and to regulate additional characteristics. A revision to the TC rule was published in the Federal Register (55FR 11798) which added 25 organic constituents, and a later revision [2] added quality control measures that require that the bias determined from matrix spike recoveries be used to correct the analytical data. In January of 1991 EPA extended bias correction requirements to the Land Disposal Restriction Rules, and has proposed including bias correction in Chapter 1 of SW-846. The latter inclusion would extend bias correction requirements to all RCRA testing.

Despite the proliferation of bias correction requirements, little has been published regarding how well this technique works. If one is to really know how well bias correction works, one must know the true concentration of an analyte. Merely spiking deionized water does not provide the information needed about recoveries since one would expect uniformly good results from an "in control" analysis. For this reason two SRMs made from real environmental samples were created. A water matrix was chosen for both types of matrices in order to overcome potential mixing problems. The SRM for Cases A and B was created from 11 liters of sanitary landfill leachate. SRM Case C was created from a single monitor well from a closed remediation site. Method 1311 currently requires that spiking for correction purposes be done on a batch basis (one spiked sample per twenty samples of a similar matrix).

Proposed changes to Chapter 1 of SW-846 would also require spiking on a batch basis, but may allow correction by representative compound class. No bias correction would be required for "self-correcting" methods such as isotope dilution. Cases A, B, and C are experiments on the use of bias correction in each of the above ways. In all cases, uncorrected and corrected data were compared with the true concentrations and changes in accuracy and uncertainty calculated.

METHODOLOGY

Case A

Eleven liters of sanitary landfill leachate from the same point source were collected, composited, and three liters removed for analysis as a sample, duplicate, and spike. The remainder was spiked with the entire list of TC volatile and semivolatile parameters. This amount is subsequently referred to as the "true" concentration and was the SRM for both Case A and Case B. See Figure 1 for the processing of this SRM.

The seven liters of the SRM were then filtered in the TCLP prescribed manner for volatiles and semivolatiles. It has been our experience that leachate often contains a large amount of dissolved gases which may cause foaming during the volatile purge step. Because of this, we routinely dilute these samples prior to analysis. We had anticipated that a five fold dilution of the SRM would be adequate, but the sample foamed too badly and a ten fold dilution was needed. Prior to each analysis for volatile constituents, the extract (filtrate) was diluted ten fold and spiked with isotopically labeled volatile TC constituents. These spikes were used to produce spike recovery correction factors.

Prior to each of the 7 extractions, the semivolatile filtrate was diluted (one to five) and spiked with the entire list of isotopically labeled TC semivolatile constituents. A separatory funnel extraction was performed due to time constraints. These spikes were also used for spike recovery correction factors.

Spike amounts for volatile and semivolatile parameters varied on a compound basis. These levels had been predetermined to give adequate recoveries from a leachate matrix without exceeding regulatory levels when dilution factors are considered. Volatile analyses were performed via methods 8240/8260 from SW-846 and semivolatile analyses were performed in accordance with method 8270. Spiking levels corrected for dilution factors are reported in Table 5.

Case B

The uncorrected mean recoveries of the native compounds from Case A were experimentally inserted into a batch of nine other sanitary landfill leachates. However, each of the nine other samples in the batch of ten

had also been spiked with the entire volatile and semi-volatile TC list, and recoveries calculated. True concentrations of these nine samples were not known. Spike recoveries from each of the nine samples were used to individually correct results of the native compounds found in the SRM.

Case C

A simulated monitor well was constructed using a five foot section of Corning glass pipe fitted with Teflon [3] endcaps. Each endcap was fitted with a Teflon stopcock. Total well volume was about 12.6 liters. The top endcap of the monitor well was removed and the well filled with sample from a single contaminated groundwater monitoring well. A volatile and a semivolatile sample were removed from the bottom of the well to determine pre-spike constituents and concentrations. The well was re-filled with groundwater which had been spiked with the following classes of volatile parameters: Saturated Chlorocarbons; Unsaturated Chlorocarbons; Aromatics; Bromocarbons. The constituents within each class are found in Table 1. The endcap was replaced and the small remaining volume filled via access through the stopcock. Top and bottom stopcocks were connected by Teflon tubing to a pump calibrated to deliver one well volume every 5.6 hours. The stopcocks were opened and the pump turned on for 23 hours during which time about four well volumes were recirculated, enough for adequate mixing of the sample. At this point the well was considered to contain a SRM.

The pump was stopped, stopcocks closed and the top cap removed. A three foot top section was added to prevent overflow and the well was sampled seven times by the lab's field crew. The volatile samples were packed with ice and shipped by Federal Express to ourselves (with routing through Memphis). Just prior to purging, each of the seven samples were spiked with a specially prepared surrogate mix that contained stable isotopically labeled compounds representative of each class of compounds. Recoveries of each representative compound were then used to bias correct all amounts of native compounds within that class found in the SRM. Results were compared to the true concentration in the same way as in Cases A and B.

The simulated monitor well prepared for a semivolatile experiment in the same manner. The semivolatile classes were: Nitroaromatics; Acidic Compounds (phenols); Nitosoamines; Bases; Polynuclear Aromatics; Chlorinated Hydrocarbons; and Phthalates. Just prior to extraction, each sample was spiked with lableled representative compounds (see Table 4). Results were treated the same way as the volatiles.

Results and Discussion

Case A

Seven replicates of leachate SRM were subjected to normal statistical treatment. The sample data consisted of three sets:

1) Recovery of known value.
2) Recovery of spiked isotopes.
3) Bias correction of SRM values with recovery of labeled compounds

The mean and standard deviation for each set of data were calculated. A confidence interval at the 99% level of confidence was calculated as:

X = mean S = small population standard deviation
CI = confidence interval = (S/square root of 7)*3.707
LCL = lower control limit = X-CI
UCL = upper control limit = X+CI

The confidence interval of a data set was considered a reflection of uncertainty in the data. Changes in uncertainty that bias correction produced were calculated as follows:

$$\% \text{ uncertainty} = \frac{(\text{corrected CI} - \text{uncorrected CI})}{\text{uncorrected CI}} * 100$$

Change in accuracy is best looked at as a relative indication of the closeness of a corrected versus uncorrected result to a true value. Accuracy increases as recovery approaches 100%, but begins to decrease as recoveries exceed 100% of the true value. Changes in accuracy were calculated as follows:

UCX = uncorrected mean % recovery of true value
CRX = corrected mean % recovery of true value
ABS = absolute value
Accuracy change = ABS(100-UCX)-ABS(CRX-100)

Table 2 summarizes the uncertainty and accuracy of bias corrected data from Case A.

Case B

While Case A was an experiment of bias correction on an individual sample basis, Case B was an experiment on a batch basis. Nine leachate samples were spiked and recoveries calculated. These recoveries, tabulated in Table 3, were used to bias correct the mean native values found in the leachate SRM. Since the proposed EPA guidelines for bias correction in SW-846 Chapter 1 state that bias correction should not be done if recoveries are greater than 80%, some recoveries were not used. Accuracy and uncertainty results for corrected data are summarized in Table 5.

Case C

Case C was an experiment in bias correcting an entire class of compounds based on recovery of a single representative compound from that compound

class on an individual sample basis. Volatiles were divided into five classes and semivolatiles into six classes. Results are summarized in Tables 6 and 7.

SUMMARY

Case A

Application of bias correction on an individual compound per individual sample basis resulted in an overall increase of accuracy by about 9%. Uncertainty also increased, however, by about 19%.

Case B

Application of bias correction on an individual compound per batch basis resulted in an average reduction in accuracy of 119%. Calculation of change in uncertainty was not as straight forward since not every data point was used per EPA proposed instruction. If batch corrected data for a compound contained at least 3 data points, then the change in uncertainty was calculated as follows:

CIB = batch corrected confidence interval
CII = individual sample corrected confidence interval

$$\% \text{ uncertainty} = \frac{(CIB - CII)}{CII} * 100$$

The average percent increase in uncertainty for Case B was 352%! See Figure 2.

Case C

Application of bias correction on a class of compounds within an individual sample was averaged on a volatile and semivolatile basis. Compounds which were corrected by their own isotopes were not included for averaging purposes. Volatile data increased in percent uncertainty by 55%, but also increased in accuracy by only 8. Semivolatiles increased in accuracy by 4 units and increased in uncertainty by 13%.

The above results clearly show that bias correction on a batch basis performs very poorly. Case A was essentially an isotope dilution method. Case C gave results that were surprisingly similar to Case A on an average basis, but neither instance showed marked improvment in accuracy. Bias correction also failed to correct a glaring case of systematic error in the TC method. The average recovery of native hexachlorobenzene was a dismal 3.49%. There was no error in sample spiking, since the control sample yielded an excellent 90%. These results are consistent with other studies conducted at this laboratory: hexachlorobenzene fails to survive the TC filtration step. The mean corrected value was only 3.87% of the original concentration in the SRM.

Many people in the industry have lost sight of the fact that every laboratory in the country using GC/MS methods from SW-846 are already employing bias correction in a case C type manner. Every volatile and semi-volatile analysis goes through an extraction step and a concentration step. The volatile extraction step is usually referred to as the purge step. The volatile extract is concentrated onto a trap and then injected into the instrument. The semi-volatiles are extracted into a liquid solvent, and the extract concentrated to 1 mL. Internal standards are used for quantification. The use of internal standards means that all data is bias corrected.

The only difference between volatile and semi-volatile analysis is in when (or where) the internal standards are added. In the volatile analysis, internal standards are added prior to extraction. The semi-volatile internal standards are added after extraction. This is a critical difference which may partly explain why bias corrected data for volatile analytes seems more consistent than semi-volatile data.

Perhaps two small changes would be in order:

1) Add semi-volatile internal standards prior to extraction

2) Change the list of internal standards for both volatiles and semi-volatiles.

These changes would make data that have already been bias corrected through use of internal standards more representative of the sample. Currently, internal standards are assigned to an analyte purely on the basis of retention time. Compounds of very different chemical type share the same retention time. Careful examination indicates that data quality improves when analyte recovery is corrected by compounds which more closely resemble the analyte in terms of both chemical and physical characteristics. Recommended internal standards are:

Volatile	Semi-volatile
vinyl chloride-d3	n-nitrosodimethylamine-d6
1,1-dichloroethene-d2	phenol-d6
chloroform-13C	nitrobenzene-d5
benzene-D6	hexachloroethane-13C
chlorobenzene-D5	hexachorobenzene-13C6
bromoform-13C	aniline-d5
	di-n-butyl phthalate-d4
	pentachlorophenol-13C6
	benzo[a]pyrene-d12

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M. O'Quinn - Encotec, Ann Arbor, MI

W. Ziegler - ThermalKEM, Rock Hill, SC

Environmental Laboratory Council, Washington, DC

REFERENCES

[1] Method 1310 from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, November, 1986, Third Edition, USEPA, SW-846 and additions thereto.

[2] Federal Register, Vol. 55, No. 126, Friday, June 29, 1990, pp. 26986-98.

[3] "Teflon" is a registered trademark of the E. I. DuPont Corporation.

DLS/slm

Figure 1

Schematic Diagram of Case A & Case B

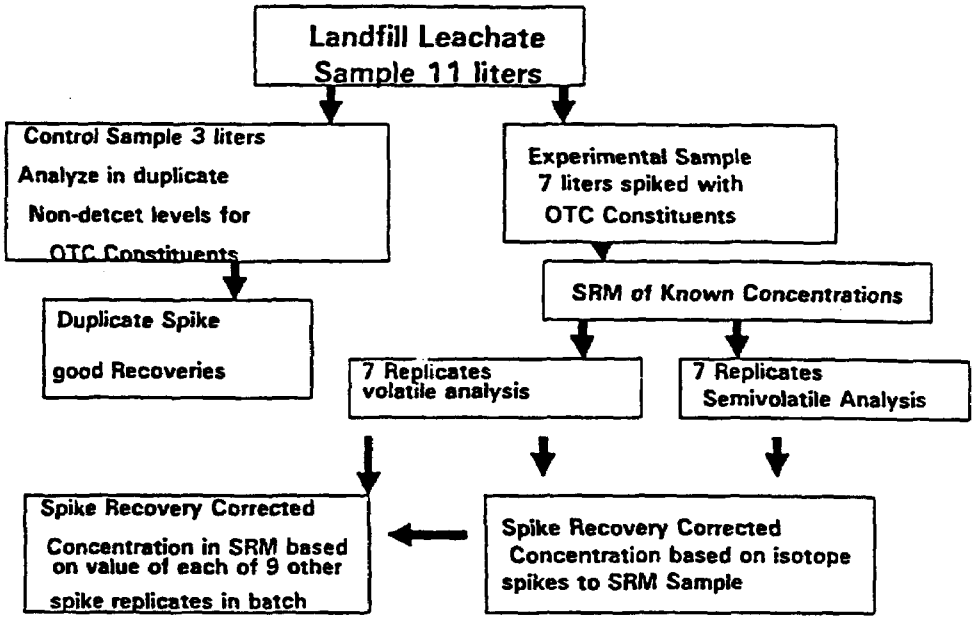

Figure 2

Comparison of Individual vs Batch Based Corrections

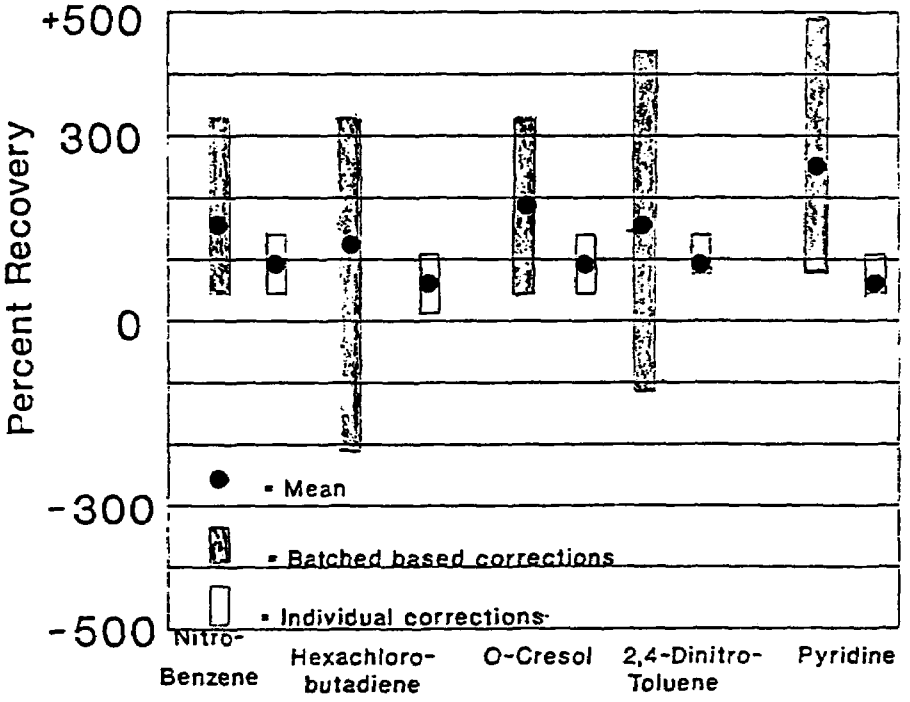

Table 1 CASE C ORGANIC VOLATILES by COMPOUND CLASS

SATURATED CHLOROCARBONS									
COMPOUND 200PPB IN DIH20	Mean	STD	CI	LCI	UCI	Mean%Re	%RSD	CH ACC	REL%UNC
CHLOROMETHANE	160	25.37059	35.54375	124.4562	195.5438	80	15.85662	11.85889	25.75486
CORRECTED RECOVERY	183.7178	31.90475	44.69799	139.0198	228.4158	91.85889	17.36617	-7.43032	-53.2495
CHLOROETHANE	168.8571	14.91564	20.89655	147.9606	189.7537	84.42857	8.833287	12.04631	-23.8756
CORRECTED RECOVERY	192.9498	11.35443	15.90736	177.0424	208.8571	96.47489	5.884657	-7.33203	132.1096
METHYLENE CHLORIDE	178.2857	26.35472	36.92251	141.3632	215.2082	89.14286	14.7823	8.595805	21.84452
CORRECTED RECOVERY	204.5227	32.11179	44.98805	159.5346	249.5107	102.2613	15.70084	-13.5244	-52.5379
1,1-DICHLOROETHANE	168.4286	15.24092	21.35227	147.0763	189.7808	84.21429	9.048894	12.2068	15.54175
CORRECTED RECOVERY	192.8422	17.60963	24.67078	168.1714	217.513	96.42109	9.131627	-15.4571	-20.1704
CHLOROFORM	165.5714	14.0577	19.6946	145.8768	185.266	80.96402	8.490417	13.54218	-70.0991
CORRECTED RECOVERY	189.0124	4.203377	5.888858	183.1236	194.9013	94.5062	2.223863	-30.8633	175.2959
CARBON TETRACHLORIDE	127.2857	11.57172	16.21178	111.0739	143.4975	63.64286	9.09114	9.076084	-29.8286
CORRECTED RECOVERY	145.4379	8.120035	11.37603	134.0619	156.8139	72.71894	5.583164	23.71317	281.4405
1,2-DICHLOROETHANE	209	30.97311	43.39278	165.6072	252.3928	103.5679	14.81967	-15.6283	-19.6459
CORRECTED RECOVERY	238.3924	24.88816	34.86788	203.5245	273.2602	119.1962	10.44	4.624747	-61.6409
1,2-DICHLOROPROPANE	170.8571	9.546877	13.37501	157.4821	184.2322	85.42857	5.587637	12.36843	8.453149
CORRECTED RECOVERY	195.594	10.35389	14.50562	181.0884	210.0996	97.797	5.293561	-20.8684	116.3545
1,1,2-TRICHLOROETHANE	153.8571	22.40111	31.38356	122.4736	185.2407	76.92857	14.55968	10.55197	-44.6627
CORRECTED RECOVERY	174.9611	12.39616	17.3668	157.5943	192.3279	87.48054	7.085093	-14.2663	-61.6337
1,1,2,2-TETRACHLOROETHANE	146.4286	4.755949	6.663001	139.7656	153.0916	73.21429	3.247965	11.03354	311.4857
CORRECTED RECOVERY	168.4957	19.57005	27.4173	141.0784	195.9129	84.24783	11.61457	-3.6764	-15.3949
1,1,1-TRICHLOROETHANE	161.1429	16.55726	23.19643	137.9464	184.3393	80.57143	10.2749	12.11037	68.79756
CORRECTED RECOVERY	185.3636	27.94825	39.15501	146.2086	224.5186	92.6818	15.07753	-5.03894	-44.8891
CHLOROFORM-13C	175.2857	15.40254	21.57868	153.707	196.8644	87.64286	8.787102	-87.6429	-100
UNSATURATED CHLOROCARBONS									
VINYL CHLORIDE	149.2857	20.5322	28.76526	120.5205	178.051	74.64286	13.75363	11.69287	-58.0827
CORRECTED RECOVERY	172.6715	8.606541	12.05761	160.6138	184.7291	86.33573	4.984345	-6.2706	28.83677
CIS-1,2-DICHLOROETHENE	161.5714	11.08839	15.53464	146.0368	177.1061	80.06513	6.862841	14.1719	63.74059
CORRECTED RECOVERY	188.4741	18.15619	25.43651	163.0376	213.9106	94.23703	9.633259	-23.8799	-27.2979
TRANS-1,2-DICHLOROETHENE	140.7143	13.19993	18.49287	122.2214	159.2072	70.35714	9.380659	12.39876	117.8068
CORRECTED RECOVERY	165.5118	28.75034	40.27872	125.2331	205.7905	82.7559	17.37056	-11.9702	-71.8245
TRICHLOROETHENE	141.5714	8.100558	11.34874	130.2227	152.9202	70.78571	5.721888	11.71105	53.97156
CORRECTED RECOVERY	164.9935	12.47256	17.47383	147.5197	182.4674	82.49677	7.559421	16.07466	90.48787
CIS-1,3-DICHLOROPROPENE	202.8571	23.75871	33.28554	169.5716	236.1427	101.4286	11.71204	-16.7135	22.66144
CORRECTED RECOVERY	236.2842	29.14277	40.82852	195.4557	277.1127	118.1421	12.33378	-23.3579	-69.4369
1,1-DICHLOROETHENE	117	8.906926	12.47845	104.5216	129.4784	58.5	7.612757	9.946844	101.749
CORRECTED RECOVERY	136.8937	17.96964	25.17515	111.7185	162.0688	68.44684	13.12671	-39.6754	-46.5632
TRANS-1,3-DICHLOROPROPENE	57.54286	9.602405	13.4528	44.09005	70.99566	28.77143	16.6874	4.729886	17.94579
CORRECTED RECOVERY	67.00263	11.32563	15.86702	51.13561	82.86965	33.50132	16.90327	15.0344	140.8324
TETRACHLOROETHENE	97.07143	27.2758	38.21292	58.85851	135.2843	48.53571	28.09869	7.431575	2.208025
CORRECTED RECOVERY	111.9346	27.87805	39.05667	72.87791	150.9912	55.96729	24.90567	37.03271	-32.51
CHLOROBENZENE	214	18.81489	26.35933	187.6407	240.3593	107	8.792004	-18.3474	93.61075
CORRECTED RECOVERY	250.6949	36.42765	51.0345	199.6604	301.7294	125.3474	14.53067	11.77602	-40.4139
1,1-DICHLOROETHENE-D2	172.8571	21.70583	30.40948	142.4477	203.2666	86.42857	12.55709	-86.4286	-100

Table 1 (Cont.)

AROMATICS									
BENZENE	1600	74.16198	103.8997	1496.1	1703.9	88.88889	4.635124	8.34939	15.60694
CORRECTED RECOVERY	1849.711	85.7364	120.1152	1729.596	1969.826	102.7617	4.635124	−50.1864	−87.8242
TOLUENE	101.9143	10.4391	14.62499	87.28929	116.5393	47.05184	10.24302	11.85815	15.60694
CORRECTED RECOVERY	117.82	12.06832	16.90751	100.9125	134.7275	58.90999	10.24302	−1.78239	55.90311
CHLOROBENZENE	214	18.81489	26.35933	187.6407	240.3593	57.1276	8.792004	19.17298	15.60694
CORRECTED RECOVERY	247.3988	21.75132	30.47321	216.9256	277.8721	123.6994	8.792004	−24.717	−65.9896
ORTHO XYLENE	109.3571	7.397715	10.36407	98.99307	119.7212	51.58356	6.76473	11.62866	15.60694
CORRECTED RECOVERY	126.4244	8.552272	11.98158	114.4429	138.406	63.21222	6.76473	−12.9701	13.33718
ETHYL BENZENE	118.5714	9.692904	13.57959	104.9918	132.151	50.24213	8.174738	23.74426	98.42748
CORRECTED RECOVERY	147.9728	19.23338	26.94564	121.0271	174.9184	73.98639	12.99792	−16.4203	−85.0339
STYRENE	116.5714	2.878492	4.032717	112.5387	120.6041	57.56614	2.469294	15.29352	521.9419
CORRECTED RECOVERY	145.7193	17.90254	25.08115	120.6382	170.8005	72.85965	12.28564	6.240875	−30.3506
(M+P)−XYLENE	170.8571	12.46901	17.46887	153.3883	188.326	79.10053	7.297915	14.44745	91.47209
CORRECTED RECOVERY	212.904	23.87467	33.448	179.456	246.352	106.452	11.21382	−12.4766	−12.0929
BENZENE−D6	162.1429	20.98752	29.40316	132.7397	191.546	81.07143	12.94385	−81.0714	−100
BROMOFORMS									
BROMOMETHANE	167.5714	12.35391	17.30761	150.2638	184.879	83.78571	7.372324	10.35554	12.35955
CORRECTED RECOVERY	188.2825	13.8808	19.44675	168.8358	207.7293	94.14125	7.372324	−19.7127	46.01783
BROMODICHLOROMETHANE	148.8571	20.26844	28.39573	120.4614	177.2529	74.42857	13.61603	9.199037	12.35955
CORRECTED RECOVERY	167.2552	22.77352	31.90531	135.3499	199.1605	83.62761	13.61603	−28.1133	37.06562
DIBROMOCHLOROMETHANE	111.0286	31.21467	43.73121	67.29736	154.7598	55.51429	28.11409	6.861316	12.35955
CORRECTED RECOVERY	124.7512	35.07266	49.13619	75.61501	173.8874	62.3756	28.11409	2.174663	−82.2813
BROMOFORM	139.4286	6.214423	8.706298	130.7223	148.1349	64.55026	4.457065	13.78039	12.35955
CORRECTED RECOVERY	156.6613	6.982497	9.782357	146.879	166.4437	78.33066	4.457065	5.455056	85.04849
BROMOFORM−13C	167.5714	12.92101	18.1021	149.4693	185.6735	83.78571	7.710745	−83.7857	−100
GASES									
CHLOROMETHANE	160	25.37059	35.54375	124.4562	195.5438	80	15.85662	8.888889	38.88889
CORRECTED RECOVERY	222.2222	35.23693	49.36632	172.8559	271.5885	111.1111	15.85662	−14.246	−41.731
VINYL CHLORIDE	149.2857	20.5322	28.76526	120.5205	178.051	74.64286	13.75363	21.68651	38.88889
CORRECTED RECOVERY	207.3413	28.51695	39.95175	167.3895	247.293	103.6706	13.75363	−11.9008	−47.6955
CHLOROETHANE	168.8571	14.91564	20.89655	147.9606	189.7537	84.42857	8.833287	−1.69048	38.88889
CORRECTED RECOVERY	234.5238	20.71616	29.02298	205.5008	263.5468	117.2619	8.833287	1.047619	−40.3658
BROMOMETHANE	167.5714	12.35391	17.30761	150.2638	184.879	83.78571	7.372324	−0.15476	38.88889
CORRECTED RECOVERY	232.7381	17.15821	24.03835	208.6997	256.7764	116.369	7.372324	−3.05952	−9.99832
VINYLCHLORIDE−D3	161.1429	15.44267	21.63492	139.5079	182.7778	80.57143	9.58322	−80.5714	−100

TABLE 2

SUMMARY OF RESULTS FOR CASE A IN TABLE 1

Compound	% Uncertainty	Change In Accuracy	
vinyl chloride	+68.70	+14.3	
1,1-dichloroethene	+ 1.37	+23.6	
chloroform	+75.53	+20.1	
1,2-dichloroethane	-15.41	+ 0.86	* corrected value >100%
carbon tetrachloride	+11.84	+11.61	
trichloroethane	-41.73	+ 6.34	
benzene	+245.2	+ 8.89	* corrected value >100%
tetrachloroethene	+59.89	- 0.77	
chlorobenzene	-49.46	-11.41	
hexachloroethane	+58.69	+26.75	
nitrobenzene	- 2.97	+ 2.60	
hexachlorobutadiene	+169.2	+25.96	
hexachlorobenzene	+ 5.99	+ 0.38	
o-cresol	- 9.43	+ 9.76	
pentachlorophenol	-55.22	+12.65	
2,4-dinitrophenol	- 6.71	+17.36	
pyridine	-69.50	+34.1	
2,4,6-trichlorophenol	-55.99	- 2.84	
2,4,5-trichlorophenol	+ 7.18	+ 4.14	
m&p cresol	-10.29	-17.00	
MEAN	+19.3	+ 9.36	

Ten parameters, or 50% had an increase in uncertainty that ranged from +1.4% to +245%. Ten parameters, or 50% had a decrease in uncertainty that ranged from -2.97% to -69.50%. Sixteen parameters, or 80% had an increase in accuracy that ranged from +0.86 to +34.1%. Two corrected values had increases in accuracy that exceeded the maximum, or true value. Four parameters experienced a decrease in accuracy with a range of -0.77% to -17%.

Overall the uncertainty increased by an average of 19% with only a marginal improvement in accuracy of 9.36%.

TABLE 3

SPIKE RECOVERY RESULTS FOR OTHER NINE SAMPLES
ANALYZED IN SAME BATCH WITH THE SRM (Case B)

	65984	66092	65058	65560	65068	65781	64697	65238	62836
vinyl chloride	95	85	85	85	95	85	130	95	120
1,1-dichloro ethene	105	95	80	75	95	100	135	105	120
chloroform	100	90	85	85	105	115	130	107	110
1,2-dichloro ethane	95	84	75	80	110	135	105	120	97
carbon tetrachloride	80	80	85	85	105	95	135	125	110
trichloroethene	95	95	90	90	95	105	95	120	100
benzene	100	85	90	95	100	90	110	112	110
tetrachloro- ethene	80	75	85	80	95	95	90	100	95
chlorobenzene	95	85	90	95	100	90	95	110	105
o-cresol	60	60	50	72	62	108	100	58	17
hexachloroethane	77	80	97	97	77	107	130	80	10
(m&p)-cresol	130	130	99	170	130	53	112	110	28
nitrobenzene	75	60	85	215	70	80	95	73	24
hexachloro- butadiene	90	94	138	70	58	106	158	96	10
2,4,6-trichloro- phenol	115	105	175	100	85	100	7	65	0.15
2,4,5-trichloro- phenol	104	100	90	116	88	172	9	60	-
2,4-dinitro- toluene	92	74	118	98	86	90	170	78	26
hexachlorobenzene	86	86	88	20	54	88	112	68	28
pentachlorophenol	114	108	104	61	104	90	8	54	-
pyridine	29	36	28	6	10	25	75	95	14

Table 4 BIAS CORRECTION by COMPOUND CLASS

Nitroaromatics									
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CH ACC	REL%UNC
NITROBENZENE	169.1429	11.90838	16.68501	152.4578	185.8279	83.73409	7.040428	9.086179	-12.9046
Corrected % Recovery	216.5031	10.37165	14.53186	201.9712	231.0349	107.1797	4.790534	-1.46312	67.98963
2,4-DINITROTOLUENE	182.7143	17.4233	24.41205	158.3022	207.1263	91.35714	9.535818	-7.1772	10.32834
Corrected % Recovery	233.9565	19.22264	26.93341	207.0231	260.8899	115.8201	8.216415	-5.96566	-39.7915
NITROBENZENE-D5	156.4286	11.57378	16.2162	140.2124	172.6448	78.21429	7.398783	-78.2143	-100
Acid Coumpounds									
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CH ACC	REL%UNC
4-NITROPHENOL	168	35.8376	50.21259	117.7874	218.2126	84	21.3319	11.24131	10.06863
Corrected % Recovery	190.4826	39.44595	55.26831	135.2143	245.7509	95.24131	20.70843	-41.3127	-48.8688
PENTACHLOROPHENOL	107.8571	20.16919	28.25935	79.59778	136.1165	53.92857	18.69991	7.328386	19.84075
Corrected % Recovery	122.5139	24.17091	33.86822	88.6477	156.3801	61.25696	19.72911	-60.0141	-95.114
O-CRESOL	2.485714	1.181	1.654717	0.830997	4.140432	1.242857	47.51151	0.154002	8.690042
Corrected % Recovery	2.793719	1.28363	1.798513	0.995206	4.592232	1.396859	45.947	87.03171	921.1366
O-CRESOL-D8	176.8571	13.10761	18.36527	158.4919	195.2224	88.42857	7.411413	-88.4286	-100
Nitrosoamines									
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CH ACC	REL%UNC
N-NITROSODI-N-PROPYLAMINE	159.8571	12.07516	16.91869	142.9385	176.7758	79.92857	7.55372	14.29381	-3.45224
Corrected % Recovery	188.4448	11.6583	16.33462	172.1101	204.7794	94.22238	6.186586	3.777619	157.7084
N-NITROSODIMETHYLAMINE	196	30.04441	42.09568	153.9043	238.0957	98	15.32678	-12.9718	-21.2709
Corrected % Recovery	229.9435	23.6537	33.14156	196.802	263.0851	114.9718	10.28674	-0.02824	-40.2117
N-NITROSODIMETHYLAMINE-D6	170	14.14214	19.81476	150.1852	189.8148	85	8.318903	-85	-100
Base Compounds									
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CH ACC	REL%UNC
ANILINE	10328.14	885.0029	1239.991	9088.152	11568.13	106.9387	8.568848	-19.374	41.90038
Corrected % Recovery	12199.28	1255.822	1759.552	10439.73	13958.83	126.3127	10.29423	12.38415	-97.4621
2-NITROANILINE	172.1429	31.87177	44.65601	127.4868	216.7989	86.07143	18.51472	-83.9578	39.84593
Corrected % Recovery	204.1354	44.57137	62.44961	141.6858	266.585	2.11364	21.83422	90.17207	42.69237
PYRIDINE	184.5714	63.59994	89.11083	95.4606	273.6823	92.28571	34.45817	-90.0627	1,283176
Corrected % Recovery	214.7	64.41604	90.25428	124.4457	304.9543	2.223028	30.00281	82.77697	-78.0456
N-NITROSODIMETHYLAMINE-D6	170	14.14214	19.81476	150.1852	189.8148	85	8.318903	-85	-100
PNA									
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CH ACC	REL%UNC
NAPHTHALENE	100.7286	4.606776	6.454622	94.27395	107.1832	38.59332	4.573455	4.769462	-3.93562
Corrected % Recovery	113.1769	4.42547	6.200593	106.9763	119.3775	43.36278	3.910225	-18.2326	-28.2652
ACENAPHTHENE	51.01429	3.174602	4.447982	46.5663	55.46227	25.13019	6.222966	-3.19512	-63.1847
Corrected % Recovery	57.25054	1.168741	1.63754	55.613	58.88808	21.93507	2.041449	37.02726	3723.99
BENZO(A)PYRENE	118.5143	44.69252	62.61936	55.89492	181.1336	58.96233	37.71066	-8.54966	0.689022
Corrected % Recovery	131.5771	45.00046	63.05082	68.52625	194.6279	50.41267	34.20084	38.73019	-73.9989
BENZO(A)PYRENE-D12	176.2857	11.70063	16.39393	161.8918	194.6796	89.14286	6.562854	-89.1429	-100
CHLORINATED HYDROCARBONS									
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CH ACC	REL%UNC
HEXACHLOROBENZENE	136.8714	60.66357	84.99664	51.87479	221.8681	68.43571	44.32157	2.306761	-14.6781
Corrected % Recovery	141.4849	51.75928	72.52071	68.96424	214.0057	70.74247	36.58289	-48.4568	-94.9907
1,2,4-TRICHLOROBENZENE	44.57143	2.592755	3.632749	40.93868	48.20418	22.28571	5.81708	1.429292	62.94392
Corrected % Recovery	47.43001	4.224737	5.919343	41.51067	53.34936	23.71501	8.907308	70.99928	432.2455
HEXACHLOROBENZENE-13C6	189.4286	22.48597	31.50544	157.9231	220.934	94.71429	11.87042	-94.7143	-100
PHTHALATES									
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CH ACC	REL%UNC
DIMETHYLPHTHALATE	0.142857	0.377964	0.529572	-0.38671	0.672429	0.071429	264.5751	0.040179	56.25
Corrected % Recovery	0.223214	0.590569	0.827456	-0.60424	1.05067	0.111607	264.5751	12.38839	1161.617
DI-N-BUTYLPHTHALATE	25	7.450727	10.43933	14.56067	35.43933	12.5	29.80291	6.58916	26.6179
Corrected % Recovery	38.17832	9.433954	13.21805	24.96027	51.39637	19.08916	24.71024	37.79655	278.034
DI-N-OCTYLPHTHALATE	113.7714	35.66355	49.96874	63.80269	163.7402	56.88571	31.34667	30.46519	34.23827
Corrected % Recovery	174.7018	47.87414	67.07717	107.6246	241.779	87.35091	27.40334	-22.1152	-56.8054
DI-N-BUTYLPHTHALATE-D4	130.4714	20.67903	28.9737	101.4977	159.4451	65.23571	15.84947	-65.2357	-100

TABLE 5

SUMMARY OF APPLICATION OF BIAS CORRECTION TO SRM FOLLOWING EPA GUIDELINES ON A BATCH BASIS (from Table 4)

Compound	True Value	Amount Found	% Recovered	Bias Corrected	Change In Accuracy
1,1-dichloroethene	100	67	75	89	+22.0
1,2-dichloroethane	100	93	75	124	-17.0
tetrachloroethene	100	75	75	100	+25
o-cresol	1250	1036	60	1727	-21.0
o-cresol	1250	1036	60	1727	-21.0
o-cresol	1250	1036	50	2072	-48.6
o-cresol	1250	1036	72	1439	+2.4
o-cresol	1250	1036	62	1671	-16.6
o-cresol	1250	1036	58	1786	-25.8
o-cresol	1250	1036	17	6094	-370
hexachloroethane	750	369	77	479	+14.7
hexachloroethane	750	369	77	479	+14.7
hexachloroethane	750	369	10	3690	-341
(m&p) cresol	2500	3595	53	6783	-128
(m&p) cresol	2500	3595	28	12839	-370
nitrobenzene	500	421	75	561	+3.6
nitrobenzene	500	421	60	762	-24.6
nitrobenzene	500	421	70	601	-4.4
nitrobenzene	500	421	73	577	+0.4
nitrobenzene	500	421	24	1754	-235
hexachlorobutadiene	125	33	70	47	+12
hexachlorobutadiene	125	33	58	57	+24
hexachlorobutadiene	125	33	10	330	-90.4
2,4,6-trichlorophenol	500	419	7	5986	-1080
2,4,6-trichlorophenol	500	419	65	645	-12.8
2,4,6-trichlorophenol	500	419	<5	279	-
2,4,5-trichlorophenol	1250	618	9	6867	-399
2,4,5-trichlorophenol	1250	618	60	1030	+33.0
2,4,5-trichlorophenol	1250	618	<5	-	-
2,4-dinitrotoluene	125	100	74	135	+12.0
2,4-dinitrotoluene	125	100	78	128	+17.6
2,4-dinitrotoluene	125	100	26	385	-188
hexachlorobenzene	125	4.4	20	22	+14.1
hexachlorobenzene	125	4.4	54	8.15	+3.0
hexachlorobenzene	125	4.4	68	6.47	+1.7
hexachlorobenzene	125	4.4	28	15.7	+9.0
pentachlorophenol	12500	10350	8	129400	-910
pentachlorophenol	12500	10350	54	19170	-36.2
pentachlorophenol	12500	10350	<5	-	-
pyridine	500	226	29	942	-33.6
pyridine	500	226	36	628	+29.2
pyridine	500	226	28	807	-6.6
pyridine	500	226	6	3767	-599
pyridine	500	226	10	2260	-297
pyridine	500	226	25	904	-26.0
pyridine	500	226	75	301	+15.0
pyridine	500	226	14	1614	-168

The entire set of data had 200 applicable data points. Forty-seven recoveries fit the requirements set by EPA guidelines for accuracy adjustment. Of these 47 bias corrections, 18, or 38%, resulted in an increase in accuracy of the number with respect to the true value averaging 14.8%. Twenty-nine of the bias corrections resulted in recoveries that reduced the accuracy of the data. This represented 62% of the corrected data. In calculating the average change in accuracy, three recoveries below 5% were not included. The overall average reduction in accuracy was 119%.

TABLE 6
SUMMARY OF RESULTS FOR CASE C SEMIVOLATILES

COMPOUND	% UNCERTAINTY	CHANGE IN ACCURACY
nitrobenzene	-12.9	9.09
2,4-DNT	10.33	-7.18
4-nitrophenol	10.07	11.24
pentachloro	19.84	7.33
o-cresol	8.69	0.15
N-nitroso-propyl	-3.45	14.29
N-nitroso dimethylamine	-21.27	-12.97
aniline	41.9	-19.37
2-nitroaniline	22.97	11.83
pyridine	1.17	-0.41
naphthalene	-3.94	4.77
acenapthalene	-6.82	3.67
benzo[o]pyrene	0.69	6.5
hexachloroethane	29.2	1.86
1,2,4-trichlorobenzene	6.46	1.43
hexachlorobenzene	-14.6	2.31
dimethylpthalate	NR	NR
di-N-butylpthalate	26.62	6.59
di-N-octylpthalate	34.24	30.46
MEAN	+13.2	+4.24

Compounds which were connected by its own isotope were not used for averaging purposes (see Table?).

TABLE 7
SUMMARY OF RESULTS FOR CASE C VOLATILES

COMPOUND	% UNCERTAINTY	CHANGE IN ACCURACY
chloromethane	25.75	11.86
chloroethane	-23.88	12.05
methylene chloride	21.84	8.60
1,1-dichloroethane	15.54	12.21
chloroform	-70.10	11.72
carbontetrachloride	-29.83	9.08
1,2-dichloroethane	-19.64	11.7
1,1,2-trichloroethane	-44.66	10.55
1,2-dichloropropane	8.45	12.37
1,1,2,2-tetrachloroethene	311.48	11.03
1,1,1-trichloroethane	68.80	12.11
vinyl chloride	-58.08	11.69
cis-1,2-dichloroethane	63.74	13.45
trans-1,2-dichloroethene	117.81	12.40
trichloroethene	53.97	11.71
cis-1,3-dichloropropane	22.66	-16.71
1,1-dichloroethene	101.75	9.95
trans-1,3-dichloropropane	17.94	4.73
tetrachloroethene	2.21	7.43
chlorobenzene	93.61	-18.35
benzene	15.61	8.1
toluene	15.61	7.38
chlorobenzene	15.61	8.7
ortho-xylene	15.61	8.0
ethylbenzene	98.43	12.45
styrene	523	14.57
(m+p)xylene	91.47	8.12
bromomethane	12.35	10.36
bromodichloromethane	12.36	9.20
dibromochloromethane	12.36	6.86
bromoform	12.36	8.62
MEAN	+55.12	+8.34

Compounds which were connected by its own isotope were not used for averaging purposes (see Table ?).

Figure 1

Schematic Diagram of Case A & Case B

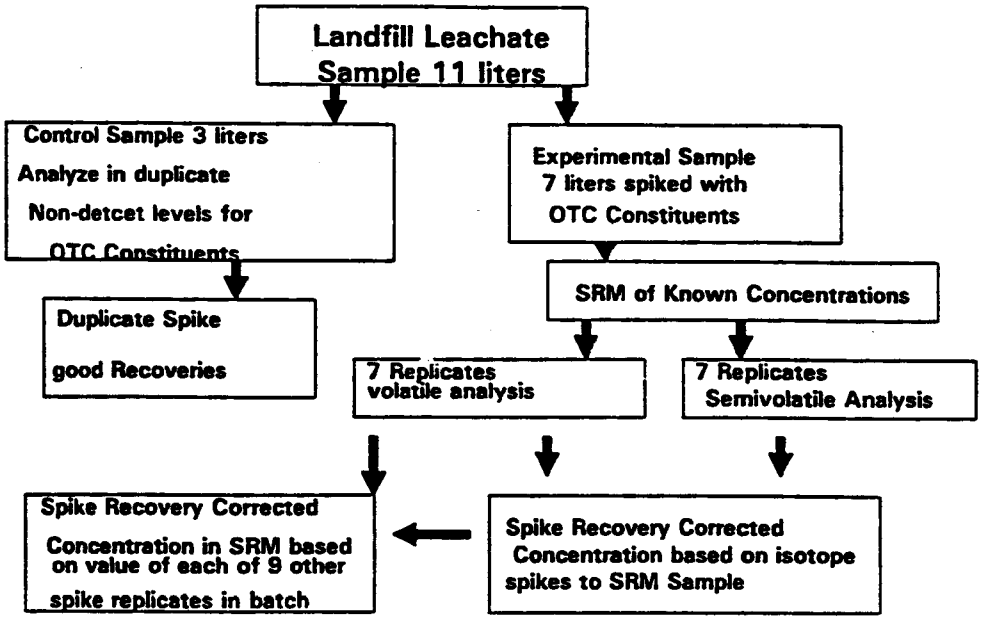

Figure 2

Comparison of Individual vs Batch Based Corrections

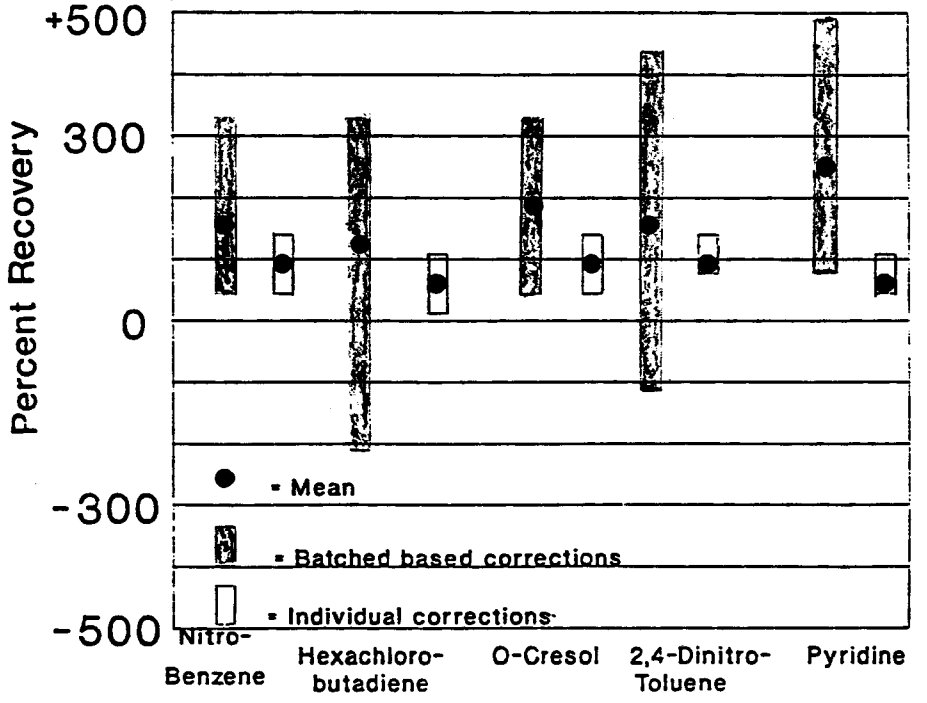

TABLE 1 CASE C ORGANIC VOLATILES BY COMPOUND CLASS

SATURATED CHLOROCARBONS COMPOUND 200PPB IN DI:H2O	Mean	STD	CI	LCI	UCI	Mean%Rec	%RSD	CH ACC	REL%UNC
CHLOROMETHANE	160	25.37059	35.54375	124.4562	195.5438	80	15.85662	11.88889	25.75486
CORRECTED RECOVERY	183.7178	31.90475	44.69799	139.0198	228.4158	91.85889	17.3661	-7.43032	-59.2495
CHLOROETHANE	168.8571	14.91564	20.89655	147.9606	189.7537	84.42857	8.833287	12.04631	23.8756
CORRECTED RECOVERY	192.9498	11.35443	15.90736	177.0424	208.8571	96.47489	5.884657	-7.33203	132.1096
METHYLENE CHLORIDE	178.2857	26.35472	36.92251	141.3632	215.2082	89.14286	14.7823	8.595865	21.84452
CORRECTED RECOVERY	204.5227	32.11179	44.98805	159.5346	249.5107	102.2613	15.70084	-13.5244	-52.5379
1,1-DICHLOROETHANE	168.4286	15.24092	21.35227	147.0763	189.7808	84.21429	9.048894	12.2068	15.54175
CORRECTED RECOVERY	192.8422	17.60963	24.67078	168.1714	217.513	96.42109	9.131627	-15.4571	-20.1704
CHLOROFORM	165.5714	14.0577	19.6946	145.8768	185.266	80.96402	8.490417	13.54218	-70.0991
CORRECTED RECOVERY	189.0124	4.203377	5.888858	183.1236	194.9013	94.5062	2.223663	-30.8633	175.2959
CARBON TETRACHLORIDE	127.2857	11.57172	16.21178	111.0739	143.4975	63.64286	9.09114	9.076084	29.8286
CORRECTED RECOVERY	145.4379	8.120035	11.37603	134.0619	156.8139	72.71894	5.583164	23.71317	281.4405
1,2-DICHLOROETHANE	209	30.97311	43.39278	165.6072	252.3928	104.5679	14.81967	-15.6283	-19.6459
CORRECTED RECOVERY	238.3924	24.86816	34.86788	203.5245	273.2602	119.1962	10.44	4.624747	-61.6409
1,2-DICHLOROPROPANE	170.8571	9.546877	13.37601	157.4821	184.2322	85.42857	5.587697	12.30643	8.453149
CORRECTED RECOVERY	195.594	10.35389	14.50562	181.0884	210.0996	97.797	5.293561	-20.8684	116.3545
1,1,2-TRICHLOROETHANE	153.8571	22.40111	31.38356	122.4736	185.2407	76.92857	14.55908	10.55197	-44.0627
CORRECTED RECOVERY	174.9611	12.39616	17.3668	157.5943	192.3279	87.48054	7.085093	-14.2663	-61.6937
1,1,2,2-TETRACHLOROETHANE	146.4286	4.755949	6.663001	139.7656	153.0916	73.21429	3.247965	11.03354	311.4857
CORRECTED RECOVERY	168.4957	19.57005	27.4173	141.0784	195.9129	84.24783	11.61457	-3.67.3	-15.3949
1,1,1-TRICHLOROETHANE	161.1429	16.55726	23.19643	137.9464	184.3393	80.57143	10.2749	12.11037	68.79756
CORRECTED RECOVERY	185.3636	27.94825	39.15501	146.2086	224.5186	92.6818	15.07753	-5.03894	-44.8891
CHLOROFORM-13C	175.2857	15.40254	21.57868	153.707	196.8644	87.64286	8.787102	-87.642	-100
UNSATURATED CHLOROCARBONS	0	0	0	0	0	0	ERR	74.64286	ERR
VINYL CHLORIDE	149.2857	20.5322	28.76526	120.5205	178.051	74.64286	13.75303	11.69287	-58.0827
CORRECTED RECOVERY	172.6715	8.606541	12.05761	160.6138	184.7291	86.33573	4.984345	-6.2706	28.93677
CIS-1,2-DICHLOROETHENE	161.5714	11.08839	15.53464	146.0368	177.1061	80.78513	6.862841	14.1719	63.74059
CORRECTED RECOVERY	188.4741	18.15619	25.43651	163.0376	213.9106	94.23703	9.633259	-23.8799	-27.2979
TRANS-1,2-DICHLOROETHENE	140.7143	13.19993	18.49287	122.2214	159.2072	70.35714	9.380659	12.39876	117.8068
CORRECTED RECOVERY	165.5118	28.75034	40.27872	125.2331	205.7905	82.7559	17.37056	-11.9702	-71.0245
TRICHLOROETHENE	141.5714	8.100558	11.34874	130.2227	152.9202	70.78571	5.721888	11.71105	53.97156
CORRECTED RECOVERY	164.9935	12.47256	17.47383	147.5197	182.4674	82.49677	7.559421	16.07466	90.48767
CIS-1,3-DICHLOROPROPENE	202.8571	23.75871	33.28554	169.5716	236.1427	101.4286	11.71204	-16.7135	22.66144
CORRECTED RECOVERY	236.2842	29.14277	40.82852	195.4557	277.1127	118.1421	12.33378	-23.3579	-69.4369
1,1-DICHLOROETHENE	117	8.906926	12.47845	104.5216	129.4784	58.5	7.612757	9.946844	101.749
CORRECTED RECOVERY	136.8937	17.96964	25.17515	111.7185	162.0688	68.44684	13.12671	-39.6754	-46.5632
TRANS-1,3-DICHLOROPROPENE	57.54286	9.602405	13.4528	44.09005	70.99566	28.77143	16.6874	4.729086	17.94579
CORRECTED RECOVERY	67.00263	11.32663	15.86702	51.13561	82.86965	33.50132	16.90327	15.0344	140.8924
TETRACHLOROETHENE	97.07143	27.2758	38.21292	58.85851	135.2843	48.53571	28.09869	7.431575	2.208025
CORRECTED RECOVERY	111.9346	27.87805	39.05667	72.87791	150.9912	55.96729	24.90567	37.03271	-32.51
CHLOROBENZENE	214	18.81489	26.35933	187.6407	240.3593	107	8.792004	-18.3474	93.61075
CORRECTED RECOVERY	250.6949	36.42765	51.0345	199.6604	301.7294	125.3474	14.53067	11.77602	-40.4139
1,1-DICHLOROETHENE-D2	172.8571	21.70583	30.40948	142.4477	203.2666	86.42857	12.55709	-86.4286	-100

TABLE 1 (continued)

AROMATICS	0	0	0	0	0	0	ERR	88.88889	ERR
BENZENE	1600	74.16198	103.8997	1496.1	1703.9	88.88889	4.635124	8.34939	15.60694
CORRECTED RECOVERY	1849.711	85.7364	120.1152	1729.596	1969.826	102.7617	4.635124	-80.1864	-87.8242
TOLUENE	101.9143	10.4391	14.62499	87.28929	116.5393	47.05184	10.24302	11.85815	15.60694
CORRECTED RECOVERY	117.82	12.06832	16.90751	100.9125	134.7275	58.90999	10.24302	-1.78239	55.90311
CHLOROBENZENE	214	18.81489	26.35933	187.6407	240.3593	57.1276	8.792004	19.17298	15.60694
CORRECTED RECOVERY	247.3988	21.75132	30.47321	216.9256	277.8721	123.6994	8.792004	-24.7.7	-65.9896
ORTHO XYLENE	109.3571	7.397715	10.36407	98.99307	119.7212	51.58356	6.76473	11.6[illegible]	15.60694
CORRECTED RECOVERY	126.4244	8.552272	11.98158	114.4429	138.406	63.21222	6.76473	-12.[illegible]701	13.33718
ETHYL BENZENE	118.5714	9.692904	13.57659	104.9918	132.151	50.24213	8.174738	23.74426	90.42748
CORRECTED RECOVERY	147.9728	19.23338	26.94564	121.0271	174.9184	73.98639	12.99792	-16.4203	-85.0339
STYRENE	116.5714	2.878492	4.032717	112.5387	120.6041	57.56614	2.469294	15.29352	521.9419
CORRECTED RECOVERY	145.7193	17.90254	25.08115	120.6382	170.8005	72.85965	12.28564	6.240875	-30.3506
(M+P)-XYLENE	170.8571	12.46901	17.46887	153.3883	188.326	79.10053	7.297915	14.44745	91.47209
CORRECTED RECOVERY	212.904	23.87467	33.448	179.456	246.352	106.452	11.21382	-12.4766	-12.0929
BENZENE-D6	162.1429	20.98752	29.40316	132.7397	191.546	81.07143	12.94385	-81.0714	-100
BROMOFORMS	0	0	0	0	0	0	ERR	83.78571	ERR
BROMOMETHANE	167.5714	12.35391	17.30761	150.2638	184.879	83.78571	7.372324	10.35554	12.35955
CORRECTED RECOVERY	188.2825	13.8808	19.44676	168.8358	207.7293	94.14125	7.372324	-19.7127	46.01783
BROMODICHLOROMETHANE	148.8571	20.26844	28.39573	120.4614	177.2529	74.42857	13.61603	9.199037	12.3595
CORRECTED RECOVERY	167.2552	22.77352	31.90531	135.3499	199.1605	83.62761	13.61603	-28.1133	37.06562
DIBROMOCHLOROMETHANE	111.0286	31.21467	43.73121	67.29736	154.7598	55.51429	28.11409	6.861316	12.35955
CORRECTED RECOVERY	124.7512	35.07266	49.13619	75.61501	173.8874	62.3756	28.11409	2.174663	-82.2813
BROMOFORM	139.4286	8.214423	8.706298	130.7223	148.1349	64.55026	4.457065	13.78039	12.35955
CORRECTED RECOVERY	156.6613	6.982497	9.782357	146.879	166.4437	78.33006	4.457065	5.455056	85.04849
BROMOFORM-13C	167.5714	12.92101	16.1021	149.4693	185.6735	83.78571	7.710745	-83.7857	-100
GASES	0	0	0	0	0	0	ERR	80	ERR
CHLOROMETHANE	160	25.37059	35.54375	124.4562	195.5438	80	15.85662	8.888889	38.88889
CORRECTED RECOVERY	222.2222	35.23693	49.36632	172.8559	271.5885	111.1111	15.85662	-14.246	-41.731
VINYL CHLORIDE	149.2857	20.5322	28.76526	120.5205	178.051	74.64286	13.75363	21.68651	38.88889
CORRECTED RECOVERY	207.3413	28.51695	39.95175	167.3895	247.293	103.6706	13.75363	-11.9008	-47.6955
CHLOROETHANE	168.8571	14.91564	20.89655	147.9606	189.7537	84.42857	8.833287	-1.69048	38.88889
CORRECTED RECOVERY	234.5238	20.71616	29.02298	205.5008	263.5468	117.2619	8.833287	1.047619	-40.3658
BROMOMETHANE	167.5714	12.35391	17.30761	150.2638	184.879	83.78571	7.372324	-0.15476	38.88889
CORRECTED RECOVERY	232.7381	17.15821	24.03835	208.6997	256.7764	116.369	7.372324	-3.05952	-9.99832
VINYLCHLORIDE-D3	161.1429	15.44267	21.63492	139.5079	182.7778	80.57143	9.58322	-80.5714	-100

TABLE 2

SUMMARY OF RESULTS FOR CASE A IN TABLE 1

Compound	% Uncertainty	Change In Accuracy	
vinyl chloride	+68.70	+14.3	
1,1-dichloroethene	+ 1.37	+23.6	
chloroform	+75.53	+20.1	
1,2-dichloroethane	-15.41	+ 0.86	* corrected value >100%
carbon tetrachloride	+11.84	+11.61	
trichloroethane	-41.73	+ 6.34	
ber zene	+245.2	+ 8.89	* corrected value >100%
tetrachloroethene	+59.89	- 0.77	
chlorobenzene	-49.46	-11.41	
hexachloroethane	+58.69	+26.75	
nitrobenzene	- 2.97	+ 2.60	
hexachlorobutadiene	+169.2	+25.96	
hexachlorobenzene	+ 5.99	+ 0.38	
o-cresol	- 9.43	+ 9.76	
pentachlorophenol	-55.22	+12.65	
2,4-dinitrophenol	- 6.71	+17.36	
pyridine	-69.50	+34.1	
2,4,6-trichlorophenol	-55.99	- 2.84	
2,4,5-trichlorophenol	+ 7.18	+ 4.14	
m&p cresol	-10.29	-17.00	
MEAN	+19.3	+ 9.36	

Ten parameters, or 50% had an increase in uncertainty that ranged from +1.4% to +245%. Ten parameters, or 50% had a decrease in uncertainty that ranged from -2.97% to -69.50%. Sixteen parameters, or 80% had an increase in accuracy that ranged from +0.86 to +34.1%. Two corrected values had increases in accuracy b... exceeded the maximum, or true value. Four parameters experienced a decrease in accuracy with a range of -0.77% to -17%.

Overall the uncertainty increased by an average of 19% with only a margin... improvement in accuracy of 9.36%.

TABLE 3

SPIKE RECOVERY RESULTS FOR OTHER NINE SAMPLES ANALYZED IN SAME BATCH WITH THE SRM (Case B)

	65984	66092	65058	65560	65068	65781	64697	65238	62836
vinyl chloride	95	85	85	85	95	85	130	95	120
1,1-dichloro ethene	105	95	80	75	95	100	135	105	120
chloroform	100	90	85	85	105	115	130	107	110
1,2-dichloro ethane	95	84	75	80	110	135	105	120	97
carbon tetrachloride	80	80	85	85	105	95	135	125	110
trichloroethene	95	95	90	90	95	105	95	120	100
benzene	100	85	90	95	100	90	110	112	110
tetrachloro-ethene	80	75	85	80	95	95	90	100	95
chlorobenzene	95	85	90	95	100	90	95	110	105
o-cresol	60	60	50	72	62	108	100	58	17
hexachloroethane	77	80	97	97	77	107	130	80	10
(m&p)-cresol	130	130	99	170	130	53	112	110	28
nitrobenzene	75	60	85	215	70	80	95	73	24
hexachloro-butadiene	90	94	138	70	58	106	158	96	10
2,4,6-trichloro-phenol	115	105	175	100	85	100	7	65	0.15
2,4,5-trichloro-phenol	104	100	90	116	88	172	9	60	-
2,4-dinitro-toluene	92	74	118	98	86	90	170	78	26
hexachlorobenzene	86	86	88	20	54	88	112	68	28
pentachlorophenol	114	108	104	61	104	90	8	54	-
pyridine	29	36	28	6	10	25	75	95	14

TABLE 4 CASE C SEMIVOLATILES BY COMPOUND CLASS

BIAS CORRECTION BY COMPOUND CLASS

Nitroaromatics										
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	CII ACC	HEL%UNC	
NITROBENZENE	169 1429	11 90838	16 68501	152 4578	185 8279	83 73409	7 040128	9 086179	-12 9016	
Corrected % Recovery	216 5031	10 37165	14 53188	201 9712	231 0349	107 1797	4 790534	-1 46312	67 9071	
2 4 - DINITROTOLUENE	182 7143	17 4233	24 41205	158 3022	207 1263	91 35716	9 535818	-7 1772	10 32834	
Corrected % Recovery	233 9545	19 22284	26 93341	207 0231	260 8899	115 4201	8 216415	-5 96546	-39 7915	
NITROBENZENE - D5	156 4286	11 57378	16 2162	140 2124	172 6448	78 21429	7 398763	-78 2143	-100	
Acid Coumpounds										
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	84	ERR	
4 - NITROPHENOL	168	35 6376	50 21259	117 7874	218 2126	84	21 33319	11 24131	10 00893	
Corrected % Recovery	190 4826	39 44595	55 26831	135 2143	245 7509	95 24131	20 70843	-41 3127	-46 8688	
PENTACHLOROPHENOL	107 8571	20 16019	28 25035	79 59779	136 1165	53 92857	18 69991	7 328386	19 84075	
Corrected % Recovery	122 5139	24 17091	33 86622	88 6477	156 3801	61 25696	19 72911	-60 0141	-95 114	
O CRESOL	2 485714	1 181	1 654717	0 830997	4 140432	1 242857	47 51151	0 154002	8 690942	
Corrected % Recovery	2 793719	1 28063	1 798513	0 995206	4 592232	1 396859	45 947	87 03171	921 1366	
O - CRESOL - D8	176 8571	13 10781	18 36527	158 4919	195 2224	88 42857	7 411419	-88 4286	-100	
Nitrosoamines										
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	79 92857	ERR	
N NITROSODI - N - PROPYLAMINE	159 6571	12 07516	16 91869	142 9385	176 7758	79 92857	7 55372	14 29181	-3 45224	
Corrected % Recovery	188 4448	11 6583	16 33462	172 1101	204 7794	94 22238	6 186586	3 777619	157 7084	
N - NITROSODIMETHYLAMINE	196	30 04441	42 09568	153 9043	238 0957	98	15 32878	-12 9718	-21 2709	
Corrected % Recovery	229 9435	23 6537	33 14156	196 802	263 0851	114 9718	10 28674	-0 02624	-40 2117	
N - NITROSODIMETHYLAMINE - D6	170	14 14214	19 81476	150 1852	189 8148	85	8 318903	-85	-100	
Base Compounds										
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	93 06127	ERR	
ANILINE	10328 14	885 0029	1239 991	9088 152	11568 13	106 9387	8 568848	-19 374	41 90038	
Corrected % Recovery	12199 28	1255 822	1758 552	10439 73	13958 83	126 3127	10 29423	12 38415	-97 4021	
2 - NITROANILINE	172 1429	31 87177	44 65601	127 4868	216 7989	86 07143	18 51472	-83 9578	39 84593	
Corrected % Recovery	204 1354	44 57137	62 44961	141 6858	266 585	2 11364	21 83422	90 17207	42 69237	
PYRIDINE	184 5714	63 52694	89 11083	95 4606	273 6823	92 28571	34 45817	-90 0627	1 283176	
Corrected % Recovery	2147	64 41604	90 25428	124 4457	304 9543	2 223028	30 00281	82 77697	-78 0456	
N - NITROSODIMETHYLAMINE - D6	170	14 14214	19 81476	150 1852	189 8148	85	8 318903	-85	-100	
PNA										
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	38 59332	ERR	
NAPHTHALENE	100 7286	4 606776	6 454622	94 27395	107 1832	38 58332	4 573455	4 769462	-3 93562	
Corrected % Recovery	113 1769	4 42547	6 206093	106 9763	119 3775	43 36278	3 910225	-18 2346	-28 2652	
ACENAPHTHENE	51 01429	3 174602	4 447982	46 5663	55 46227	25 13019	6 222966	-3 19512	-63 1847	
Corrected % Recovery	57 25054	1 168741	1 63754	55 613	58 88808	21 93507	2 041449	37 02726	3723 99	
BENZO(A)PYRENE	118 5143	44 69252	62 61936	55 89192	181 1366	58 90233	37 71066	-8 54966	0 685022	
Corrected % Recovery	131 5771	45 00046	63 05132	68 52625	194 6279	50 41267	34 20084	38 73019	-73 9969	
BENZO(A)PYRENE D12	178 2857	11 70063	16 39193	161 8938	194 6796	89 14288	6 562954	-89 1429	-100	
CHLORINATED HYDROCARBONS										
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCL	UCL	MEAN %RE	%RSD	68 43571	ERR	
HEXACHLOROBENZENE	136 8714	60 66357	84 99064	51 87479	221 8681	68 43571	44 32157	2 306781	-14 6781	
Corrected % Recovery	141 4849	51 75928	72 52071	68 96124	214 0057	70 74247	36 58289	-48 4588	-94 9507	
1 2 4 - TRICHLOROBENZENE	44 57143	2 592755	3 632749	40 93868	48 20418	22 28571	5 81708	1 429792	62 91392	
Corrected % Recovery	47 43001	4 224737	5 919343	41 51067	53 34936	23 71501	8 907308	70 99028	432 2455	
HEXACHLOROBENZENE - 13C6	169 4286	22 48597	31 50615	157 9231	220 934	84 71429	11 87042	-91 7143	-100	
PHTHALATES										
ANALYTE 200PPB MW MATRIX	Mean	STD	CI	LCI	UCL	MEAN %RE	%RSD	0 071429	ERR	
DIMETHYLPHTHALATE	0 142857	0 377964	0 529572	-0 386715	0 672429	0 071429	264 5751	0 043179	6 25	
Corrected % Recovery	0 223214	0 590569	0 827456	-0 60424	1 050667	0 111607	264 5751	12 38039	1161 617	
DI - N - BUTYLPHTHALATE	25	7 450727	10 43933	14 56067	35 43933	12 5	29 80291	6 588016	2 631579	
Corrected % Recovery	39 17632	9 431954	13 21805	25 95827	51 39437	19 68816	24 71024	37 70655	276 934	
DI - N - OCTYLPHTHALATE	113 7714	35 66155	49 96874	63 80269	163 7402	56 88571	31 34067	30 41519	94 29827	
Corrected % Recovery	178 7018	47 87414	67 07717	107 6246	241 779	89 35091	27 40334	-22 1152	-56 8804	
DI - N - BUTYLPHTHALATE - D4	130 4714	20 67903	28 9737	101 4977	159 4451	65 23571	15 84947	-65 2357	-100	

TABLE 5

SUMMARY OF APPLICATION OF BIAS CORRECTION TO SRM FOLLOWING EPA GUIDELINES ON A BATCH BASIS (from Table 4)

Compound	True Value	Amount Found	% Recovered	Bias Corrected	Change In Accuracy
1,1-dichloroethene	100	67	75	89	+22.0
1,2-dichloroethane	100	93	75	124	-17.0
tetrachloroethene	100	75	75	100	+25
o-cresol	1250	1036	60	1727	-21.0
o-cresol	1250	1036	60	1727	-21.0
o-cresol	1250	1036	50	2072	-48.6
o-cresol	1250	1036	72	1439	+2.4
o-cresol	1250	1036	62	1671	-16.6
o-cresol	1250	1036	58	1786	-25.8
o-cresol	1250	1036	17	6094	-370
hexachloroethane	750	369	77	479	+14.7
hexachloroethane	750	369	77	479	+14.7
hexachloroethane	750	369	10	3690	-341
(m&p) cresol	2500	3595	53	6783	-128
(m&p) cresol	2500	3595	28	12839	-370
nitrobenzene	500	421	75	561	+3.6
nitrobenzene	500	421	60	762	-24.6
nitrobenzene	500	421	70	601	-4.4
nitrobenzene	500	421	73	577	+0.4
nitrobenzene	500	421	24	1754	-235
hexachlorobutadiene	125	33	70	47	+12
hexachlorobutadiene	125	33	58	57	+24
hexachlorobutadiene	125	33	10	330	-90.4
2,4,6-trichlorophenol	500	419	7	5986	-1080
2,4,6-trichlorophenol	500	419	65	645	-12.8
2,4,6-trichlorophenol	500	419	<5	279	-
2,4,5-trichlorophenol	1250	618	9	6867	-399
2,4,5-trichlorophenol	1250	618	60	1030	+33.0
2,4,5-trichlorophenol	1250	618	<5	-	-
2,4-dinitrotoluene	125	100	74	135	+22.0
2,4-dinitrotoluene	125	100	78	128	+17.6
2,4-dinitrotoluene	125	100	26	385	-188
hexachlorobenzene	125	4.4	20	22	+14.1
hexachlorobenzene	125	4.4	54	8.15	+3.0
hexachlorobenzene	125	4.4	68	6.47	+1.7
hexachlorobenzene	125	4.4	28	15.7	+9.0
pentachlorophenol	12500	10350	8	129400	-910
pentachlorophenol	12500	10350	54	19170	-36.2
pentachlorophenol	12500	10350	<5	-	-
pyridine	500	226	29	942	-33.6
pyridine	500	226	36	628	+29.2
pyridine	500	226	28	807	-6.6
pyridine	500	226	6	3767	-599
pyridine	500	226	10	2260	-297
pyridine	500	226	25	904	-26.0
pyridine	500	226	75	301	+15.0
pyridine	500	226	14	1614	-168

The entire set of data had 200 applicable data points. Forty-seven recoveries fit the requirements set by EPA guidelines for accuracy adjustment. Of these 47 bias corrections, 18, or 38%, resulted in an increase in accuracy of the number with respect to the true value averaging 14.8%. Twenty-nine of the bias corrections resulted in recoveries that reduced the accuracy of the data. This represented 62% of the corrected data. In calculating the average change in accuracy, three recoveries below 5% were not included. The overall average reduction in accuracy was 119%.

TABLE 6
SUMMARY OF RESULTS FOR CASE C SEMIVOLATILES

COMPOUND	% UNCERTAINTY	CHANGE IN ACCURACY
nitrobenzene	-12.9	9.09
2,4-DNT	10.33	-7.18
4-nitrophenol	10.07	11.24
pentachloro	19.84	7.33
o-cresol	6.69	0.15
N-nitroso-propyl	-8.45	14.29
N-nitroso dimethylamine	-21.27	-12.97
aniline	41.9	-19.37
2-nitroaniline	22.97	11.83
pyridine	1.17	-0.41
naphthalene	-3.94	4.77
acenapthalene	-6.82	3.67
benzo[a]pyrene	0.69	6.5
hexachloroethane	29.2	1.86
1,2,4-trichlorobenzene	6.46	1.43
hexachlorobenzene	-14.6	2.31
dimethylpthalate	NR	NR
di-N-butylpthalate	26.62	6.59
di-N-octylpthalate	34.24	30.46
MEAN	-15.2	-4.24

Compounds which were connected by its own isotope were not used for averaging purposes (see Table 4).

TABLE 7
SUMMARY OF RESULTS FOR CASE C VOLATILES

COMPOUND	% UNCERTAINTY	CHANGE IN ACCURACY
chloromethane	25.75	11.86
chloroethane	-23.88	12.05
methylene chloride	21.84	8.60
1,1-dichloroethane	15.54	12.21
chloroform	-70.10	11.72
carbontetrachloride	-29.85	9.06
1,2-dichloroethane	-19.64	11.7
1,1,2-trichloroethane	-44.66	10.55
1,2-dichloropropane	8.45	12.37
1,1,2,2-tetrachloroethene	311.48	11.05
1,1,1-trichloroethane	68.80	12.11
vinyl chloride	-58.06	11.69
cis-1,2-dichloroethane	63.74	13.45
trans-1,2-dichloroethene	117.81	12.40
trichloroethene	53.97	11.71
cis-1,3-dichloropropane	22.66	-16.71
1,1-dichloroethene	101.75	9.95
trans-1,3-dichloropropane	17.94	4.75
tetrachloroethene	2.21	7.43
chlorobenzene	93.61	-18.35
benzene	15.61	8.1
toluene	15.61	7.38
chlorobenzene	15.61	8.7
ortho-xylene	15.61	8.0
ethylbenzene	91.43	12.45
styrene	522	14.57
(m-p)xylene	91.47	8.12
bromomethane	12.35	10.36
bromodichloromethane	12.36	9.20
dibromochloromethane	12.36	6.86
bromoform	12.36	8.62
MEAN	-55.12	-8.34

Compounds which were connected by its own isotope were not used for averaging purposes (see Table 1).

18 **Matrix Spiking: From Sampling to Analysis**

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Abstract

Currently there is little knowledge about how much change in analyte concentration occurs during the steps from sampling from the sample source (e.g. a monitor well) to analysis. A series of experiments were performed for metal, volatile, and semivolatile parameters with various stages of handling from the sampling of a simulated monitor well to analysis; percent recoveries were determined, and conclusions drawn.

Introduction

Current EPA methodology using the SW-846[1] procedures requires a matrix spike relatively close to the point of analysis for volatile (VOA) organics, semivolatile (SV) organics, and metals. Specifically, volatile matrix spikes are performed immediately prior to analysis, semivolatile spikes during the extraction step, and the metals spiked prior to digestion. Matrix spikes are performed using analytes listed in the appropriate sections in SW-846; it is assumed that these analytes were chosen by EPA because they felt these were representative of the analytes routinely analyzed.

Currently the purpose of these matrix spikes is to provide QA/QC for the labs performing the analysis by demonstrating that the analyses being performed in the batch associated with the matrix spike are "in control." The results from the matrix spike are compared to the appropriate control charts, and if they fall within an acceptable range the analyses in that batch are deemed within "control." In a similar vein, the organic analyses are tracked with surrogate spiking compounds added during the extraction step. The function of the surrogates is to track "in control" performance on a sample by sample basis.

The advent of spike correction, however, changes the role of the matrix spike. This type of spike correction requires the substitution of the particular analytes of interest versus the standard spike list, and replaces the "in control" aspect of the matrix spike with an adjustment to the data from the associated batch of samples based on percent recoveries of the analytes of interest in the spike. Part of the stated reasons for moving to spike correction is to provide data more representative of what is actually in the sample source (e.g. monitor wells, leachate, etc.).

Regardless of the appropriateness of spike correction as a method, this raises an interesting question: how much does the sample change from the time of sampling to analy-

sis? To examine this question in detail we performed a series of experiments designed to determine change in analyte concentration at each conceivable stopping point from sampling to analysis. This was done by spiking different sets of replicates at the possible locations, letting the sample then proceed through the process as normal, and analyzing the samples. The locations at which it was determined to spike for the organics (see Figure 1) were: 1. Sample Source; 2. Water Sample (post sampling, pre-transportation); 3. Water Sample (post-transportation); 4. Organic Toxicity Characteristic (OTC) Filtered Water Sample; 5. Extract. For the metals all the samples originated from the same source, then underwent different degrees of processing along the metals pathway (see Figure 2) and differences in concentrations determined. The concentrations from the samples were compared to spiked amounts and percent recovery determined. The recovery data from various stages was compared to determine trends in analyte concentration through the sample pathway.

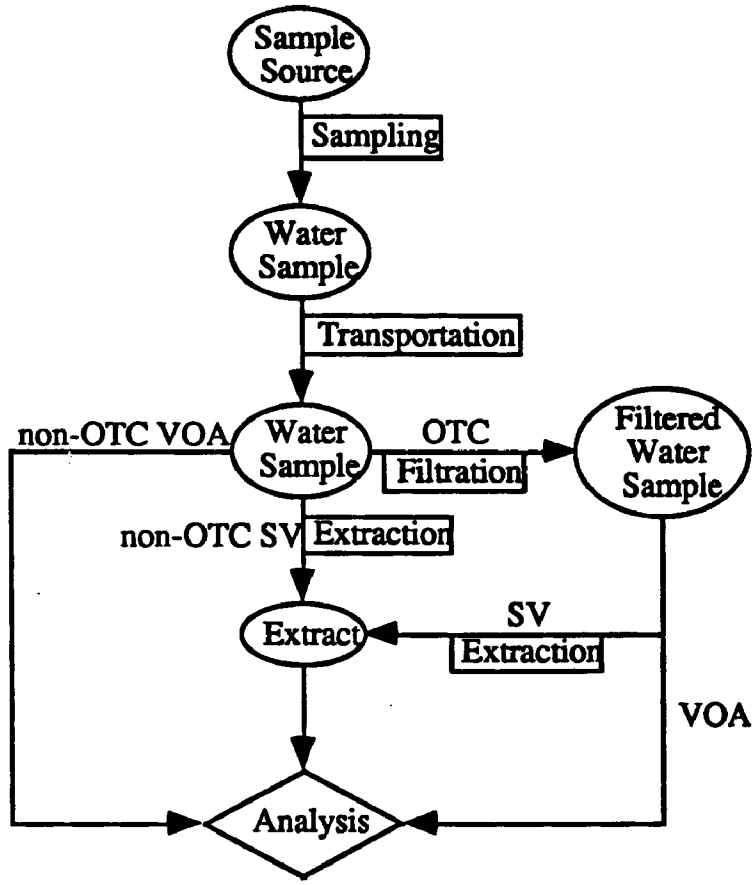

Figure 1: Organic Sample Pathway

Methodology[2]

For the metal constituents a spike was performed in a simulated monitor well which yielded the

Metal	Concentration (ppm)
As	2.51
Ba	2.51
Cd	1.18
Cr	2.51
Pb	1.96
Se	2.51
Ag	1.18
Ca	5.10
Fe	2.51
Mg	5.10
Mn	2.51
Ni	1.96
Zn	1.96

Table 1: Metals Spike Concentrations

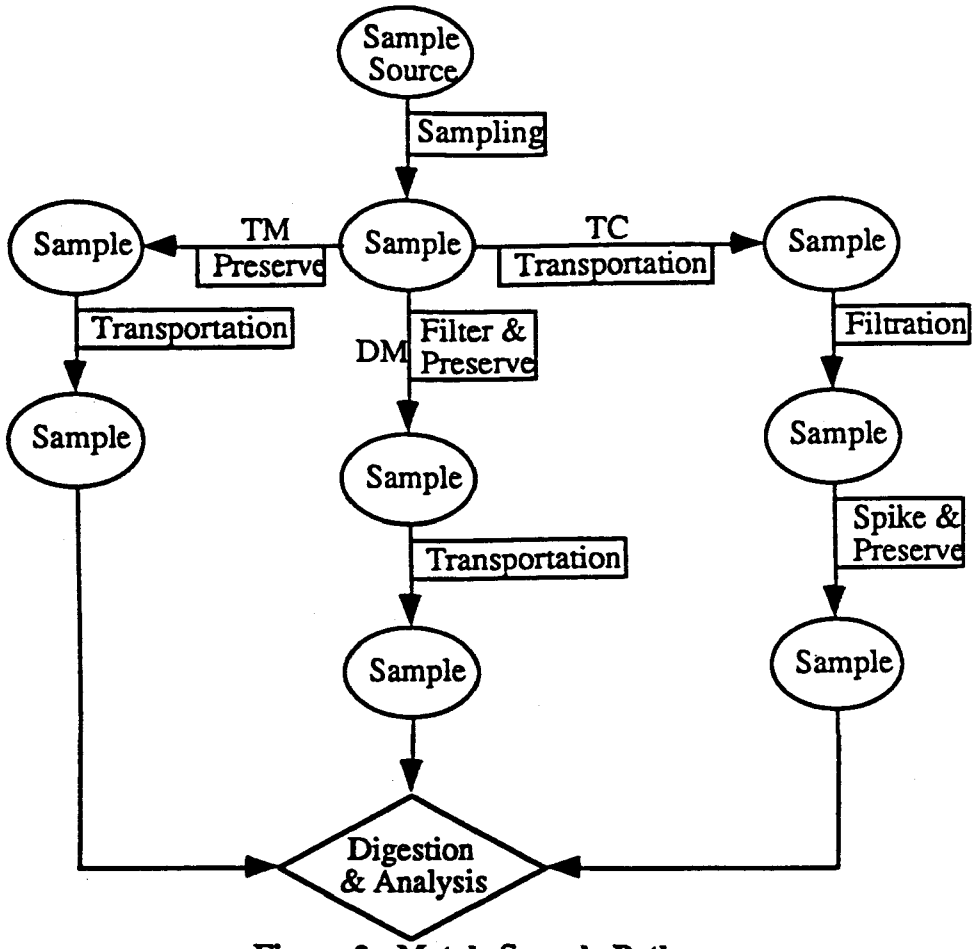

Figure 2: Metals Sample Pathway

concentrations indicated in Table 1. The monitor well was constructed using a five foot section of Corning conical glass pipe with Teflon[3] endcaps, each endcap fitted with a Teflon stopcock. The simulated well was stood vertically in its frame, the bottom sealed with an endcap and partially filled with deionized (d.i.) water. The spiking solutions were added, the remainder filled, and the top capped. The remaining small volume was filled via access from the top stopcock, and a Teflon tubing was used to connect the bottom stopcock to a pump calibrated to deliver one well volume (~12.58 l) in ~5.6 hours, then connected to the top stopcock. The stopcocks were opened, and the simulated well allowed to recirculate for ~23 hours. This allowed a total of approximately four well volumes to be recirculated, and was deemed satisfactory for adequate mixing of the sample.

After stopping the recirculation process the stopcocks were closed, and the teflon tubing removed. One liter of sample was drained from the bottom and analyzed for the complete list, then the top endcap removed and the simulated well sampled. Eight one liter samples were then distributed as follows:

1. One sample was preserved in the manner appropriate for total metals (TM) analysis, then analyzed for Ba, Cd, Ca, Cr, Fe, Mn, Mg, Ni, and Zn.

2. One sample was preserved as above, then shipped overnight and analyzed for Ba, Cd, Ca, Cr, Fe, Mn, Mg, Ni, and Zn.

3. One sample was analyzed immediately after sampling for the complete list.

4. One Sample was field filtered and preserved in the manner appropriate for dissolved metals analysis, then analyzed for Ba, Cd, Ca, Cr, Fe, Mn, Mg, Ni, and Zn.

5. One sample was filtered and preserved as above, then shipped overnight and analyzed for Ba, Cd, Ca, Cr, Fe, Mn, Mg, Ni, and Zn.

6. One sample was shipped and analyzed for As, Ba, Cd, Cr, Pb, Se, and Ag (the TC metals except for Hg).

7. One sample underwent TC (Toxicity Characteristic) filtration, then was preserved and analyzed for As, Ba, Cd, Cr, Pb, Se, and Ag.

8. One sample underwent TC filtration, then was spiked with the appropriate metals, preserved, and analyzed for As, Ba, Cd, Cr, Pb, Se, and Ag.

All analyses were performed in replicates of five, and the results averaged. The averages were compared versus known spike amounts, and percent recovery computed.

For the semivolatile organics an experiment was performed in which the simulated monitor well was spiked as above at a level of 200 ppb with seven sets of compounds deemed to be representative of the priority pollutant analytes. These sets consisted of:

1. Acids: 4-Nitrophenol, pentachlorophenol, o-cresol.

2. Bases: Aniline, 2-nitroaniline, pyridine.

3. Chlorocarbons: Hexachloroethane, 1,2,4-trichlorobenzene, hexachlorobenzene.

4. Nitroaromatics: Nitrobenzene, 2,4-dinitrotoluene.

5. Nitrosamines: N-Nitrosodi-n-propylamine, N-nitrosodimethylamine.

6. Phthalates: Dimethyl phthalate, di-n-butyl phthalate, di-n-octyl phthalate.

7. Polynuclear Aromatics: Naphthalene, acenaphthene, benzo[a]pyrene.

The well was allowed to recirculate ~23 hours, then five one liter samples pulled from the bottom of the well via the stopcock. The top endcap was removed, and five one liter samples taken from the top in the normal sampling method. These samples were then sent through the normal process (see Figure 1) and analyzed.

In addition four other sets of samples were spiked and sent through the remaining steps of the pathway:

1. Five liters spiked at 200 ppb, then shipped overnight and proceeding through extraction to analysis.

2. Five liters spiked at 200 ppb, then proceeding through extraction to analysis.

3. Five liters spiked at 200 ppb, then proceeding through the TC filtration process, extraction, and to analysis.

4. Five vials spiked at 200 ppm (simulating the 1000:1 concentration factor) and analyzed.

During the extraction step a set of isotopically labeled compounds consisting of the following were spiked:

o-cresol-d_8	pyridine-d_5	hexachlorobenzene-$^{13}C_6$
nitrobenzene-d_5	di-n-butyl phthalate-d_4	benzo[a]pyrene-d_{12}
N-nitrosodimethylamine-d_6		

These were considered as surrogates in substitution of the standard surrogates which are listed in SW-846, and used to track the quality of the extraction and analytical stages. Note that since these compounds are representative of the compounds of interest, they may also serve as a matrix spike, and are added at the location stated for such.

As for the metals, percent recoveries were determined for each set of replicates.

The volatile organics were treated essentially the same as the semi-volatile organics, except the exclusion of the extraction step. The analytes of interest were:

1. Saturated Chlorocarbons: Chloromethane, chloroethane, methylene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,2-dichloropropane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and 1,1,1-trichloroethane.

2. Unsaturated Chlorocarbons: Vinyl chloride, 1,1-dichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, trichloroethene, cis-1,3-dichloropropene, trans-1,3-dichloropropene, chlorobenzene, and tetrachlorothene.

3. Bromocarbons: Bromomethane, bromodichloromethane, dibromochloromethane, and bromoform.

4. Aromatics: Benzene, toluene, o-xylene, ethylbenzene, styrene, and m- & p-xylenes.

5. Gases: Chloromethane, vinyl chloride, bromomethane, chloroethane; these are compounds from the above list which may be separated from the above chemical classifications in addition due to their physical properties.

Isotopically labeled surrogate/matrix spike compounds for the volatiles were:

chloroform-^{13}C	1,1-dichloroethene-d_2	vinyl chloride-d_3
bromoform-^{13}C	benzene-d_6	

Following the normal analytical procedures percent recoveries were calculated as before for the metals and semivolatiles.

Results and Discussion

The metals data are summarized in Tables 2 and 3. The data in the tables represent averages of the percent recoveries for all five replicates, except for the TC Spike, which indicates the recovery of the TC analytes spiked at the appropriate location. The %RSD (percent relative standard deviation) indicates that very little, if any, loss occurs in any of the processes; the only exception being a consistently slight loss during the TC filtration stage.

	Bottom/Well	Top/Well	Transport	TC Filter	TC Spike	%RSD
As	100%	100%	101%	94%	94%	3%
Ba	99%	99%	100%	98%	96%	2%
Cd	99%	99%	101%	92%	99%	3%
Cr	99%	99%	100%	94%	98%	2%
Pb	92%	93%	93%	86%	98%	5%
Se	100%	102%	100%	91%	94%	5%
Ag	97%	97%	96%	96%	94%	2%

Table 2: Metal Recoveries for TC Analytes (except Hg)

	Bottom/Well	Top/Well	Filter/ Preserve(DM)	Preserve(TM)	Trans(DM)	Trans(TM)	%RSD
Ba	92%	92%	94%	90%	93%	92%	2%
Cd	86%	88%	87%	86%	90%	88%	2%
Ca	100%	99%	102%	100%	102%	106%	2%
Cr	93%	92%	94%	91%	94%	93%	1%
Fe	98%	97%	97%	93%	101%	98%	2%
Mn	94%	94%	96%	92%	95%	94%	1%
Mg	94%	94%	95%	91%	94%	93%	1%
Ni	92%	92%	92%	90%	93%	92%	1%
Zn	92%	93%	95%	91%	92%	91%	2%

Table 3: Metal Recoveries for Non-TC Analytes

The volatile organic results are summarized in Tables 4 and 5 (see end of paper). Table 4 displays the recovery data for the initial attempt at performing this experiment. The overall trend displays higher recoveries for the samples drawn from the bottom of the well via the stopcock and the samples sampled in the normal manner than those samples which were simply spiked and carried through their respective processes. These results obviously represent aberrant experimental procedure, but where is the question.

The most obvious conclusion is poor spiking methodology. The spiking methods employed in the initial experiment used four spiking solutions, each at 2000 µg/ml. The appropriate amount was then spiked from each individual solution into the simulated well, followed by individual spikes of the appropriate containers of d.i. water.

To determine whether the methodology was at error a second set (three replicates instead of five) of samples was analyzed with new spiking solutions. In this set the steps in which samples were just spiked and run and those that were spiked, filtered, and run were repeated with spikes being performed as previously and also in a composite manner using septum capped vials (Table 5). In addition, a single replicate was performed in which a sample was spiked in the previous manner using the original set of solutions and analyzed. Obvious degradation of the integrity of the original set had occurred, although the numbers are comparable to those obtained from the data from the spiked and run set versus the original experiment.

Although some improvement can be seen in the quality of the data in going from the previous spiking method to the composite/septum vial method, the improvement is not enough by itself to explain the variance in the original data. The most likely explanation is that the spiking solutions degraded during the length of the original spiking process, causing erratic results. Examination of the new spike data is ongoing.

Of interest, however, are the exceptional recoveries obtained in the samples acquired from both sampling via the bottom stopcock and those sample from the top via the normal method. This would suggest that very little is lost during the sampling process, and in the steps later on. Obviously these conclusions must be taken with a grain of salt, however, due to an incomplete set of comparable data. The available data also suggests that spiking technique is critical when performing volatile organic spikes.

The semivolatile results are summarized in Figures 3 through 9 (see end of paper). The observed trends:

1. Acids - No excessive decrease from sampling to analysis. Filtration provided the greatest reduction in analyte concentration. Note must be taken, however, that d.i. water is an ideal matrix, and our experience has been that the acids suffer greatly from matrix interferences in actual matrices.

2. Bases - Although the bases did not suffer greatly as a group in the process from sampling to analysis, it is important to note that their recoveries were highly erratic. The best actor overall was 2-nitroaniline, which is the least basic and least water-soluble of the three. Pyridine's erratic behavior may be attributed to the factors of basicity, solubility, and volatility (i.e. during the concentration stage).

3. Chlorocarbons - A trend is obvious which displays that with increased handling from sampling to analysis there is a reduction in analyte concentration. Of particular interest is the total failure to recover hexachlorobenzene from the sample which underwent TC filtration. This result concurs with previous experiments performed in this laboratory, and begs questioning the validity of TC hexachlorobenzene results.

4. Nitroaromatics - No significant trends exist. In general, these compounds are good actors from sampling to analysis.

5. Nitrosamines - Overall this classification can also be considered good actors, the only exception being the erratic behavior of N-nitrosodimethylamine. The most likely explanation of this erratic behavior is its volatility, which could provide problems during the concentration stage.

6. Phthalates - The obvious trends are higher recoveries as molecular weight increases, reflective of a solubility phenomenon, and loss in analyte concentration with increased handling, especially at the filtration stage. Of particular interest is the failure to recover dimethyl phthalate, consistent with poor recoveries for this analyte seen previously in studies at this laboratory.

7. Polynuclear Aromatics - The most striking trend is the large loss of analyte concentration with increased handling time and/or length of time containerized. This trend increased with molecular weight, with extremely poor recoveries being demonstrated for benzo[a]pyrene. This is especially so during the TC filtration stage.

Conclusions

Experience has shown that the matrix plays a very significant factor in analyte recoveries, and all results and conclusions reported herein should be taken with note that these experiments were performed in an ideal matrix, that being d.i. water.

1. Metals - Current metals methods from sampling to analysis give data which is representative of the actual analyte concentration within the sample source; therefore no need is seen for modification of procedures in involving metals samples.

2. Semivolatiles - Over the classes defined, it was seen that some classes performed adequately with respect to recovery, but that on the whole increased handling showed decreased recoveries. Of interest to note is the erratic behavior of some analytes, defying efforts to determine trends for these analytes. Erratic recoveries for samples which were measured in a replicate basis demonstrate that if spike recovery corrected values for these analytes were used, the values must be taken with a grain of salt.

It is our recommendation that the current semivolatile surrogate list, which is not representative of typical analytes, be changed to the more representative list below:

Di-n-butyl Phthalate-d_4

Hexachloroethane-^{13}C

Hexachlorobenzene-$^{13}C_6$

Benzo[a]pyrene-d_{12}

Aniline-d_5

N-Nitrosodimethylamine-d_6

Phenol-d_6

Pentachlorophenol-$^{13}C_6$

Nitrobenzene-d_5

We feel that this list is representative of the typical analytes in terms of reactivity, volatility, and solubility. In addition, if a list such as this were used in place of the current surrogate list, the recoveries determined could be used in place of the traditional matrix spike to monitor "in control" performance.

The benefits of changing the list of spike compounds would be to provide a more representative list of analytes to determine laboratory performance on a sample by sample basis. In addition, elimination of the superfluous matrix spike, required on a minimum one spike per twenty sample batch basis, would allow one additional analysis per batch.

3. Volatiles - Obviously the data is inconclusive; the most apparent conclusion to be drawn is that spiking methodology and handling of the spiking solution is a critical step. It may be that with proper handling there is little loss in analyte concentration from sampling to analysis.

Acknowledgements

The authors wish to thank the field crew, extraction, GC/MS, and wet lab personnel for their willingness to devote intense energy towards this project. None of this data would have arisen without their dedication.

References

1. Method 1310 from "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," November, 1986, Third Edition, USEPA, SW-846 and additions thereto.

2. Methods for sampling and analysis obtained from SW-846.

3. Teflon is a registered trademark of the E. I. Dupont Corporation.

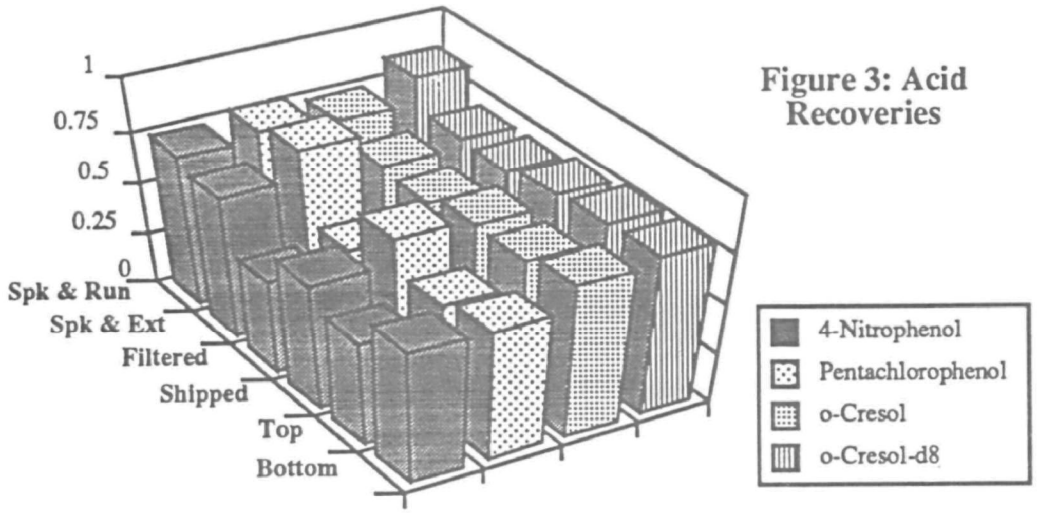

Figure 3: Acid Recoveries

	Bottom	Top	Shipped	Filtered	Spk & Ext	Spk & Run
4-Nitrophenol	66%	52%	62%	46%	70%	74%
Pentachlorophenol	65%	59%	74%	51%	83%	77%
o-Cresol	76%	70%	71%	65%	67%	74%
o-Cresol-d8	79%	78%	75%	71%	71%	85%

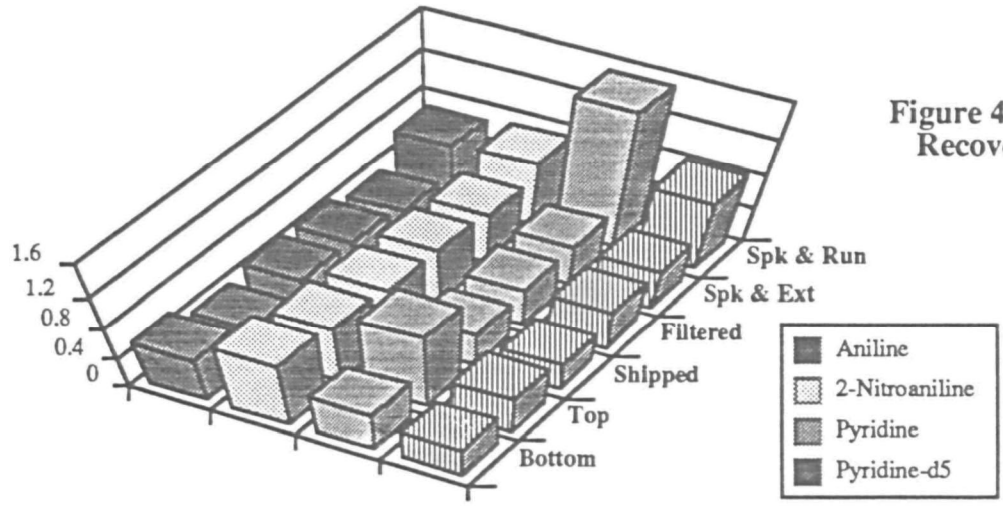

Figure 4: Base Recoveries

	Bottom	Top	Shipped	Filtered	Spk & Ext	Spk & Run
Aniline	59%	42%	52%	48%	38%	70%
2-Nitroaniline	87%	76%	70%	66%	60%	74%
Pyridine	54%	99%	45%	47%	50%	155%
Pyridine-d5	40%	48%	36%	49%	47%	83%

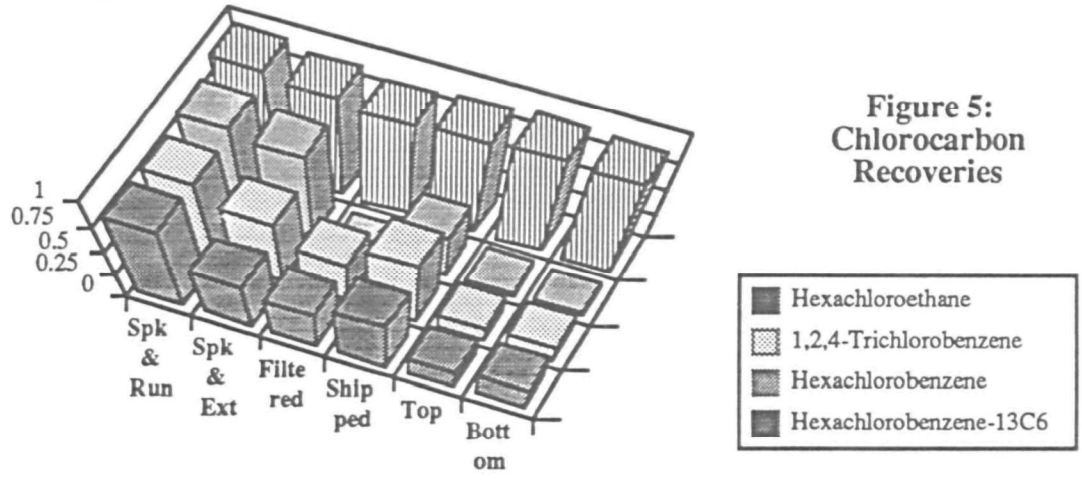

Figure 5: Chlorocarbon Recoveries

	Bottom	Top	Shipped	Filtered	Spk & Ext	Spk & Run
Hexachloroethane	24%	19%	51%	38%	46%	80%
1,2,4-Trichlorobenzene	17%	14%	62%	41%	61%	79%
Hexachlorobenzene	2%	3%	42%	0%	79%	86%
Hexachlorobenzene-13C6	88%	90%	87%	84%	89%	94%

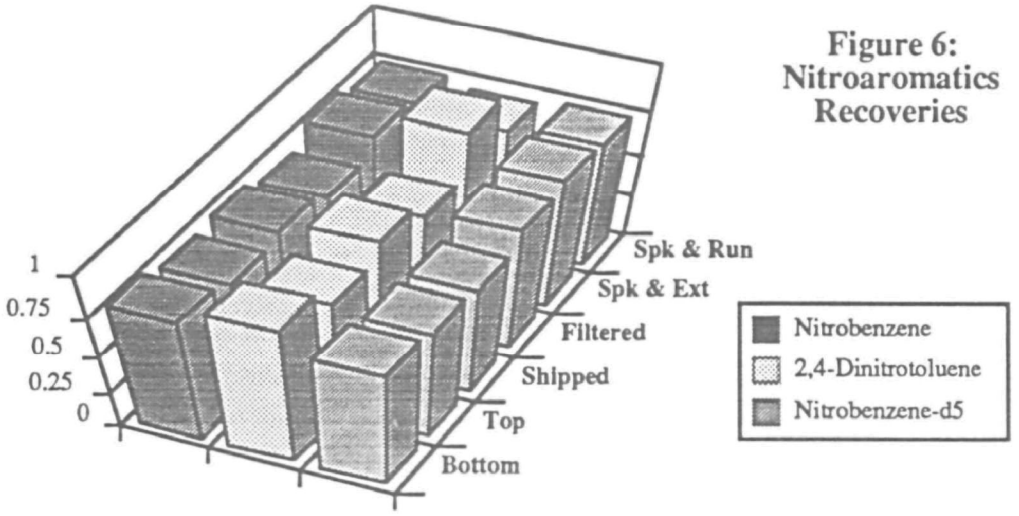

Figure 6: Nitroaromatics Recoveries

	Bottom	Top	Shipped	Filtered	Spk & Ext	Spk & Run
Nitrobenzene	80%	74%	77%	71%	81%	76%
2,4-Dinitrotoluene	89%	76%	84%	72%	94%	71%
Nitrobenzene-d5	77%	72%	69%	76%	79%	74%

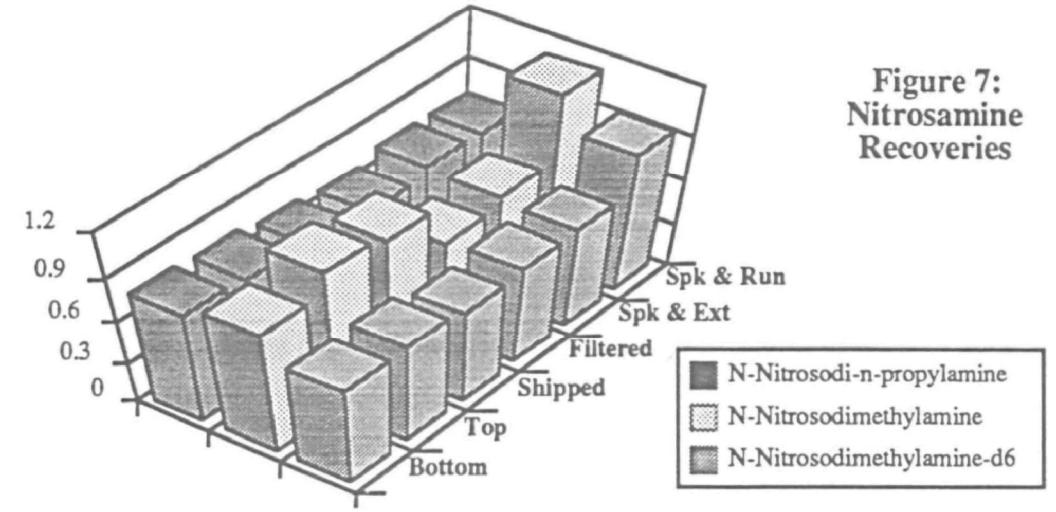

Figure 7: Nitrosamine Recoveries

	Bottom	Top	Shipped	Filtered	Spk & Ext	Spk & Run
N-Nitrosodi-n-propylamine	79%	76%	72%	70%	76%	74%
N-Nitrosodimethylamine	88%	101%	95%	67%	74%	114%
N-Nitrosodimethylamine-d6	71%	72%	66%	69%	69%	94%

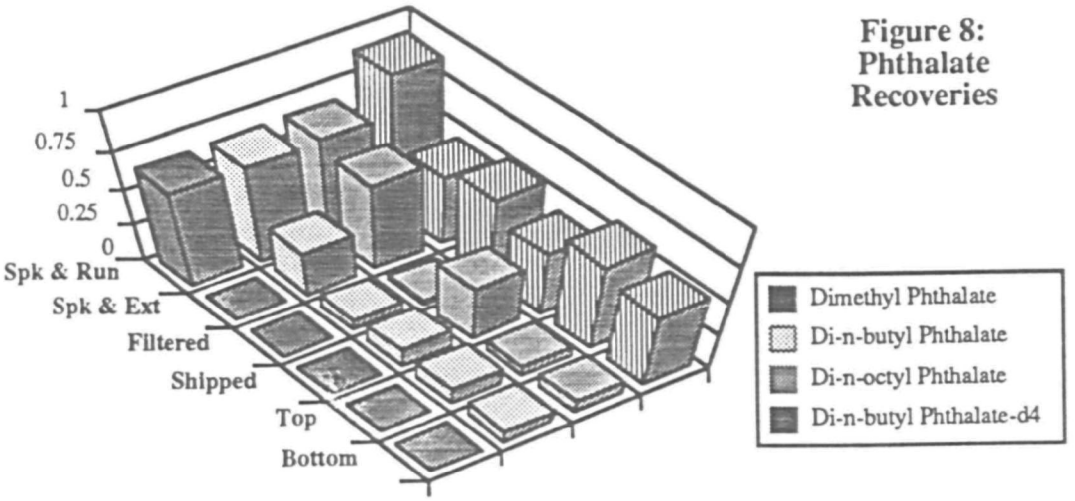

Figure 8: Phthalate Recoveries

	Bottom	Top	Shipped	Filtered	Spk & Ext	Spk & Run
Dimethyl Phthalate	0%	0%	0%	0%	0%	65%
Di-n-butyl Phthalate	9%	12%	12%	7%	30%	65%
Di-n-octyl Phthalate	9%	7%	37%	2%	59%	66%
Di-n-butyl Phthalate-d4	52%	60%	43%	55%	47%	90%

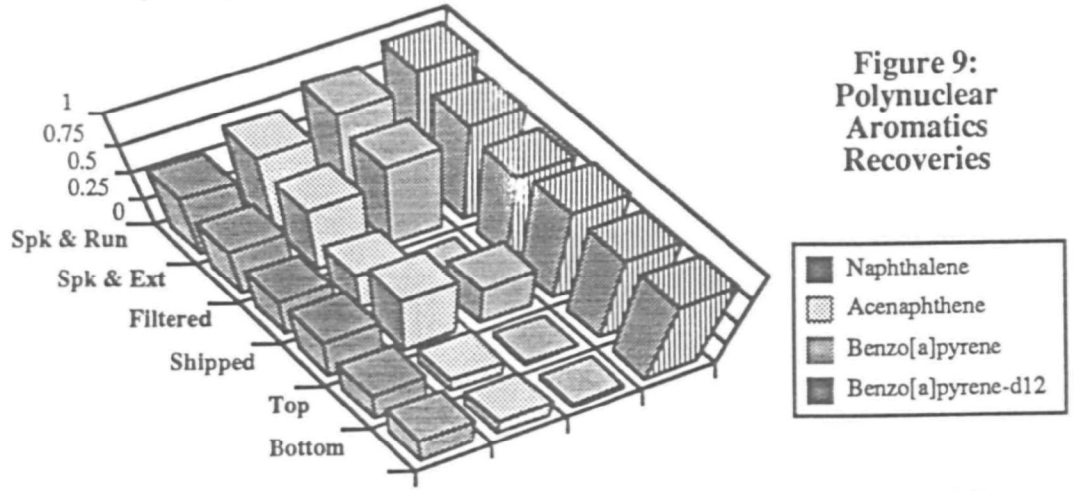

Figure 9: Polynuclear Aromatics Recoveries

	Bottom	Top	Shipped	Filtered	Spk & Ext	Spk & Run
Naphthalene	32%	31%	43%	38%	46%	55%
Acenaphthene	17%	15%	58%	37%	59%	70%
Benzo[a]pyrene	2%	2%	39%	0%	75%	84%
Benzo[a]pyrene-d12	86%	86%	87%	80%	87%	96%

	Bottom	Top	Shipped	Filtered	Spiked & Run
Chloromethane	103%	103%	27%	54%	15%
Vinyl Chloride	99%	113%	36%	65%	20%
Bromomethane	162%	164%	64%	100%	48%
Chloroethane	136%	144%	57%	85%	43%
1,1-Dichloroethene	66%	74%	43%	55%	34%
Methylene Chloride	72%	69%	37%	57%	36%
1,1-Dichloroethane	77%	76%	55%	68%	51%
cis-1,2-Dichloroethene	74%	74%	48%	57%	43%
Chloroforom	73%	74%	54%	65%	54%
trans-1,2-Dichloroethene	68%	71%	44%	53%	39%
Carbon Tetrachloride	63%	73%	52%	61%	51%
1,2-Dichloroethane	69%	72%	51%	60%	50%
Benzene	77%	79%	55%	60%	51%
Trichloroethene	66%	72%	56%	71%	55%
1,2-Dichloropropane	77%	80%	55%	65%	53%
Bromodichloromethane	64%	64%	42%	58%	43%
cis-1,3-Dichloropropene	110%	100%	102%	114%	88%
Toluene	53%	56%	50%	52%	41%
trans-1,3-Dichloropropene	36%	46%	33%	44%	28%
1,1,2-Trichloroethane	83%	117%	51%	83%	50%
Dibromochloromethane	98%	100%	54%	64%	53%
Chlorobenzene	74%	70%	65%	62%	56%
o-Xylene	63%	60%	54%	54%	50%
Ethylbenzene	65%	61%	82%	87%	66%
Styrene	66%	62%	58%	58%	54%
Bromoform	66%	66%	56%	65%	56%
1,1,2,2-Trichloroethane	77%	76%	57%	67%	59%
Tetrachloroethene	58%	62%	68%	75%	57%
1,1,1-Trichloroethane	71%	78%	58%	69%	51%
m- & p-Xylene	107%	98%	117%	121%	106%
Chloroform-13C	77%	81%	75%	77%	79%
1,1-Dichloroethene-d2	92%	95%	82%	83%	81%
Benzene-d6	82%	83%	82%	84%	87%
Vinyl Chloride-d3	104%	107%	99%	109%	112%
Bromoform-13C	75%	84%	80%	72%	71%

Table 4: Initial Volatile Organic Results

	Spike & Run			Spike, Filter, & Run	
	Old Way Old Sol'n	Old Way New Sol'n	New Way New Sol'n	Old Way New Sol'n	New Way New Sol'n
Chloromethane	11%	108%	90%	120%	157%
Vinyl Chloride	19%	126%	106%	143%	138%
Bromomethane	48%	157%	141%	182%	135%
Chloroethane	49%	146%	131%	168%	136%
1,1-Dichloroethene	34%	65%	60%	73%	109%
Methylene Chloride	42%	57%	54%	68%	86%
1,1-Dichloroethane	68%	56%	74%	90%	105%
cis-1,2-Dichloroethene	57%	75%	73%	85%	112%
Chloroforom	45%	50%	56%	60%	113%
trans-1,2-Dichloroethene	54%	79%	71%	85%	118%
Carbon Tetrachloride	62%	76%	81%	88%	110%
1,2-Dichloroethane	68%	64%	72%	79%	123%
Benzene	58%	78%	87%	89%	108%
Trichloroethene	67%	79%	84%	95%	113%
1,2-Dichloropropane	68%	81%	88%	98%	114%
Bromodichloromethane	60%	75%	75%	87%	91%
cis-1,3-Dichloropropene	93%	103%	118%	105%	154%
Toluene	34%	42%	49%	52%	98%
trans-1,3-Dichloropropene	32%	25%	30%	31%	44%
1,1,2-Trichloroethane	72%	54%	65%	74%	101%
Dibromochloromethane	57%	65%	62%	63%	127%
Chlorobenzene	80%	88%	99%	104%	100%
o-Xylene	60%	66%	78%	78%	97%
Ethylbenzene	93%	101%	105%	104%	105%
Styrene	66%	72%	86%	85%	106%
Bromoform	37%	36%	44%	42%	90%
1,1,2,2-Trichloroethane	64%	59%	74%	69%	88%
Tetrachloroethene	62%	57%	56%	66%	121%
1,1,1-Trichloroethane	74%	84%	97%	93%	105%
m- & p-Xylene	145%	161%	175%	177%	195%
Chloroform-13C	90%	90%	87%	88%	97%
1,1-Dichloroethene-d2	102%	97%	87%	100%	100%
Benzene-d6	93%	89%	83%	84%	103%
Vinyl Chloride-d3	106%	91%	85%	88%	103%
Bromoform-13C	79%	74%	75%	70%	79%

Table 5: Spike Method Comparison

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LAND DISPOSAL RESTRICTIONS PROGRAM DATA QUALITY INDICATORS FOR BDAT CALCULATIONS: PAST AND FUTURE

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ABSTRACT

The Land Disposal Restrictions (LDR) Program is continuing to develop and re-examine treatment standards for each of the listed hazardous waste codes using data of known quality from well-designed and well-operated treatment systems. The numerical treatment standards are based on the level of treatment achieved, the accuracy of the data, and the inherent variability of the treatment processes, sampling, and analytical data. Analytical data are collected by EPA or submitted by industry for the LDR Program on an ongoing basis. Consistent with the quality assurance/ quality control (QA/QC) program mandated by the Office of Solid Waste and Emergency Response, the quality and usability of the data being evaluated are assessed based on the following data quality indicators: detection limits, bias, precision, representativeness, and comparability.

EPA OSW's newly issued Quality Assurance/Quality Control Methodology Background Document (QMBD) explains in detail the LDR Program's requirements for data quality as well as the history behind existing LDR standards. This paper discusses these data requirements in order to present the "whole picture" of QA/QC in the LDR Program.

To verify that substantial treatment has occurred, when a treatment system is evaluated as a candidate for BDAT, EPA examines data characterizing the untreated waste and the treatment system residuals. Since treatment systems frequently reduce the hazardous constituents in many wastes to levels below detection limits, a detection limit is often used as the numerical measure of the level of treatment that occurred. The detection limit is also a factor considered in determining the applicability of the analytical method for the waste matrices analyzed.

The LDR Program's QA protocols define bias as percent recovery of laboratory matrix spikes. The results of the matrix spikes are used to bias correct the data as well as to determine the extent of matrix interferences on the usability of the data.

Similarly, precision is defined in terms of relative percent difference of the matrix spike and matrix spike duplicate. The results of relative percent difference are used to determine the reproducibility of the

analytical procedure and can provide additional insight into matrix interferences.

Representativeness is addressed through selection of appropriate sampling locations and procedures. For the data to be applicable for calculating treatment standards, the samples must be determined to be representative of the waste and the treatment system.

Comparability is addressed through use of the same sampling and analytical procedures. If data from more than one study are used, the results should be comparable. Therefore, the samples should be collected using the same procedures (i.e., grab or composite) and the analytical procedures should be either the same or comparable for all the results to be applicable for calculating treatment standards.

If the results of the data quality indicators meet the program's objectives, then the data are defensible and can be used to evaluate the treatment technology to determine whether it is the best demonstrated available technology and to calculate concentration-based treatment standards based on that technology.

INTRODUCTION

Under the Land Disposal Restrictions Program, EPA's Office of Solid Waste (OSW) developed and promulgated regulations for the following scheduled wastes:

- Solvents and Dioxins - November 7, 1986
- California Rule Wastes - July 8, 1987
- First Third Wastes - August 8, 1988
- Second Third Wastes - June 8, 1989
- Third Third Wastes - May 8, 1990

Currently, EPA-OSW's Waste Treatment Branch is developing standards for newly listed wastes (i.e., wastes listed since the 1984 HSWA Amendments). EPA-OSW will also re-examine promulgated treatment standards as new information on treatment technologies or analytical methods become available to the EPA. As discussed in recent Advance Notices of Proposed Rulemaking, EPA is actively soliciting treatability information for both groups of wastes. Since treatment standards developed and promulgated under the LDR Program were, and will continue to be, based on the best data available for treatment systems that were determined to be well-designed and well-operated. The Quality Assurance Methodology Background Document is intended to present EPA's criteria for accepting treatability data as the basis of subsequent numerical treatment standards.

Analytical data used to develop concentrated-based treatment standards can come from many sources both inside and outside EPA. These may be collected by EPA for the LDR Program or for other EPA programs (e.g., Office of Water's Effluent Guidelines Program) or may be submitted to EPA

by industry, trade associations, etc., to be considered for inclusion in the LDR Program's data base. The quality and usability of the data is evaluated based on the data quality indicators--detection limit, accuracy, precision, representativeness, and comparability.

EVALUATION OF DATA QUALITY INDICATORS

The results of the data quality indicators are important to determine:

- Appropriateness of the analytical method for the constituents analyzed.
- Bias of the analytical procedure, especially for bias-correction of the data.
- Determination of matrix interferences or other analytical problems.
- Reproducibility of the analytical results.
- Comparability of data, especially for comparability of data sets submitted from more than one source.
- Representativeness of samples, especially for comparison of data from more than one treatment system.

The LDR Program has established quantitative or qualitative guidelines for each of the data quality indicators. The guidelines are used to evaluate the acceptability of the data for developing treatment standards. EPA OSW's Quality Assurance/Quality Control Methodology Background Document (QMBD) explains in detail the LDR Program's requirements for data quality as well as the history of the existing LDR treatment standards.

Detection Limits

To verify that substantial treatment has occurred, data characterizing the untreated waste and the treatment system residuals are examined. Since the hazardous constituents in many wastes are treated to non-detect levels, especially for destruction technologies, a detection limit is often used to quantify the level of treatment that has occurred and to develop the treatment standards.

The detection limit may also be used to evaluate the appropriateness of the analytical procedures. One of the goals of the LDR Program was to obtain the best data with the lowest detection limits. A target detection limit of at least 1 ppm was established for data collected specifically for the LDR Program. However, lower detection limits were achieved for most of the data collected. The reported detection limit is especially important in evaluating data reported as non-detect. Data may be judged to be unacceptable for calculating treatment standards if it could be

determined that an inappropriate analytical procedure was used based on the reported detection limits. For example, in the case of metals, if the residuals and TCLP extracts were analyzed by flame atomic absorption methods instead of graphite furnace or ICP methods, the detection limits may be considered to be too high for the purpose of developing treatment standards and lower limits could have been achieved if the best analytical method was used.

Bias

Matrix spikes are completed to evaluate whether the laboratory is performing adequately or whether there is a methodological problem such as the presence of an interference or a systematic laboratory error. For the LDR Program, a matrix spike and matrix spike duplicate are required for the parameters of interest for treatment tests completed specifically for the LDR Program. A minimum recovery value of 20 percent was determined to be acceptable for the LDR Program. Data with recovery values below 20 percent are deemed to be unreliable, since the low recovery values indicated the presence of matrix interferences and may indicate difficulty in obtaining reproducible analytical results. Therefore, data with low recoveries are not used to develop treatment standards.

All data used to develop the treatment standards for the First, Second, and Third Thirds were bias-corrected. If a matrix spike and a matrix spike duplicate were completed, the lowest recovery value for the constituent to be regulated is used. If a spike was not completed for the constituent to be regulated, the lowest average recovery for the subset of constituents that are representative of the constituent class and analyzed by the same method (e.g., volatile organics, base-neutral organics, acid extractable organics, etc.) may be used. It should be noted that, for the Second and Third Thirds, data were not adjusted if the spike recoveries were above 100 percent.

All data used to develop treatment standards for newly listed wastes or for revising promulgated standards will also adjust for recovery in order to bring the reporting concentration of the target analyte closer to the true concentration, thus improving the overall accuracy of the value that serves as the basis for the promulgated standard.

Precision

Precision is defined in terms of relative percent difference of the matrix spike and matrix spike duplicate. The results of relative percent difference (RPD) are used to determine the reproducibility of the analytical procedure. No criteria were established for an acceptable RPD, however, the RPD is evaluated to gain additional insight into any matrix interference and to evaluate the reproducibility of the laboratory's performance. Engineering judgment is used to evaluate the analytical data with RPD's exceeding 20 percent for all of the constituents spiked.

Representativeness

Representativeness is addressed through selection of appropriate sampling locations and procedures. For the data to be applicable for calculating treatment standards, the samples must be representative of the waste and the treatment system. For a specific waste code, EPA uses data for the most difficult to treat waste to develop the treatment standards, i.e., for most cases, that would affect waste with the highest concentrations of the BDAT constituent present. Therefore, to evaluate the information for this data quality indicator it is important to evaluate both the untreated waste and the treatment residuals that may be land disposed.

For the treatment residuals, the data must also be representative of the material to be regulated. Since organic constituents can be destroyed, the treatment standards are based on total composition analysis. For metals, treatment technologies usually remove or immobilize the metal, data are evaluated for both total composition and the TCLP extract for both the untreated waste and the treatment residual to determine the leachability of the metal.

Comparability

Comparability is addressed through use of the same sampling and analytical procedures. If data from more than one study are used, the results must be comparable. Therefore, documentation on how the samples were collected (i.e., grab or composite) and on the analytical procedures used is reviewed.

Most of the treatment standards were developed based on grab samples analyzed using EPA approved methods published in SW-846. However, this does not preclude the use of composite data or samples analyzed using other solid analytical procedures.

BDAT CALCULATIONS FOR TREATMENT STANDARDS

The general approach for developing treatment standards was promulgated as part of the November 7, 1986 Solvents and Dioxins Rule. Based on this approach, EPA's treatment standards are based on the performance of the "best demonstrated available technology" (BDAT) and are stated as (1) concentrations of hazardous constituents in nonwastewater and wastewater residues, (2) specific treatment technologies for the waste, or (3) a combination of a specific treatment technology for a type of residue and constituent concentrations.

All valid data available to the Agency will be considered in establishing the treatment standards. All data either collected by EPA or submitted by industry, etc. for a specific waste code are available to the public in the Administrative Record either during proposal or promulgation (depending upon the data of submission) of the rulemaking for the specific waste code. Whatever the information source, however, the data underlying

the performance standards must meet standards of quality assurance and quality control. Therefore, information for the data quality indicators are evaluated as discussed earlier. If insufficient information is available for some of the indicators, engineering judgment may be used to determine the adequacy of the data. If the data for the indicators is totally nonexistent or judged to be substandard, the data may be discarded. All data evaluations are presented in either the background document for the specific waste and/or in the Administrative Record.

Information for the data quality indicators is collected during all of the treatment tests conducted by EPA-OSW specifically in support of the LDR Program. The adequacy of the data is evaluated on a case-by-case basis and only data meeting the criteria described previously is used to develop concentration-based treatment standards.

The final step in setting a performance standard is to define the maximum acceptable constituent levels in treatment residuals based on the performance of the technologies proven to be both demonstrated and available for the waste.

All concentration data with spike recoveries between 20 and 100 percent are bias-corrected. The average treatment value observed in all of the acceptable data is then multiplied by the "variability factor." The variability factor takes into account the fluctuations in performance that may result from inherent mechanical limitations in treatment control systems, treatability variations caused by changing influent levels, variations in procedures for collecting treated samples, or variations in sample analysis.

Only one major change was made between November 1986 and June 1990 in the methodology used to calculate the treatment standards. In the solvents and dioxins rule, the treatment standards were based on TCLP results for both the organic and inorganic constituents. For the Thirds, the standards and all subsequent regulations were based on total composition data for organic constituents and TCLP extract data only for the metal constituents.

If analytical data of adequate quality or an appropriate analytical procedure are not available, the Agency set a performance standard based on a specific treatment method.

SUMMATION

Data collected by EPA for the LDR Program has sufficient information available to evaluate all of the data quality indicators. No changes in the basic methodology are expected to be made for future regulations. Any changes in the methodology would be proposed and published for comment before the change would be implemented. As new data become available or new analytical procedures are developed, EPA may re-examine promulgated treatment standards to determine if a revision in the standard is necessary.

Therefore, data submitted for potential inclusion in the future rulemakings should have at a minimum information on the following:

- Analytical data for untreated waste
- Analytical data treatment residuals (total composition and TCLP extracts for all inorganic constituents)
- Analytical methods used and any modifications
- Detection limits
- Matrix spike recoveries
- Analytical precision (from matrix spike and matrix spike recoveries or from duplicate analysis)
- Sampling method (i.e., grab or composite)

REFERENCES

U.S. EPA. 1986. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846 (3rd Edition), Washington, D.C., November 1986.

U.S. EPA. 1987. U.S. Environmental Protection Agency, Office of Solid Waste. OSW's Generic Quality Assurance Project Plan for Land Disposal Restrictions Program (BDAT). March 1987. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1991. U.S. Environmental Protection Agency, Office of Solid Waste. Draft. Best Demonstrated Available Technology (BDAT) Background Document for Quality Assurance/Quality Control Procedures and Methodology (QMBD).

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COMPARISON OF QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS FOR DIOXIN/FURAN METHODS

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ABSTRACT

Fundamental areas of quality assurance/quality control are compared for several dioxin/furan analysis methods which use high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). These methods are used for analyzing various environmental matrices and for testing emissions from combustion sources. General areas of compatability and differences are discussed, while comparative items are categorized into tables for EPA Methods 8290, 23, and 1613, and also California ARB Method 428.

INTRODUCTION

Numerous analytical methods exist for the determination of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Many of these methods have been promulgated or drafted under federal and state agencies for use in environmental programs. These methods involve diverse matrices, and some are targeted toward specific regulatory applications, such as testing of hazardous waste incinerators under TSCA, CERCLA site remediations, and for development of national effluent limitation guidelines.

Although the basic techniques of isotope dilution, gas chromatography, and mass spectrometry used in identifying and quantifying these compounds are similar across these reference methods, regulatory applications are complicated by subtle variances in quality assurance/quality control (QA/QC) requirements imposed by the selection of a particular method. The goal of this paper is to simplify the technical review and application of these methods by comparing the various QA/QC elements. This information is categorized for some of the more commonly used methods into general descriptions, procedural checks, calibration controls, validation criteria, and external verification

recommendations. These comparisons may be helpful in formulating test plans and in data review.

DIOXIN METHODS

For this paper, the following four methods were examined:

- **EPA Method 8290**—"Analytical Procedures and Quality Assurance for Multimedia Analysis of PCDDs and PCDFs by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)," EMSL-Las Vegas draft dated May 1987. Although this method has never been promulgated, it has been widely used to analyze a wide variety of matrices including soil, sediment, water, biota, etc. It includes matrix-specific extraction and analyte-specific cleanup techniques.

- **EPA Method 23**—"Determination of PCDDs and PCDFs from Stationary Sources," Final Rule, *Federal Register*, February 13, 1991. This method has been promulgated to regulate emissions from municipal waste combustors and is also being used for trial burns on hazardous waste incinerators. The method includes descriptions of stack sampling procedures and recovery of the sampling train components for the PCDD/PCDF analyses.

- **ARB Method 428**—"Determination of PCDD, PCDF, and PCB Emissions from Stationary Sources," California Air Resources Board, March 1988. Similar to Method 23, this state-promulgated method also involves a modified Method 5 source sampling system for collection, recovery, and analysis of source emissions for PCDD/PCDF.

- **EPA Method 1613**—"Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS," Revision A, October 1990. This method was developed by the Industrial Technology Division with the U.S. Environmental Protection Agency's Office of Water Regulations and Standards to provide regulatory test data on waters, soils, sludges, and other matrices.

As indicated in Tables 1 through 6, there are many similarities and also subtle differences between the methods. The following sections present some general discussions in these areas.

GENERAL AND PROCEDURAL DIFFERENCES IN METHODS

One fundamental difference between these methods is in sampling. Two of the methods (23 and 428) include protocols for sample collection and recovery from combustion sources, while the other two procedures focus on the analysis, with only limited discussion relating to field sampling activities.

Of the sampling procedures, Method 23 and ARB 428, although very similar, do differ in solvent recovery protocols for the sampling train. Both add labeled congeners to the XAD adsorbent of the sampling train, prior to sample collection, to monitor train performance. Method 428 also requires correction of source emission results, if field surrogate recoveries are below 70%.

For the analytical methods, 1613 has more restrictive criteria for data acceptance than the draft Method 8290, primarily in the increased number of labeled congeners added prior to extraction, in specifications for initial demonstration of precision and recovery, and in continuing calibration verification limits.

Control blanks are required for all methods in the forms of blank sampling trains, sampling equipment rinsates, and laboratory method blanks.

Sample holding times are only discussed in Method 1613, although the QA sections of SW-846 provide holding time guidance for aqueous matrices which would be applicable to Method 8290.

General and procedural comparisons for the methods are presented in Tables 1 and 2.

CALIBRATION REQUIREMENTS

As shown in Table 3, only Method 8290 requires the use of a 7-point initial calibration curve, while the other methods require 5-point curves. Differences occur in acceptance

limits for both native and labeled congeners, although none of the methods discuss the rationale for the selection of these limits. Requirements for ion abundance ratios are the same for all methods. Mass spectrometer tuning and column performance checks are standard across the methods.

Continuing calibration requirements are significantly lower for some congeners in Method 1613, as low as ±6% difference for some congeners versus 20% to 30% difference used by the other methods. This is an important control parameter in that it triggers the need to stop analyses and recalibrate the instrument.

VALIDATION CRITERIA

As presented in Table 4, qualitative determination of dioxin/furan congeners are similar in most respects except for differences in matching requirements of relative retention times for samples to standards. Confirmatory analyses are required by all methods for positive identification of 2,3,7,8-substituted congeners.

Most of the methods discuss handling of non-detect values and the estimation of detection limits as a reportable value. This generally involves estimation of concentrations based on background noise or reporting values as "maximum possible concentration" for chemical hits which may match standard retention times but are outside of ion ratio criteria.

Because these methods involve trace analysis, there are discussions on reagent screening techniques, glassware tracking, glassware cleaning, and decontamination throughout the methods. However, the methods do not always indicate how to handle blank contamination problems other than to discard contaminated sources and restart the analytical process. Method 8290 does discuss criteria for acceptable method blanks.

Duplicate analysis of field samples (and criteria for acceptance) is only discussed in Method 8290. However, source testing typically involves multiple runs and samples that are representative of 1 test condition which may be used for comparison. Surrogate recoveries across like matrices, as discussed in Method 1613, also provides a means to evaluate analytical precision.

Acceptance criteria for surrogate recoveries of labeled congeners vary significantly by method, ranging from 25% to 150% recoveries. The concept and use of the isotope dilution technique for quantitation allows these tolerances without invalidating the test data. Poor surrogate recoveries, similar to poor detection limits, may be due to real matrix effects and/or interferences, and not reflective of analyst performance. As described in Method 1613, the technique of adding a known amount of a labeled compound to every sample prior to extraction allows the native compound to be corrected for recovery because the native compound and its labeled analog exhibit similar effects through extraction, concentration, and gas chromatography.

Table 6 lists the calibration ranges, native and labeled congeners for each method.

EXTERNAL VERIFICATION CHECKS

Because these complex methods are routinely used in regulatory-based decisions, all the methods specify that an ongoing quality assurance program be implemented by the laboratory. This encompasses many more areas of QA/QC than are presented in the methods, such as document control, audits, control charting, etc. However, the methods suggest several ways that this may be accomplished, including: using standards traceable to EPA reference materials or other certified standards, using EPA audit samples (spiked XAD) for source testing, and using field-associated QC samples (field replicates, rinsates, etc.) to demonstrate the overall quality of sampling and analysis test data.

SUMMARY

In researching this paper, several observations were apparent:

- Successful use of these methods require a comprehensive QC system that incorporates procedural elements which are common to all the methods, including laboratory management, sample handling, instrument operating parameters, and elimination of potential sources of contamination. In addition, a QA program is needed to ensure that test data for environmental programs are both internally consistent and comparable to other EPA data.

- Control limits and acceptance criteria vary by method for initial/continuing calibrations, surrogate recoveries, and control samples.

- Validation of test data relies on proper calibration, acceptable method blanks, surrogate recoveries, qualitative identification criteria, certification of standard reference materials, and confirmatory analysis of suspect samples. Documentation of these control parameters is essential for completing technical reviews and audits.

Notwithstanding the inherent method similarities and differences discussed above, the authors' discussions of particular technical areas vary in degree of clarity and emphasis, so that there is complimentary information shared by all methods. This diversity of information gives the reader a better understanding of dioxin analysis techniques, regardless of the actual method chosen for an environmental program.

TABLE 1. PCDD/PCDF METHOD COMPARISONS

	Application	Status	Sampling protocol	Field spiked surrogates	Preclean & screen reagents & glassware	Sample train recovery	Analysis
METHOD 8290	PCDD/PCDF in soil, sediment, water, fly ash, sludge, fuel oil, paper, biological samples	EPA Draft, May 1987	No	NA	Yes	NA	• Spike samples with internal standards • Extract aqueous with methylene chloride • DB-5 column recommended • Confirmation column required for positive identification of all isomers
METHOD 23	PCDD/PCDF from stationary sources	EPA final rule, *Federal Register*, February 1991	Yes, Modified Method 5 (filter/XAD)	Yes	Yes	1. Acetone 2. Methylene chloride 3. Toluene (separate analysis as "QA rinse")	• Spike XAD with internal standards • Reduce aqueous component and combine with XAD • Soxhlet extract with toluene • Split sample in half for archiving • Column cleanup: —silica gel —alumina —carbon/Celite • no acid cleanup discussed • HRGC/HRMS with DB-5 column • Confirmation using SP-2330 on SP-2331
ARB 428	PCDD/PCDF & PCB emissions from stationary sources (regulatory compliance)	Adopted March 23, 1988 by CARB	Yes, modified California version of Method 5 (filter/XAD) [minimum 3 tons @ 3 h each]	Yes	Yes	1. Methanol 2. Benzene 3. Methylene chloride	• Spike XAD with internal standards (none is added to aqueous) • Extract aqueous with methylene chloride then add to & extract with filter/XAD • Extract with benzene or toluene • Acid cleanup • Column cleanup —silica gel —alumina —carbon/Celite • HRGC/HRMS with DB-5 • Confirmatory analysis using SP-2330 on SP-2331
METHOD 1613	PCDD/PCDF in water, soil, and other solid matrices	USEPA, Revision A, October 1990	No	NA	Yes, protocol specifies	NA	• Spike samples with 15 labeled analogs • Labeled TCDD added after extraction to measure efficiency of cleanup steps • Internal standards added prior to analysis for quantitation • Sample cleanup by GPC, HPLC, or column chromatography described (column calibration required)

TABLE 2. PROCEDURAL QA/QC

	Lab method blank	Matrix spike/MSD	Holding times	Homogenization of sample	Field blank	QC check sample
METHOD 8290	Yes, 1 per batch of 24	Yes, duplicate spike per batch of 24	Not discussed; refer to SW-846	Yes (% moisture of soils)	Rinsate of sampling equipment; 1 "uncontaminated" field blank per 24	One performance evaluation sample in all batches
METHOD 23	Yes	All XAD traps are spiked with labeled congeners prior to sampling	Not discussed	Complete analysis (except for toluene "QA" rinse)	Blank train	EPA audit sample required for regulatory basis
ARB 428	Ongoing	All XAD traps are spiked with labeled congeners prior to sampling	Not discussed	Complete analysis	1 blank train per three runs	EPA or other independent audit sample
METHOD 1613	1 blank control matrix per batch of 20 samples	Initial demonstration of recovery and precision from 4 matrix spikes is required. Also, 1 control sample per batch is analyzed.	1 yr @ 4°C for samples; 40 d @ 4°C for extracts	Yes, % moisture of soils	Recommended.	Ongoing precision and accuracy control samples

TABLE 3. CALIBRATION QA/QC

	Number of standards in calibration curve	Initial calibration precision	Ion abundance ratios	Continuing calibration (every 12 hr)	M5 tuning and accuracy check	GC column performance check
METHOD 8290	7-point	20% RSD	±15% of theory	20% D (bracketing RRFs used for quantitation if RRF is between 20-25% D)	PFK (every 12 h)	Initially and every 12 h: • First and last eluters labeled on chromatograms • Presence (current switching) of both 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF
METHOD 23	5-point (option for two levels)	25% RSD (30% RSD for native OCDF and some labeled congeners)	±15% of theory	25% D (30% D for OCDF and some labeled congeners)	PFK	Initially (daily): • 25% valley for 2,3,7,8-TCDD • Established RT windows for homolog series
ARB 428	5-point (replacement of calibration standards every 6 months)	15% RSD	±15% of theory	30% D	PFK (every 12 h)	Initial (daily): • 25% valley for 2,3,7,8-TCDD • Meets ion abundance ratio criteria • Minimum S/N of 5:1 • Mass correction for *m/e* 328 for native TCDD • Retention windows for homolog series
METHOD 1613	5-point standard solutions are analyzed within 48 h of preparation and on a monthly basis to check for degradation	< 20% coefficient of variation for calibration by isotope dilution; < 35% coefficient of variation for calculation by internal standard	±15% of theory	Varies from 6% to 20% D allowed	PFK (every 12 h)	Initially and every 12 h: • Mass drift correction using PFK • Verify ion abundance ratios, minimum levels, and signal-to-noise ratios • Column window-defining mix

TABLE 4. QC DATA AND ACCEPTANCE CRITERIA

	Identification	Method blanks	Field surrogates	Internal standard recovery	Duplicate sample analysis	MS/MSD	Detection limits
METHOD 8290	• Ions maximize within 2 s • S/N ≥ 2.5 for both ions • RT match of -1 to +3 s of standard • Ion abundance ratio within ±15% limit • RT within homolog window • Confirmatory analysis on second column (quantitation is specified by column & congener) • No PCDPE interference	• Method blank per batch (daily, before samples) —internal standards > 10:1 S/W —background below < 10% of target detection limit	NA	40-120% R	≤ 25% D for 2,3,7,8-congeners	≤ 20% D for 2,3,7,8-congeners	Concentration corresponding to 7.5x the background noise
METHOD 23	• Simultaneously (±2 s) detection of ions • S/N ≥ 2.5 for both ions • RT match of ±3 s of standard • Ion abundance ratio within ±15% limit • RT within homolog window • Confirmatory analysis on second column (quantitation is specified by column & congener) • No PCDPE interference	• No blank criteria given	70-130% R (correct test results if R < 70%)	40-130% R (tetra-hexa) 25-130% R (hepta-octa) (data are still acceptable if S/N ≥ 10 for detected PCDD/PCDF)	Not discussed	Not discussed	Report "Theoretical Minimum Quantifiable Level (TMQL)" as: TMQL (PG) = lowest STD (pg/μL) x final extract volume/recovery of internal standards
ARB 428	• Simultaneous (±2 s) detection of ions • S/N ≥ 2.5 for standards > 10 for samples (both ions) • Ion abundance ratio within ±15% limit • RT within homolog window • Confirmatory analysis on second column (quantitation is specified by column & congener) • No PCDPE interference	• No blank criteria given	60-140% R	40-120% R	Field replicates (no criteria given)	Not discussed	• Concentration corresponding to 2.5x noise level or ions outside ion abundance criteria as "estimated maximum possible concentration"
METHOD 1613	• Ions maximize within ±2 s of one another • S/N ≥ 2.5 for sample extract and ≥ 10 for a calibration standard • Ion abundance ratios within ±15% limits • Relative retention time windows within column performance mix • Confirmatory analysis for 2,3,7,8-congeners using second column • No PCDPE interference	• All materials must be demonstrated to be interferant-free • Glassware tracking recommended	NA	25-150% R	Not discussed	Acceptance criteria for initial and continuing performance tests are listed	Minimal levels are listed for water, solid, and extract

TABLE 5. EXTERNAL VERIFICATION

	Reporting requirements	Method recommendations
METHOD 8290	• Results of at least one GC column performance check first ("F") and last ("L") eluters labeled on chromatogram • Results of 2 mass resolution checks and continuing calibration checks during a 12-h period • Toxic equivalency factors (if needed)	• Calibration standards traceable to EPA (EMSL-LV) reference materials —verification data and supporting records on file —1 to +3 s match in RT times —≤ 20% difference in concentration between standards and EPA reference —standard preparation and traceability records on file
METHOD 23	• Internal standard percent recoveries • Field surrogate recoveries • Analysis results of toluene QA rinse • TMQLs (detection limits) • Results for 2,3,7,8-congeners and totals	• EPA audit sample (for regulatory tests)
ARB 428	• Detection limits = 2.5 x noise • "Maximum Possible Concentration" for hits that do not meet ion abundance criteria • Deviations from method • Totals and specific 2,3,7,8-substituted congeners • Sample numbers, source, and chain-of-custody records • Dates of submittal and GC/MS analysis • Raw data (mass intensities) • Ion ratios for PCDD/PCDF detected • % recoveries of internal standards • Recovery of spiked samples • Summary of calibration data —mean RRFs —RSDs for 5-point curve —acceptable continuing calibration checks for each 12 h • Traceability records and sequence of analysis	• Verification of 2,3,7,8-TCDD standards to EPA reference materials • Formal QA program —ongoing analysis of spiked samples —records of past performance —ongoing screens and method blanks —field replicates for overall S&A precision
METHOD 1613	• Report values to 3 significant figures • Multiple forms provided for reporting QC and test data • Control charting required	Standards must be certified for purity, concentration, and authenticity

TABLE 6. ANALYTE LIST AND CALIBRATION RANGES

Desig-nation	Compound	RRF reference standard	Method 8290	Method 23	Method 428	Method 1613
	Calibration range:		2.5-1,000 pg/µL	0.5-1,000 pg/µL (low) 5-10,000 pg/µL (high)	5-10,000 pg/µL	0.5-2,000 pg/µL
	UNLABELED ANALYTES (17)					
1	2,3,7,8-TCDD	A	X	X	X	X
2	2,3,7,8-TCDF	B	X	X	X	X
3	1,2,3,7,8-PeCDD	C	X	X	X	X
4	1,2,3,7,8-PeCDF	D	X	X	X	X
5	2,3,4,7,8-PeCDF	D	X	X	X	X
6	1,2,3,4,7,8-HxCDD	E	X	X	X	X
7	1,2,3,6,7,8-HxCDD	E	X	X	X	X
8	1,2,3,7,8,9-HxCDD	E	X	X	X	X
9	1,2,3,4,7,8-HxCDF	F	X	X	X	X
10	1,2,3,6,7,8-HxCDF	F	X	X	X	X
11	1,2,3,7,8,9-HxCDF	F	X	X	X	X
12	2,3,4,6,7,8-HxCDF	F	X	X	X	X
13	1,2,3,4,6,7,8-HpCDD	G	X	X	X	X
14	1,2,3,4,6,7,8-HpCDF	H	X	X	X	X
15	1,2,3,4,7,8,9-HpCDF	H	X	X	X	X
16	OCDD	I	X	X	X	X
17	OCDF	I	X	X	X	X

(continued)

TABLE 6 (continued)

Desig-nation	Compound	RRF reference standard	Method 8290	Method 23	Method 428	Method 1613
	INTERNAL STANDARDS (10)—(SPIKED ONTO SAMPLE PRIOR TO EXTRACTION)					
A	$^{13}C_{12}$-2,3,7,8-TCDD	AA	X	X	X	X
B	$^{13}C_{12}$-2,3,7,8-TCDF	AA	X	X	X	X
C	$^{13}C_{12}$-1,2,3,7,8-PeCDD	AA	X	X	X	X
D	$^{13}C_{12}$-1,2,3,7,8-PeCDF	AA	X	X	X	X
E	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	BB	X	X	X	X
F	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	BB	X	(1,2,3,6,7,8)[a]	(1,2,3,6,7,8)	X
G	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	BB	X	X	X	X
H	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	BB	X	X	(1,2,3,4,7,8,9)	X
I	$^{13}C_{12}$-OCDD	BB	X	X	X	X
	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	BB	-	-	-	X
	RECOVERY STANDARDS (2)—(SPIKED INTO EXTRACT PRIOR TO ANAYSIS)					
AA	$^{13}C_{12}$-1,2,3,4-TCDD	-	X	X	X	X
BB	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	-	X	X	(1,2,3,4,7,8)	X
	SURROGATE STANDARDS (6)—(SPIKED ONTO SAMPLE PRIOR TO SAMPLING					
18	^{37}Cl-2,3,7,8-TCDD	A	-	X	X	X[b]
19	$^{13}C_{12}$-2,3,4,7,8-PeCDF	D	-	X	X	X[c]
20	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	E	-	X	-	-
21	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	F	-	X	X	X[c] (1,2,3,6,7,8)
22	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	H	-	X	(1,2,3,4,6,7,8)	X[c]
23	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	F	-	(alternate)	X	X[c]

[a] Brackets indicate alternate or other congener specification by method.
[b] Spiked into sample after initial extraction prior to clean-up to check column performance.
[c] Method 1613 uses these labeled congeners as internal standards, i.e., spiked into sample prior to extraction.

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A STUDY OF METHOD DETECTION LIMITS IN ELEMENTAL SOLID WASTE ANALYSIS

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ABSTRACT

Two types of data are generated when determining the concentrations of regulated elements in solid matrices (e.g., sediments, sludges, soils, spent catalysts, press cakes, slags, powders, etc.). These are numerical values, that indicate the amount of analyte present, and "None Detected" or "Less Than" values. The latter values define, for a given analyte, the smallest amount that can be quantified. A positive numerical value is usually defined within a set of precision and accuracy criteria. A "less than" value on an analytical report is as much a data point as a numerical value and should be determined with equivalent precision and accuracy.

By far the most common method for determining these "less than" values is the U.S. E.P.A.'s Method Detection Limit (MDL)[1,2] based on the work of Glazer et al.[3] This method was developed for trace analysis of organic analytes in water matrices. MDLs have, however, been used extensively for inorganic analyses and solid matrix analyses without examination of its applicability.

This study attempts to assess the applicability of the MDL method to solid matrix analysis. The study compares the calculated MDLs for five analytes in soil, arsenic, cadmium, molybdenum, selenium, and thallium with method performance at concentrations above and below the calculated MDL. The MDL method is examined both for its empirical suitability for solid waste analysis and whether it has the proper theoretical tools for solid matrices.

INTRODUCTION

When determining the concentration of regulated elements in solid matrices (e.g., sediments, sludges, soils, spent catalysts, press cakes, slags, powders, etc.) two types of data are generated, numerical values indicating the amount of an analyte present and "None Detected" or "Less Than" values that let the data user estimate the smallest amount of the analyte that can reasonably be quantified. A positive numerical value is usually defined within a set precision and accuracy. A "less than" value on an analytical report is as much a data point as a numerical value and should be determined with equal precision and accuracy. The most common method for determining this "less than" value is the U.S. E.P.A.'s Method Detection Limit (MDL) based on the work of Glazer et al. This method was developed for trace analysis of organic analytes in water matrices. MDLs have, however, been used extensively for inorganic and solid matrix analyses without an examination of their applicability to the procedures.

This study attempts to assess the applicability of the MDL method to solid matrix analysis. A comparison of the calculated MDLs for five analytes in soil (arsenic, cadmium, molybdenum, selenium, and thallium) with method performance at concentrations above and below the calculated MDL. The MDL method is examined both for its empirical suitability for solid waste analysis and its appropriateness as a theoretical tool for estimating MDLs in solid matrices.

METHODS

A) The USEPA's MDL and Glazer et al. are both six step procedures. These procedures are designed to be used on any matrix. The five step portion of these procedures that are applicable to solid wastes are presented below.

1) Estimate the MDL by one of four procedures:

   a) The concentration that corresponds to an instrument signal to noise ratio of 2.5 to 5.

   b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water.

   c) The concentration value that corresponds to the region where there is significant change in sensitivity at low analyte concentrations.

   d) The concentration value that corresponds to the known instrument limitations.

   (This will be referred to as the estimated MDL)

2) Obtain a solid material corresponding to the matrix type for which the MDL is to be determined. The material must have a concentration of the analyte(s) of interest at one to five times (but not to exceed ten times) the estimated MDL.

3) Take a minimum of seven (7) aliquots of the material and process each through the entire analytical procedure. Calculate the results back to solid phase with the appropriate units such as mg/kg or ug/g.

4) Calculate the standard deviation (S) using equation 1, as follows:

$$S = \frac{\sqrt{\Sigma X_i^2 - \Sigma \bar{X}_i^2}}{n - 1}$$

Eq. 1

5) Calculate the MDL by equation 2 as follows:

$$MDL = t * S$$

Eq. 2

where t is the student's value approximate for a 99% confidence level for n - 1. Since n is equal to seven the student's t value would be 3.143. (This will be referred to as the calculated MDL).

6) There is an optional step which calls for the preparation of a material spiked exactly at the calculated MDL and repeating steps 3-5. This will be referred to as the **iterative procedure**. If the calculated MDL results in a spiked concentration that does not allow qualitative identification then repeat steps 3 - 5 with a higher spiked concentration. If the spiked concentration is qualitatively identifiable but the standard deviation of the seven replicates of the spike (S_b)is 3.05 times greater than the standard deviation of the calculated MDL determination (S_a) then an other spiked material must be prepared. If the ratio of S_a/S_b is less than 3.05 then the MDL is recalculated by pooling the data following equations 3 and 4:

$$S_{pooled} = \frac{\sqrt{(6S_a)^2 + (6S_b)^2}}{12}$$

Eq. 3

$$MDL = 2.681\ (S_{pooled})$$

Eq. 4

(This will be referred to as the pooled MDL).

B) Percent Inaccuracy (%I) is defined here as the absolute difference between the spiked value (X_s) of a soil and the mean measured value (X_m) divided by the spiked value times 100.

$$\%I = \frac{X_s - \overline{X_m}}{\overline{X_s}} * 100$$

Eq. 5

C) Percent Relative Standard Deviation (%RSD) is defined as the standard deviation as defined above divided by the mean value times 100.

$$\%RSD = \frac{S}{\bar{X}_m} * 100$$

Eq. 6

EXPERIMENTAL SECTION

A) Study Design. To assess the applicability of the MDL method to solid waste elemental analysis it will be necessary to determine the MDL by means of the five steps outlined above for a solid matrix, in this case a loamy soil.

Three instruments were used: a Jobin-Yvon JY-50P simultaneous Inductively Coupled Plasma Atomic Emission Spectrometer (ICP) a Perkin-Elmer PE-5500 sequential ICP, and a Thermo Jarrel- Ash Video 12E Flame Atomic Absorption Spectrometer (FAA). The estimated MDL was determined by each of the four methods for each instrument in step one for arsenic, cadmium, molybdenum, selenium, and thallium for the two ICP-AESs. The same was performed for cadmium, molybdenum, and thallium on the FAA.

Five soils were spiked at several concentrations for each element (see below) corresponding to the estimated MDLs. Seven aliquots of each soil were digested and the calculated MDLs were determined for each element for each instrument. When necessary, the pooled MDL was also determined. Finally, the estimated, calculated, and pooled MDL values was evaluated for both precision and accuracy for solid waste analysis.

B) Analytical Procedures. The soils were digested using an aqua regia method here designated as the SCL method[4,5,6]. 2.00 grams of the soil were placed in a 150 mL Phillips beaker. 10 mL of concentrated HCl and 2.5 mL of concentrated HNO_3 was added and heated to 95° C on a heating block. When there was no more reddish-brown gas (NO_2), the beakers were removed from the heating block and the digestate was filtered through a Whatman 41 filter paper and collected in a 100 mL volumetric flask. The residue and filter paper were then washed with 5 mL of hot (95° C) concentrated HCl and then 20 mL of hot de-ionized water which is also collected into the 100 mL flask. The filter paper and residue were then placed back into the Phillips beaker and heated with 5 mL of concentrated HCl until the filter paper dissolves and then this second digestate is filtered and collected into a second 100 mL volumetric flask. Both filtrates were then analyzed and the results were mathematically combined.

Instrumental analysis methods used to analyze these materials was EPA SW 846[6] methods 6010 for both the sequential and simultaneous ICP using a 100 ug/mL standard for all elements.

Both ICPs used two background correction points for each analytical line.

Methods 7130, 7480, and 7840 were used for the Flame AA and a deuterium lamp was used for all analyses for background correction.

C) **Materials.** A local soil was dried, sieved and then analyzed for of arsenic, cadmium, molybdenum, selenium, and thallium. The amounts found were far below 1 ug/g. These elements were then spiked into the soils to produce the following concentrations:

	Sample A	Sample B	Sample C	Sample D	Sample E
Arsenic	4,000	500	50	5	-
Cadmium	500	50	5	-	5,000
Molybdenum	30	5	-	5,000	500
Selenium	5	-	5,000	500	50
Thallium	-	5,000	500	50	5

Here and throughout this paper the dash mark, -, is used to indicate that the analyte in question was not spiked. Soluble salts of each element were dissolved in water and spiked into the soils. Additional water was added to form a slurry which allowed for easy homogenization. The soils were then dried, milled and sieved. (for a more complete discussion of the preparation of spiked soils, see "Preparation and Validation of Proficiency Evaluation Samples" by Kimbrough, D.E. and J.R. Wakakuwa in these proceedings.) One additional material was prepared, designated "K", which was made up of 100 g of the same soil and was spiked with 20 mL of a 100 ug/mL Cd and Tl standard. This material was treated exactly as the other materials were. Its concentration was 20 ug/g.

RESULTS

A) **Arsenic.** Table I lists all of the data for arsenic. Using the estimation procedures, four estimated MDLs were determined for both types of ICP. A wide range of estimates were obtained, so three different spiked materials with concentrations of 500, 50, and 5 ug/g were used to determine the calculated MDL as well as an unspiked background material.

For the simultaneous ICP, using the 500 ug/g material the calculated MDL is 30 ug/g. Following the iterative procedure then a 30 ug/g material should be analyzed. For this step the 50 ug/g PE sample was used which produced a calculated MDL of 41 and the ratio of S_{500} to S_{50} is far less than 3.05. The pooled MDL is 29.

For the sequential ICP the 500 ug/g material yields a calculated MDL of 17 ug/g. The 5 ug/g material could be used for the iterative procedure except the results were not qualitatively identifiable. The 50 ug/g material is qualitatively identifiable and yields a MDL of 8.4. The ratio

of S_{500} to S_{50} is less than 3.05 and the pooled MDL is 10.3 ug/g.

B) Cadmium. Three materials were used as with arsenic, 500, 50, and 5 ug/g as well as an unspiked background material. Table II lists the estimated MDLs.

Using the 500 ug/g material to calculate the MDL on the simultaneous ICP, the value of the MDL is 17 ug/g. If the iterative step is followed then the 5 ug/g material should be used. The 5 ug/g sample is qualitatively distinguishable but the ratio of S_{500} to S_5 is far greater than 3.05. The same is true for 50 ug/g material. If the 20 ug/g material is used here a qualitatively identifiable signal is generated which has a standard deviation less than 3.05 times the standard deviation of the 5 ug/g material. The pooled MDL is 0.8 ug/g.

The sequential ICP analyzing the 500 ug/g material yields a calculated MDL of 22 ug/g. The 5 ug/g material could be used for the iterative procedure except the results were not qualitatively identifiable. The 50 ug/g material is qualitatively identifiable and yields a MDL of 8.4. The ratio of S_{500} to S_{50} is greater than 3.05. The 20 ug/g material produced no qualitatively identifiable signal.

For the FAA the 50 ug/g material produces a calculated MDL of 4.4 ug/g. The 5 ug/g material was qualitatively identifiable and yields a MDL of 3.1. The ratio of S_{50} to S_5 is less than 3.05. The pooled MDL is 3.0

C) Molybdenum. Following the estimated MDLs on Table III, the 500 ug/g material was used to determine the calculated MDL on the simultaneous ICP, which had a value of 72 ug/g. The 30 ug/g material was used for the iterative procedure but the ratio of S_{500} to S_{30} is far greater than 3.05. Using data from the 30 ug/g material, the calculated MDL is 8.6 ug/g. However, the 5 ug/g material yielded no qualitatively identifiable signal.

The sequential ICP analyzing the 500 ug/g material yields a calculated MDL of 56 ug/g. The 50 ug/g material is qualitatively identifiable and yields a MDL of 8.4. The ratio of S_{500} to S_{30} is greater than 3.05. Using data from the 30 ug/g material, the calculated MDL is 7.5 ug/g. However, the 5 ug/g material yielded no qualitatively identifiable signal.

For the FAA the 30 ug/g material produces a calculated MDL of 9.2 ug/g. The 5 ug/g material was qualitatively identifiable and yields a MDL of 5.0. The ratio of S_{30} to S_5 is less than 3.05. The pooled MDL is 6.7

D) Selenium. Table IV lists the estimated MDLs and other data. The 500 ug/g material was used to calculate the MDL on the simultaneous ICP, which had a value of 29 ug/g. The 50 ug/g material was used for the iterative procedure producing and calculated MDL of 17 and the ratio of S_{500} to S_{50} is less than 3.05.

The sequential ICP analyzing the 500 ug/g material yields a calculated MDL

of 63 ug/g. The 50 ug/g material is qualitatively identifiable and yields a MDL of 30. The ratio of S_{500} to S_{50} is less than 3.05 and the pooled MDL is 38.

E) Thallium. Table V lists the estimated MDLs. Using the 500 ug/g material to calculate the MDL on the simultaneous ICP, the value of the MDL is 23 ug/g. The iterative step using 50 ug/g material produced an MDL of 11 ug/g. The pooled MDL is 14 ug/g. This is identical with the calculated MDL for the 20 ug/g material which has a S_{20} of less than 3.05 times the standard deviation of either the 5 ug/g or the 50 ug/g materials.

The sequential ICP using the 500 ug/g material yields a calculated MDL of 26 ug/g. The 50 ug/g material is qualitatively identifiable and yields a MDL of 22. The ratio of S_{500} to S_{50} is less than 3.05. The pooled MDL is 19. The 20 ug/g material produced not qualitatively identifiable signal.

The FAA analyzing the 50 ug/g material produces a calculated MDL of 26 ug/g. The 5 ug/g material was qualitatively identifiable and yields a MDL of 4.5. The ratio of S_{50} to S_5 is less than 3.05. The pooled MDL is 5.0

DISCUSSION

The MDL process as applied to arsenic using simultaneous ICP produced three estimates 30,41, and 29 ug/g which were in close agreement. These numbers, however, were indistinguishable from the 34.6 ug/g value that was obtained from the unspiked soil. Further, the inaccuracy found in the 50 ug/g material was quite high despite the good precision. For the method used in this study, two grams of soil digested by aqua regia and analyzed by ICP, any results below 50 ug/g are highly inaccurate even if they were statistically distinguishable from zero. This is also true for selenium values, the poor accuracy and precision obtained at 50 ug/g would make lower results quite dubious. Cadmium and thallium had accuracy and precision reasonable results at 50 ug/g but highly inaccurate results at 20 ug/g, which is far above the calculated and pooled MDLs. Molybdenum results for 30 ug/g were both accurate and precise but the calculated MDL of 8.6 does not appear reasonable given the fact that the 5 ug/g material was not qualitatively identifiable.

The sequential ICP results for arsenic exhibit the same type of data as that obtained from the simultaneous ICP. The three measurements of the estimated MDL were 17, 8.4, and 10 ug/g. However, the 5 ug/g produced no measurable signals on the ICP making it indistinguishable from the blank. This raises serious questions as to the accuracy and precision of measurements near this point, as was the case for all of the other analytes. Furthermore, the sequential ICP results for thallium and selenium were very inaccurate even at 50 ug/g so lower values were even more doubtful. Cadmium, on the other hand, produced accurate results at 50 ug/g but no signal at 20 ug/g, again far above the calculated and pooled MDLs. Likewise, molybdenum results for 30 ug/g were quite good but

the calculated MDL of 7.5 ug/g is unlikely in light of the results from the 5 ug/g material. Again the MDL procedure generated values that can only be described as highly inaccurate.

The FAA data were quite different from that obtained from either of the ICPs. Estimated MDLs for cadmium were 30, 5, 5, and 5 ug/g. The calculated MDLs were 4.4 and 3.1 while the pooled MDL was 3.0 ug/g. The 5 ug/g material was accurate, %I = 1.4 and the precision was acceptable, %RSD = 19. This was also true for the molybdenum and the thallium. The MDL method seems to produce values that are accurate and precise for the FAA.

SUMMARY AND RECOMMENDATIONS

The EPAs method detection limit procedure is not adequate for the determination of "less than" values for elemental solid waste analysis using ICP. As the data clearly shows, the MDL too often predicts a "less than" value that is at a concentration that either generates no signal at all or is subject to unacceptable high inaccuracy. Interestingly enough, precision generally was not a problem.

The EPA's MDL procedure seems to predict reasonably accurate values for Flame AA determinations. The calculated and pooled MDLs produced results that were both precise and accurate when using real solid matrix materials. Even for Flame AA however, the amount of work needed to generate these MDLs is quite prohibitive.

The EPA MDL procedure is designed to determine the lowest concentration of an analyte where there is a 99% confidence that the concentration is not zero. The determination of this value is based entirely on the precision of the method without considering accuracy. The smallest amount of analyte that has an acceptable precision (i.e., MDL) is not the correct question. For the regulatory solid waste community the question should be "what is the smallest amount of an analyte that can be quantified within quality control limits of both precision and accuracy".

REFERENCES

1. Appendix A, July 1982 to Methods for Chemical Analysis of Wastewater EMSL-Cincinnati, USEPA, June 1982

2. Appendix B to Part 136 CFR 40, October 26, 1984, Federal Register Vol. 49, No. 209, Pages 198 - 204.

3. Glaser, J.A., Forest, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., "Trace Analysis for Wastewaters," Environmental Science & Technology, 15, 1426, December 1981

4. Kimbrough, D.E. and J.R. Wakakuwa, "Acid Digestion for Sediments, Sludges, Soils, and Solid Wastes. A Proposed Alternative to EPA SW 846 Method 3050." ; Environmental Science and Technology, 23, pages 898-900,

July 1989.

5. Kimbrough, D.E. and J.R. Wakakuwa, "Report of an Interlaboratory Study of an Interlaboratory Study Comparing EPA SW 846 Method 3050 and an Alternative Method from the California Department of Health Service"; Proceedings of the Fifth Annual USEPA Symposium on Solid Waste Testing and Quality Assurance, Washington, D.C. July 1989. Reprinted in Waste Testing & Quality Assurance: Third Volume, ASTM STP 1075, C.E. Tatsch, Ed., American Society for Testing and Materials, Philadelphia, 1991

6. Kimbrough, D.E. and J.R. Wakakuwa, "A Report of the Linear Ranges of Several Acid Digestion Procedures "; Proceedings of the Sixth Annual USEPA Symposium on Solid Waste Testing and Quality Assurance, Washington, D.C. July 1990.

7. Test Methods for Evaluating Solid Wastes (EPA SW 846 Volume 1A) 3rd Edition. Office of Solid Waste and Emergency Response, U.S.Environmental Protection Agency:Washington, D.C., November 1986

TABLE I

ARSENIC		
ESTIMATED MDLs IN µg/g		
SIMULTANEOUS ICP		SEQUENTIAL ICP
a)	268	71
b)	165	165
c)	5.0	50
d)	5.0	50

CALCULATED MDL IN µg/g SIMULTANEOUS ICP				
Spiked Value	500	50	5	_
Mean	506	78.7	51.4	34.6
Calculated MDL	30	41	5.7	7.7
% Inaccuracy	1.2	57.4	902	-
Standard Deviation	9.7	13.3	1.8	2.3
% RSD	1.9	3.5	3.5	6.7

CALCULATED MDL IN µg/g SEQUENTIAL ICP				
Spiked Value	500	50	5	_
Mean	479	42.9	<1	<1
Calculated MDL	17	8.4	-	-
% Inaccuracy	4.2	14.2	-	-
Standard Deviation	5.3	2.7	-	-
% RSD	1.1	6.2	-	-

TABLE II

CADMIUM					
ESTIMATED MDLs IN µg/g					
	SIMULTANEOUS ICP	SEQUENTIAL ICP	FAA		
a)	30	113	30		
b)	115	120	5.0		
c)	5.0	50	5.0		
d)	5.0	50	5.0		
CALCULATED MDLs IN µg/g SIMULTANEOUS ICP					
Spiked Value	500	50	20	5	-
Mean	518	55.5	7.1	7.8	1.5
Calculated MDL	19	4.0	0.9	1.1	-
% Inaccuracy	3.6	11.0	74.5	56.0	-
Standard Deviation	6.1	1.3	0.3	0.4	0.07
% RSD	3.9	2.3	3.9	4.5	10.2
CALCULATED MDLs IN µg/g SEQUENTIAL ICP					
Spiked Value	500	50	20	5	-
Mean	500	41.8	-	-	-
Calculated MDL	22	5.4	-	-	-
% Inaccuracy	0.0	16.4	-	-	-
Standard Deviation	6.9	1.7	-	-	-
% RSD	1.4	4.1	-	-	-
CALCULATED MDLs IN µg/g FLAME ATOMIC ADSORPTION					
Spiked Value	500	50	5	-	
Mean	508	50.4	5.1	-	
Calculated MDL	15	4.4	3.1	-	
% Inaccuracy	2.0	0.8	2.0	-	
Standard Deviation	4.8	1.4	1.0	-	
% RSD	0.95	2.8	19.2	-	

TABLE III

MOLYBDENUM				
ESTIMATED MDLs IN µg/g				
	SIMULTANEOUS ICP	SEQUENTIAL ICP		FAA
a)	140	163		30
b)	135	30		4.5
c)	5.0	50		5.0
d)	5.0	50		5.0
CALCULATED MDLs IN µg/g SIMULTANEOUS ICP				
Spiked Value	500	30	5	-
Mean	439	28.3	-	-
Calculated MDL	72	8.6	-	-
% Inaccuracy	12.2	5.7	-	-
Standard Deviation	23	2.73	-	-
% RSD	5.2	9.7	-	-
CALCULATED MDLs IN µg/g SEQUENTIAL ICP				
Spiked Value	500	30	5	-
Mean	473	10.8	-	-
Calculated MDL	56	7.5	-	-
% Inaccuracy	5.4	64.0	-	-
Standard Deviation	18	2.4	-	-
% RSD	3.8	22	-	-
CALCULATED MDLs IN µg/g FLAME ATOMIC ADSORPTION				
Spiked Value	500	30	5	-
Mean	453	37.6	4.3	-
Calculated MDL	46	11.0	5.0	-
% Inaccuracy	9.4	25.3	14.0	-
Standard Deviation	14	3.5	1.6	-
% RSD	3.2	9.2	37.0	-

TABLE IV

SELENIUM				
ESTIMATED MDLs IN µg/g				
SIMULTANEOUS ICP		SEQUENTIAL ICP		
a)	460	94		
b)	210	120		
c)	5.0	50		
d)	5.0	50		
CALCULATED MDLs IN µg/g SIMULTANEOUS ICP				
Spiked Value	500	50	5	_
Mean	394	6.56	<1	<1
Calculated MDL	29	11	-	-
% Inaccuracy	21.2	86.9	-	-
Standard Deviation	9.1	3.5	-	-
% RSD	4.2	53.0	-	-
CALCULATED MDLs IN µg/g SEQUENTIAL ICP				
Spiked Value	500	50	5	_
Mean	425	12.9	<1	<1
Calculated MDL	63	30.0	-	-
% Inaccuracy	15.0	74.2	-	-
Standard Deviation	20.0	9.5	-	-
% RSD	1.1	74.0	-	-

TABLE V

THALLIUM					
ESTIMATED MDLs IN µg/g					
	SIMULTANEOUS ICP	SEQUENTIAL ICP	FAA		
a)	120	200	25		
b)	110	150	10.5		
c)	5.0	50	25		
d)	5.0	50	25		
CALCULATED MDLs IN µg/g SIMULTANEOUS ICP					
Spiked Value	500	50	20	5	-
Mean	452	41.9	12.1	-	-
Calculated MDL	23	11	14	-	-
% Inaccuracy	9.6	16.2	39.5	-	-
Standard Deviation	7.4	3.6	4.4	-	-
% RSD	0.96	8.6	36.5	-	-
CALCULATED MDLs IN µg/g SEQUENTIAL ICP					
Spiked Value	500	50	20	5	-
Mean	450	28.6	-	-	-
Calculated MDL	26	22.0	-	-	-
% Inaccuracy	10.0	43.8	-	-	-
Standard Deviation	8.2	6.9	-	-	-
% RSD	1.5	24	-	-	-
CALCULATED MDLs IN µg/g FLAME ATOMIC ADSORPTION					
Spiked Value	500	50	5	-	
Mean	446	54.7	7.0	-	
Calculated MDL	20	26.0	4.5	-	
% Inaccuracy	9.8	9.4	40.0	-	
Standard Deviation	6.3	2.5	1.4	-	
% RSD	1.4	4.56	20.6	-	

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PREPARATION AND VALIDATION OF PROFICIENCY EVALUATION SAMPLES FOR SOLID WASTE ANALYSIS

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ABSTRACT

Development, validation, and use of Proficiency Evaluation (PE) samples for solid waste analysis has generally been performed by private firms supplying them on a self-analysis basis to private laboratories. This paper discusses preparation and validation of two sets of proficiency evaluation samples.

For the purpose of this study PE samples are defined as materials used to evaluate laboratory (as opposed to method, instrument, or analyst) performance for a given matrix specific analysis. Any material which have a method defined mean value and homogeneity can be used. The easiest and most practical approach is to spike a known amount of analyte into a well defined homogeneous matrix. This not only meets the criterion for a PE sample but also gives a "true value" in addition to a mean value.

The first set of PE samples consists of five soils spiked with Aroclor 1260, and the second of five soils spiked with arsenic, cadmium, molybdenum, selenium, and thallium. The samples were first analyzed at Southern California Laboratory (SCL) and then sent to twenty eight laboratories outside of California for analysis.

This validation study was designed to test the PE sample preparation procedures used at SCL. The data and statistical analysis for this study are presented.

INTRODUCTION

The last ten years have seen an explosive growth in the field of environmental chemistry. Concomitant with this growth has been the development of laboratory accreditation programs for environmental laboratories. The federal government does not accredit environmental laboratories. Almost every state either has or is developing an accreditation program for environmental laboratories. It is generally agreed that Proficiency Evaluation (PE) samples should be an integral part of a comprehensive laboratory accreditation program. Significant progress has been made in developing PE samples for water matrices,

there has been virtually no progress in the development of solid matrix PE samples. This is due, in part, to the newness of programs accrediting laboratories analyzing solids and the relative simplicity of preparing aqueous PE samples as compared to solid matrix samples.

The California Department of Health Services (DOHS) through its Environmental Laboratory Accreditation Program (ELAP) is responsible for the accreditation of laboratories analyzing water, waste water, and solid waste doing business in the state. ELAP is mandated by California law to distribute PE samples to laboratories they accredit.

PROFICIENCY SAMPLE THEORY

There is significant confusion about the distinctions between PE samples, Laboratory Control Samples (LCSs), and Standard References Materials (SRMs). Also a lack of consensus as to how to prepare these solid matrix PE samples. A number of issues have contributed to this lack of consensus. The most important of which is the debate between spiked PE samples vs."real world" PE sample. This debate revolves around the benefits of "true values" versus mean values or of "real" samples versus the artificial. For the purposes of this pilot project a set of definitions was developed for LCSs, SRMs, and PE samples.

A Laboratory Control Sample (LCS) is a material used by a laboratory for quality control/quality assurance purposes for a method or set of methods. It contains the analytes of interest in concentrations within the working range of the method or methods. It is homogeneous, of the same matrix type as the samples and is analyzed with each batch of samples. The results for each batch should fall within established control limits. This data can be used to monitor long term trends and method performance. It is immaterial whether the LCS is spiked or not, since only a mean value and standard deviations are needed to create a control chart and set control limits.

A Standard Reference Material (SRM) is used to determine the applicability, **on a particular matrix,** of a method, method comparison, instrument, or instrumental performance. It should be a "real world" sample, homogeneous and must not be spiked. The analytes of interest should be present in measurable amounts .

Proficiency Evaluation samples are used to evaluate the performance of the entire laboratory system for a given analyte, not just the methods or instruments. This includes sample tracking, sample preparation, record keeping, method selection, method application, and data

reduction. Like the other materials, PE sample must have the analytes of interest present in concentrations that are within the linear range of the methodology. It must be homogeneous and of a matrix that approximates that of actual samples. Laboratories analyzing solid wastes cannot be evaluated using a reagent water PE sample.

Although laboratories use PE samples internally for self-evaluation, the most important use of PE samples is as part of a laboratory accreditation program. The accrediting agency submits the samples blind to the laboratory. The laboratory's performance is evaluated based on the results obtained. The material can also be used for double blind analysis, that is it can be submitted to the laboratory without the knowledge of its personnel. As a result, a PE sample should have a physical appearance that will not give it away as a PE sample. For laboratories analyzing soils, the PE sample should look like a soil.

Theoretically, a laboratory can be put out of business if it fails a PE sample. This leaves the accreditation program with a large window of liability. So in addition to the above mentioned factors, PE sample must be legally defensible This means PE samples must be validated prior to distribution.

All of these needs are best met by using a spiked sample. Spiking allows for choice of analytes, their concentrations, the matrix, and can establish a "true" value. This last point is important in increasing the PE samples legal defensibility. Spiked samples are also easier and less expensive to prepare.

EXPERIMENTAL SECTION

Experimental Design: To test this approach to PE samples, a pilot project was designed. The project had two goals. The first was to test the PE sample preparation process. The second was to test the validation procedure for PE samples.

PE Sample Preparation

From previous experience in the preparation of soils spiked with inorganic analytes[1,2] it was decided to use water soluble salts of the target elements. The use of water soluble salts means that it will be easy for laboratories to solubilize the target elements using any digestion procedure. It is also easier to make spiking materials using water soluble salts. Strong oxidizers can attack the organic component of the soil and volatilizing it, leaving the heavier silica and alumina portions. This increases the

density of the soil and changes the concentration of the spiked analytes. The appearance of the soil is also altered making it look more artificial. For PE samples to be used as double blind checks they should appear as natural as possible.

A large amount of a local soil was collected, milled, and sieved through U.S. Standard No. 10 (2 cm^2) sieves. It was analyzed for native amounts of sixteen elements regulated by the State[3]. Chromium, cobalt, copper, lead, nickel, vanadium, and zinc were found to be present in excess of 5 mg/kg. Since, most laboratories use EPA SW 846 method 3050[4] as the digestion procedure antimony, barium, and silver will be poorly solubilized. These three elements were not be used. Beryllium was not used as most of the water soluble salts are either unavailable commercially or are extremely toxic. Beryllium sulfate is relatively safe but has a very small mole fraction of beryllium. This would require such large amounts of beryllium sulfate that the soil matrix would be disturbed. This left arsenic, cadmium, molybdenum, selenium, and thallium as the target elements. The inorganic samples were prepared in the following fashion:

	Sample A	Sample B	Sample C	Sample D	Sample E
Arsenic	4,000	500	50	5	-
Cadmium	500	50	5	-	5,000
Molybdenum	50	5	-	5,000	500
Selenium	5	-	5,000	500	50
Thallium	-	5,000	500	50	5

(Here and throughout this paper the dash mark, -, will be used to indicate that the analyte in question will not be spiked and the analyte is at background concentration.)

California ELAP accredits about 200 laboratories for inorganic hazardous materials analysis. Five kilograms of each sample was prepared enough to provide a 20 gram aliquot of each sample to the individual laboratories. Spiking solutions were prepared for each of the salts listed below. These solutions were diluted one to one hundred and checked against standards prepared from different stock materials. All of the solutions were well within 10% of the expected value.

Salt	MF	Mass Element	Mass Salt	Conc.
As_2O_3	0.757	100 g	132 g	100g/L
$3Cd(SO_4)\cdot 8H_2O$	0.438	50 g	114 g	50g/L
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	0.543	5 g	9.2 g	5 g/L
H_2SeO_3	0.612	50 g	82 g	50g/L
Tl_2SO^4	0.808	5 g	6.19 g	5 g/L

MF = Mole Fraction

The amount of each salt that was to be added to each soil was calculated and totaled as noted below. The amount of salts to be spiked was subtracted from the 5 kilograms of soil. Thus when the salts were added, the total weight would be 5 kg. Due to the limited solubility of ammonium molybdate and thallium sulfate, dry salts were added for the 5,000 mg/kg materials. The appropriate mass of soil was placed in a plastic tray and mixed with enough de-ionized water to make a slurry. The slurries are then spiked with the amounts of the salts as indicated below.

	Sample A	Sample B	Sample C	Sample D	Sample E
Arsenic Trioxide	26.4g (200 ml)	3.30g (25 ml)	0.38g (250 ml 1:100)	0.04g (25 ml 1:100)	-
Cadmium Sulfate	5.12g (50 ml)	0.51g (50 ml 1:10)	0.05g (5 ml1:10)	51.2g -(500 ml)	
Ammonium Molybdate	0.28g (30 ml)	0.05g (5 ml)	- (500ml)	46.1g	4.6g
Selenium Trioxide	0.04g (5 ml 1:10)	-	41g (500 ml)	4.1g (50 ml)	0.41g (50 ml1:10)
Thallium Sulfate	-	30.7g	3.07g (500ml)	0.31g (50 ml)	0.03g (5 ml)
Total Mass of Salts	39 g	34 g	44 g	50 g	62 g

This mass was removed from each 5.00 kg batch.

Mass of Soil	4.961kg	4.966 kg	4.956 kg	4.950 kg	4.948 kG

The slurries were then dried at 95^{o} C with frequent mixing. After drying, the materials were again milled and sieved through a U.S. Standard No. 10 sieve.

The PBC Aroclor 1260 was used to spike the same native soil as was used to make the inorganic PE samples. The soil was found to be free of PCBs, although low level interferences from decomposed vegetable matter was detected. The soil was milled, sieved, and autoclaved (to kill any bacteria that might be present). Approximately 150 laboratories are certified for PCB analysis by California ELAP. Ten kilograms of each PE sample was prepared so that each laboratory could be provided with about 25 grams per PE sample. The five PE samples were prepared in the following concentrations in mg/kg:

	Sample F	Sample G	Sample H	Sample I	Sample J
Aroclor 1260	100	10	1.0	0.1	-

Two solutions were prepared; one contained 10 g Aroclor 1260 in 1 liter of hexane, while a second was made form a 1 to 100 dilution of the first solution. The Aroclor 1260 was made up from neat PCB and checked against EPA derived standards and found to be within 5% of the expected value. These solutions were spiked in the following fashion:

	Sample F	Sample G	Sample H	Sample I	Sample J
Aroclor 1260	100 ml	10 ml	100 ml (1:100)	10 ml (1:100)	-

The samples were slurried with n-hexane, homogenized, and dried at room temperature with periodic mixing.

Validation

A two step validation was used. The initial validation was performed in-house. The inorganics were digested seven times using an aqua regia method[5] (which in previous publications was referred to as the SCL method[1,2,5]) for analysis by simultaneous inductively coupled plasma atomic emission spectroscopy (ICP-M), sequential ICP (ICP-Q), and Flame Atomic Absorption Spectroscopy (FAA). For Graphite Furnace Atomic Absorption Spectroscopy (GFAA) EPA SW-846 method 3050 was used. Analytical methods include EPA SW-846 methods 6010, 7061, 7130, 7131, 7480, 7481, 7740, 7840, and 7841. The organic samples were analyzed in duplicate using EPA SW-846 method 3540, 3620, and 8081. All of the results were within 20% of the expected values and had a relative standard deviation of less than 30%.

The samples were validated by having at least twenty (20) laboratories which are not accredited by California ELAP analyze the materials. The samples would be considered valid if the mean value from these laboratories was within 20% of the spiked value and the percent relative standard deviation (%RSD) is less than 20% for the two higher concentrations for each analyte. It is to be expected that the %RSD for an analyte will increase as the concentration decreases, all other things being the same. In the case of the inorganic materials each low concentration analyte was in a material with a high concentration analyte. So for the lower concentrations inorganic analytes, the analyte is considered validated if the mean value was within of 20% the spiked value and the high concentration analyte in the same sample had an %RSD of less than 20%.

RESULTS

For the inorganic samples, the majority of the laboratories prepared the samples by an acid digestion, in most cases by EPA SW 846 method 3050 or a similar method. Two laboratories used chelation extraction for some of the analytes. For the energy dispersive X-ray fluorescence instrument (EDXRF) the samples were ground to pass a U.S. Standard sieve No. 200.

The digestates and extracts of the PE samples were analyzed on a number of different instruments, ICP-MS, simultaneous and sequential ICPs, FAA, GFAA, hydride generation atomic absorption (HGAA), colorimeter, and fluorescence spectrometer. The soils were also analyzed directly by EDXRF. Again all of the mean values were within 20% of the spiked values except for arsenic at 5 mg/kg. See Table I.

The PCB results were more complex. All of the mean values were within 20% of the true value and % RSD was less than 30% for all except the lowest sample. As can be seen on Table II the mean tends to be low and the %RSDs high. However, this is consistent with previous efforts with solid matrix PCB materials. The data was unlike the inorganic materials where there was a normal distribution about a mean. The data for the three highest PCB materials, samples F, G, and H were bi-modally distributed, with one mode at around 95% recovery and another at 75%.

Outliers

Two types of outliers were identified; even multiples and base line interferences. Even multiples are values that are an even factor off of the true value. These are caused by either omission or inclusion of dilution factors or bad standards. For example, there is a Cadmium outlier for sample C. It is exactly 40 times the true value and the worksheet indicates that a 1:40 dilution occurred. Similar errors seem to have occurred three other times in the inorganic samples. Bad standards account for the five arsenic outliers which were all five to seven times the true value and the five high PCBs from laboratory number 1.

Base line interferences occurred in the inorganic samples. This is caused by an interference that raises the analytical background. Without appropriate background correction, the instrument reads significant amounts of the analyte in the blank soil. This caused elevated results in the lowest spiked value. This can be seen for two laboratories with molybdenum and thallium. Every laboratory except two, both with high reporting limits, measured significant amounts of arsenic in the unspiked

sample (E).

DISCUSSION

Almost all of the inorganic PE materials were validated. The accuracy and homogeneity was within acceptance criteria. The mean values were all well within 20 percent of the spiked values and the %RSDs for the high concentration analytes were all less than 12%. The exception to this rule was arsenic at 5 mg/kg level in sample D and the unspiked sample E. In almost every case the readings from sample E, when subtracted from the results of sample D, produced results within 20 % of the spiked value. From this it can be concluded that, in fact, there was a small amount of arsenic present in the native soil. This is not surprising since arsenic is commonly found in soils in the low ug/g range[8]. As can be seen on table I the mean value for arsenic for sample D is 13 ug/g and 8.8 ug/g for sample E, the difference being 4.2 ug/g, 88% of the spiked value. Table III shows the results for arsenic instrument by instrument. As can be seen, for each instrument type, the difference between the mean value for samples D and E is about equal to the spiked value of 5.0 ug/g. The ICPs obviously had a high spectral background problem was well.

One point is clear, that if an analyte is going to be spiked at a concentration that is near the lower quantitation limit, to properly validate it, an internal standard must be spiked in as well at the same time as the analyte. The internal standard should be at a much higher concentration and should be an easily analyzable analyte such as beryllium or cadmium. It is also possible to use background analytes, in soils this internal standard could be iron or calcium. For future validation studies where low concentration spikes are planed, it is suggested that a liquid standard also be analyzed containing these analytes at low concentrations.

The data for the PCBs is more difficult to interpret. As can be seen, the data is bi-modal for samples F, G, and H while the results for sample I is more normally distributed. Specifically, There are nine sets of results clustered around the spiked value (labs 2 - 10) and another eight sets clustered around 70% recovery. The clustering is not evident in the results for sample I. The source of this bi-modality appears to be a result of instrument calibration bias. This conclusion is by means of elimination. Laboratories in both clusters used the same extraction equipment, solvents, methods, instruments, columns, and procedures. The only remaining difference was the calibration procedures. One possibility is the base-

line selection procedure used during integration.

One conclusion is evident, the PCB PE samples themselves are homogeneous. This can be shown by two facts: Samples F, G, an H all produced results equal to or *lower* than the spiked value with one exception. Second, the response was generally linear i.e., F, G, and H were proportionally lower in each case. It would be unreasonable to expect a set of heterogeneous materials to respond in this fashion.

There is also a question of accuracy. For example, sample F was spiked at 100 ug/g but the mean value is 85 ug/g. A similar situation exists with samples G and H. Sample I, on the other hand, was spiked at 0.10 ug/g and had a mean value of 0.109. Were then, samples F, G, and H made incorrectly leaving these materials with 85% of the expected value? If the data were distributed normally about an 85% recovery this might be reasonable. But as has been noted, there are two normal distributions, one around 95% recovery and another around 75% recovery. For samples F, G, and H there are no more than 15% of the results are near the mean value (80 to 89%). Further, since H and I were prepared from the exactly the same solution and base soil, and F and G were made from the same stock as H and I, it would be unreasonable to conclude that the materials contain a concentration other than the spiked value. Rather, there are two distinct populations of laboratories analyzing the same materials and getting two different sets of results.

SUMMARY

Using spiked materials is a useful and economical approach to preparing PE samples for solid waste laboratory evaluation. The preparation steps used in this study generate accurate and homogeneous materials. Difficulties occur when very low concentrations are spiked and this should be avoided or combined with an internal standard. PCB spikes are difficult, not due to the preparation steps but to the linearity problems obvious in the analysis process. More study is needed to identify the source of this problem in PCB analysis and so the use of PCBs spikes for PE samples must be used with discretion.

ACKNOWLEDGMENTS

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Douglas Laboratory

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State Laboratory Division

California Department of Health Services
Hazardous Materials Laboratory

COMPUCHEM Laboratories Inc.

Connecticut Department of Health Services
Bureau of Laboratories
Environmental Chemistry Section

Hittman Ebasco Associates Incorporated of Columbia Maryland

Hawaii Department of Health
Chemistry Branch

Indiana State Board of Health
Environmental Laboratory Division

Lower Colorado River Authority
Environmental Laboratory
Maine Department of Environmental Protection
Bureau of Administration
Division of Laboratory Services

Michigan Department of Natural Resources
Environmental Laboratory

Minnesota Department of Health
Chemical Laboratory

Mississippi State Chemical Laboratory

Ohio Environmental Protection Agency
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Oregon Department of Environmental Quality
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Tennessee Valley Authority
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U.S. Department of Interior
Bureau of Reclamation
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Research & Laboratory Services Division

U.S. Geological Survey
National Water Quality Laboratory

REFERENCES

1. Appendix A, July 1982 to Methods for Chemical Analysis of Wastewater EMSL-Cincinnati, USEPA, June 1982

2. Appendix B to Part 136 CFR 40, October 26, 1984, Federal Register Vol. 49, No. 209, Pages 198 - 204.

3. Glaser, J.A., Forest, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., *"Trace Analysis for Wastewaters,"* Environmental Science & Technology, 15, 1426, December 1981

4. Kimbrough, D.E. and J.R. Wakakuwa, "Acid Digestion for Sediments, Sludges, Soils, and Solid Wastes. A Proposed Alternative to EPA SW 846 Method 3050." ; Environmental Science and Technology, 23, pages 898-900, July 1989.

5. Kimbrough, D.E. and J.R. Wakakuwa, "Report of an Interlaboratory Study of an Interlaboratory Study Comparing EPA SW 846 Method 3050 and an Alternative Method from the California Department of Health Service"; Proceedings of the Fifth Annual USEPA Symposium on Solid Waste Testing and Quality Assurance, Washington, D.C. July 1989. Reprinted in Waste Testing & Quality Assurance: Third Volume, ASTM STP 1075, C.E. Tatsch, Ed., American Society for Testing and Materials, Philidelphia, 1991

6. Kimbrough, D.E. and J.R. Wakakuwa, "A Report of the Linear Ranges of Several Acid Digestion Procedures "; Proceedings of the Sixth Annual USEPA Symposium on Solid Waste Testing and Quality Assurance, Washington, D.C. July 1990.

7. Test Methods for Evaluating Solid Wastes (EPA SW 846 Volume 1A) 3rd Edition. Office of Solid Waste and Emergency Response, U.S.Environmental Protection Agency:Washington, D.C., November 1986

8. Arsenic; Committee on Medical and Biological Effects of Environmental Pollutants, National Academy of Science, Washington D.C., 1979

TABLE I

INORGANIC RESULTS

Arsenic N = 25	All Results Are In Micrograms/Gram				
True Value	4000	500	55	10	5
Mean Value	4000	480	48	13	8.8
SD	440	58	13	10	12
%RSD	11	12	27	77	140
Reporting <pql			1	1	2
Outliers	1	1	1	1	1
Cadmium N = 25					
True Value	5000	500	50	5	<1
Mean Value	4900	500	50	5.8	1.9
SD	330	41	3.5	1.1	1.9
%RSD	6.7	8.1	7.0	19	100
Reporting <pql				1	13
Outliers				1	
Molybdenum N = 21					
True Value	5000	500	30	5	<1
Mean Value	4800	450	34	5.8	2.1
SD	410	55	9.5	3.8	3.0
%RSD	8.6	12	28	65	140
Reporting <pql				7	10
Outliers				2	2
Selenium N = 24					
True Value	5000	500	50	5	<1
Mean Value	4500	470	47	4.6	0.5
SD	450	71	10	4.0	0.3
%RSD	10	15	21	87	68
Reporting <pql			1	5	16
Outliers		2		1	
Thallium N = 20					
True Value	5000	500	50	5	<1
Mean Value	4400	460	44	4.3	0.2
SD	470	70	8.5	1.5	0.03
%RSD	11	15	19	35	13
Reporting <pql			1	3	12
Outliers		1	2	2	2

Instruments Used: ICP-MS, ICP-Sequential, ICP-Simultaneous, Flame AAS, Hydride Generation AAS, Graphite Furnace AAS, Colorimetry, Fluoresence spectroscopy, Energy Dispersive X-Ray Fluoresence.

TABLE II
PCB RESULTS IN MICROGRAMS/GRAM

Sample	F	G	H	I	J
Spiked Value	100 ug/g	10 ug/g	1.0 ug/g	0.1 ug/g	<Report Limit
LAB 1	160	15	1.4	0.19	<0.05
LAB 2	110	11	1.0	0.1	<0.1
LAB 3	100	10	0.84	0.10	0.01
LAB 4	99.2	9.1	0.93	0.09	<0.05
LAB 5	95	9.5	0.95	0.12	<0.04
LAB 6	95	8.8	0.92	0.12	<0.1
LAB 7	94	9.2	0.77	0.11	<0.05
LAB 8	92.6	9.1	1.4	<0.5	<0.5
LAB 9	93.0	8.44	0.935	0.138	0.0206
LAB 10	91.3	10.4	1.0	0.2	<0.1
LAB 11	83.5	6.93	0.72	0.090	0.011
LAB 12	79.0	7.50	0.71	0.083	<0.018
LAB 13	78.7	7.09	0.94	<0.20	<0.20
LAB 14	78.0	8.7	0.820	0.10	<0.021
LAB 15	75.8	8.00	0.89	0.124	<0.005
LAB 16	70	9.3	0.70	0.083	<0.01
LAB 17	65.8	6.0	0.60	0.1	<0.0221
LAB 18	61.9	6.02	0.802	0.074	<0.060
LAB 19	52.3	4.6	0.205*	0.041	<0.01
LAB 20	36	3.1	0.33	<0.1	<0.1
Mean	85	8.4	0.84	0.109	0.015
SD	26	2.51	.280	0.040	0.0029
%RSD	30	30	33	37	21
N =	20	20	19	17	3
<RL	0	0	0	3	17
Outliers	0	0	1*	0	0

TABLE III

Data from Verification of PE Samples for Arsenic

Total Results	All Results Are In Micrograms/Gram				
N = 25					
ID	A	B	C	D	E
True Value	4000	500	55	10	5
Mean Value	4000	480	48	13	8.8
SD	440	58	13	10	12
%RSD	11	12	27	77	140
Reporting <pql			1	1	2
Outliers	1	1	1	1	1
Data for ICPs	(Incuding ICP-MS)				
Mean Value	4000	480	52	23	14
SD	370	48	19	15	13
%RSD	9.2	10	36	65	97
N =	10	10	9	6	5
Data for GFAA					
Mean Value	3800	460	48	9.6	5.0
SD	390	58	6.1	3.4	4.8
%RSD	10	13	13	35	95
N =	8	8	8	11	11
Data for HGAA					
Mean Value	3900	470	47	8.1	4.1
SD	600	82	6.1	1.4	2.2
%RSD	15	18	13	17	54
N =	4	4	5	5	5
Outliers	1	1	1	1	1
	N = 1 for all of the below				
Data for ICP-MS					
Value	3720	458	71	12	2.8
Data for EDXRF					
Value	4920	565	<50	<50	<50
Data for Colorimetery					
Value	4200	510	24	9	-

23

OBSERVATION OF QUALITY ASSURANCE ANOMALIES IN SUPERFUND ACTIVITIES

by

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The Superfund Program consists of numerous components, programs, contracts and documents which have contributed to placing sites on the NPL, PRP and remedial actions. During this process, quality assurance activities within EPA and the States have continually evolved. Accordingly, there are QA requirement for activities under the Clean Water Act, Safe Drinking Water Act, Clean Air Act, RCRA, and the NCP, as well as State programs which can affect Superfund actions as ARAR's. Historically, the Superfund paper-trail process makes use of field sampling plans, QA program and project plans, and ultimately, Records of Decisions (ROD). When a site is to be remediated, additional RI/FS work may be necessary for RD/RA design.

A review of numerous QA documents within the Superfund process indicates that anomalies do occur in the process. As examples, RODs have been reviewed in which numerous compounds were mis identified or reported as isomers based on incorrect R fits or mass spectra, and compounds were reported in aqueous media at values greatly exceeding solubility maxima. In other reviews, wrong analytes are listed on wrong lists with intermixed methods, or the ARAR end point MDL is mismatched with the CLP CRQL. This paper will present a synopsis of QA anomalies observed in reviewing QA activities.

PAPER.DS

24 FUNCTIONAL EVALUATION OF Q C SAMPLES, A PROACTIVE APPROACH

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Abstract

An aggressive and systematic approach in using and evaluating Quality Control (QC) samples provides improved data quality and reduced costs for environmental sampling. Unlike the traditional approach, where evaluation of QC samples has typically been performed after all sample results have been received from the laboratory and the process of data validation/evaluation is underway, a proactive approach involves strategic QC sampling, rapid analytical turnaround, and preliminary review of QC sample results. This "just-in-time" approach allows for decisions to be made regarding isolation of contamination, minimization of error associated with data, and avoiding unnecessary sample analysis costs. This information provides the sampling team with necessary data to identify, isolate, and eliminate sources of contamination and provides a definitive means to determine if resampling is required while still in the field, thus avoiding remobilization costs. Additional savings result from eliminating unnecessary sample analysis and reducing the need to resample. Data quality is improved by reducing data qualifiers and minimizing data gaps. The goal of this manuscript is to summarize the decision-making process in identifying the feasibility of the proactive approach and to provide a framework for that process by means of a decision-tree flowchart.

Introduction

Quality assurance (QA) and quality control (QC) are programmatic and systematic procedures to ensure that a product of known quality is produced. This "quality" is defined for environmental sampling by quantitative data characteristics, accuracy, precision, and minimum acceptable detection limits. The measure of how close our data comes to the true concentration of the contamination present at the site defines accuracy. Precision is a measure of how reproducible our results are. Minimum acceptable detection limits determine the amount of contaminant necessary to be present for detection. These key elements are defined during the establishment of data quality objectives (DQOs) for the scope of work. Based upon the decisions which will be made with the sampling data and the consequences of failure, a minimum acceptable level will become evident. Cost effective sampling strategies can minimize the number of samples required to obtain the required data necessary for the decision making process. The result of this strategy is that as the number of samples is reduced, the quality of each sample data point becomes increasingly more

critical. If information from a sample representing a given area is deleted or becomes unusable, a gap in the data will exist. Depending upon the importance of this information to the achievement of the scope of work, the data gap created by missing or substandard data may be sufficient for resampling to be required. For example, qualitative data may be acceptable for preliminary site investigations. This situation may not justify the additional costs associated with the proactive evaluation of QC samples, requiring rapid turnaround, as qualitative (estimated) data may be satisfactory. On the other hand, data necessary to support closure or permitting activities would require quantitative data.

Traditional sampling and analysis plans call for critical samples to be analyzed under rigorous analytical standards at qualified analytical laboratories such as laboratories participating in the Contract Laboratory Program or one of several interlaboratory comparison programs. Unfortunately, this process is time consuming. Constraints from laboratory scheduling, holding times and documentation requirements result in a routine 45 day turnaround time for the results from a sampling event. It is at this point that the data are reviewed and evaluated. The consequence of discovering that a sample or batches of samples fail to meet the minimum criteria at this point has serious implication on both cost and scheduling.

Minimum criteria for sampling are measured by the results of the QC samples. If the QC samples are discovered to have a significant level of contamination on review after the typical 45 day wait, it may be too late to remedy the situation at this point. However, if the QC samples had been evaluated earlier before the other associated (within the same sample batch) samples were analyzed, several options would then be available: 1) discarding the data completely, thus eliminating the data for that point or area; 2) finding the source of the problem and eliminating it with subsequent resampling and reanalysis; 3) only using the data with analyte concentrations significantly above background data ($\geq$ 5X or 10X above the concentration found in the blanks); or 4) accepting qualitative data (instead of quantitative), as all data less than 5X or 10X above the concentration found in the blanks will be qualified as estimated (J) (EPA Functional Data Validation Guidelines).

Conclusions

This "just-in-time" approach allows for decisions to be made regarding isolation of contamination, minimization of error associated with data, and avoidance of unnecessary sample analysis costs. This is accomplished by reviewing the QC sample results which are scheduled for rapid turnaround (24 to 48 hours) analysis before other associated samples are analyzed. This provides initial review of QC results and the option of cancelling associated sample analyses if it is decided that estimated data are or will not be acceptable. It is vital that the rapid turnaround data be evaluated immediately so that real-time decisions can be made. For example, sources of contamination can be identified, isolated and eliminated (see Figure 1),

thus preventing further contamination of QC and associated samples; and decisions can be made to resample while still in the field, thus avoiding remobilization costs (see Figure 2). These options may result in further cost savings by avoiding unnecessary analyses. Scheduling delays are reduced as a result of faster evaluation (as opposed to the traditional 45 day, standard turnaround wait). If these decisions are used to avoid the cost of remobilization, eliminate unnecessary analyses, and insure that data meet DQOs, then thousands, or possibly million, of dollars in project and analytical costs will have been saved. The likelihood of poor decision making is reduced, and the project tasks will have been performed as efficiently and cost-effectively as possible.

Contamination Source Isolation Process

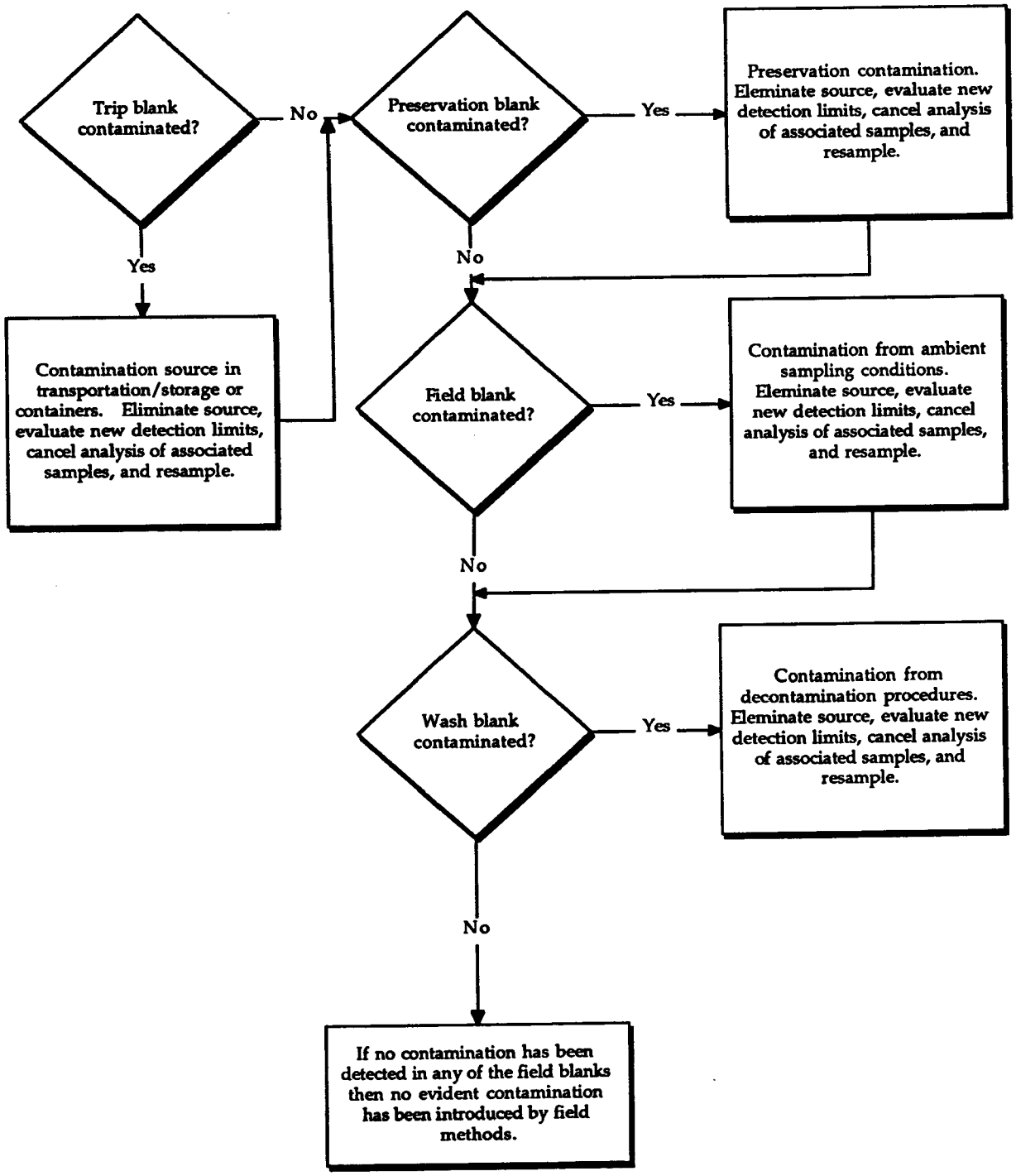

Figure 1

Pro-active QC Decision Tree

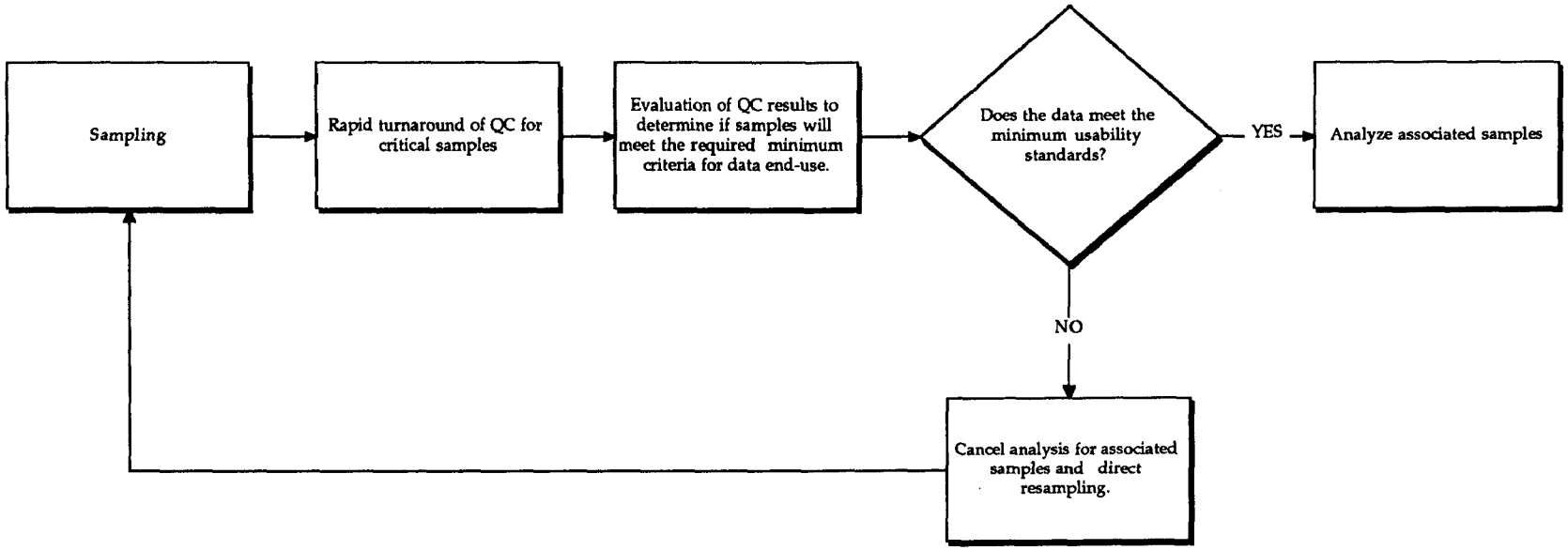

Figure 2.

25 **FEATURES OF THE U.S. EPA-QUALITY ASSURANCE MATERIAL BANK STANDARDS**

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ABSTRACT

The U.S. EPA currently provides organic solution standards to its Contract Laboratory Program (CLP) laboratories under the Quality Assurance Material Bank (QAMB). These standards ensure comparability between laboratories and traceability to U.S. EPA materials. ManTech Environmental operates the current QAMB program over which U.S. EPA maintains a strong quality assurance oversight role.

The quality assurance requirements for QAMB organic solutions standards have a number of distinct features and this presentation addresses each. For example, one requirement is the characterization of the neat materials with purity analyses, including moisture analyses of hygroscopic compounds, and confirmation of the compound identity. An U.S. EPA-supervised, independent laboratory analyses the purity to verify the original assay. Furthermore, the identity confirmation procedures are designed to be unequivocal.

Each lot of standards is analyzed to verify its concentration by ManTech Environmental and again by an U.S. EPA-supervised, independent laboratory. Reanalysis of the standards is required periodically to verify stability, according to a schedule optimized for each standard. Strict control limits are placed on each of these analyses and will be presented. The details of these specific requirements and their implications on confidence intervals associated with the standards will be presented.

The probable error of each step in the solution standard production process has been evaluated and used to assess the overall probable error. This information, along with the analytical method performance data for the quality control, serve to define the quality of the standards available under the QAMB program. The results of this evaluation will be presented.

26 AUTOMATED DATA VALIDATION--PANACEA OR TOOL

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ABSTRACT

The increased emphasis on the clean-up of hazardous waste sites and the quality assurance (QA) of environmental data has caused a substantial increase in the amount of analytical data that must be reviewed. Computer programs such as Computer-Aided Data Review and Evaluation (CADRE) for the review of Contract Laboratory Program data and "E-DATA" for the review of analytical data from emergency response teams have been developed to help deal with that large amount of data. Such programs can be of great value to the data reviewer; however, the user must be aware of what these programs can and cannot accomplish. The types of QA measures that may be checked by computer such as calibrations, holding times and analytical sequences will be described. The limitations of computerized checking will also be discussed including the areas of analytical methodology, electronic data formats, chromatographic quality and professional judgement. The needs for standardization and QA of the electronic data will be considered.

Notice: Although the information discussed in this article has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to Agency review and does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

27 BUILDING DATA QUALITY INTO ENVIRONMENTAL DATA MANAGEMENT

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ABSTRACT

With the volume of environmental data increasing and the need to make rapid, accurate decisions, managing the data is essential. Data Management includes consolidating all information into central, consistent, accurate data bases. From these data bases, information can be selected, queried and electronically transferred to statistical, graphical and reporting packages. By establishing a database with output to decision support software, accuracy and speed of decision making is improved. An essential part of computerizing the data is establishing a credible data base. This paper describes methods to improve the quality, integrity, and connectivity of information.

INTRODUCTION

There are many different programs requiring collection and analysis of environmental data. Among these are those required under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA). In addition, the National Pollutant Discharge Elimination Systems (NPDES) requires that any effluent from a facility be monitored regularly according to permit requirements. Other regulations require monitoring of air and drinking water. No matter which program is discussed, data must be collected and evaluated. The problem is that if the project is large or if monitoring data is collected for several years, one is inundated with information. This information becomes difficult to sort and evaluate. While many of begun using spread sheets and other similar tools, the amount of data can quickly exceed the capacity of many tools. The other problem is that the technical staff and managers typically do not enjoy entering the data. Even if diskette deliverables are presented, someone must map and move the data into the existing database. Many databases have been established only to find that the information is inaccurate, inconsistent and difficult to retrieve. The purpose of this paper is to outline issues in data management and an strategy for success. The information is based on the experience which Automated Compliance Systems has had in managing databases of over 3,000,000 records on over 100 projects. These projects have included CERCLA, RCRA, NPDES, air monitoring and other environmental projects.

PLANNING

Some regulations such as CERCLA, SARA and RCRA require that planning documents be written. Others require that data be documented but do not require specific planning documentation such as sampling plans and QA/QC Plans. Most projects do not include a data management plan. Millions of dollars are spent collecting and evaluating the data however, little thought is given to planning how the data will be passed between parties, what information will be captured and passed, and who will be responsible for this process. The first recommendation for large projects is to outline a plan for managing the data.

The goal of any data management system should be to consolidate the data and allow the end user to be able to use and evaluate the information. The primary purpose of a data management plan is the communication of how information will be captured, accessed, entered, and used. Data management plans should include:

1) Data Dictionary
2) Data Naming Conventions
3) Data Entry Criteria
4) Data Consistency Filters
5) A Traffic Control System
6) QC Data Elements and Relationships
7) System Design Strategy
8) Audit Trails and Entry Serial Numbers
9) Connectivity Requirements
10) Tools for Compliance Screening/Data Validation
11) Staff Responsible for Data Management

The following sections will outline issues and provide some examples of success when these areas are addressed.

DATA DICTIONARY

Data dictionaries often include the elements of data to be captured and the definitions of these elements. Some data dictionaries include the location of information in the database and diagrams of the relationships between the data. While this is useful, the most important information is the data elements and terms. This assures that all project members have consistent understanding of the pieces of information to be captured.

Another critical issue in establishing a data dictionary is that the geologist will not look at data the same way the laboratory looks at the same piece of information. The data dictionary needs to be reviewed by project team members with different view points. This insures that the same data element will be understood by all parties. A benefit of the dictionary is that redundancy in the data system can be reduced. (1)

DATA NAMING CONVENTIONS

The planning document should include a method of naming and identifying samples. Samples are often collected by one group, analyzed by another and evaluated by yet another group. The key information which is passed along is the sample identity. If all parties do not know the convention for numbering samples mistakes can be made.

One issue with naming a sample is how much information to include in the name. Many projects have met disaster because the convention included more fields than the sampling, lab or end user database would allow. If this occurs the identity may be truncated and make matching the data

with the sample number difficult. It is important that all the parties involved understand how data is collected and entered into the respective databases along the data processing path. As an example if the sample collection team had understood that the laboratory computer could only accept 12 digits for the customer sample number, then the sample number could have been appropriately sized. Long naming conventions increase the chance of data entry errors. If the name is exceedingly long, the laboratory and end users often have trouble accurately entering the number for laboratory sample tracking and for using the information. If this occurs the association between the data and the sample may be incorrect. Keeping sample location and numbers at less than 10-12 characters is suggested. This is especially true if bar code readers are not used.

ACS's experience has shown that unique pieces of information should be tracked separately and not aggregated together. With the power of relational databases, the data can still be related without elaborate naming conventions which encode all pieces of information. As an example, a sampling location such as SB-12/A/10-15/3-91 may mean the soil boring (SB) was collected from location number 12 in zone A at a depth of 10-15 feet in sampling event of May 1991. It is very easy for data entry mistakes to be made in entering this number into sampling and laboratory databases. With modern relational databases, there is no reason for this type of naming. With a well designed system all the information could easily be tied to Soil Boring number 12. This could be printed on chain-of-custodies and labels without being encoded.

The recommendation is that the sampling location names or numbers should be short and unique. Other data should be related to this point name. Information typically related to the point name is the sampling coordinates, the depth of collection, complete sampling and analytical data including analytical data and dates of collection, receipt by all parties. Data from multiple sampling events can be associated to a single location. Data from each event is designated by sampling and analysis date and by the laboratory and sampling numbers used in sample identification.

A location and sample number system should be established and documented and used by all contractors performing work. Often the most confusion occurs when several organizations collect samples at the same site over several years. Without an agreed upon location naming convention, the data is difficult to connect to the correct location. Having this information available to all staff performing work is important in maintaining accurate and traceable data.

Since the location name and sample numbers are critical pieces of information, it increases accuracy if these are passed between the field teams and laboratories via computer generated chain of custody forms. Many projects have suffered major problems because of difficulty in transcribing data from a hand written chain of custody to a laboratory computer tracking system. If the project planning information is entered for early tracking, the sample names and numbers, this can be easily done. In addition to the forms, bar codes can be placed both on the forms and the bottles. The bar codes should contain the sample location, sample number, depths, analysis requested and any other pertinent information. By putting more information on the code than the number, sample login in the laboratory can be quick and accurate. If changes occur while samples are being collected, information can be hand written on the forms. (2)

DATA ENTRY CRITERIA

Data entry is accomplished via manual entry, scanning or electronic transfer. Criteria should be specified for all areas. It has been ACS's experience that scanning of documents which are not neatly typed results in 5-10% errors requiring reentry and correction. This is particularly critical for sampling logs, boring logs and other documents which are typically hand written. If these are manually entered into the database, the data can be electronically searched and moved to logs and construction diagrams. This results is typed, legible forms while entering the data only once.

If manual entry is needed, the best method is to double key the information by separate staff with the computer making a comparison between the entries. If it is not practical for two people to enter the information, it should be entered at least twice by the same person followed by computer comparison of the entries. The computer should print out differences between the entries. These differences should be resolved prior to moving the data from temporary holding files or tables to the final database tables.

If electronic transfer is used, typically ASCII files should be transferred. All parties should agree on the information to be entered and transferred and its location in the file. Two major issues are that many organizations performing analysis do not have double key entry processes nor do they have electronic download from the instruments to the central database. This is especially true of laboratories. As a result the data is rekeyed from the instrument output to the database. This is why so many differences are normally found between hard copy and electronic transmittals. Data errors between these two media run from 5-10%. In some cases they are greater. In auditing laboratory information processes, ACS has found as many as four transcriptions of the same data prior to entering it into a file for electronic transfer.

As a result, ACS recommends that criteria be outlined for data entry of sampling data, laboratory data, validation of data and other information needed for the permanent records. These criteria should include not only the method of transfer of data, but the way the data enters the database initially. This means that if a laboratory does not have electronic transfer between instruments, double key entry may be needed. Trend analysis and other checks may be used to further assure that data is consistent and correctly reported.

DATA CONSISTENCY FILTERS

Many problems in using data result in inconsistencies in the reporting. As an example, ACS mapped data from a project. The engineering firm had observed a 20ft water level difference at the site when ground water samples were collected. Prior to ACS involvement, much money had been spent on models to explain these inconsistencies. After the original well logs and methods of measuring water level were discussed, ACS determined through consistency checks that the problem was inaccurate survey information.

The consistency checks are performed via computer and via data inventory printouts. These consistency checks. The consistency checks include identifying:

- Missing sample locations
- Duplicate data and samples
- Improper parameter names
- Duplicate Test Names
- Samples with missing data
- Data with missing location information
- Time traveling samples
- Incorrect location and episode data
- Illogical Units
- Illogical Qualifiers
- Missing Detection Limits

Any data management process should look for and correct problems in these areas. While software can help identify these issues, it takes dedicated staff to correct these problems. In order for these corrections to occur, all the members of the project team must be easily contacted regarding these problems. It is also helpful if these problems are identified as early as possible in the project. This allows for correction of inconsistencies prior to use of the data.

When new data is received, a mechanism must be in place to examine the incoming data and compare it to the existing data in the central database. The mechanism should also look for inconsistencies similar to those outlined previously in the new incoming data. The information upload to the central database should allow only the new data to be entered. If the entire database must be uploaded, hours may be wasted in data processing. In order to facilitate these data transfers, special utility programs need to reside on the system which maintains the central database.

DATA TRAFFIC CONTROL SYSTEM

A major part of managing the data is knowing when deliverables are due and assuring that they meet schedules and that the data required is delivered. This is particularly critical for sampling and analytical data. The traffic control system varies depending on the project need. As an example, for CERCLA/SARA projects the proposed number of samples and QC samples must be compared to the number actually collected and analyzed. This information is used to alert project managers of missing information and be able to assist in cost tracking. In the systems used, all the proposed samples, matrix, methods of analysis, and QC for delivery are entered. The computer compares incoming data to the proposed data. Printouts of differences were available immediately after receipt of data. These reports must occur quickly. This allows rapid corrective action. Having the cost information available also allows contractual issues to be quickly resolved.

For NPDES type of projects, not only is the laboratory data tracking important, but sampling staff need to be alerted to collect specific samples from outfalls on specific days. In addition, the final reporting of data should be compared to permit requirements. This comparison should include the analytes, analyte concentration limits, and date reported. Anything exceeding permit criteria must be flagged and managers notified immediately.

The traffic control system described is important since typically, there are large amounts of incomplete data or data which does not meet acceptance criteria. By allowing early notification of these problems, project schedules can be met. Without using computers, tracking the large number of samples, sample results, cost and schedule become difficult and tedious for technical staff. The data management system must address these needs. The method of handling these issues should be outlined in the plan.

QC DATA ELEMENTS AND RELATIONSHIPS

Another critical item is defining the QC samples in the planning document and a numbering scheme for these samples. The critical item which is often missed is the definition of what the sample is and how it is collected. Currently at least 10 definitions exist for Field blanks and rinsates. With this many definitions, all parties in the process should understand what the samples are.

The other critical information is how the QC samples are related to the actual samples. These relationships must be captured or the QC data will not be useful. As an example if five trip blanks were collected and shipped in 5 coolers, one must be able to relate the correct blank with the correct cooler or to the samples in the cooler. This is typically done via the chain of custody and the sampling date, time, and person collecting. However, a more successful method is to number the QC samples and state which samples by number were associated with the QC samples. This method of association should be included in the definitions in the data dictionary.

Similar issues occur in the laboratory. Many laboratories do not track batch numbers for samples. Samples may only be related to QC by date. This leads to problems when multiple instruments are being used for the same task and when several similar sample preparations are performed on the same day. More problems arise when the laboratory must reanalyze a sample. Reanalysis results in two or more batches of QC being related to a sample. If the lab system cannot assist in managing this, confusion as to which data should be reported may occur. All QC should be available. This means that QC should be associated to the samples by unique batch numbers. When reanalysis occurs both the old and new batch number should be available with a comment on why reanalysis was performed. Batch numbers will also serve to tie the instrument, method, and person performing analysis to the samples. Without knowing which samples are associated with specific QC samples, data validation and evaluation becomes difficult.

SYSTEM DESIGN STRATEGY

The system must be flexible enough to handle all the sampling, project scheduling and analytical data. The database must be able to manage large and small projects. The entry process must allow easy addition of parameters, sampling data points and other information which may not be identified in the early planning stages. The system must be able to handle numeric and textual data. A design which has proven to be flexible, thinks of data as three type, sites, locations and episodes. Site data is the area of study or the site name. This could be a building, facility, or area name. The next type of information is associated with the location. This information is fixed in time. It includes information such as soil lithology, sample coordinates (x,y, and z), and the name of the sampling location. The last division of data is the episodic data. This data includes information which changes with time. These data elements include but are not limited to water level, parameter names, analytical results, detection limits, units, dates sampled, dates prepared and analyzed, methods used and other information related to the sampling events.

Using this design strategy makes data entry flexible and easy to add information when the need arises. No matter how much planning occurs there is always the need to add information during the project. Once data is entered in this manner, it can be extracted in many different methods to allow one to examine data by locations, parameters, methods and other queries appropriate for data review.

Another issue of design is the method of handling data qualifiers. These qualifiers are used to easily indicate QC problems, detection limits and other pieces of information needed to evaluate the data. In many databases the qualifiers are coded as part of the result. This makes passing data to modeling programs, and statistical programs difficult. These programs accept only numeric results. If the qualifiers such as Us, Bs, Js are part of the result field, it is difficult to extract the data and move it to user programs. It is critical that qualifies be placed in separate data fields. The recommendation is that reporting and usage requirements should not drive the data entry. By allowing the computer to reformat data rather than have data entry dictated by the reporting additions can be made quickly and by the user.

Other issues for data base design include the use of relational database tools which can be moved to various hardware systems without rewriting software. This will allow upscale of hardware as the database grows in size. It also allows end users to have smaller systems and to easily upload and download between smaller and larger systems. In addition the ANSI computer standards require use the Structured Query Language to facilitate data communication between systems. Because of these features, ACS has had the best success using ORACLE Relational Data Management Systems with a design built on a row based entry system consisting of sites, locations and episodic data.

AUDIT TRAILS and ENTRY SERIALS

The computer must be able to track the entry and changing of information. An effective method is to establish unique computer generated serial numbers for each entry session. The audit trail should be kept for both manual and electronic entry. The person performing entry or download, of the data, the origin of the information, and the date entered must be kept by the computer. The entry serial number ties this information together. By performing this task, an audit trail is kept on the data entry. Changes to the database should follow a similar strategy.

CONNECTIVITY REQUIREMENTS

In communicating data from planning to field crews, to the laboratory, and back to the data users, a path with consistent methods of transfer must occur. Without documentation and a well designed path, data will be transcribed and reentered many times. This results in errors and project delays. The best strategy is to outline file structures and information which must be passed. Typically ASCII files can be passed between organizations. However, information sometimes is not in consistent locations within files. A data exchange language which assists in this process is a useful tool. This exchange language can parse files apart even when information is not in consistent locations.

As mentioned in the Data Consistency Filter section, as data is uploaded checking for consistent information should be performed. These checks should be available to all parties moving data. By doing this, early warning for missing and inconsistent information occurs.

The recommendations are to use ASCII files, to agree on the information to be transferred and a general format prior to beginning the project, to use a data exchange tool which will assist in parsing files even if data moves within the file, and to provide upload and download software which performs consistency checks on the incoming and outgoing data.

TOOLS FOR COMPLIANCE SCREENING/DATA VALIDATION

Contract Compliance Screening is the systematic verification that the deliverables specified in the governing contract meet delivery and general QC requirements. It also includes verifying the frequency of QC analysis, and limit checks. Examination of the raw data (chromatograms and mass spectra) are not included. The process of screening generates both summary and detailed lists of samples failing criteria with associated notes about how they failed.

Data Validation is a systematic review of the data which includes QC frequency and limit checks. It also includes review of the raw data, flagging of data which does not meet criteria and technical judgement in assessing the information.

The part of screening and validation amenable to automation is the QC frequency and limit checks, and much of the data flagging. Once the initial flags are applied, some evaluation using

technical judgement must be done by a qualified technical person to assess the flags. By automating much of this process, staff will be better utilized, screening will be improved, consistency is improved, and faster execution will occur. Currently, much of this process is poorly automated.

Software used for this purpose needs to allow the limits to changed to meet the objectives of the project. It must also generate summary reports outlining the number of compliant and non-compliant items per sample. Detailed reports outlining specific non-compliant data should also be presented. Ultimately final data with flags should be presented. This should be similar to an EPA Contract Laboratory Protocol Form 1 with additional validation flags. The system should be able to handle textual data so that explanations of flags and non-compliance can be related to the numerical results.

After the screening/validation is complete, the electronic download to a central database should be easy and menu driven. The data from the central database should then be moveable to other packages such as statistics and mapping packages. This will allow the central repository to maintain upto date data. The last issue is that an audit trail on the changes should be maintained.

DATA MANAGEMENT STAFF

A key person(s) should be identified in each organization to manage data. This individual must be a part of all planning from the initial stages. A budget should be set aside for this task. The items above should be addressed in the planning and continuing phases of the project. The data manager(s) should be familiar with the types of data collected in the particular process, they should have a desire to create systems which place data in the users hands, and should be willing to communicate with the entire project team. This person or organization becomes a focal point to manage the data traffic.

CONCLUSION

Data management is an integral part of environmental projects. The need to quickly obtain and assess data continues to be an important factor in successful completion of projects. Multiple companies and organizations typically work on these projects, the management of the information is critical. If a central process is established for data management from the beginning, projects can be successfully completed. Key elements include computerized chain of custody and tracking, establishing common terms and meanings, and establishing location naming conventions which are documented and used by all parties. In order to maintain consistency and integrity, audit trails and consistency checks are required. To track the information, a traffic control system is needed to determine the planed samples versus those obtained. Screening and validation must be automated to prevent data review bottlenecks. The data must be made available to users for decision support in a timely manner. By considering these issues in the planning and implementation project, high quality and timely results can be generated.

References

1. Phyllis Koslow,"Data Dictionaries," Database Programming & Design, April 1991, 26-29.

2. Butterfield, S.; Deinse, H.V.; Rumford, Greg; Penalba, Jorge; "Data Management of a Multimedia Remedial Investigation Program," Presented at Annual Conference of the Air and Waste Management Association, Vancouver, British Columbia, June 16-21, 1991.

28 A SOFTWARE APPROACH FOR TOTALLY AUTOMATING THE QUALITY ASSURANCE PROTOCOL OF THE EPA INORGANIC CONTRACT LABORATORY PROGRAM

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ABSTRACT

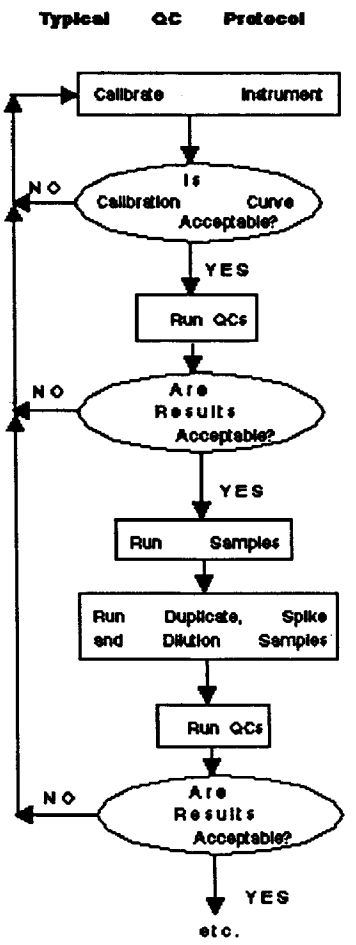
The EPA's Inorganic Contract Laboratory Program requires the determination of 23 elements in a wide variety of matrices. ICP-OES and ICP-MS, because of their multielement capabilities, are ideal techniques for this type of analysis. Although ICP-OES has gained full approval by the EPA, ICP-MS, while rapidly gaining momentum, is still not fully approved for all the EPA Inorganic Programs. However, regardless of the technique chosen, the quality assurance protocol associated with a CLP analysis is very complex and time consuming. Traditionally this has been a manual operation that can involve the rechecking, recalibrating, rerunning or even rejecting samples, standards, blanks and spikes that fall outside certain specified ranges.

This paper will describe a software program, which shall be called "QC Expert™", that totally automates the operation of both ICP-OES and ICP-MS for this very tedious quality control protocol. This is achieved by controlling both the instrument and the autosampler with the software. During an analysis, if the quality of the data is considered unacceptable, then pre-established procedures to restore the quality will be undertaken. These will be monitored and then directed by the software.

The major tasks for establishing the proper criteria for this type of analysis are divided into two separate steps. The first step involves setting the analytical method (standard concentrations, QC limits, predefined actions, etc.) and the second step involves setting up the sample parameters (sample id's, weights, and volumes, etc.). The logic behind this, is that once an analytical method has been set up to perform a C.L.P. analysis, it will not drastically change. On the other hand, the sample information will almost definitely change on a regular basis. For this reason, these two quite different tasks are separated and simplified to provide for a quick and easy set up for each analysis.

INTRODUCTION

The EPA's Inorganic Contract Laboratory program has quality control requirements that are very stringent. Laboratories participating in ths program find that these analyses can be extremely time-consuming on the analyst's part, and would rather not have an analyst spend all of his or her time monitoring the analysis of samples, to insure that good quality control of the data is maintained. Yet, that is exactly what many laboratories must do. Many instruments still require some user intervention to both ascertain the quality of the analysis and to control it.



A typical analysis requiring extensive QC is shown in the flowchart above. The protocol shown here is very similar to that mandated by the EPA for the Contract Laboratory Program. Once the autosampler tray has been loaded with samples and the appropriate sample IDs and perhaps weights and volumes have been entered into the instrument software, the analysis is started by establishing a calibration curve. The analyst must be present at this point to verify that the calibration curve meets the requirements for the method, for example, the correlation coefficient of the curve must be 0.9995 or better. In some cases, the correlation coefficients must be hand calculated by the analyst. If the correlation coefficients do not meet the established limit, an action from the analyst is required. This action is likely to be initiation of a recalibration.

After the calibration curve requirements have been met, a suite of QC standards that must be run. The result for each element in each QC standard must be within some established limits. If the results for an element or a number of elements fail to meet the requirements, an action by the analyst again must be taken. A typical action would be to recalibrate, confirm the calibration curve and rerun the QC standards until all of them meet the established criteria. Finally, samples may be run and the analyst may take a break from closely monitoring each result. However, the analyst may need to know when the results for an element are below the instrument detection limit, requiring that the sample be rerun by a more sensitive technique, or when the results for an element are above the linear range, requiring that the sample be diluted and rerun. In both of these

cases, the results are not reportable. Rather than searching through the data to see where the results fall, the analyst may choose to continually check on the results after each sample is run, to flag the samples that must be rerun. In either case, after 10 samples have been run, the analyst must return to monitor the results for the next set of QC standards to verify the continuing quality of the results. As you can see from this scenario the analyst has little time for other tasks and the potential for errors is great. Just imagine the task of making sure 23 elements in 10 QC standards are within the allowable limits.

Automation of this analysis would provide benefits to the analyst and ultimately to the laboratory. The greatest benefit would be that the analyst would be free to multi-task and would not be required to make any decisions during the analysis or to physically take any action. The analyst could be responsible for the analysis but at the same time attend to other challenging tasks and be assured that the quality of the data was being assessed and controlled by the software. The potential for human error disappears. The lab would also be assured of the quality of the data under the close supervision of the software.

SUMMARY

This proposed automation could be met with the QC Expert software which is designed to provide intelligent quality control for ICP Emission spectrometry and ICP Mass spectrometry. If the quality of the data is determined to be unacceptable, pre-established procedures to restore quality will be undertaken in real-time.

Software Structure

The strategy of this software design was to intelligently separate the various tasks that are required to set up an analysis. The instrumental parameters such as element mass or wavelength, integration time, etc. are set up with the normal instrument software. What we are calling the analytical parameters are established in the QC Expert software. The analytical parameters are divided into two parts or files. One is called the Analytical Method File and contains all the information necessary to run the analysis except for the sample information. The other file is the Sample Description file which includes information specific to the individual samples. The Analytical Method file and the Sample Description file are then combined into an Autosampler Worksheet File, which is basically a script for the instrument or a log of the analytical sequence. Results obtained during the analysis may be used later to create a variety of reports and a variety of QC charts.

Specifically the Analytical Method File contains information on the calibration standards and the type of calibration algorithm to use. It also contains information on all the QC standards that will be run in the analysis and the allowable limits for them. All actions for out of limit conditions are chosen in this file. The internal standard elements that will be used are selected here as well as the allowable drift limits for the internal standard element intensities. This file also contains information on how often a QC standard will be run during the analysis.

The information about the calibration and QC standards are stored in separate files. This allows for flexibility in the selection of QC standards and calibration standards. Once a standard is created it may be used with any number of methods, it is not necessary to re-enter the standard information in each Analytical Method file. A standard file may be created which contains every element one ever expects to determine. This file could then be used with any method, but the software would only use the information for the elements in that method and ignore the others.

QC Limits

The allowable limits for several measurements are established in the Analytical Method file. Each measurement that a limit has been set for may have an action associated with it that will be taken if any of the limits are exceeded. Limits may be set for the following:

* Correlation coefficients for each element
* QC standards
* Intensities for the internal standards
* Duplicates, spikes and dilutions
* Elements in the samples

An example of when one might use the sample limit feature of the software, would be to monitor when the concentrations of the elements in the samples are below the detection limit or above the linear range. In both or either case, an action could be selected. A message would be printed which might simply flag the data and tell the user that the sample must be rerun for that particular element. For example, the message "Se concentration is below the Detection Limit, RERUN by GFAA" could appear when the concentration of Se is below the lower limit. The message "Ca concentration is beyond the Linear Range, DILUTE and RERUN" could appear when the concentration of Ca exceeded the upper limit.

Actions

An action may be chosen for every measurement for which a limit was set. This would include: correlation coefficients, all QC standards, upper sample limit for each element, lower sample limit for each element, intensity drift for each internal standard element, duplicates, spikes and dilutions. It is also possible to qualify when an action should take place. Rather than have an action, say recalibration, occur when any element out of a suite of 20 is out of limits, it is possible to establish which elements or how many elements must be out of limits before an action will occur. A recalibration takes time and it may not be worth the time if only one element is out of limits, especially if it is an element that may be determined later by a more sensitive technique anyway.

There are nine available actions for each measurement for which you have established limits. Two actions may be selected for each measurement. The second action becomes the alternative action that will be taken if the first action does not solve the problem. This would be analagous to a user reruning a QC standard if it did not meet the established limits. For the QC Expert this would be action 1. If the QC standard still

failed, the user would recalibrate and then rerun that standard. This would be action 2 for the QC Expert.

When an out of limit condition is detected by the software, the selected actions are executed. The actions available are as follows:

* Stop
* Continue
* Recalibrate and Continue
* Recalibrate and Rerun
* Wash for X seconds and Rerun
* Wash for X seconds and Continue
* Rerun current sample/standard
* Continue from... (specify sample or standard ID)
* User Defined Program

User Defined Program

The User Defined Program action allows the user to do virtually anything that a program can be written for. A User Defined Program is a batch file containing whatever commands are needed to accomplish the desired task. When this action is executed, the QC Expert software is temporarily exited and the User Defined Program is run. When the program is completed, the QC Expert software is automatically returned to and the analysis continues. The User Defined Program could turn on or off a switch or turn on a dilution system or even call you at home.

Every time an out of limit situation occurs the message in the message column would be printed on the printout. This message could be as long as 80 characters, the full width of a page.

The utility of a User Defined program as well as the utility of establishing limits for elemental concentrations in samples are best illustrated in a process control situation. An example of a process that requires good control is the discharge of effluent from a factory. Depending on what body of water the effluent is being discharged into, the limits for the various heavy metals monitored vary. In this example, the effluent is being discharged into a trout stream thus the allowable levels of many heavy metals are very low. The allowable level for the discharge of Pb, mandated by the EPA, is as low as 15 μg/L in some states. The QC Expert software in conjunction with an ELAN 5000 could easily be used to both monitor the level of Pb in the effluent as well as control the discharge of it. The sample limits feature of the software could be used to determine when the concentration of Pb exceeds 15 μg/L in the effluent. When the level of Pb does exceed 15 μg/L, the action that the QC Expert would initiate would be a User Defined program. This User Defined program could control a switch that would divert the effluent to a holding tank where it could be treated to precipitate the Pb before discharging the effluent into the trout stream.

Customizing a Method

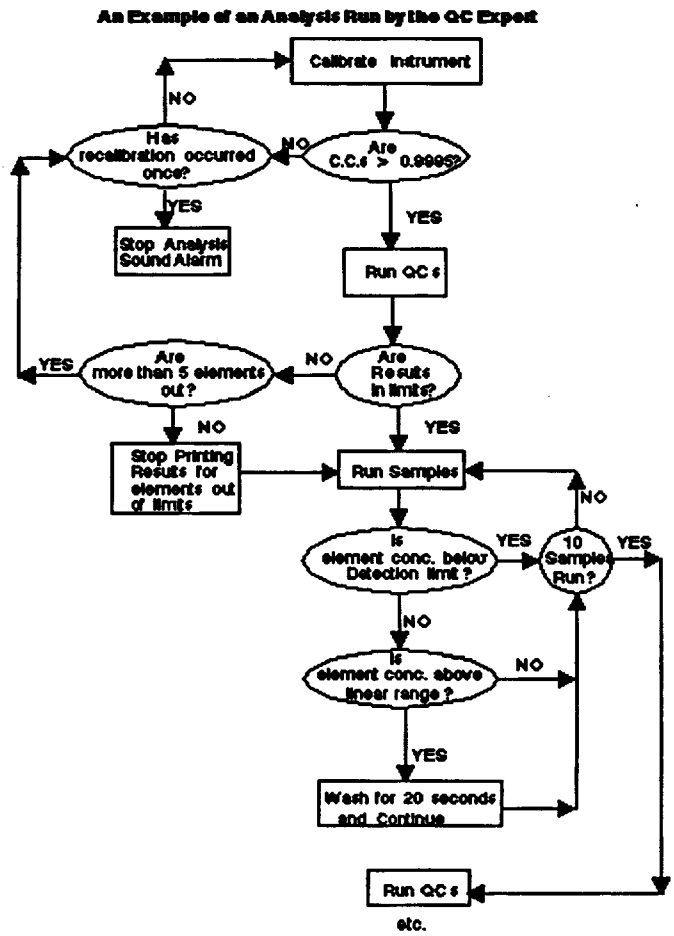
The QC Expert software has a number of features that allow one to customize a method. This makes it easy to follow any QC protocol required. Units are available for the standards, the weights and volumes for the samples and the final concentrations reported for the samples. It is possible to use different units for each element. Several commonly used units are available in the software and it is possible to teach the software any other unit desired. The software is smart enough to know the various conversion factors needed to calculate the final sample concentrations in the units specified.

It is possible to report the sample concentrations to a certain number of significant figures or a certain number of decimal places. Each element may also be reported differently. The available calibration curve algorithms are selectable on a per element basis and there are a number of linear and non-linear choices available. The samples have two possible labels, a 15 character batch ID and a 15 character sample ID. It is easy to copy and increment these IDs.

Once a method has been created and all the sample IDs and weights have been entered, the analytical sequence is automatically created by the software and assembled into an Autosampler Worksheet. The software is able to create this worksheet by combining information on the autosampler tray layout, the calibration and QC standards to be run and the sample information. This autosampler worksheet is readily edited. It is possible to print this worksheet according to the analytical sequence so the user knows how the analysis will proceed or it is possible to print the worksheet according to autosampler positions so the user can fill the autosampler tray easily.

Running an Analysis

An example of how an analysis is run automatically by the QC Expert is shown in the flowchart below. The calibration is initiated by the software. The correlation coefficients are compared to the minimum acceptable value of 0.9995. If any of the correlation coefficients are 0.9995 or less, the software directs the instrument to recalibrate for those elements. However, if a recalibration had already occurred once, the software will simply stop the analysis and sound an alarm to alert the user to the problem. If all the correlation coefficients are acceptable, the analysis will proceed and all the QC standards are run. After each QC is run, the results are be compared to the acceptable limits. If the results are unacceptable for more than five elements, a recalibration occurs. If a recalibration for this QC had already occurred, the analysis is stopped and an alarm is sounded to alert the user of the problem. If five elements or less were out of limits, the analysis continues with the samples. However, the elements that were out of limits are no longer reported to avoid having data on the printout that is not useable.



After each sample is run, the elemental concentrations are compared to the allowable upper and lower limits. If a concentration for a particular element is below the lower limit, a message is printed, telling the user that the concentration for that particular element is below the detection limit and it has to be run again by a more sensitive technique. If the elemental concentration is above the lower limit, it would be compared to the upper limit to check that it does not exceed this. If the elemental concentration does exceed the upper limit, the autosampler would be directed to wash for 20 seconds and then continue on with the next sample. This would avoid carryover between samples. A message would also be printed out telling the user that the concentration for that element exceeded the linear range and the sample would have to be diluted and rerun. After each sample is run, the sample count is checked. Once 10 samples have been run, the QC standards are run again as already described. This process continues on in this fashion with QC standards being run inbetween batches of 10 samples. After the last sample, a set of QC standards are run again with a similar protocol.

Without the automation of the QC software, the user would have been required to intervene at all of the stages, to make a decision and/or to physically take action. The user would also have been required to wait after each intervention to see that the problem was solved and the analysis could continue. If the problem had not been solved, a second action would have to be initiated by the user. Again, the potential for errors allowing "bad" data to slip through cannot be overstated. With the QC software, the user has only

to be present to start the analysis. The user may want to be within ear shot if he wants to know when the analysis is completed or if the analysis has stopped.

When the analysis is completed, the printout will contain all the information necessary to track the analysis. Time and date appear for each sample. When QC standards and diluted samples are run, percent recoveries are calculated and printed. When spiked samples are run, spike recoveries are calculated and printed. For duplicate samples a percent difference is printed. All user specified messages will be printed for all out of limit situations.

If the printout is not what is needed as a final report, one can use the Report Generator included which will provide a variety of reporting formats. It is also possible to monitor the quality of the data over time by using the QC Charting mode of the software. In the QC Charting mode, one can monitor any measurement of any standard and element over time. For example, one can plot the concentration for each element in each QC standard over time (an X-bar chart) or the %RSDs for each element in each QC standard over time.

The QC Expert software totally automates the analysis, allowing the analyst to attend to other tasks. Actions that would normally be taken by the analyst to assure the quality of the analysis can be executed by the software. The laboratory can become very efficient by having the analyst tend to other more challenging and important tasks than "watching" an instrument. The quality of the data is assured by the software as it executes the protocol established by the user.

29 AUTOMATED REPORTING OF ANALYTICAL RESULTS AND QUALITY CONTROL FOR USEPA ORGANIC AND INORGANIC CLP ANALYSES

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ABSTRACT

The U.S. Environmental Protection Agency's Contract Laboratory Program (CLP) for environmental analyses follows a detailed protocol for analysis, quality control, and reporting. The formal reporting procedure involves submission of a deliverable data package, which includes a number of predefined forms and a diskette containing data in an "Agency Standard" format. Attention to detail in the reporting process is important, both to assure verifiable, usable data for the Government, and to guarantee full compensation for the contractor laboratories. Automation of the reporting detail is necessary, if compliant deliverables are to be generated with regularity.

The QC calculation and reporting process lends itself to automation through the use of PC-based programs for data reduction. This paper will discuss the factors involved in developing and maintaining such programs for both the Organic and Inorganic CLP programs.

Automation of the reporting process begins with electronic data acquisition from the analytical instruments being used. Some beginning efforts at standardization of data output format among instrument manufacturers has resulted in the ability to include "standard" data import routines in CLP report generation software. For organic analyses, the "reduced result" file has been selected as a standard import structure. For inorganic analyses, a "comma delimited ASCII" import routine has been selected, which is compatible with some manufacturer's AA and ICP instruments. For both organic and inorganic analyses, where instrument output does not match one of the "standard" structures, special custom data file import routines have been devised for automatic data acquisition.

After instrument data has been accumulated into the CLP reporting software, additional required information may be added by keyboard entry. Once all required data is present, software routines process data to calculate reported results

according to EPA approved calibration routines, compare results to specified limits and conditions, flag results which lie outside these limits or otherwise meet conditions for data qualification, and finally, generate the formal printed and computer readable reports.

Until recently, two formats for computer readable data were allowed. These were known as Format A and Format B. Over the past year, the intention to go to a single "agency standard" format was announced. The specifications for this format, as it applies to CLP diskette deliverables, was introduced earlier this year. This paper will discuss the status of automated CLP reporting software to provide "agency standard" diskettes for organic and inorganic CLP software.

While the CLP program was devised strictly as a protocol for sample analysis and reporting of data by EPA contractors to the EPA, a trend has emerged for use of CLP, or at least a "CLP-like" format, as a reporting standard for other environmental analyses. In such cases, it may be desirable to modify some of the details of the report, to achieve modified goals. The modifiability of the CLP reporting software to address special reporting needs will be discussed.

INTRODUCTION

Telecation Associates began as a consulting company providing on-site training, instrument setup and method development for analytical laboratories. In 1985, while helping a laboratory setup for compliance with the Contract Laboratory Program's inorganic Statement of Work 7/85, we became aware of the detailed calculations and comparisons required to produce a CLP printed data package. It was quite obvious that a PC-based software program designed to perform the calculations and the logic required to fill in the forms would provide an automated means of generating compliant deliverables with both regularity and considerable savings of time.

Somewhat later a new inorganic Statement of Work, SOW 7/87 was released. This contract required the laboratory to not only prepare the printed set of forms for each group of samples, but also submit the package data on a DOS readable diskette, in accordance with one of two very specific computer formats. Computer automated reporting of analytical results for CLP analyses had now become a requirement.

In October of 1987, Telecation introduced a commercial software product which automated the QC calculations and the report and diskette generation for Inorganic CLP, SOW 7/87. Since then we have continued providing CLP reporting software to comply with subsequent contracts under Statements of Work 7/88 and 3/90, in addition to numerous official revisions and "interpretation updates" issued by EPA for each contract.

In the spring of 1990, Telecation expanded its CLP software product line to include the new Organic CLP contract for SOW 3/90. In May 1990, Telecation began shipping QC and reporting software for all three organic protocols, including volatiles, semi-volatiles, and pesticides. From the viewpoint offered by our extensive background in developing software for both inorganic and organic CLP, we will discuss the technical and economic factors which prevail in the automation of the QC and reporting requirements of USEPA's CLP program. We will also identify opportunities to substantially enhance the benefits of automation for CLP-like applications, where the restrictions imposed by USEPA may not be a factor.

REVIEW OF THE REQUIREMENTS

Before examining the factors affecting the development of CLP reporting software, we will first review some of the elements of CLP, which the software must address. The analytical protocols for CLP describe the analysis of set lists of analytical parameters. In addition to the actual field samples, a series of QC samples must be analyzed. The QC samples include such things as blanks, duplicates, spikes, matrix spike duplicates, control samples, and various instrument performance checks. The analytical results and other sample related details, as well as the QC, sample preparation, instrument calibration and performance checks, are summarized on printed forms, the format of which is precisely defined for each reporting protocol. There are 14 different forms plus a cover page required for the inorganic data package, and 36 different forms for organics.

The CLP reporting requirements do not allow a simple transfer of information to a fixed format form. All raw analytical results must first be compared to both actual instrument detection limits and to the reporting limits required by the contract to determine which of the values is to be reported. Each form has different requirements regarding the reporting of data corrected for sample preparation factors, the reporting of significant figures, decimals, and values rounded according to the EPA rounding rules. Data

qualifiers, or "flags", summarize the analytical performance. And, in some cases the forms interact with one another, inasmuch as the results or the flags appearing on one form may also have to appear on another form in place of, or in addition to, information which would normally appear there. And, last but definitely not least, these results must also be submitted on a computer readable diskette according to a very fixed format, which is now entirely different than the format of the data appearing on any form.

In addition to the demands imposed by the contract details of the CLP statements of work, the practical considerations in making the software versatile enough to address modified CLP needs must be considered. When the Contract Laboratory Program was established, it was originally intended as a standardized protocol for analysis and reporting by contractor laboratories who worked under contract to the USEPA. Soon, however, the quality control standards set by the program began to be applied to other environmental work, as well.

Since legal decisions rest heavily on established precedent, the analytical and reporting protocols of CLP, which were developed specifically to provide legally defensible data, were accepted as a defacto standard for such analyses. Because laboratories of all types are now being held legally accountable for the data they release, CLP-type reports are being requested by state environmental agencies, industrial accounts, environmental engineers, and practically every facility that is submitting data for any type of environmental monitoring, especially if they are concerned that the data may become involved in litigation.

The emergence of other users of CLP reports, besides the USEPA, has created a demand for a software product which can automate the generation of a CLP-like reporting package, which may be substantially the same as strictly interpreted CLP, but modified in certain details. Even the USEPA, themselves, has issued special bid requests, which deviate from the "Routine Analytical Services" contracts. These include protocols for analysis of "Low Concentration Organics", "High Concentration Inorganics", and others.

The market place for CLP software is small to begin with, relative to the development effort required to implement the complex requirements. These special purpose modifications to standard CLP serve to reduce the market size even further. In the case of EPA special bids, the entire market size may consist of only two or three laboratories. Therefore, the only feasible way to address the many variations of CLP and

"CLP-like" applications, is to design flexible software, which allows the user to modify certain aspects of the software's performance. The features to be modified may include the list of analytes or compounds to be reported, variations in quantitation limits (CRDL's and CRQL's), and the format or file structure in which data is to be recorded on the printed forms and/or the diskette deliverable. Some applications may not require all of the printed forms, and others may require a modified file structure for the diskette deliverable. Finally, even the actual analysis details, including the nature of quality control and associated calculations to be performed, may be different from USEPA CLP specifications.

To create a software package which automates the complex requirements of CLP would be, in itself, a difficult challenge. To also make it flexible to address any number of modified specifics, while keeping the final product easy to use, becomes an almost impossible task. Combining the above goals with the ever-changing nature of the USEPA requirements for CLP makes an optimum software solution for all applications extremely illusive.

In spite of the challenge presented above, Telecation provides a solution in its "ENVIROFORMS/Inorganic" and "ENVIROFORMS/Organic" software products, which have historically provided notably accurate compliance with strict CLP standards, while providing the flexibility required to allow the user to address most "CLP-like" applications, through the use of software utilities for modifying output. No special knowledge of a programming language or use of optional compilers is required to implement modified output through the use these utilities.

BARRIERS TO AN OPTIMUM SOFTWARE SOLUTION: CONTINUAL CHANGES

Working with the EPA's Contract Laboratory Program can cause both the contract laboratories and the software vendor considerable frustrations. Not only do these contracts contain a profusion of technical and bureaucratic detail, but also these details are in a constant state of flux. To the software vendor, once a contract is issued, the program code necessary to implement the terms of the contract is written, tested, and documented. But even as samples are being released for analysis, revisions to the protocol are issued. Sometimes the official revisions note errors in calculations or documentation in the original contract. Other times these amendments are actually "interpretations" intended to clarify an ambiguous point, or in cases where the contract

contradicts itself, indicate which statement should prevail. Inasmuch as the CLP approach is now several years old, it might be expected that the number and frequency of revisions would be diminishing. But in fact, this has not been the case. Wholesale changes in analytical protocol, QC calculations, and diskette file structure have led to a new round of contract problems, the fix to which frequently creates more problems.

Each time revisions are issued by the EPA, the software vendor is required to make the corresponding changes to the software, if the product is to remain viable. Since the nature of CLP software is so interactive, even the smallest change to the software in one area requires thorough testing to detect possible problems in other areas, which occur as a result of the change. This process ultimately identifies "bugs", which require further changes followed by a new round of testing. Then, the documentation for the software must be updated to reflect these latest changes. It should be noted, that revisions which the EPA might consider "minor" may in fact have a major effect on software. The code is written around all of the details specified in the contract, and a "minor" change in procedure may have a devastating impact on the logic used for program development.

Besides testing and documenting the updated software, the vendor must also consider the effect of updating their current users, considering among other things, how installing the changes will affect "work in progress" at the laboratory site. Lastly, all new software and documentation must be distributed to the users.

The instability of CLP contract terms, therefore, sets into motion a series of events, which can only lead to further changes. Each contract change which necessitates a software change, requires that new logic and code be developed, followed by performance testing, software bug fixes and retesting, and issuance of updated software and documentation. This is usually followed by identification of contract flaws, which require new contract modifications, which sets the whole process in motion again. Meanwhile, as this moving target progresses through a never ending evolution, the contract laboratories and software vendors are expected to "conform" to what ever the latest interpretation happens to be. Any deviations from this volatile "standard" result in compensation penalties exacted against the submitting laboratory.

Because of the continuous EPA revisions to the requirements for CLP analysis and reporting, most software vendors offer a

type of software maintenance contract designed to keep the end user up to date with the latest EPA revision. Some laboratories view the price of these "Maintenance Contracts" as expensive, and indeed they are relative to maintenance contract prices for most software. But the demands outlined above are not a part of most software. The software vendor who conscientiously strives to update its clients in a timely manner after being notified of yet another change, must be prepared to divert development, testing, and documentation resources from other projects to CLP projects on a moment's notice. If commercial software for CLP work is to continue to be available, the software vendor must be compensated for the never-ending development and untimely diversion of resources. In fact, the software vendors, like the contract laboratories, themselves, realize nominal profit margin on CLP work, relative to other, less demanding tasks. Laboratories, who bear the cost for software and software maintenance, should understand what is behind that cost.

BARRIERS TO AN OPTIMUM SOFTWARE SOLUTION: OTHER

The goal of CLP software is to automate QC calculations and reporting in as expeditious a manner as possible. There are a number of details of the CLP contract which impede the ultimate achievement of this goal. The inorganic contract SOW 7/85, which was produced prior to the need for computerization, included some features which defied computerization. One such detail was the requirement to "circle" preprinted options on the forms. Since computers cannot "circle" choices, this was changed for SOW 7/87 to take advantage of the benefits which computer technology had to offer. However, at least one requirement, which is almost equally incompatible with computer technology still exists today, the EPA rounding rule.

The EPA rounding rules call for the evaluation of numerical data in a way which is foreign to computers. Computers can round on their own very nicely, but the rounding required by the Contract Laboratory Program calls for a special evaluation routine to be performed on each and every value.

Since the rounding rule is nothing new, the software routine has been developed a long time ago to perform the calculation. But this does not mean that the rounding rule does not still impact CLP software in a negative way. First of all, the necessity to round by a special routine frequently complicates the implementation of other EPA imposed changes. Further, the ever present requirement to evaluate every number by a special rounding routine impacts

the speed of software operation. When it is realized that a typical sample delivery group contains thousands, if not tens of thousands of calculated numbers, the special rounding rule is responsible for a significant increase in software operation time.

As to the value of the rule, it has been stated that in order to make the data legally defensible, it is necessary to precisely define the rounding conditions. This appears to us, however, to be a flawed argument, since it is highly unlikely that the outcome of a legal action would ever hinge on the difference in rounding of a number in the least significant digit. A competent attorney would see to that. The USEPA has deemed this rule to be valuable for their purposes, and hence, it is by definition a part of all software intended for generating data for EPA use. For all other applications, the EPA rounding rule serves only to reduce the automation benefit which would otherwise be realizable in a 1990's computer technology.

A new impediment to efficient compliance with the CLP protocols is the "Agency Standard" diskette format. Prior to the more recent contract terms, data could be recorded on diskette in one of two formats, Format A or Format B. Format A has been the choice of most software vendors, since that format closely matches the printed form, and a software routine which is set up to print the hard copy forms can, without great difficulty, also produce the Format A file structure. By contrast, the "Agency Standard" format, which does not follow the forms, and in fact contains information which is not contained on any form, requires all new software code, involving additional data manipulation, to produce the diskette. This incremental software development will impact the cost of future software and maintenance contracts. Software users should also expect increased software operation time, to complete the additional data manipulation required to create the Agency Standard diskette.

A recent occurrence has added a new element to the already uncertain nature of CLP contract details. This occurrence attacks at the heart of every software vendor's confidence that after expending the time and resources described earlier to develop a product to address a new CLP contract, there will be a market for that product.

When a new CLP contract is issued the required dates for complete compliance are also stipulated. At a CLP data management caucus held in Raleigh, North Carolina in the spring of 1990, the software vendors were asked if they would be able to respond to the proposed Statement of Work 3/90 for

volatiles, semi-volatiles, and pesticides by a date specified by EPA. It was explained to the vendors that it would be important for software to be available at that time for use with Performance Evaluation samples distributed in response to an Invitation For Bid appearing in Commerce Business Daily. Because of this and prior commitments made to EPA to meet the required schedules, Telecation redirected resources to address the new Statement of Work, and ENVIROFORMS/Organic SOW 3/90 was ready to ship in May, 1990. However, EPA later recanted their previously announced schedule, thereby eliminating all need for the product.

The impact on software cost emanating from the frequent changes imposed by EPA has already been discussed. Issuing modification instructions and asking for crash development efforts, only to have the demand removed after the development effort has been expended, compounds the economic impact of the changes. The development effort expended toward a protocol which is never, in fact, implemented has to be absorbed in the cost of future CLP software products and maintenance contracts. It should be noted that the software vendors affected most by this failure of EPA to follow through with its announced contracts, are those which strive the hardest to provide prompt updates to the changes. Such a practice can only serve to discourage the software vendor from reacting quickly to future USEPA changes.

OPPORTUNITIES IN CLP-LIKE PROTOCOLS

As discussed earlier, there is an increasing number of laboratories who wish to report data in a format resembling CLP, but differing in certain details. For such applications, the limitations discussed above may not apply. It is not the authors' intention to second guess the USEPA on the necessity for the details contained in its contracts, nor to question the need to frequently change those details. It is our purpose to identify the stumbling blocks which stand in the way of automating the good analytical protocol of CLP, and discuss the benefits that would accrue to non-USEPA applications, if these stumbling blocks were removed.

As discussed earlier, non-USEPA applications have need to change various performance and output features, including such things as the list of target analytes or compounds, quantitation limits, and report and diskette formats. ENVIROFORMS/Inorganic and ENVIROFORMS/Organic offer this flexibility to the user. Further, the user may select less than the total CLP form set for printing. The items mentioned above are modifiable by the user without programming, because

the items are controlled by user accessible data bases, as opposed to program code.

Some modifications for which we have received requests, involve changes to the analytical and QC procedures from standard CLP protocols. Since much of the program logic and calculations are based on the standard CLP procedures and calculations, applications which require a departure from standard CLP procedures and calculations are more difficult or, in some cases, impossible to change without changes in actual program code.

One such application was recently introduced by EPA, itself. The statement of work for "Low Concentration Inorganics" introduced a new technique (ICP/MS), added several additional forms, and reported detail which was not previously required. Since these and other changes struck down the program logic assumed for standard CLP, it was impossible to use the standard CLP software to address Low Concentration Inorganics. Similarly, certain state programs, which model themselves after CLP but alter certain critical logic elements, destroy the possibility of using off-the-shelf CLP software to totally automate the response.

A potential solution exists, which would add the ability to change many procedural issues, in addition to the currently modifiable characteristics of the software. This solution, which is currently under investigation by Telecation, would make the software operation largely independent of analytical procedure and would put the QC calculation formulas in the hands of the user. Such a software product would benefit both the contract laboratory and contractor agency, alike, in that it would now be technically and economically feasible to address special contracts, with differing analytical and QC requirements. If it is easy enough for the user and/or the vendor to make the changes necessary to address the special requirements, then such changes can be economically made, even for low volume work.

Whether or not such a concept is workable rests heavily on the flexibility of the contractor agency regarding some of the issues which have complicated CLP in the past. In order to provide the degree of user control necessary to make the concept work, the software code will have to be less regimented. This means that some of the issues which are now handled by the regimented code, must be sacrificed. The issues which cause particular problems with this concept are: (1) the EPA rounding rule, and (2) the Agency Standard diskette.

The rounding rule, as discussed earlier, offers very questionable benefit, either from a standpoint of scientific significance or legal defensibility. However, its presence would require the software to execute specific rounding routines, which in turn, would require the software to have predefined knowledge of the calculations, which eliminates the desired goal of user-definable formulas.

The Agency Standard diskette format introduces a new and formidable barrier to development of a generic software package for CLP-like work. The format, which includes such things as special data delimiters, hexadecimal calculation of checksums, and unique file formats precludes any possibility of user configuration. On the other hand, a simple file format based around a comma-delimited ASCII output of information contained on the forms, would make it possible to generate a diskette under user control, by allowing the user to simply indicate the sequence of fields to be written to the diskette file.

It is our understanding that the Agency Standard has been decreed as Government policy even to those responsible for generation of CLP contract terms. Therefore, it is assumed that Agency Standard is a nonnegotiable point for USEPA applications. This simply means that software to address special low volume USEPA contracts will probably never be commercially available. Other contractors, who are not under this constraint, should consider the complications of Agency Standard very carefully, before adopting this approach and promulgating more barriers to efficient automation of CLP type work.

SUMMARY

The technical and non-technical complications discussed in this paper do not necessarily go hand in hand with the goals of CLP analyses. For those who have need to develop a good regimented QC program accompanied by a standardized reporting format, we would encourage adopting the sound analytical features of CLP, while excluding the detail which complicates the process without return of a corresponding benefit. For state agencies which have not finalized their requirements, we would encourage allowing flexibility, where such flexibility does not compromise the quality of the data or quality control. We would advise against requirements for special rounding rules, and suggest a less rigid diskette format based around the printed forms. Such flexibility will not only reduce the cost of both analysis and automation, it will also lead to a more reliable deliverable, due to the reduced complexity.

Telecation has been dedicated to providing state-of-the-art software to address CLP applications, since the first diskette deliverable requirement for Inorganic CLP. The current ENVIROFORMS/Inorganic and ENVIROFORMS/Organic address detailed compliance to the USEPA's contract terms. We have provided timely updates to EPA issued changes, by conscientiously applying development resources to the CLP challenge. As an historical supplier of CLP software, Telecation intends to continue its past policy of providing the detailed compliance and prompt updates necessary for USEPA contract laboratories, consistent with what is technically possible and economically viable.

We are, however, not content with the limitations imposed by USEPA details and the effect they have on non-EPA applications for CLP-type analyses. We will, therefore, also explore new approaches to CLP-like software, which retain the analytical benefit of CLP, without the cost and operational complexity burdens which accompany USEPA CLP requirements. Since USEPA applications will undoubtedly continue to present obstacles to automation, future developments will probably involve a CLP software product line, consisting of two separate product categories, one for USEPA contracts in its strictest detail, and one for other, more flexible applications. This allows strict compliance to be maintained for our EPA contract laboratories, while offering expanded capability and flexibility for those who are not so constrained.

For such a segregated software product line, the costs associated with the changes and complexity imposed by the EPA could be applied to the price of the software intended for USEPA applications. The more flexible CLP products, would thereby be less expensive to laboratories, since they would not carry the cost liability of the complexity and frequent changes imposed by the EPA program. This would, of course, make the software for USEPA applications much more expensive than it is currently, since there would be a smaller market over which to amortize the development expense. On the other hand, such a segregation of product application would put the cost where it really belongs, without penalty to all those other applications, which are not so constrained.

The authors would again like to clarify that the purpose of this paper is not to provide an evaluation of the necessity and value of the items discussed to the USEPA's program. It is impossible for us to know all of the factors behind the terms of USEPA contracts. We are, however, qualified to identify the effects of these terms on software performance and flexibility, and evaluate the enhanced features and

benefits which could be made available for CLP-like applications, where the constraints of the EPA program are not a factor.

30 A CUSTOMIZABLE GRAPHICAL USER-FRIENDLY DATABASE FOR GC/MS QUALITY CONTROL

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Abstract

Standard methods for GC/MS analysis require a significant amount of data gathering operations to demonstrate good quality control (QC) practices. Both volatile and semi-volatile analysis require the use of surrogates, internal standards, matrix spikes and matrix spike duplicates. Laboratories are required by the corporate quality assurance (QA) program to control the analysis within fixed method specific criteria. Additionally, laboratories are required to calculate their own control limits.

At Chemical Waste Management (CWM), we developed a customized application to facilitate the collection, analysis and viewing of GC/MS quality control (QC) data. The Customizable Graphical User-Friendly Database for GC/MS Quality Control was designed according to the guidelines specified in EPA SW-846 Methods 8240 and 8270. Compounds for the QC section use the recommended surrogate standards from the two methods. Ranges for recovery data are taken from Table 8 of Methods 8240/8270, which contains multi-laboratory performance-based limits for soil and aqueous samples. Compounds selected for the duplicate and fortification analysis section were selected from the recommended compounds listed in EPA SW-846 Method 3500. Ranges for the matrix spike and matrix spike duplicate compounds were selected from the forms following Chapter 1 in SW-846, which correspond to the CLP limits for these compounds. In addition to meeting standard QC practices for collecting, analyzing and viewing GC/MS QC data, this application allows for the creation of acceptance limits in matrices other than those matrices allowed by the methods specified within the database.

Surrogate recovery data are compared to these fixed criteria and are used to calculate the laboratory specific criteria. Relative percent difference and percent recovery data are accumulated and compared to the fixed acceptance and laboratory generated criteria. QC data can be viewed, edited and graphically displayed based upon a wide range of selection criteria (e.g., sample id, matrix, dates, analyst, instrument, etc.). Use of this application has already significantly increased the efficiency and effectiveness of QC practices within the company.

Introduction

Analytical methods promulgated by the USEPA which use gas chromatograph/ mass spectrometer instruments require a considerable amount of quality control practices. The complexity of the matrices and the sensitivity of the instrumentation and volume of data combine to create a situation which requires substantial use of data evaluation to show the accuracy and precision of the analytical process. In the methods covering volatile and semi-volatile organics, a large number of compounds of interest are included, and the number of surrogate compounds and matrix spike compounds are significant. Moreover, the methods require specific trend analysis procedures and specific data evaluation techniques to demonstrate acceptable performance.

A laboratory using one of the GC/MS methods must calculate the average recoveries for all surrogate compounds added to the calibration standards, blanks, and samples. The laboratory must compare its variability to the allowable variability in the method. The lab's own entries should be developed and used for control from this accumulated data. The mean percent recoveries and standard deviations need to be calculated and reviewed in a timely manner. Additionally, the CWM QC Policy requires that the laboratories performing GC/MS analysis report pertinent quality control data to the central quality assurance unit. Quality Control policy also mandates that each VOA and Semi-VOA assay act as its own QC sample with spike duplicates required every 20th sample.

A fully integrated software package was determined to be the best way to accomplish these tasks, but no such package was commercially available. The GCMS Application, described in this paper, was developed to fulfill these quality control requirements.

Specification

The specification for GCMS evolved over time as the developers interacted with members of the Quality Assurance group and the laboratory. Quality Assurance required flexible access to GCMS QC data to assure the quality of sample analysis and a means to compare GC/MS quality across the corporation. The lab required flexibility in data input, reporting, and graphing, plus the ability to isolate potential quality control problems of instruments, analysts, or matrix inferences. Other requirements included the ability to selectively query and graph surrogate data, compare our surrogate recoveries to regulatory limits, and the capability to distribute the application inexpensively throughout the CWM laboratory system.

Base Software

GCMS was developed in Clarion®, a comprehensive and flexible database development language. Clarion® satisfied our database requirements and included built-in graphing tools to allow for visual display of surrogate recoveries. Clarion® applications are compilable, which facilitated distribution throughout the corporation.

Features

From the specifications described above, an initial prototype was built and demonstrated to the users for immediate feedback. This process continued through several iterations until the final application emerged. Ultimately, a "top down" versatile and responsive screen/menu application was produced. The resulting GCMS application is a feature-rich quality assurance quality control tool. Major features include:

Customizable Database

GCMS allows all CWM labs to customize the application to local site requirements. Laboratories incorporate instruments and GCMS personnel specific to their site, enabling each laboratory to isolate quality performance and quality trends before they become significant issues. GCMS also acts as a repository for regulatory surrogate recovery limits and allows for creation of new acceptance limits in matrices other than those listed in the regulations. GCMS allows for the accumulation of QC data over a 5 year period with appropriate control limits for each year.

Data Input

Results are entered by selecting the appropriate method and pressing the [Insert] key. Like data (analyst, instrument, matrix, etc.) are copied into the new record. As the analyst enters QC data, the results are automatically compared to the pertinent limits for that method and matrix. Out of control results are immediately flagged. GCMS can also be shared on a network, allowing simultaneous access by analysts, management and quality control staff.

Data Queries and Reports

GCMS has summary screens which show the quality performance for volatile and semi-volatile analyses. The summary screens are queried for all data found in a specific date range. The search can optionally be qualified for a particular analyst, instrument, matrix or compound. The summary screen enables the reviewer a quick view of the quality performance for a range of samples. The screen summarizes, in an easily read format, the sample identification, the surrogates analyzed, the acceptability of the surrogate (e.g., by signifying if the result is in or out of limits), and a summary of the total performance of the assay (i.e., by listing the total number of surrogates out of control). Since GCMS allows for qualified searches, the data can be reviewed to identify specific quality problems in the lab.

GCMS is capable of generating two types of reports. The first report is a listing of all surrogates and spikes entered into the application (Figure 1). The report looks similar to the CLP format for reporting surrogate results and can be printed using all of the filters used for the summary screens. The other report present in GCMS is the QA/QC report which lists all surrogate parameters and gives a total of the number of analyses entered, the number of samples, and QC calculations that include: percent of analyses that are within QC limits, the upper and lower limits along with a mean and the co-efficient of variation. The mean percent recovery, mean percent error, along with the standard deviations for both spikes and duplicates are also reported. This report is placed in a DOS file and can be printed or copied on disk and sent to the Quality Assurance unit.

Chemical Waste Management, Inc.
GC/MS QC Report for VOA Surrogate Recovery

Date Analyzed: 11/30/90 TO 11/30/90 Waste Matrix: AQU - AQUEOUS
Instrument ID: * - Analyst Name: * -

AID	Sample-ID	DBF	12D	TO8	BFB	T-OUT	D
KH1	34052 TC	98	104	102	101	0	N
PD1	34147 ZHE	110	113	93	88	0	N
PD1	34148 ZHE	109	95	93	86	0	N
PD1	34196 ZHE	119*	117*	102	96	2	N
PD1	34197	119*	119*	102	91	2	N
KH1	BLANK VOA	100	94	92	99	0	N
PD1	BLANK VOA	96	100	103	96	0	N

Report Summary

Glossary

AID: Analyst ID
T-OUT: Total # OUT of QC Limits
D: Surrogates Diluted OUT
*: Values outside Req. QC Limits
-1: Represents Null Field/Data

Surrogates

		QC Limits Low Hgh
DBF:	Dibromofluoromethane	86-118
12D:	1,2-Dichloroethane-d4	76-114
TO8:	Toluene-d8	86-110
BFB:	Bromofluorobenzene	86-115

Figure 1: QC Report

Graphing

One of the more useful features of GCMS is its graphical capabilities. GCMS uses two graph formats, a QC graph and fortification/duplicate graph. The data to be graphed can be selected by range of dates, surrogate, matrix, instrument or analyst. The QC graph plots the individual surrogate recoveries, the upper and lower method and laboratory limits by method/matrix, and the mean of the surrogate analysis. The duplicate/fortification graph plots the surrogate recoveries for each duplicate, the relative percent difference of the duplicate recoveries and the method limits (Figure 2). GCMS plots 110 individual graphs (one plot per surrogate, per matrix). The lab limits displayed are those calculated from the beginning of the year to date.

Each graph summarizes the limit information in the upper right hand corner of the display. If users require more information about a datapoint, they click on the point of interest using a mouse, and the details of the analysis are displayed in the upper left hand corner. If users require a hard copy of the graph, they click on the print icon to send the graph to a local printer.

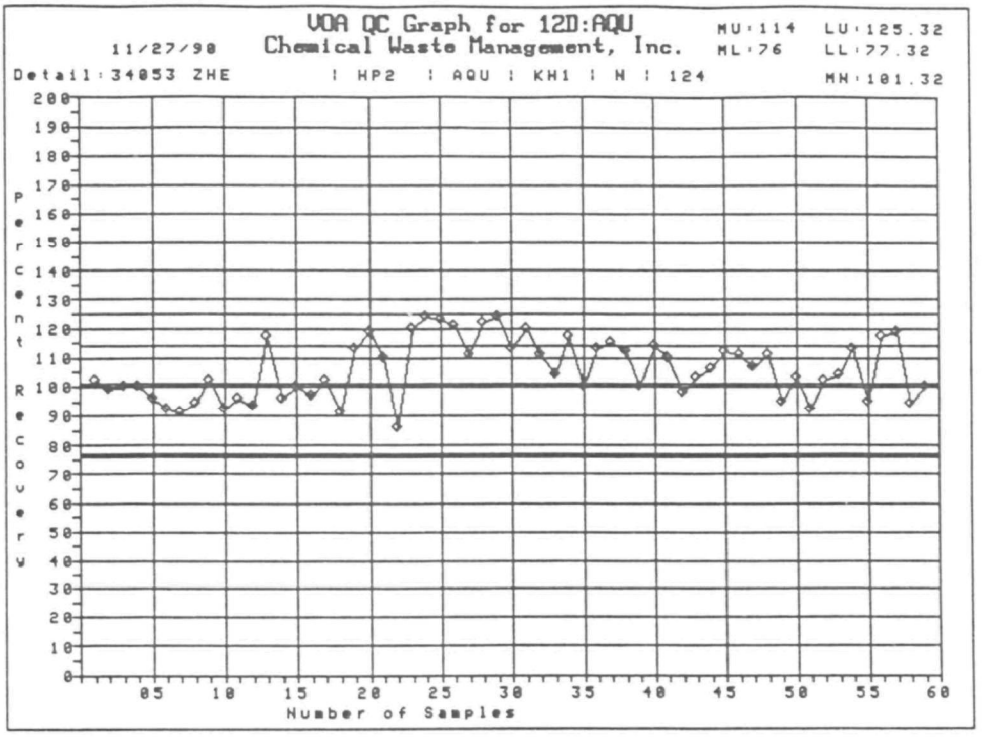

Figure 2: QC Graph

Benefits

The following examples demonstrate how the GCMS Application makes quality problem-solving a quick and relatively painless operation:

Approximately 25% of the volatile surrogates in a laboratory were found to be running bias-high upon analysis. The problem was present on the two instruments used to run the volatile analyses. When the surrogate data was filtered through GCMS, a pattern emerged that showed that a large percentage of one analyst's surrogate recoveries were high. Since this analyst used a different stock solution of surrogates, the stock was re-analyzed and found to be incorrectly constituted.

Samples, of a specific matrix, received from one customer were found to have low surrogate recoveries. Two years before the same customer submitted similar samples. By using GCMS to retrieve the surrogate/ matrix data for the older samples, it was shown that the lab had similar analysis problems.

A large group of samples in the middle of the month had low surrogate recovery. By using GCMS it became apparent that all of the samples were analyzed on a specific instrument. The instrument calibration was examined and found to contain a wrong (or incorrect) number. Upon correction, all surrogate recoveries were recalculated and found to be within range.

Conclusion

GCMS gives a laboratory with multiple instruments from different manufacturers and with many analysts the ability to view all of the quality control data at one time. The ability to group samples by matrix allows the laboratory to quickly and easily calculate its own quality control limits for the many different matrices an environmental lab needs to analyze. The GCMS application is a simplified way to satisfy these requrirement, and allows the laboratory to satisfy the method requirements in a relatively simple way. The GCMS application also allows the laboratory to not only gather quality control data, but to also put it to good use. From the many sheets of paper and printouts that the GC/MS laboratory had previously used to accumulate the quality control data, we now are able to put all of the data into this application in a minimal amount of time. More importantly, by using GCMS we are able to retrieve the most useful information from the inputted data. In a larger sense this application can help gather information from a large group of labs doing GC/MS analysis to study the affect of matrix on surrogates and to evaluate new methods as they are approved.

31 **COMPUTER-ASSISTED TECHNICAL DATA QUALITY EVALUATION**

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ABSTRACT

Assessing environmental contamination and designing and implementing remediation strategies are invariably based on analytical data. Sound decisions for managing environmental assessments and cleanups can only be made if the analytical data are of a known and documented quality. Manually assessing the quality of analytical data generated in an environmental study is a resource intensive endeavor, and frequently the results of the assessment are not delivered to the end users of the data. This paper describes an automated system developed for the Air Force Human Systems Division Installation Restoration Program (IRP) Office (HSD/YAQ) to automatically evaluate the quality of technical data and to store the data with their respective data qualifiers in an electronic database. The data processed by this system are generated as part of the Air Force IRP efforts and are stored in the IRP Information Management System (IRPIMS). IRPIMS currently contains sampling and analysis data for IRP efforts at 76 Air Force installations which comprise nearly one million analytical results.

The process of automated data validation must be considered as two distinct but interrelated activities. One of these activities is the preparation of the electronic data files by contractors. The second activity is the automatic evaluation of these data by the Air Force. The Air Force has developed software tools that support these activities. Two personal computer tools have been developed to assist contractors in the preparation of their data submissions. One of these tools (the Contractor Data Loading Tool) provides the contractor with a convenient means of manually entering the technical data that are to be processed. The other tool (the Contractor Quality Checking Tool) enables the contractor to evaluate the data integrity of a submission. The final software tool developed by HSD/YAQ (the Batch Loading Tool) is used at Brooks Air Force Base (AFB) to automatically evaluate the submission for consistency with IRPIMS data requirements and the technical correctness of the data (e.g., holding times met, contamination in blanks, logic of well completion records,

etc.) Data assessment reviews that would require staff weeks of effort can be done in hours with this automated system. The technical data processed by this batch loading tool are stored in electronic form fully qualified for all the technical evaluations that were automatically done during batch loading.

This discussion covers the two automated data validation activities, and the three distinct pieces of software that have been developed by the Air Force to support them.

INTRODUCTION

The analytical data that are procured by the Air Force as part of its IRP are required to be both scientifically sound and legally defensible. Procurement of technical data that meet these requirements must be based on a structured procurement strategy that includes clearly defined performance criteria and a quality assurance review of received data for conformance with these established criteria. The manual implementation of such a procurement strategy is very resource intensive, and a manually implemented review system is prone to errors. This paper describes an automation tool that has been developed by the Air Force to facilitate the implementation of a structured technical data procurement strategy that is capable of 100 percent check of all data against the established performance criteria.

The description of this automated tool will be presented in three sections. The first section will describe the electronic data loading tool (i.e., the Batch Loading Utility) that is resident on the VAX 8600 at Brooks AFB. Included in this discussion will be a description of the organizational process that supports the operation of the Batch Loading Utility. This discussion will be followed by a description of the various data quality reports that are being produced while the technical data are being processed by the Batch Loading Utility. Finally, a brief discussion of the various forms of assistance the Air Force is providing to its contractors to help them prepare suitable electronic data submissions will be presented.

THE ELECTRONIC DATA LOADING PROCESS

The technical data that are generated as part of Air Force IRP studies cross several disciplines, and the electronic collection of these data must be supported by various technical and administrative personnel. Additionally, the electronic data loading process consists of activities that must be done by contractors and other activities that must

be done by Air Force personnel. The Air Force's electronic data loading process is based on a standard operating procedure that defines the roles and responsibilities of the various technical and administrative staff and describes the electronic data loading review and decision making processes. The illustration in figure 1 schematically depicts this process. The review and decision making processes and the roles and responsibilities of the various staff are described below.

ROLES AND RESPONSIBILITIES

Collection of quality data suitable for making decisions regarding remediating hazardous waste sites is a team effort. The roles and responsibilities of the various team members include the following:

The Remedial Investigation/Feasibility Study Contractor. The remedial investigation/feasibility study contractor is responsible for conducting the field investigation, performing the laboratory analyses, and preparing the electronic data submission. The electronic data submission contains a record of quality assurance/ quality control (QA/QC) activities in the field and in the laboratory. HSD/YAQ has provided tools to assist the contractor in preparing electronic data submissions. Those tools are described in a subsequent section of this article.

Contracts Administrative Branch. Electronic data submissions are treated exactly like any other IRP deliverable. The data submissions are received by contract administrators, who record the receipt of the deliverables, and based on the advice of the technical project managers, accept the deliverables from the contractor or require the contractor to resubmit the electronic report with revisions.

Technical Project Managers. The technical project manager (TPM), with the assistance of the data administrator and hydrogeology and chemistry consultants, is responsible for accepting or rejecting the contractor's data submissions. The data submissions may be rejected for two reasons. If the data does not conform to the standard IRPIMS data format, they may be rejected, and the contractor may be required to reconstruct the electronic data submission. If the reports generated by the automated QA/QC tool indicate that the contractor did not meet the data quality objectives identified for the project, the contractor may be required to repeat field work and/or laboratory analyses.

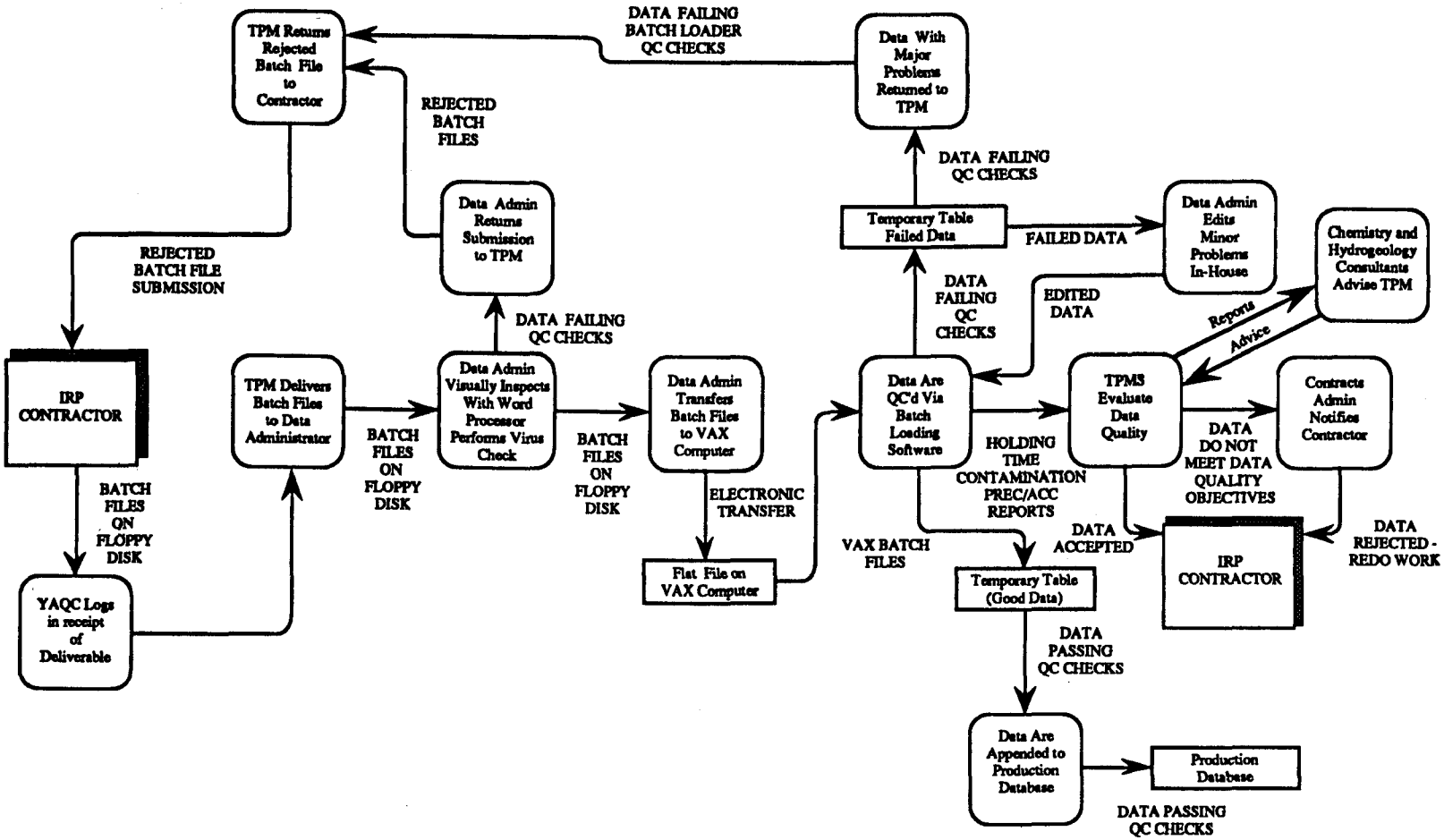

Figure 1. Data Flow Diagram of Batch Loading Process

Hydrogeology and Chemistry Consultants. The hydrogeology and chemistry consultants provide the TPM with expert advice in interpreting the output of the data QA/QC modules.

The IRPIMS Data Administrator. The data administrator is responsible for overseeing the work of the contractor that operates the batch loading software. The data administrator is ultimately responsible for maintaining the integrity of the IRPIMS database. He maintains the lists of valid codes (e.g., codes for analytes, analytical methods, sampling methods, etc.) that the batch loading software uses to evaluate the quality of the electronic data submissions. He provides the TPM with expert advice regarding the quality of a contractor's data submission from the database integrity perspective as opposed to the hydrogeology/chemistry perspective.

The Operator of the Electronic Data Loading Software. The operator of the electronic data loading software is responsible for physically loading the electronic submission onto the IRPIMS computer, running the data quality checking software, distributing the resulting reports to the appropriate HSD/YAQ staff, and providing technical support in interpreting the output. If the TPM decides to accept the electronic data submission, the operator then appends the electronic data submission into the production technical database.

REVIEW AND DECISION PROCESS

As illustrated in figure 1, the electronic data submission is first received by the contracts and administrative branch, where it is logged as received. The submission is then delivered to the technical project manager responsible for the IRP project. The TPM delivers it to the IRPIMS data administrator. An operator designated by the data administrator checks the data submission for computer viruses, and then performs a visual inspection of the data using a word processor. If the submission fails the visual inspection, it is returned to the TPM, who advises the contracts administrative branch that the submission has been rejected, and should be resubmitted. Data that passes the visual inspection is loaded onto the IRPIMS computer, and run through the data quality assessment software. Data that passes all of the QA/QC checks are loaded into a set of temporary tables that can be appended to the production database. Data that fail the QA/QC checks are loaded into a set of temporary tables that can be edited in house or converted into standard ASCII files to be returned to the contractor. The quality assessment software generates a series of reports that are distributed to the TPM and

chemistry and hydrogeology consultants. The TPM, with the assistance of the technical consultants and data administrator, ultimately decides whether to accept the data submission and whether the reports indicate that the contractor should be required to repeat a portion of the field and/or laboratory work.

THE ELECTRONIC DATA LOADING SOFTWARE

The IRPIMS system resides on a Digital Equipment Corporation VAX computer, running the VMS operating system. The database is managed by relational database management system software from the Oracle Corporation. The quality assessment software is written in the "C" programming language, with embedded structured query language (SQL) statements. The electronic data submissions are quite large (typically 25,000 to 50,000 records), and a single record may contain 10 or more coded fields. To improve the performance of the software, many of the checks to verify that coded fields contain valid codes are instituted in memory rather than via lookups to tables on disk. A throughput of approximately 40,000 records per hour has been achieved using this algorithm.

The software evaluates the data for three different types of quality issues. First, the software evaluates individual records from the computer scientist's point of view. The software verifies that key and required fields are not blank; that numeric fields contain numbers; that date fields contain dates; and that coded values are drawn from a list of valid values. Second, the software evaluates the data from the chemist's and hydrogeologist's perspective. For instance, analytical results are evaluated for conformance with holding times, contamination, precision, and accuracy conformance criteria, and well completion details are evaluated for conformance with specifications identified for the project. Finally, the software evaluates the data from a database integrity point of view. For instance each analytical result must be associated with an extraction event; each extraction event must be associated with a sampling event; and each sampling event must be associated with a known sampling location. Details regarding reports generated by the electronic data loading software are given below.

DATA QUALITY REPORTS

The Batch Loading Utility does a number of quality checks on the technical data that it processes, and it produces a very comprehensive set of evaluation reports. Several examples of these reports will be presented in the figures of this

section. A complete discussion of all the checks done by the Batch Loading Utility and presentation of all the reports that are produced by this utility is beyond the scope of this discussion.

The quality evaluations of the chemistry data generated to support environmental decision making are perhaps the most universally acknowledged. These evaluations typically address the quality concerns of contamination, precision, accuracy, and the maintenance of sample integrity during sampling and analysis. The analysis of environmental samples is almost always accompanied with the analysis of QC samples that are used to gauge the success of the sampling and analysis activities. These QC samples are used to document the precision and accuracy of the analyses and the presence of contamination introduced in the sampling or analysis process. The integrity of analytes in environmental samples can be compromised if the samples are held for periods longer than their specified holding times.

A typical IRPIMS Batch Loading Utility holding times report is shown in figure 2. Every test that is submitted to IRPIMS is checked for compliance with regulator specified holding times. Tests performed outside the holding times are presented in the holding times report. These tests that are not in compliance with regulatory specified holding times can be rejected and not entered into the database, or they can be entered into the database with flags that indicate the holding times have been missed.

The IRPIMS Batch Loading Utility produces a complement of reports on the many type of QC samples that accompany field sampling and subsequent analysis. Contamination concerns are addressed by a series of four reports that are produced by the Batch Loading Utility. An example of one of these reports is shown in figure 3. A series of six reports summarize the QC data that document precision concerns and another series of six reports summarize the QC data that document accuracy concerns. These reports list the normal environmental samples that are associated with these questionable QC samples. The Batch Loading Utility also sets contamination, precision, and accuracy flags for all normal environmental samples as passed, failed, or could not determine. Finally, two reports summarize the QC samples that accompanied each analytical test reported in the electronic submission.

Submission Identification

Base: XXXXX XXX XXX X xxxxx
Contract: 85-4533 Delivery Order: 06
Contractor: xxxxxxxxxxxxxxxxxxxxxx
Submission Date: 05-MAR-91 Analysis Date: 26-MAR-91

Method: SW8270 GC/MS for Semivolatile Organics: Capillary Column Technique
Matrix: S Standards: 7 40 47

SAMPLE ID						DATES			HOLDING TIMES (DAYS)		
AFIID	LOCID	MATRIX	SBD	SED	SA	SAMPLING	EXTRACTION	ANALYSIS	SAMPLE TO EXTRACTION	EXTRACTION TO ANALYSIS	SAMPLE TO ANALYSIS
XXXXX	TR-10F	S	0.00	0.00	N	21-DEC-89	19-JAN-90	22-JAN-90	28	3	31
XXXXX	TR-16F	S	0.00	0.00	N	21-DEC-89	19-JAN-90	22-JAN-90	28	3	31
XXXXX	TR-17F	S	0.00	0.00	D	21-DEC-89	19-JAN-90	22-JAN-90	28	3	31
XXXXX	TR-17W	S	0.00	0.00	D	21-DEC-89	30-DEC-89	16-JAN-90	9	16	25
XXXXX	TR-18F	S	0.00	0.00	N	21-DEC-89	19-JAN-90	22-JAN-90	28	3	31
XXXXX	TR-5F	S	0.00	0.00	N	21-DEC-89	19-JAN-90	22-JAN-90	28	3	31
XXXXX	TR-5W	S	0.00	0.00	N	21-DEC-89	30-DEC-89	16-JAN-90	9	16	25
XXXXX	TR-18W	S	0.00	0.00	N	21-DEC-89	30-DEC-89	16-JAN-90	9	16	25
XXXXX	TR-17W	S	0.00	0.00	N	21-DEC-89	30-DEC-89	16-JAN-89	9	-1	-1
XXXXX	TR-17F	S	0.00	0.00	N	21-DEC-89	19-JAN-90	22-JAN-90	28	3	31
XXXXX	TR-16W	S	0.00	0.00	N	21-DEC-89	30-DEC-89	16-JAN-90	9	16	25
XXXXX	TR-10W	S	0.00	0.00	N	21-DEC-89	30-DEC-89	16-JAN-90	9	16	25

(The -1 in row 9 indicates the analysis data is recorded incorrectly.)

Figure 2. Installation Restoration Program Information Management System Batch Loading Utility Holding Times Report

IRPIMS Batch File Loader
Chemistry Report
Part 2 - Contamination Summary
Section D - Normal Environmental Samples Associated with Contaminated Lab Blanks

Submission Identification

Base: BLTST Batch loading test ID
Contract: 99-XX99 Delivery Order: 01
Contractor: N/A ERROR-N/A
Submission Date: 22-MAR-91 Report Date: 01-APR-91

Analysis Date: 09-NOV-88 Lab Lot Ctl #: 8809-775 Laboratory: XXXXX

Analyte	Location	Laboratory Sample ID	Detection Limit	Actual Result	Units
ALDRIN	00-110-P	8809775001	0.0500	0.0000	UG/L
ALPHA BHC (ALPHA HEXACHLOROCYCLOHEXANE)	00-110-P	8809775001	0.0500	0.0000	UG/L
BETA BHC (BETA HEXACHLOROCYCLOHEXANE)	00-110-P	8809775001	0.0500	0.0000	UG/L
DELTA BHC (DELTA HEXACHLOROCYCLOHEXANE)	00-110-P	8809775001	0.0500	0.0000	UG/L
GAMMA BHC (LINDANE)	00-110-P	8809775001	0.0500	0.0000	UG/L
ALPHA-CHLORDANE	00-110-P	8809775001	0.5000	0.0000	UG/L
GAMMA-CHLORDANE	00-110-P	8809775001	0.5000	0.0000	UG/L
DIBUTYLCHLORENDATE	00-110-P	8809775001	0.0000	108.0000	UG/L
DIBUTYLCHLORENDATE	LABQC	8809775PBLK	0.0000	101.0000	UG/L
p,p'-DDD	00-110-P	8809775001	0.1000	0.0000	UG/L
p,p'-DDE	00-110-P	8809775001	0.1000	0.0000	UG/L
p,p'-DDT	00-110-P	8809775001	0.1000	0.0000	UG/L
DIELDRIN	00-110-P	8809775001	0.1000	0.0000	UG/L
ALPHA ENDOSULFAN	00-110-P	8809775001	0.0500	0.0000	UG/L
BETA ENDOSULFAN	00-110-P	8809775001	0.1000	0.0000	UG/L
ENDOSULFAN SULFATE	00-110-P	8809775001	0.1000	0.0000	UG/L
ENDRIN	00-110-P	8809775001	0.1000	0.0000	UG/L
ENDRIN KETONE	00-110-P	8809775001	0.1000	0.0000	UG/L
HEPTACHLOR EPOXIDE	00-110-P	8809775001	0.0500	0.0000	UG/L
HEPTACHLOR	00-110-P	8809775001	0.0500	0.0000	UG/L

Figure 3. Installation Restoration Program Information Management System Contamination Summary Report

Another set of technical quality concerns that are addressed by the IRPIMS Batch Loading Utility are construction and maintenance details of groundwater monitoring wells. A schematic diagram of a typical monitoring well is given in figure 4. The Batch Loading Utility report shown in figure 5 identified two types of problems in the construction records for monitoring wells in a particular data submission. The first error identifies wells that have a total depth recorded that is deeper than the driller reported in the hole. Obviously, this is a recordkeeping error that must be resolved before these well completion records can be accepted. The other error identified could be much more serious. This error indicated the filter pack length is only 6 inches in length and the screened interval of the well is 10.00 feet. From the schematic diagram of the monitoring well in figure 4, the filter pack should extend the length of the screen to ensure the proper production from the well. This error could be a simple recordkeeping problem or a more serious construction error in the installation of these wells.

In addition to the technical quality evaluations, the IRPIMS Batch Loading Utility checks the submission to insure that all information required was submitted and that it makes good logical sense. Figure 6 cites analytical result records that were submitted without the analyte identified (one instance), without the analytical result stated (three instances), and no laboratory detection limit reported (244 instances). Figure 7 reports nine sample extraction dates reported before the sample was taken, 34 analysis dates reported before the sample was taken, and 15 analysis dates that preceded the date the sample was extracted. Three instances are also identified on this report where the units "MG/KG" were used for water samples.

AIR FORCE ASSISTANCE TO CONTRACTORS

The success of electronic data loading depends on the ability of contractors to prepare the electronic submissions. The Air Force offers a variety of assistance to its contractors who are preparing these files. Two personal computer "tools" are provided to assist contractors in the preparation and preliminary evaluation of their submissions. The Contractor Data Loading Tool provides IRP contractors with a convenient means of manually entering the various technical data collected by IRPIMS. This tool performs many integrity checks, provides complete list of IRPIMS acceptable codes online, and offers technology that reduces the number of keystrokes required to make the submissions. The Contractor QC Tool provides the

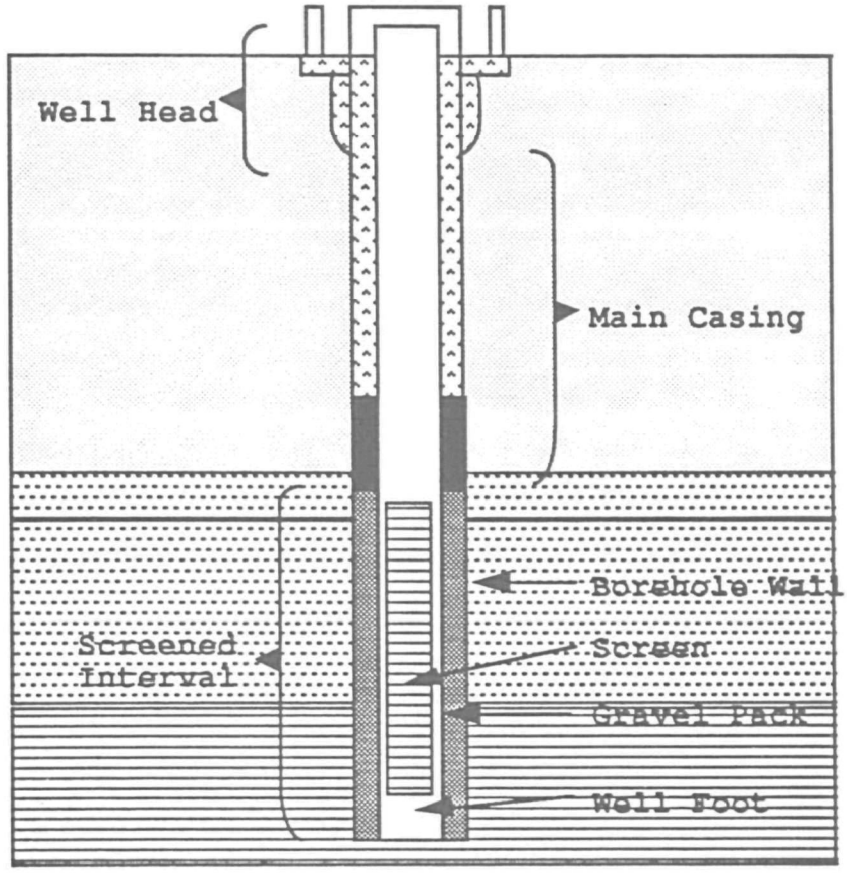

Figure 4. Schematic Diagram of an Environmental Monitoring Well

File BCHWCI

Detailed Listing of Errors and Warnings

Submission Identification

Base: XXXXX XXX XXX X xxxxx
Contract: 85-4533 Delivery Order: 06
Contractor: xxxxxxxxxxxxxxxxxxxxxxxx
Submission Date: 05-MAR-91 Analysis Date: 26-MAR-91

Error/ Warning	Description of Problem with Data			Number of Occurences
Error	Total casing depth exceeds borehole depth (TOTDEPTH > DEPTH) for the following records:			
	AFIID	LOCXREF	TOTDEPTH	DEPTH
	XXXXX	BG-1	20.00	19.0	1
	XXXXX	BG-8	20.40	20.0	1
	XXXXX	C-12	25.10	25.0	1
	XXXXX	C-14	25.50	25.0	1
	XXXXX	C-8	20.30	20.0	1
	XXXXX	C-9	22.00	20.0	1
	XXXXX	DG-5	24.20	24.0	1
	XXXXX	MW-2UWLB	23.70	23.5	1
	XXXXX	MW-4UWLB	25.60	25.5	1
	XXXXX	MW-8HF	12.60	12.5	1
	XXXXX	MW-8UWLB	25.30	25.0	1
Warning	Screen length exceeds filter pack (SCRLENGTH > FPL) for the following records:			
	AFIID	LOCXREF	SCRLENGTH	FPL	
	XXXXX	BG-1	10.00	0.50	1
	XXXXX	BG-2	9.90	0.50	1
	XXXXX	BG-3	10.00	0.50	1
	XXXXX	BG-4	10.00	0.50	1
	XXXXX	BG-5	10.00	0.50	1
	XXXXX	BG-6	10.00	0.50	1
	XXXXX	BG-7	10.00	0.50	1
	XXXXX	BG-8	10.00	0.50	1
	XXXXX	C-10	10.00	0.50	1
	XXXXX	C-11	10.00	0.50	1
	XXXXX	C-12	10.00	0.50	1
	XXXXX	C-14	10.00	0.50	1
	XXXXX	C-8	10.00	0.50	1

Figure 5. Installation Restoration Program Information Management System Batch Loading Utility Well Completion Information Error Report

File BCHRES

Detailed Listing of Errors and Warnings

Submission Identification

Base: XXXXX XXX XXX X xxxxx
Contract: 85-4533 Delivery Order: 06
Contractor: xxxxxxxxxxxxxxxxxxxxxxxxxxxx
Submission Date: 05-MAR-91 Analysis Date: 26-MAR-91

Error/ Warning	Description of Problem with Data	Number of Occurences
Error	Key field PARAMETER LABEL (PARLABEL) was left blank	1
Error	Required field PARAMETER VALUE (PARVAL) was left blank	3
Error	Required field LAB DETECTION LIMIT (LABDL) was left blank	244
Error	Required field EXPECTED VALUE (EXPECTED) was left blank	609
Warning	Contamination in the laboratory of field blank samples were detected for the following tests/analytes:	
	ANMCODE	
	E418.1	2
	SW6010	11
	SW7191	4
	SW8240	35
	SW8270	13

Figure 6. Installation Restoration Program Information Management System Batch Loading Utility Analytical Results Error Report

File BCHTEST

Detailed Listing of Errors and Warnings

Submission Identification

Base: XXXXX XXX XXX X xxxxx
Contract: 85-4533 Delivery Order: 06
Contractor: XXX XXXXXXXXXXXXXXXXX
Submission Date: 05-MAR-91 Analysis Date: 26-MAR-91

Error/ Warning	Description of Problem with Data	Number of Occurences
Error	The extraction date must be on or after sampling date	9
Error	The analysis date must be on or after sampling date	34
Error	The analysis date must be on or after extraction date	15
Error	The following soil or tissue records did not have a value in the field BASIS:	
	AFIID LOCXREF LOGDATE SBD SED MTX SAC	
	XXXXX MW-7UWLB 16-NOV-89 5.00 5.00 S N	1
Error	The following UNITS OF MEASURE (UNITMEAS) are not applicable to a water sample:	
	UNITMEAS	
	MG/KG	3

Figure 7. Installation Restoration Program Information Management System Batch Loading Utility Sample Preparation Error Report

contractors with an onsite means to evaluate the format of their electronic submissions. In addition to these tools, the Air Force also provides a guidance document, training, and telephone support of the contractor data loading effort.

SUMMARY

The Air Force has implemented a comprehensive technical data evaluation process that includes a high level of automation and results in the technical data being stored in a easily retrievable electronic format. The data processed by the Batch Loading Utility are reviewed for a number of technical quality concerns and the results of this review is stored with each record in the database. The Air Force anticipates that this data will eventually be used to supply data to various graphical (including geographical information systems) and modeling tools that will facilitate IRP remediations.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Mr. Stephen Shieldes of OAO Corporation, the implementation programmer who coded the IRPIMS Batch Loading Utility.

SAMPLING/FIELD

32 Preparation and Stabilization of Volatile Organic Constituents of Water Samples by Off-Line Purge and Trap

by

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Purge-and-trap gas chromatographic analysis has a 20 year history of successfully analyzing volatile organics in water. The technique is quantitative, sensitive, and able to be automated. Purge-and-trap is used in all major EPA monitoring programs; RCRA, CERCLA, NPDES industrial wastewater, and drinking water.

A conventional system is integrated, i.e. the purge vessel and sorbent trap are connected directly to the gas chromatograph in a laboratory environment. Water samples must be collected in the field, chemically stabilized, atmospherically sealed, and shipped to a laboratory while chilled. When received at the lab, they must be stored at 4°C. until analyzed, and at least for CERCLA, these samples must be analyzed within 10 days of receipt. While this existing analytical system works well, this paper will demonstrate that it is not necessary for the purging to be done in proximity to the chromatographic analysis.

Purge-and-trap systems which incorporate an integral (on-line) thermal desorption device have been found to suffer from several limitations. These limitations can adversely affect the practical performance of such on-line systems. Among the limitations are:

- RISK OF CARRYOVER BETWEEN SAMPLES. This can occur when a particularly high concentration sample is analyzed.
- RESTRICTED COMPATIBILITY WITH HIGH RESOLUTION CAPILLARY GC + MS DETECTION.
- RESTRICTED STORAGE TIME FOR WATER SAMPLES.
- INCREASED CHANCE OF SAMPLE CONTAMINATION. This can happen because of stabilizers added to the sample to prevent haloform formation, or from atmospheric contamination of the aqueous sample from improper sample seals.

One solution to overcoming these potential problems is to separate the purge-and-trap volatile chemical collection and concentration from the desorption-chromatographic analysis. In other words, perform the chromatography off-line from the sample concentration.

Using portable traps in combination with an automatic off-line purge unit enables water to be sampled using conventional EPA purging methodology at field sampling stations. Once sampling is completed, the tubes may be capped and transferred for thermal desorption GC analysis at a central laboratory facility. This approach immediately overcomes two of the major drawbacks of conventional on-line methodology:

- NO RISK OF CARRYOVER BETWEEN SAMPLES.
- GREATLY EXTENDED MAXIMUM SAMPLE STORAGE TIMES.
- DISTRIBUTED FIELD SAMPLING COMBINED WITH CENTRALIZED LABORATORY ANALYSES.

Commercial automatic thermal desorption instruments allow multiple sample tubes or traps to be analyzed without operator attendance. These traps, in the form of sampling tubes, are compatible with the method detection limits specified by EPA 500 and 600 series methods, as well as those purge-and-trap methods in the RCRA SW-846 analytical method manual. For long term storage, the sorbent tubes can be capped with brass Swagelok ™caps and one-piece PTFE ferrules. Such tubes, spiked with benzene, toluene and m-xylene, are available as certified standards (Ref.1), and have been shown to be stable for up to two years of storage time.

In addition, data reported by the Netherlands Organization for Applied Scientific Research shows that chlorinated hydrocarbons on Tenax ™ are stable for over 2 years. Multiple analyses for trichloroethylene and tetrachloroethylene carried out over a two year period had a reproducibility with less than 10% RSD at storage temperatures ranging from 4™ to 40 °C (Ref. 4).

STABILITY OF VOLATILE CHLOROALKANES ON TENAX

Storage Temperature °C	Component	Initial Mean Charge ng	RSD%	# Rep	24 Month Mean Recovery ng	% Rec.
4°	Trichloroethylene	840	2.0%	15	856	102%
	Tetrachloroethylene	806	1.9%	15	781	97%
20°	Trichloroethylene	840	2.0%	15	816	97%
	Tetrachloroethylene	806	1.9%	15	756	94%
40°	Trichloroethylene	840	2.0%	15	842	100%
	Tetrachloroethylene	806	1.9%	15	765	95%

Ref: TNO Division of Technology for Society: Netherlands Organization for Applied Scientific Research, Report No. R90/268.

The ATD-400 also overcomes another limitation of conventional procedures, i.e. incompatibility with high resolution capillary GC, by using an optimized two-stage thermal desorption process.

REFERENCES

1. Certified Standard Material Reference No. CRM 112. Available from the European Community Bureau of Reference:
   Community Bureau of Reference (BCR)
   Rue de la Loi 200
   B-1049 Brussels
   Belgium

2. *How Efficient are Capillary Cold Traps?*, J. W. Graydon and K. Grob, Chrom. 15, 327, 1983, pp. 265-269.

3. *Modified Analytical Technique for Determination of Trace Organics in Water Using Dynamic Headspace and Gas Chromatography-Mass Spectrometry.* Bianchi, Varney, and Phillips, J. of Chrom. 467 (1989), pp 111-128.

4. *Stability of Chlorinated Hydrocarbons on Tenax*, F. Lindqvist and H. Bakkeren, Netherlands Organization for Applied Scientific Research, TNO Division of Technology for Society, Report No. 90/268.

33 A REMOTE WATER SAMPLER USING SOLID PHASE EXTRACTION DISKS

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ABSTRACT

In order to reduce costs and inconveniences associated with the sampling, preservation, storage, shipping and analysis of large volumes of water for the analysis of trace levels of pesticides, we have designed and developed a remote water sampler employing porous extraction disks. Commercially available disks were studied in the laboratory for their ability to extract the pesticides alachlor, butachlor, ametryn, prometryn, and terbutryn from both laboratory and groundwaters. Extraction efficiencies were determined as functions of pesticide type, concentration, flow rate through the disks, disk pretreatment, storage temperature, and storage interval. Results were encouraging enough to pursue design and construction of the remote sampler, made possible by the extensive modification of an existing commercially available water sampler. Evaluation of the resulting sampler using extraction disks showed that it was reliable and accurate enough to be used in the field.

INTRODUCTION

One of the larger expenses in any ground or surface water monitoring project entails proper collection, preservation, storage, and transportation of the water samples to be studied. This is particularly true when transient events, such as a moving groundwater plume or a single surface contamination event, occur. Being able to effectively sample in a continuous manner over a period of hours, days, or even weeks would allow for the observation of such an event, and prevent it from escaping unnoticed.

Most approved USEPA numbered methods for the analysis of trace organics in water, (500 and 600 series) including pesticides, require the collection of large volumes of water, typically one liter. Transporting multiple one liter quantities, when multiple analytical methods are to be employed, or when sampling over regular intervals is to be undertaken, requires expensive transportation and storage techniques. And when they arrive at the laboratory, they are typically extracted with large quanitities of expensive and hazardous solvents, such as methylene chloride. Some methods allow the water to be extracted on-site with solid phase extractors (SPEs; 1 - 3), with subsequent transportation back to the laboratory for elution and chemical analysis, usually by gas or high performance liquid chromatography. These SPE devices are small cylindrical cartridges packed with intermediate size silica particles, usually chemically coated with an alkyl material, such as octyl groups. They adsorb organics from water when it is drawn through by pressure or vacuum, and then release the organics to a small amount of solvent that is passed through the cartridge.

While on-site extraction via the SPEs obviates several problems, there still is the requirement that personnel be transported, housed, maintained, and paid if sampling is to be done over time. In order to eliminate the requirement for collecting, storing, and transporting large volumes of water, while at the same time minimizing costs for the presence of on-site personnel, we conceived the idea of creating a remotely located "dosimeter", which could be placed at a remote surface or well water site, programmed to collect one liter samples at various intervals, perform the sampling unattended, process the sample water through a solid phase extractor, direct the processed water to waste, shut itself off and await return of personnel. It was our initial intention to employ SPE cartridges that have been commercially available. However, as the engineering of the device began, it became readily apparent that switching a stream of water

into and away from an array of SPEs would be very difficult, if not impossible to achieve, given the pressures required to achieve reasonable flow rates through the SPEs. Attention turned to the more recently developed extraction disks, developed by the 3M Company (4,5). These disks have proved their worth for such an application, as we now report here.

We evaluated the C_8 disks for the extraction of the pesticides ametryn, prometryn, terbutryn, alachlor, and bromacil from laboratory and three typical Florida groundwaters; some evaluations were done in the laboratory in filter holders, and some within the "dosimeter".

DISK EXTRACTION EFFICIENCIES

EXPERIMENTAL

All studies were performed on the 4.7 cm C_8 Empore extraction disks (Analytichem, Harbor City, CA). They were held by a glass Millipore model KGS-47TF filter holder, attached to a 250 mL graduated funnel that was clamped hold the disk. The filter holder was placed into a 1 liter suction flask that was attached by Tygon tubing to a Millipore vacuum pump, model 5KH10GGR28S. This vacuum pump was equipped with a needle valve for adjusting the vacuum present in the flask.

Pesticide analyses were conducted on a Hewlett-Packard gas chromatograph, model 5890, equipped with a nitrogen-phosphorus (NP) detector, and an electron capture detector. The instrument was capable of automatic sample injection and peak integration. Separation of the pesticides under study was accomplished on a DB-5 bonded fused silica column, 30 meters long x 0.25 mm ID, with a film thickness of 0.25μm (J and W Scientific, Folsom, CA). Injections were made, 2 μL, in the splitless mode with a 45 second delay. Carrier gas was helium at 30 cm/sec linear velocity. Injector temperature, 250°C; NP detector temperature, 300°C; EC detector temperature, 300°; oven temperature programmed from 60°C to 300°C at 4°C/min.

Pesticides studied were ametryn, prometryn, terbutryn, alachlor, and bromacil, all obtained in 99.9% pure analytical standard form from the EPA Pesticide Repository (Research Triangle Park, NC).

All solvents were HPLC grade (Fisher Scientific or Burdick and Jackson). Wetting agents (CETABS, polyethylene glycol, octanol, etc) were ACS reagent grade from Fisher.

Since reverse phase disks, the C_{18} and the C_8, are hydrophobic by their nature, and require pretreatment with a water miscible solvent to allow activation of the reverse phase material, and to allow for water flow, various wetting agents, neat and dissolved in water, were examined for their abilities to wet the Empore disks so as to allow water flow by gravity. Efforts were made to select water miscible alcohols and surfactants that would be involatile, so that pretreatment could be done in the laboratory before assembly of the disks. The disks were soaked in the following agents, for 1 hour and 30 minutes, then they were removed, placed in the Millipore filter holder, 100 mL of HPLC grade water added to the funnel, and allowed to drain by gravity, without vacuum from the vacuum pump.

Three procedures were studied for their ability to extract the pesticides ametryn, prometryn, and terbutryn from water. They were designed with an eye toward their implementation in the dosimeter, since it was known that the dosimeter would place some constraints on how disk pretreatment could be accomplished. We wanted to determine what steps in the Analytichem procedure could be either reduced or eliminated, while still giving good extraction efficiencies, so that the dosimeter design could be kept as simple as possible. The selected extraction method was then validated on other pesticides (alachlor

and butachlor) during additional extraction efficiency studies at high water flow and during volatility studies, where losses from disks used to extract the pesticides from water were determined (see subsequent section).

These three extraction procedures were:

(1) Modified Analytichem (created from the procedure recommended by Analytichem in Appendix A by omitting the 5 mL addition of methanol to the water, and by presoaking the Empore disks in ethyl acetate, rather than passing it through the disks once they were placed in the holder).
-Presoak disk in 5 mL of ethyl acetate for 6 hours; discard solvent.
-Place disk in Millipore filter apparatus.
-Apply vacuum for 5 minutes.
-Add 20 mL of methanol, apply vacuum; do not let disk go dry.
-Repeat above step with 20 mL of HPLC grade water.
-Begin adding water sample.
-After sample is processed, pull air through disk for 5-30 minutes.
-Place test tube at tip of filter base inside flask.
-Add 10 mL ethyl acetate, pull half of the solvent through, let stand for approximately minute, then pull the rest through.
-Repeat with a second 10 mL aliquot.
-Sample is ready for analysis or may be concentrated to a smaller volume by dry nitrogen at ambient temperature.

(2) PRL Procedure #1.
-Presoak disk in 5 mL of ethyl acetate for 6 hours; discard solvent.
-Place disk in Millipore filter apparatus.
-Wash with methanol:water (40 mL of 1:1).
-Apply vacuum.
-Add sample.
-After sample is processed pull air through disk for 5-30 minutes to remove any water remaining on disk.
-Elute sample as per modified Analytichem procedure above.

(3) PRL Procedure #2. (As for PRL #1, except 20 mL methanol used rather than methanol:water).

Since the Millipore vacuum pumps used in the laboratory are capable of pulling water through the Empore disks at a higher rate than can be done in the dosimeter, and since high flow rates would be desirable when extracting 1 liter samples, a study was done to determine what effect maximum flow rates would have on extraction efficiency. Consequently, we studied the two flows of 20 mL/min and 80 mL/min for several pesticides in HPLC grade water at several concentrations.

The ability of the Empore disks to function at such high flow rates (80 mL/min) allowed for the collection of 1 liter samples if plugging did not result and if "breakthrough" did not result. It was conceivable to us that "breakthrough" might occur for these large volumes. Since the Empore disks are simply very short and very permeable reverse phase HPLC columns, and even though 100 % water causes organic compounds to move only slowly down these columns, there is some volume of water that would cause the compounds to "breakthrough" and exit the disks. Whether or not this would occur within the 1 liter of water being sampled was part of this study, as determined by measuring percent recoveries.

Consequently, replicate one liter samples were fortified at concentrations of 0.1, 1.0, and 10.0 ppb with the pesticides alachlor, bromacil, ametryn, prometryn, and terbutryn, and the PRL #2 procedure was used for extraction and analysis. All determinations were done in triplicate with duplicate sample injections on the gas chromatograph. Unfortunately, some of the 0.1 μg/L samples were not quantifiable due to method sensitivity limitations (alachlor and bromacil).

In order for the Empore extraction disk concept to be functional in the dosimeter in the field for extended periods approaching 30 days, it was important to determine whether after extraction, the pesticides would remain on the disks without unusual precautions so that they could be transported to the laboratory for analysis. It was also important to consider that the disks could conceivably experience elevated temperatures as a result of a "greenhouse" effect as they sat in the dosimeter.

Consequently, we studied all the pesticides at 15 and 30 days storage at 25°C (nominal ambient), and also studied alachlor, bromacil, and prometryn at 40°C for those intervals. We also studied alachlor and bromacil for 1 day and 10 day intervals. HPLC grade water was fortified at the 10.0 μg/L level, exactly 100 mL was passed through fresh Empore extraction disks at 80 mL/min, and the disks subjected to the #2 PRL procedure for extraction and analysis. All samples were prepared and analyzed in triplicate with duplicate injections on the gas chromatograph.

RESULTS AND DISCUSSION

How the disks responded to pretreatment with alcohols and surfactants in terms of water flow is shown in Table 1.

Table 1: Flow Through Alcohol and Surfactant Treated Disks, Gravity.

Wetting agent	Observation
none	No flow observed
MeOH	0.76 mL/min
80 % MeOH	0.7 "
50 % MeOH	No flow observed
30 % MeOH	Disk floated; no wetting
Octanol	No flow observed
80 % Octanol	"
50 % Octanol	"
30 % Octanol	Disk floated; no wetting
Ethylene glycol	No flow observed
80 % ethylene glycol	No wetting observed
50 % ethylene glycol	"
30 % ethylene glycol	"
Acetonitrile	0.6 mL/min
80 % acetonitrile	0.6 mL/min
50 % acetonitrile	0.5 mL/min
30 % acetonitrile	No flow observed
Polythelene glycol 8000 (0.5 g/100mL)	Disk floated; no wetting
CETAB (0.04 g/100mL)	No flow observed
Tetrahydrofuran	0.6 mL/min
80 % tetrahydrofuran	0.7 mL/min
50 % tetrahydrofuran	0.7 mL/min
30 % tetrahydrofuran	0.6 mL/min

These data showed that of the alcohols and surfactants studied, only methanol, acetonitrile, and tetrahydrofuran would wet the disks adequately for water flow. We then studied the effect of these solvents on water flow through prewet disks under vacuum. Empore disks were soaked in each of the three solvents that gave flow under gravity, and water was passed through at a vacuum of either 5 or 10 pounds per square inch (PSI). Table 2 summarizes these results.

Table 2: Flow Through Solvent Treated Disks, Vacuum.

Solvent	Vacuum (PSI)	Flow (mL/min)
Tetrahydrofuran (THF)	5	54
"	10	88
Methanol	5	50
"	10	79
Acetonitrile	5	59
"	10	74

Even though both THF and acetonitrile gave slightly greater flows than did methanol, methanol was chosen for further studies, so that our studies could be compared with those already done and with those yet to follow by others, who probably would use the methanol recommended by Analytichem. Since we felt that a 10 PSI vacuum could be achieved in the dosimeter using the pumps selected for it, a flow of 79 mL/min would be adequate. This flow would certainly permit 1 liter samples to be collected within 1 hour, a goal we set, if acceptable recoveries could be achieved at this flow. These studies showed that some way of pretreating the disks within the dosimeter on site before each water sample was extracted would have to be accomplished, since 100 mL subsamples of water would not pass through an unactivated Empore disk. This would have to be accomplished within the dosimeter by a separate delivery system for methanol.

How well the pesticides were recovered from the Empore disks using the three pretreatment and extraction procedures is shown in Table 3.

Table 3: Recovery of the Pesticides Ametryn, Prometryn, and Terbutryn from 100 mL of HPLC Grade Water Using Various Procedures and the Empore Disks.

Pesticide	Procedure	Conc.(ppb)	n[a]	% Rec.	%RSD
Ametryn	Modif. Analy.	105	1	117	--
	PRL #1	105	1	68	--
	PRL #2	105	14[b]	106	6.8
Prometryn	Modif. Analy.	110	3	65	12
	PRL #1	110	1	83	--
	PRL #2	110	11[c]	95	9.3
Terbutryn	Modif. Analy.	110	2	79	7.2
	PRL #1	110	1	75	--
	PRL #2	110	11[c]	88	6.1

[a] Number of individual determinations; each determination injected in duplicate on the gas chromatograph. All flows through the filter were at approximately 18 mL per min.
[b] Eleven (11) of these extracted with the same Empore disk.
[c] Extracted with the same Empore disk.

This data shows that there are little if no consistent differences in the three extraction procedures used. Consequently, since the PRL #2 procedure is simpler than the other two, it was used throughout the remaining studies, unless otherwise stated. Acceptable reproducibility exists for replicate determinations, although we would like to improve on this as the studies continue. It also shows that the disks can be reused many times without suffering fracturing, erosion, or loss of the silica particles, all of which would lead to diminished

recoveries.

Table 4 summarizes these results for the effect of flow rate on recoveries from the disks.

Table 4: Effect of Flow Rate Through Empore Disks on Extraction Efficiencies[a].

Pesticide	% Recovery	
	20 mL/min	80 mL/min
Alachlor	89	96
Bromacil	36	46
Prometryn	93	92

[a] Average of triplicate determinations for 10 μg/L samples; average RSD less than 6%.

These results show that extremely high flow rates can be handled with no loss of extraction efficiency. This ability to rapidly process samples in the laboratory allowed us to work with 1 liter samples, giving an improvement in method limit of detection, and would also allow for high sample throughput if similar vacuum could be established within the dosimeter.

Table 5: Extraction Efficiencies of Pesticides from Empore Disks Using High Water Sample Flows (80 mL/min).[a]

Pesticide	Concentration (μg/L)	Average % Recovery
Alachlor	10.0	89
	1.0	92
	0.1	--[b]
Bromacil	10.0	36
	1.0	58
	0.1	--[b]
Ametryn	10.0	91
	1.0	69
	0.1	89
Prometryn	10.0	93
	1.0	91
	0.1	76
Terbutryn	10.0	83
	1.0	79
	0.1	35

[a] Averages of triplicate determinations, with duplicate injections for each on the gas chromatograph. Average % RSD for triplicate determinations less than 8%.
[b] Unable to quantitate due to sensitivity problems.

From the above data, it is apparent that only bromacil gives low recoveries at all concentrations. There is also an apparent recovery problem with terbutryn but only at the lower concentrations. Subsequent studies on pesticide losses due to volatility (see Table 6 below) indicated that low recoveries of bromacil may be due to factors other than that of poor adsorption by the Empore disks.

Table 6: Pesticide Losses from Empore Extraction Disks with Storage at Extended Intervals and at Elevated Temperatures.[a]

Pesticide	Storage Interval	Temperature	Average % Recovery
Alachlor	1 day	25°C	99
	10 "	"	87
	15 "	"	91
	15 "	40°C	98
	30 "	25°C	87
Bromacil	1 day	25°C	95
	10 "	"	97
	15 "	"	64
	15 "	40°C	83
	30 "	25°C	78
Prometryn	15 day	25°C	43
	15 "	40°C	30
Ametryn	15 day	25°C	30
Terbutryn	15 day	25°C	4

[a] Average of triplicate determinations, 10 μg/L; duplicate injections on the gas chromatograph. Average % RSD less than 10%.

From these data it is obvious that ametryn, prometryn, and terbutryn cannot withstand 15 day storage intervals at 25°C on the Empore disks. Surprisingly, both alachlor and bromacil are recoverable even up to 30 days with average percent recoveries greater than 78%. Even more surprising is that bromacil, which had shown very poor recoveries upon immediate extraction of the disks with ethyl acetate (see **Table 5**), now gives excellent recoveries after sitting for days after extraction of the water samples. Apparently, aging the disk stabilizes bromacil, or, makes it more amenable to ethyl acetate extraction. Whether this phenomenon would occur for other pesticides that were not studied here is yet to be determined, and merits investigation.

Raising the storage temperature from 25°C to 40°C caused little additional loss of pesticide for the three studied at the higher temperature. This may be a very important aspect for long term use of the dosimeter when temperatures may become very high in the field.

Also of potential value is the fact that during these long term studies, all Empore disks were placed in the open in fume hoods, susceptible to an array of

microbes attached to air particles which would "fall out" on them. Despite this, none of the pesticides were significantly degraded by exposure to the atmosphere. This is self evident from a "prima facie" aspect when the mechanism for retention of pesticides on the 8μ irregular shaped silica Empore particle is considered. It is well recognized that retention occurs at the alkyl (C_8) bristle which is deep inside the pores of the particle. These pores are only 60 Angstroms in diameter; expressed in microns (μ), that amounts to 10^{-4} μ. However, microbial cells are larger than 2 x 10^{-1} μ in diameter, making them much too large to penetrate into the pores of the silica particles of the Empore disks. Therefore, microbial degradation of pesticides adsorbed by Empore disks is, from first principles, impossible. For this reason, difficulties we faced in getting water flow through the 0.2 μ microbial filters are of only academic concern.

EXTRACTION DISK WATER SAMPLER DESIGN, CONSTRUCTION, AND VALIDATION

Introduction

There were several goals that were established to be met in the design of the dosimeter. The device needed to be battery powered and capable of operating unattended over extended intervals of time, as long as one month. Battery drain should be such that as many as 24 samples, of one liter volume, could be taken in as little as 24 hours. Sampling volume accuracy should be as good as + or - 10%. It ought to be programmable, such that variable volumes could be sampled at variable time intervals. It ought to be capable of processing more than one sample through the same disk. Only minimal redesign and modifications of an existing inexpensive water sampler ought to be required. While still being highly portable, the dosimeter ought to have a large enough internal volume to accommodate at least 24 Empore disk holders.

An American Sigma Streamline water sampler (Middleport, NY), was chosen as the nucleus of the disk water sampler (See Fig. 1). It came equipped with an "advanced programming" mode present in the EPROM software that allowed much flexibility in the programming in regard to sample volume, intervals, multiple sampling, etc. However, its main feature, which was not apparent until it became obvious that vacuum would have to be applied to the bottom of each Empore disk holder, was that the motor that was used to position the sample distribution arm over the sample bottles could be synchronized with a somewhat similar motor which would rotate a valve for selecting which filter holder received vacuum. This was a critical aspect in the successful design of the dosimeter.

Also critical was the fact that electronic timing circuitry was in place and enabled the installation of a switch as a means of acctuating a methanol pump at the appropriate time for each sample.

The device as modified will accept up to 24 holders. During operation, 1000 mL of water is processed through each holder, in ten 100 mL increments. In this report these 100 mL increments are referred to as sub-samples. The machine can be programmed to vary the time between increments and also set real time start and stop times for each 1000 mL sample as well as continuous operation once started.

The number of 1000 mL samples can be selected as any value up to a maximum of 24. If the multiple stop-start method of programming is to be used and the machine set to shut off after the desired number of samples have been taken, holders must be placed in the machine in direct sequence, 1 to whatever number desired, in a counter clockwise direction from position 1.

After completion of the sampling program, the holders can be brought back to the lab where the Empore disks can be processed without removal from the holder.They

are processed by elution of the adsorbed pesticides from the disk material with a solvent suitable for the type of analysis to be used.

The device, as described here, comes equipped with an intake tube of 3/8 in. internal diameter, and a weighted intake strainer for sampling surface waters. An interface remains to be constructed for monitoring wells.

Preparation of Holders

For use in this device, the Empore extraction disks are held in a modified disposable filter funnel (See Fig. 2). These filter funnels are manufactured by Micron Separations, Inc. of Westborough, Mass. (cat.# DFN-P4SGS-S1) and are supplied with various types of filter media. For this work, all of the supplied filter media, except the supporting membranes is discarded, making space for the stacked disks described below.

The remaining support disk is modified by trimming it to 40 mm in diameter. The trimmed support is then centered in the lower half of the holder and cemented in place with silicon rubber cement. After this re-work is performed, the holder is then reassembled in the following manner:

1st layer (bottom) - one original support disk (trimmed to 40 mm)
2nd layer - Empore™ cat. # 1214-5002, C8 disk (Analytichem International)
3rd layer - Whatman Multi-grade filter, # GMF150

The two halves of the holder are then placed together and held with moderate downward pressure while tape is applied to assemble them. If the holder is to be reused ordinary duct tape 3/8 in. wide has proven satisfactory. Care was exercised while assembling the holder to limit downward pressure to prevent the multigrade filter being cut allowing bypass of the sample around it.

Description of System for Wetting Extraction Disks

Before passing any water through the Empore disc, it must be wet with methanol. In this machine, this is accomplished in the following manner. Methanol is placed in a 500 mL reservoir (See Fig. 3). At the beginning of the sampling interval, the main pump runs in reverse for several seconds in order to purge the intake line to the pump. After that, the methanol pump is turned on, which delivers approximately 10 mL of methanol to the main pump discharge funnel on top of the distributor arm. The methanol flows by gravity down to filter holder number one and wets the disc. On the following pump cycles the methanol pump is held off until there is counted a total of 20 reverse run times (two for each sub-sample interval). Runs in the forward direction are ignored due to the action of a diode. After twenty run times, the circuit is reset and is ready to pump methanol again for the next sample. See Fig. 4 for a summary of the parts added to the Streamline water sampler, and Fig. 5 for a logic diagram of the control circuits, both original and added.

Description of the Vacuum Pump Circuit

At the same time the methanol pump starts, a vacuum pump is turned on to pull the methanol through the filter, and controlled by a four minute timer. A vacuum of approximately 15 in. of Hg is applied to the bottom of each individual disk holder for drawing the sub-sample through the disk. This vacuum is supplied by a small 12V powered vac pump and distributed by a 24 port rotary valve. The rotary valve is synchronized manually before the beginning of the program by rotating the distribution arm and the valve to position #1 individually. Thereafter, the interface circuitry advances the rotary valve in synchronism with the distribution arm allowing time for the sub-sample to be drawn through the

disk before advancing the valve to the next position.

Modification to Main Pumping System

The main pump flow rate is approximately 3500 mL/min as supplied by the manufacturer. Since sub-sample increments of only 100 mL are used, this high flow rate resulted in splashing and control problems. In order to reduce these problems the pumping rate was changed by reducing the size of the tubing used in the pump and the suction line. In addition, it was found that a small amount of water was trapped in the pump due to sagging of the tubing,resulting in a small carryover between sub-samples. The tubing was shortened to eliminate this sag and insure that the pump was blown dry during the purge cycle.

Materials were chosen for the dosimeter construction and evaluation that were of high quality, reliable, and economical, all readily obtainable from suppliers within the United States.

Empore Filter Design Considerations

Study design called for lake water, with 3 levels of algae, to be tested in the dosimeter, as well as 3 groundwater (well) samples with 3 levels of hardness. Therefore, a filter holder was identified that could accommodate multiple, or a stacked array of filters. We erroneously believed that some sort of microbial filter would have to be incorporated in the filter holder to prevent microbes from reaching the Empore extraction disk during water filtration.

Overflow Detection When Filter Becomes Plugged

A convenient way was devised to determine when filter holder overflow would occur, and which filter had overflowed, ostensibly as a result of Empore filter plugging, either by algae or other microparticulates. This was accomplished by ringing the top portion of the filter holder with paper tape impregnated with water soluble ink (Sanford's Mr. Sketch). As the water begins to overflow the washing away of the ink begins. This feature ought to be quite useful in that it would prevent the analytical work from being performed in the laboratory on samples that plugged in the field.

Dosimeter Pump Accuracy and Reproducibility

The accuracy and reproducibility of the dosimeter peristaltic pump were determined by evaluations with Fisher HPLC grade water. Before beginning the study, the pump was calibrated for flow. The pump was then programmed to pump 10 sequential 100 mL samples at 12 minute intervals. Water was collected in a 1000 mL graduated cylinder and measured after each sample. Of the 10 samples collected, 3 of them were exactly 100 mL, while 7 of them varied plus or minus 5 mL. Total volume delivered was 995 mL, very well within the manufacturers specifications for the pump.

Four more similar tests were run, with an average delivered volume per sample of 98.9 mL, excellent accuracy and reproducibility.

Lake Water Extraction Efficiencies

Three lake waters were selected with varying amounts of algae as determined by Secchi disk. Secchi numbers (see Table 7 below) are the number of feet that a black and white disk can be lowered before definition of its outline is lost. One gallon (4 L) brown jugs were filled, taken to the laboratory for storage at 4°C, fortified at 10 μg/L with all eight pesticides, and processed in 100 mL subsamples through the dosimeter to give a total of 1 L for each sample. These

studies were done on stacked filters that did not include the 0.2 μ microbial filters, but did include the GMF multigrade. The support filter had not been trimmed for these. Three filter aids were also tested for their ability to filter out the algae onto the multigrade filter: (1) Solka Floc, James River Corp., (2) Hyflo Super Cel, Johns-Manville Corp., and (3) white sea sand. Exactly 15 mL of each were placed into the filter holders, along with several controls (no filter aid), and the waters were run through.

Table 7: Dosimeter Extraction of Several Lake Waters Fortified with Eight Test Pesticides; Effect of Various Filter Aids [a]

Lake Water	Secchi Disk Reading
Lake Alice	1.5
Bivens Arm	1.8
Lake Wauberg	2.0
Newnans Lake	1.8
Red Water Lake	3.2
Lake Lochloosa	3.5
Riley Lake (Putnam Co.)	8.0

[a] Fortified at 10 μg/L. All samples plugged the filter stack and flow stopped at 300 mL of water, + or - 50 mL, whether filter aid was present or not.

These results clearly showed that the tested version of the Empore extraction disks cannot be used for the extraction of 1 liter quantities of lake water, even when a multigrade filter is present and even when 15 mL of filter aid are present in the filter holder.

Extraction of Groundwater Samples Fortified with the Eight Test Pesticides

Three groundwater samples of various hardnesses were to be collected, fortified with the eight test pesticides and extracted with the dosimeter. Those three chosen were: (1) Murphree well field, City of Gainesville, well #1, (2) shallow well at a private residence, Gainesville, FL, and (3) private shallow well on Riley Lake, Putnam County, FL. These wells ranged widely in their hardnesses. For example, the Gainesville well was the most hard, with 320 mg/L (ppm) of bicarbonate, followed by the Murphree well #1, with 208.6 mg/L. The Putnam County well was least hard, with a bicarbonate of only 10.2.

Samples were collected (8 L of each) in one gallon brown jugs and transported to the laboratory where they were fortified at 10 μg/L with the five test pesticides and stored at 4°C before extraction by the dosimeter. Exactly 1 liter samples of each were extracted in triplicate. Alachlor, bromacil, ametryn, prometryn, and terbutryn were analyzed by gas chromatography as previously described. Table 8 summarizes the recoveries.

Table 8: Extraction Efficiencies of Eight Test Pesticides Extracted from Three Florida Groundwaters Using the Dosimeter Equipped with Reduced Size (40 mm) Support Disks.[a]

Well	% Recoveries alachlor	prometryn	ametryn
Murphree	109	107	108
Gainesville, FL	113	110	114
Putnam Co., FL	100	102	106

Well	% Recoveries bromacil	terbutryn
Murphree	119	106
Gainesville, FL	91	109
Putnam Co., FL	100	100

[a] Averages of three separate determinations, fortifications at 10 μg/L; RSD less than 5%.

Although somewhat high, these recoveries were similar, from pesticide to pesticide and from well to well. Relative standard deviations for triplicate analyses averaged less than 5% for all pesticides and wells, not much larger than what could be expected for instrumental error.

FIELD TEST OF DOSIMETER

The pumping capacity and accuracy of the dosimeter in the field was briefly examined by placing it on the shore of Riley Lake, Putnam County, FL. The dosimeter was programmed to sample 24 one liter samples in 100 mL subsamples over a 24 hour period, beginning at 1:06 PM on Nov. 29 and ending at 1:06 PM on Nov. 30. Since previous runs on Riley Lake water showed that the Empore filter disks plugged at approximately 300 mL, they were not placed in the disk holders for this study. Only the support disk and the GMF 150 multigrade disk were installed in each of the 24 holders. All water pumped through the disks was collected in large carboys and transported back to the laboratory for volumetric measurement. After all samples were completed, the overflow detection tape was examined on each holder. Battery voltage was measured before starting the sampling and immediately following completion of sampling.

No overflow was observed for any of the samples, nor was there evidence of splashing inside the dosimeter around the filter disk holders. Exactly 20.83 liters of water were collected, 87 % of the programmed volume. This accuracy falls outside the specifications set by the manufacturer, however, it may be explained by the extreme cold temperatures the dosimeter experienced on the morning of Nov. 30 when 40°F was measured. Battery dropped very little, from 12.75 volts to 12.48 volts, indicating that much more sampling could be accomplished before recharging.

SUMMARY

We have shown that the pesticides alachlor, bromacil, ametryn, prometryn, and terbutryn can be extracted from laboratory and well waters at trace levels using C_8 Empore extraction disks and one liter samples. Drying of the disks was required for the near complete recovery of bromacil. Several lake waters plugged the disks at approximately 300 mL, whether filter aids and multigrade prefilters were employed or not. For laboratory water, extraction efficiencies decrease little with increasing flows, maximum flow being determined by disk rupture. The

pesticides alachlor and bromacil could be kept on disks at ambient temperatures (25°C) and elevated temperatures (40°C) for up to 30 days without loss. All five pesticides could be efficiently extracted from three different well waters varying widely in hardness using the dosimeter. Pumping accuracy, in the field, was not as good as observed in the laboratory, although it could be measured and used for sample volume corrections.

ACKNOWLEDGEMENTS

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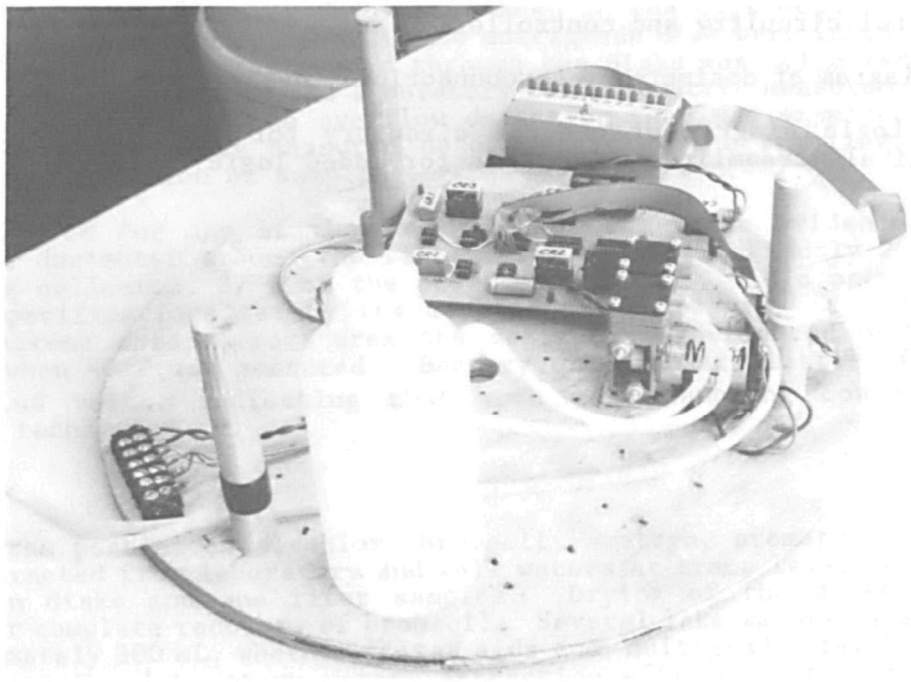
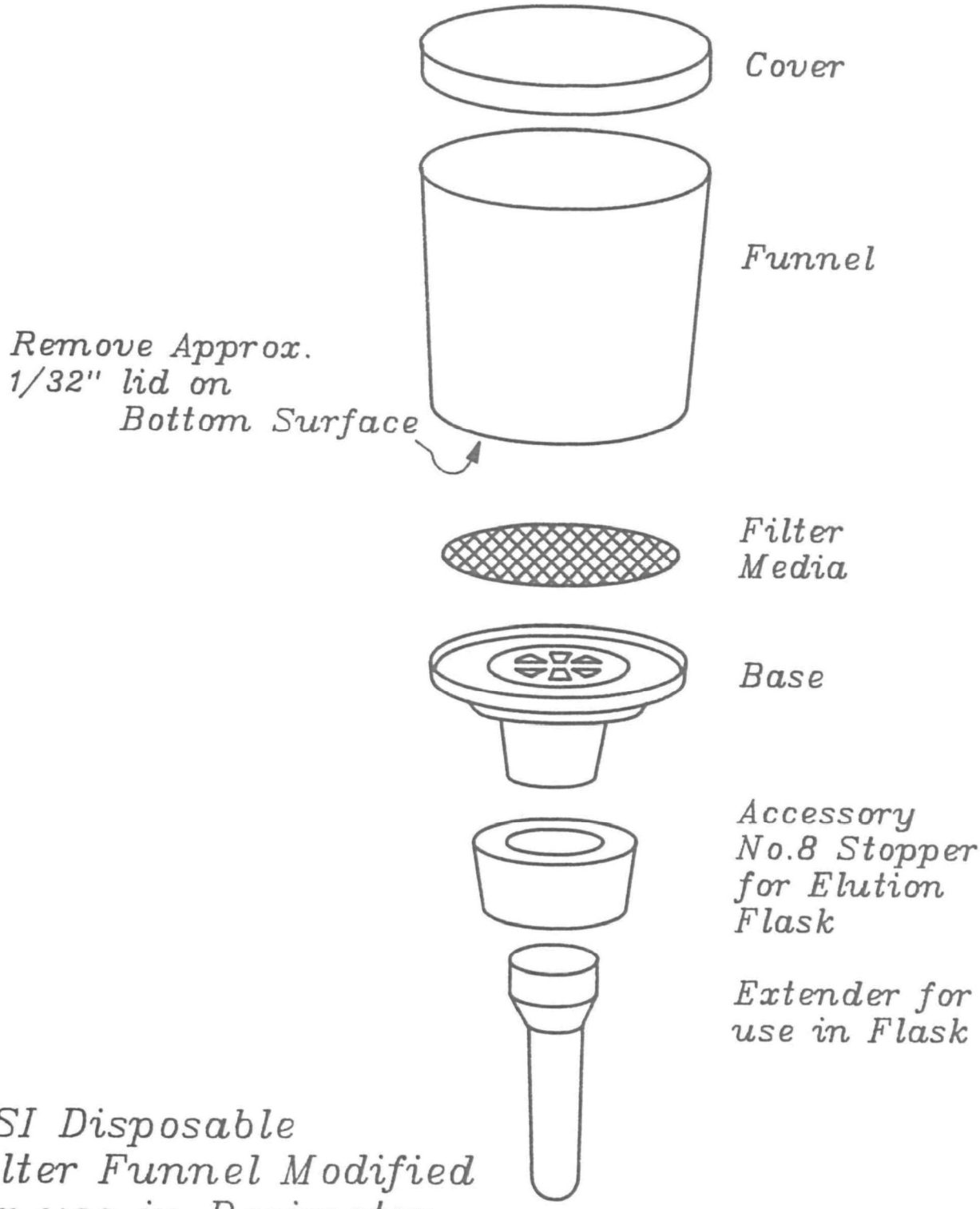
REFERENCES

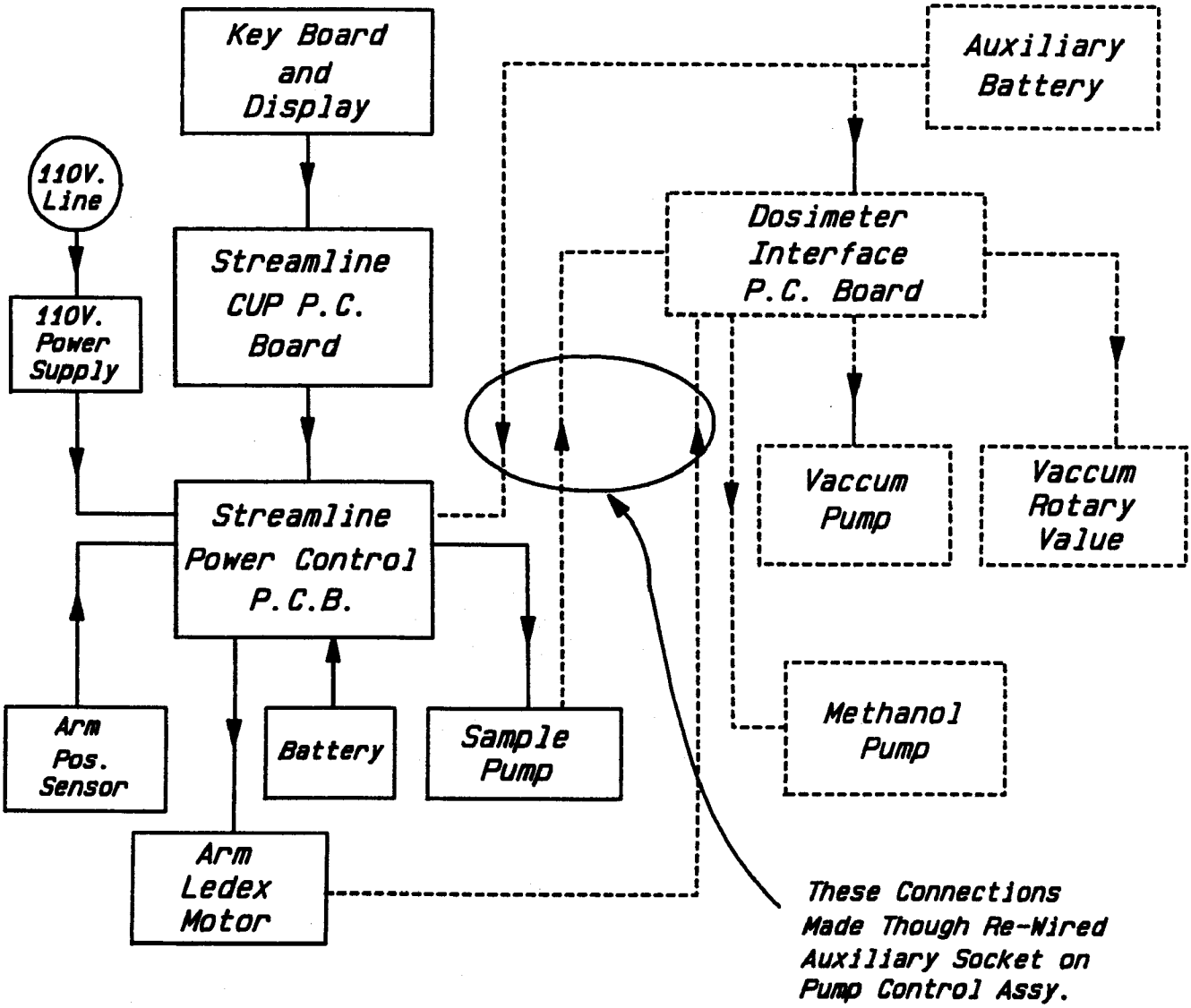
1. Cochrane, W. P.; Lanouette, M.; and Trudeau, S; J. Chrom. 243(2), 307-314 (1982).
2. Jones, A. S.; and Jones, L. A.; J. Agric. Food Chem. 30(5), 997-999 (1982).
3. West, S. D.; and Day, E. W. Jr.; J. Assoc. Off. Anal. Chem. 64(5), 1205-1207 (1981).
4. Brouwer, E. R.; Lingeman, H.; and Brinkman, U. A. Th.; Chromatographia 29(9/10), 415-418 (1990).
5. Hagen, D. F.; Markell, C. G.; Schmitt, G. A.; and Blevins D. D.; Analytica Chimica Acta 236, 157-164 (1990).

LIST OF FIGURES



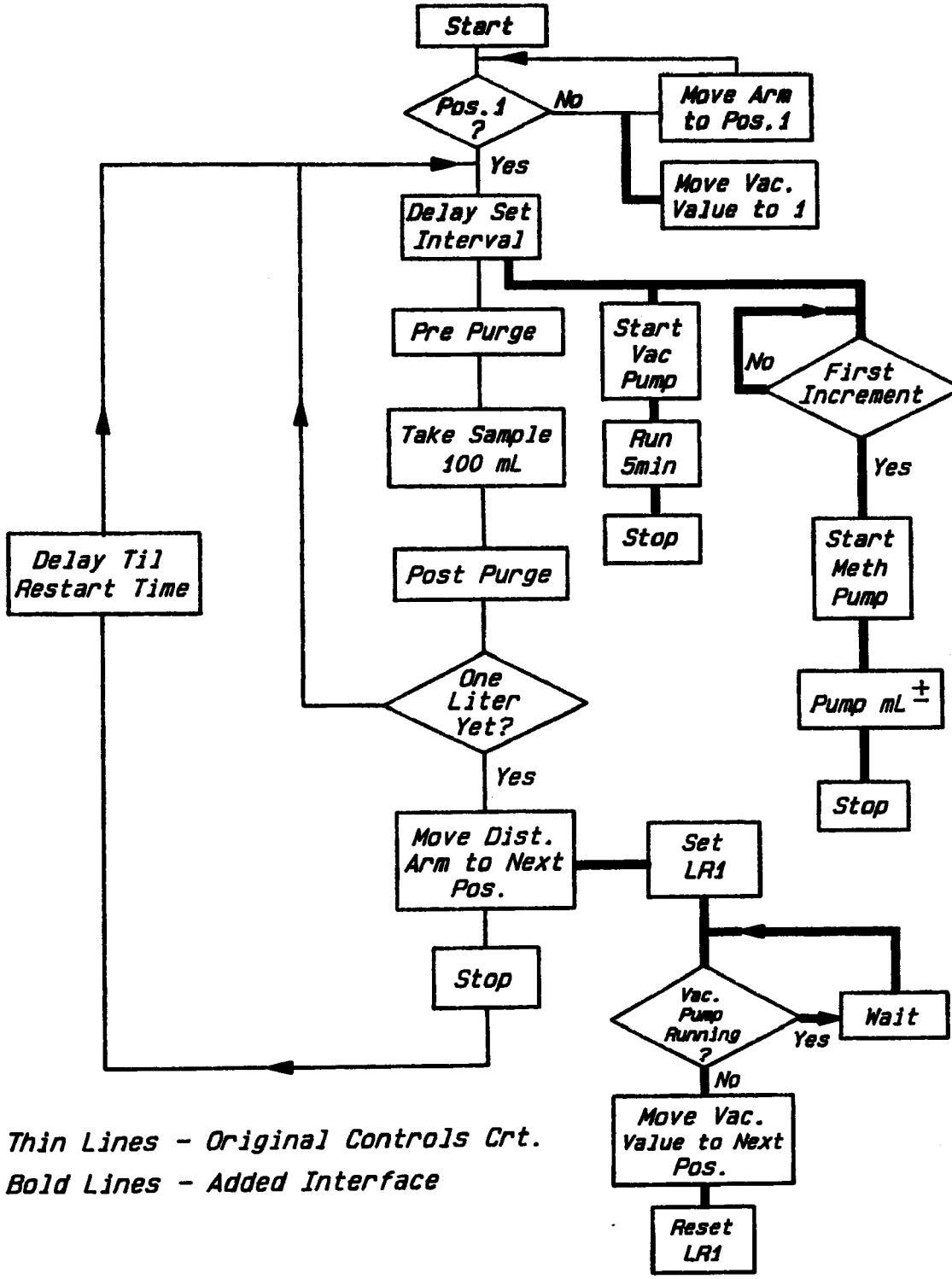


MSI Disposable Filter Funnel Modified for use in Dosimeter



Block Diagram of Interconnections Dashed Lines Denote Added for Dosimeter

Flow Chart for Control Crts.



Thin Lines - Original Controls Crt.

Bold Lines - Added Interface

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REPRESENTATIVE SAMPLING FOR THE REMOVAL PROGRAM

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ABSTRACT

In addition to addressing catastrophic releases, the Removal Program is involved in meeting objectives such as identifying the threat a site poses to public health, welfare, and the environment; delineating sources and extent of contamination; evaluating waste treatment and disposal options; and confirming the achievement of cleanup standards. To help meet these ends, EPA assembled the U.S. EPA Committee on Representative Sampling for the Removal Program to develop guidance documents for collecting representative samples at removal sites. The goal of a representative sampling plan is to accurately depict variations in pollutant presence and concentration across a site for a given medium (e.g., soil, groundwater). Five representative sampling guidance documents, addressing different environmental media, are in various stages of planning and development. Guidance documents for soil and air sampling are scheduled for publication in late FY91. Guidance documents for biological sampling, waste sampling, and groundwater/surface water/sediment sampling will be completed during FY92. Each document has information unique to its medium, but follows the overall objectives and recommendations for effective representative sampling. The documents address: assessing available information; selecting an appropriate sampling approach (including the selection of sampling locations); properly selecting and utilizing sampling and field analytical screening equipment; utilizing proper sample preparation techniques; incorporating suitable types and numbers of QA/QC samples; and interpreting and presenting the resulting data. Each document presents a case study to illustrate how a representative sampling plan may be developed to meet Removal Program objectives. A representative sampling training program and an air sampling methods database are also being developed.

INTRODUCTION

The EPA Removal Program

Under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), the EPA may respond to a release (or threat of a release) of hazardous materials. CERCLA authorized both long-

term activities (called remedial actions) and emergency response activities (called removal actions), and a Hazardous Waste Trust Fund ("Superfund") to pay for them.

A removal action is a short term action intended to stabilize or clean up an incident or site which poses a threat to public health or welfare or to the environment. Removal actions may include but are not limited to:

- removing and disposing of hazardous substances;
- constructing fences, posting signs, and other security measures to restrict access to the site;
- providing an alternative water source to local residents where water supplies have become contaminated; and
- temporarily relocating residents.

CERCLA also defined the duration and cost of removal actions. Removal actions were limited to six months duration and a total cost of $1 million. Exemptions would be required in cases where the action exceeded these time and cost limitations. In 1986 the Superfund Amendments and Re-Authorization Act (SARA) changed the limitations to 1 year and $2 million.

In cases where imminent threats have been addressed but long term threats remain, the site is referred to EPA's Remedial Program for further assessment and investigation. However, remedial actions are only conducted at sites that have been placed on EPA's National Priorities List (NPL). Removal actions may be necessary at remedial sites if an emergency arises. EPA has responded with multiple removal actions at sites with complex hazards.

Program Implementation

Superfund program implementation is guided by the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), which outlines the roles and responsibilities of the Federal agencies who respond to releases of hazardous substances. The U.S. Coast Guard has responsibility for releases in or near coastal waters and EPA has responsibility over those which occur inland.

The initial step in a removal action is the discovery of the incident. EPA may be notified by the National Response Center, which is operated 24 hours a day by the U.S. Coast Guard, or be notified directly. Once EPA has been notified, an EPA On-Scene Coordinator (OSC) evaluates the situation. Based on this evaluation, EPA decides whether Superfund money will be used to respond to the incident (if the responsible party cannot or will not do so, or if state or local officials cannot or are unable to respond). EPA notifies or calls for assistance from other agencies, as necessary.

Once EPA determines that a removal action is required, the OSC assembles the equipment and resources necessary to respond. During an initial site

assessment, air monitoring equipment help to determine the nature of the on-site hazards. After assessing on-site conditions, the OSC establishes a site command post and, if there is no immediate emergency, begins monitoring and sampling on-site materials or contaminants. A variety of media may be sampled, including soil, air, surface water, groundwater, waste piles, and drums or other containers. Once sampling is completed, the necessary equipment is mobilized to stabilize the site. Stabilization can include: building berms/dikes, establishing water treatment systems, excavating contaminated soil, erecting fences, and other activities.

REPRESENTATIVE SAMPLING

Representative sampling is the degree that a sample or a group of samples accurately characterizes site conditions. Representative samples reflect the concentration of parameters of concern at a given time. Analytical results from representative samples illustrate the variation in pollutant presence and concentration across a site.

The U.S. EPA Committee on Representative Sampling for the Removal Program, comprised of U.S. EPA, state, and contractor representatives, is planning and developing five representative sampling guidance documents, each addressing a different environmental medium. Guidance documents for soil and air sampling are scheduled for publication in late FY91. Guidance documents for biological sampling, waste sampling, and groundwater/surface water/sediment sampling will be completed during FY92. The documents are medium-specific, for ease of use, however, multimedia sampling is usually necessary at removal sites. Each document covers aspects unique to its medium, but follows the overall objectives and recommendations for effective representative sampling. The documents address: assessing available information; selecting an appropriate sampling approach (including the selection of sampling locations); properly selecting and utilizing sampling and field analytical screening equipment; utilizing proper sample preparation techniques; incorporating suitable types and numbers of QA/QC samples; and interpreting and presenting the resulting data. The air document also addresses analytical techniques and atmospheric modeling. The documents address the above considerations within the objectives and scope of the Removal Program.

Each document presents a case study to illustrate how a representative sampling plan may be developed to meet Removal Program objectives. The case study illustrates the concepts discussed in each chapter. For the soil guidance, the case study illustrates how "interactive" field analytical screening and other cost-effective field techniques such as geophysical surveys can be used to characterize a site, from selecting sampling locations to confirming cleanup.

USE OF REPRESENTATIVE SAMPLING TO MEET REMOVAL PROGRAM OBJECTIVES

Although field conditions and removal activities vary from site to site, the primary Removal Program sampling objectives include:

1. Establishing Threat to Public Health or Welfare or to the Environment -- CERCLA and the NCP establish the funding mechanism and authority which allow the OSC to activate a Federal removal action. The OSC must establish that the site poses a threat to public health or welfare or to the environment. Sampling is often required to document the hazards present on site. The analytical data are often needed quickly to activate the removal action.

2. Locating and Identifying Potential Sources of Contamination -- Sampling is conducted to identify the locations and sources of contamination. The results are used to formulate removal priorities, containment and cleanup strategies, and cost projections.

3. Defining the Extent of Contamination -- Where appropriate, sampling is conducted to assess horizontal and vertical extent of contaminant concentrations. The results are used to determine the site boundaries (i.e., extent of contamination), define clean areas, estimate volume of contaminated soil, establish a clearly defined removal approach, and accurately assess removal costs and timeframe.

4. Determining Treatment and Disposal Options -- Sampling is conducted to characterize waste and contaminated soil for in-situ or other on-site treatment, or excavation and off-site treatment or disposal.

5. Documenting the Attainment of Cleanup Goals -- During or following a site cleanup, sampling is conducted to determine whether the removal goals or cleanup standards were achieved, and to delineate areas requiring further treatment or excavation as appropriate.

Development and Execution of a Sampling Plan

The representative sampling guidance documents outline how a sampling plan can be designed to meet these objectives. The sampling plan design consists of the following steps:

- Review existing historical site information,
- Perform a site reconnaissance visit,
- Evaluate potential migration pathways, receptors, and routes of exposure,

- Determine the sampling objectives,
- Utilize field screening techniques,
- Select parameters to be analyzed,
- Select an appropriate sampling approach, and
- Determine the locations to be sampled.

Unless the site is considered a classic emergency, every effort is made to first review relevant information concerning the site. An historical data review examines past and present site operations and disposal practices, providing an overview of known and potential site contamination and other hazards. Sources of information include: federal, state, and local files (e.g., prior site inspection reports and legal actions); facility maps; blueprints; historical aerial photography; and interviews with facility owners and operators, current and former facility employees, and local residents. A site reconnaissance, conducted either prior to, or in conjunction with sampling, assesses site conditions, evaluates areas of potential contamination, evaluates potential hazards associated with sampling, and helps to develop a sampling plan. During the reconnaissance, Removal Program personnel observe and photodocument the site, noting site access routes, process, waste disposal, and other potential contaminant source areas, and potential routes for contaminant transport off-site.

A representative sampling plan considers pollutant migration pathways, receptors, and routes of exposure. Pollutant migration pathways include surface drainage, vadose zone and groundwater transport, air transport, and human activity (such as foot or vehicle traffic). In urban areas, man-made pathways, such as storm and sanitary sewers and underground utility lines can influence contaminant transport. Human receptors include children who can come into direct contact with or ingest pollutants by playing in a contaminated area. Environmental receptors include Federal- and state-designated endangered or threatened species, habitats for these species, wetlands, and other Federal- and state-designated wilderness, critical, and natural areas.

The scope of the sampling program depends on the Removal Program sampling objectives previously discussed. In order to attain these objectives, the quality assurance components of precision, accuracy, completeness, representativeness, and comparability are considered.

Samples are analyzed by an established and approved off-site laboratory, or are screened or analyzed on-site using various portable direct reading instruments. Field analytical screening equipment utilized by the Removal Program includes the X-ray fluorescence (XRF) meter, photoionization detector (PID), flame ionization detector, and field test kits. Some field analytical screening instruments, such as the PID and some XRF units, can be used in-situ (without collecting a sample). Field analytical screening methods may be utilized to narrow the possible groups or classes of chemicals for laboratory analysis. When used appropriately, field screening can cost-effectively evaluate a large number of samples

for the purpose of selecting a subset for off-site analysis. The detection limits and accuracy of the screening method is evaluated by sending a minimum of 10% of the samples to an off-site laboratory for confirmation. Field screening techniques and confirmatory sampling can be used together to identify or delineate the extent of contamination and to confirm cleanup. Once a contaminated area has been identified with screening techniques, an appropriate confirmatory sampling strategy substantiates the screening results. Used in tandem, field analytical screening and confirmatory sampling provide data more representative of the problem at the site than off-site laboratory analysis alone. Field screening is also utilized in the Removal Program for air monitoring during removal activities and for on-site health and safety decisions.

Geophysical techniques such as ground penetrating radar (GPR), magnetometry, electromagnetic conductivity (EM) and resistivity surveys may also be conducted during removal actions. Geophysical surveys, in conjunction with field analytical screening, helps delineate areas of subsurface contamination, locations of buried drums or tanks, and disturbed areas. Geophysical data can be obtained relatively rapidly, often without disturbing the site.

Locating sampling points for field screening and laboratory analysis entails choosing the most appropriate sampling approach. The sampling objectives, the site setting, limitations in the sampling and the analytical methods, and available time and resources are all considerations. Representative sampling approaches include *judgmental, random, stratified random, systematic grid, systematic random, search and transect methodologies*. A representative sampling plan may combine two or more of these approaches (as defined below). Although some approaches (such as judgmental and random sampling) are applicable to a variety of media, it should be noted that systematic, search, and transect sampling techniques are specific to soil and sediment sampling.

- Judgmental Sampling - Judgmental sampling is the subjective selection of sampling locations at a site, based on historical information, visual inspection, and on best professional judgment of the sampling team. Judgmental sampling is most often used to identify the contaminants present at the highest concentrations (i.e., worst case conditions). This is often the basis for supporting the removal funding request. Judgmental sampling has no randomization associated with the sampling strategy, and therefore prevents statistical interpretation of the sampling results.

- Random Sampling - Random sampling is the arbitrary collection of samples within the area of concern. Random sample locations are chosen using a random selection procedure (such as a random number table). The arbitrary selection of sampling points requires each sampling point to be selected independent of the location of all other points, and results

in all locations within the area of concern having an equal chance of being selected. Randomization is necessary in order to make probability or confidence statements about the sampling results. Random sampling may be performed for all media, however random sampling assumes that the site is homogeneous with respect to the parameters being monitored. The higher the degree of heterogeneity, the less the random sampling approach will adequately characterize true conditions at the site. For soil and sediment media (which are rarely homogeneous), other statistical sampling approaches (discussed below) provide ways to subdivide the site into more homogeneous areas, and may be more appropriate than random sampling for sampling soil and sediment at removal sites. Figure 1 illustrates random sampling.

- Stratified Random Sampling - Stratified random sampling often relies on historical information and prior analytical results (or field screening data) to stratify the sampling area. Each stratum is more homogeneous than the site is as a whole. Strata can be defined based on various factors, including: sampling depth, contaminant concentration levels, and contaminant source areas. Sample locations are selected within each of these strata using random selection procedures. Stratified random sampling imparts some control upon the sampling scheme (e.g., collection of more samples from depths or areas having higher contaminant concentrations) but still allows for random sampling within each stratum. Different sampling approaches may also be selected to address the different strata at the site. Figure 2 illustrates a stratified random sampling approach for soil where strata are defined based on depth.

- Systematic Grid Sampling - Systematic grid sampling (of soil and sediment) involves subdividing the area of concern by using a square or triangular grid and collecting samples from the nodes (intersections of the grid lines). The distance between sampling locations in the systematic grid is determined by the size of the area to be sampled and the number of samples to be collected. Systematic grid soil sampling is often used to meet Removal Program sampling objectives for locating and identifying potential sources of contamination, defining the extent of contamination, and documenting the attainment of cleanup goals. Figure 3 illustrates a systematic grid sampling approach.

- Systematic Random Sampling - Systematic random sampling (of soil and sediment) involves subdividing the area of concern by using a square or triangular grid and collecting samples from within each cell using random selection procedures. Systematic random sampling is a useful and flexible design for

FIGURE 1 - RANDOM SAMPLING

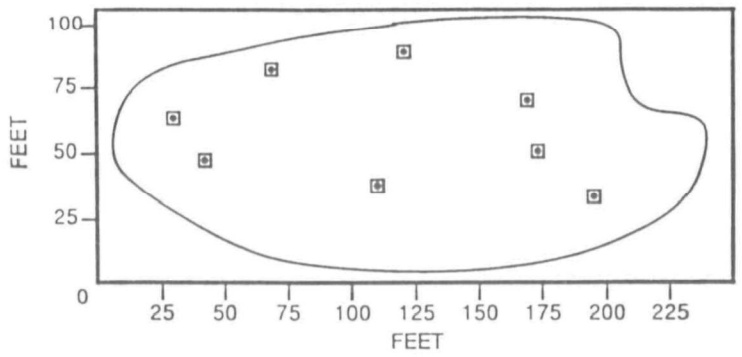

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FIGURE 2 - STRATIFIED RANDOM SAMPLING

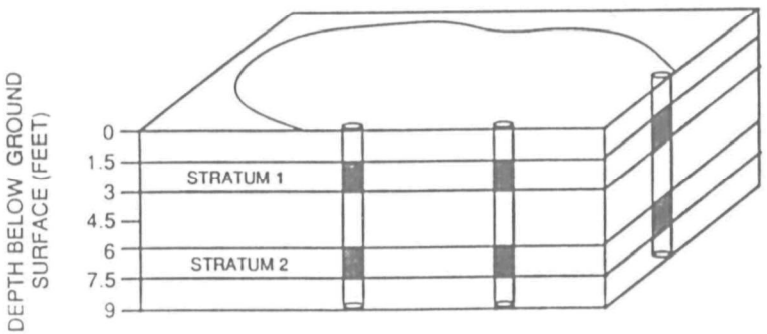


FIGURE 3 - SYSTEMATIC GRID SAMPLING

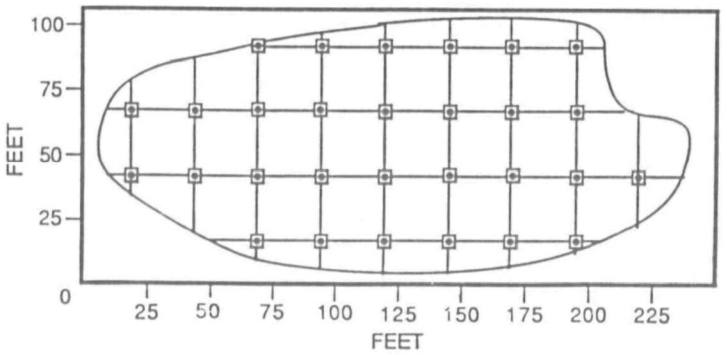
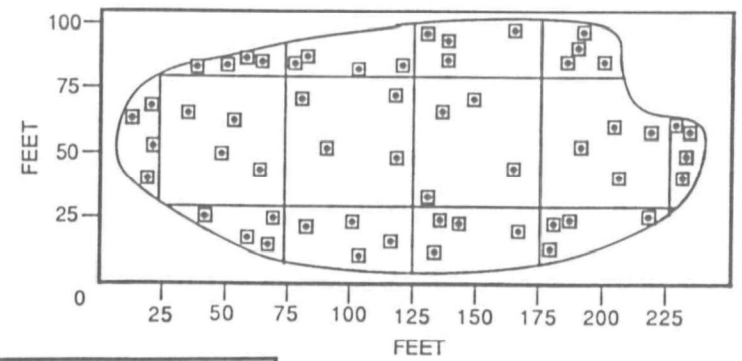
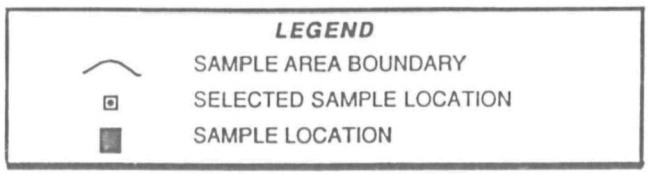


FIGURE 4 - SYSTEMATIC RANDOM SAMPLING





After: U.S. EPA, 1989, EPA/230/02-89-042

estimating the average pollutant concentration within each cell of the grid. Also, systematic random sampling allows for the isolation of cells that may require additional sampling and analysis. Figure 4 illustrates a systematic random sampling approach.

- Search Sampling - Search sampling utilizes either a systematic grid or systematic random sampling approach to search for hot spots (i.e., areas where contaminants in soil and sediment exceed applicable cleanup standards). The number of samples collected and the grid spacing used are determined on the basis of the acceptable error (i.e., the chance of missing a hot spot). When conducting search sampling, initial assumptions must be made about the size, shape, and depth of the hot spots to be searched for. The smaller and/or narrower the hot spots are, the smaller the grid spacing (i.e., the more samples) necessary to locate them. In addition, the smaller the acceptable error of missing hot spots, the smaller the grid spacing must be.

- Transect Sampling - Transect sampling involves establishing one or more transect lines across the surface of a site. Soil or sediment samples are collected at regular intervals along the transect lines at the surface and/or at one or more given depths. The spacing between sampling points along a transect is determined by the length of the transect line and the number of samples to be collected. Multiple transect lines may be parallel or non-parallel to one another. A primary benefit of transect sampling over systematic grid sampling is the ease of establishing and relocating individual transect lines versus an entire grid. Transect sampling is often used to delineate the extent of contamination and to define contaminant concentration gradients. Transect sampling has also been used, to a lesser extent, in compositing sampling schemes.

Selection and Use of Sampling Equipment

The manner in which a sample is collected is based on the objectives stated in the site-specific sampling plan. Sample collection requires an understanding of the capabilities of the sampling equipment in obtaining a sample which accurately depicts current site conditions. The use of inappropriate equipment (or the incorrect use of sampling equipment) may result in biased samples.

The mechanical method by which a sampling tool collects a sample may impact sample representativeness. For example, if the goal is to determine the concentrations of contaminants at each soil horizon interface, using a hand auger would be inappropriate. Obviously, the

augering technique would disrupt and mix soil horizons, making the precise horizon interface difficult to determine. In addition, all sampling devices used are of sufficient quality to not contribute contamination to samples (e.g., painted surfaces which could chip off into the sample) and the sampling equipment are either easily decontaminated, or cost-effective if considered to be expendable.

Sample Preparation

Field sample preparation includes all aspects of sample handling after collection, until the sample is received by the laboratory. Sample preparation techniques are specific to the sample medium and sampling plan. For soil and sediment sample preparation, common techniques are: removing extraneous material, sieving, homogenizing, splitting, and compositing samples.

Proper sample preparation and handling maintains sample integrity and provides a representative sample from the total material collected. Improper handling can result in a sample becoming unsuitable for the type of analysis required. For example, homogenizing, sieving, and compositing of soil samples all result in a loss of volatile constituents and therefore, are inappropriate when volatile contaminants are of concern.

Homogenization is the mixing or blending of a soil or sediment sample in an attempt to provide uniform distribution of contaminants. Ideally, proper homogenization assures that portions of the containerized samples are equal or identical in composition and are representative of the total sample collected. Incomplete homogenization may increase sampling error. Quartering, as per ASTM Standard C702-87, can be used to simultaneously homogenize and split a sample. Split samples are most often collected in enforcement actions for comparing sample results obtained by EPA with those obtained by the potentially responsible party (PRP). Split samples also provide a measure of the sample variability, and a measure of the analytical and extraction errors. Split soil and sediment samples are commonly collected. Splitting may also be done, in some cases, with water and air samples.

Compositing is the process of physically combining and homogenizing several individual soil and sediment aliquots. Compositing samples provides an average concentration of contaminants over a certain number of sampling points, which reduces both the number of required lab analyses and the sample variability. Compositing can be a useful technique, but must always be considered and implemented with caution. Since compositing dilutes high concentration aliquots, the applicable detection limits should be reduced accordingly. If the composite value is to be compared to a selected action level, then the action level must be divided by the number of aliquots that make up the composite in order to determine the appropriate detection limit (e.g., if the action level for a particular substance is 50 ppb, a detection limit of 10 ppb should be used when

analyzing a 5-aliquot composite).

To help maintain sample integrity and assure representativeness, it is sometimes possible to ship samples to the laboratory directly in the sampling equipment. This is the case for air sampling media. For soil core samples, the ends of a Shelby tube can be sealed with caps, taped, and sent to the laboratory for analysis. To help maintain the integrity of VOA soil samples, soil cores can be collected using acetate sleeves and sent in the sleeves to the laboratory. To ensure the integrity of the sample after delivery to the laboratory, laboratory sample preparation procedures are made part of laboratory bid contracts.

Quality Assurance/Quality Control (QA/QC)

Quality assurance/quality control (QA/QC) measures are an integral part of representative sampling. QA/QC samples provide information on the variability and usability of environmental sample results. They also evaluate the degree of site variation, whether samples were cross-contaminated during sampling and sample handling procedures, or if a discrepancy in sample results is due to laboratory handling and analysis procedures.

In the Removal Program, field replicate, collocated, background, and rinsate blank samples are the most commonly collected field QA/QC samples. Performance evaluation, matrix spike, and matrix spike duplicate samples, either prepared for or by the laboratory, provide additional measures of control for the data generated. QA/QC results may suggest the need for modifying sample collection, preparation, handling, or analytical procedures if the resultant data do not meet site-specific quality assurance objectives.

Three QA/QC objectives (QA1, QA2, and QA3) have been defined by the Removal Quality Assurance Program, based on the EPA QA requirements for precision, accuracy, representativeness, completeness, comparability, and detection level. QA1 standards are used when a large amount of data are needed quickly and relatively inexpensively, or when preliminary screening data, which do not need to be analyte or concentration specific, are useful. QA1 requirements are used with data from field analytical screening methods for a quick, preliminary assessment of site contamination. Examples of QA1 activities include: determining physical and/or chemical properties of samples; assessing preliminary on-site health and safety; determining the extent and degree of contamination; assessing waste compatibility; and characterizing hazardous wastes.

QA2 verifies analytical results. The QA2 objective is intended to provide a certain level of confidence for a select portion (10% or more) of the preliminary data. This objective allows Removal Program personnel to focus on specific pollutants and concentration levels quickly, by using field screening methods with laboratory verification and quality assurance

for at least 10% of the samples. QA2 verification methods are analyte specific. Examples of QA2 activities include: determining physical and/or chemical properties of samples; defining the extent and degree of contamination; verifying site cleanup; and verifying screening objectives obtainable with QA1, such as pollutant identification.

QA3 assesses the accuracy of the concentration level, by determining the analytical error as well as the identity of the analyte(s) of interest. QA3 data provide the highest degree of qualitative and quantitative accuracy of all QA objectives by using rigorous methods of laboratory analysis and quality assurance. QA3 is intended to provide a high level of confidence so that the decisions can be made with regard to: treatment; disposal; site remediation and/or removal of pollutants; health risk or environmental impact; cleanup verification; and pollutant source identification.

Sources of Error

Quantifying the error associated with a sampling activity can be difficult, but is important in order to identify the possible sources of error or variation in sampling and laboratory analysis and to limit their effect(s) on the data. Four potential sources of error are:

- Sampling design -- Site variation (the non-uniform conditions which exist at a site) include the identities and concentration levels of contaminants. The goal of representative sampling is to accurately identify and define this variation. However, error can be introduced by the selection of a sampling design which "misses" site variation. For example, a sampling grid with relatively large distances between soil sampling points or a biased sampling approach (i.e., judgmental sampling) may allow significant contaminant trends to go unidentified.

- Sampling methodology -- Error can be introduced by sampling methodology and sample handling procedures, as in cross-contamination from inappropriate use of sample collection equipment, unclean sample containers, improper decontamination and shipment procedures, and other factors. The use of standard operating procedures for collecting, handling, and shipping samples allows for easier identification of the source(s) of error, and can limit error associated with sampling methodology. Trip blanks, field blanks, replicate samples, and rinsate blanks are used to identify error due to sampling methodology and sample handling procedures.

- Sample heterogeneity -- Sample heterogeneity is a potential source of error, especially for soil and sediment samples. These media are rarely homogeneous and exhibit variable

properties with lateral distance and with depth. This heterogeneity may also be present in the sample container unless the sample was homogenized in the field or in the laboratory. The laboratory uses only a small aliquot of the sample for analysis; therefore thorough sample homogenization is important to assure that the analytical results are representative of the sample and of the corresponding site.

- Analytical procedures -- Error which may originate in analytical procedures includes cross-contamination, inefficient extraction, and inappropriate methodology. Matrix spike samples, replicate samples, performance evaluation samples, and associated quality assurance evaluation of recovery, precision, and accuracy, can be used to distinguish analytical error from error introduced during sampling activities.

A common objective of the evaluation of soil analytical data is to delineate the extent of site contamination. One cost-effective approach used in the Removal Program is to correlate inexpensive field screening data with laboratory results. When field screening techniques, such as XRF, are used along with laboratory methods (e.g., atomic absorption (AA)), a regression equation can be used to predict a laboratory value based on the screening results. The model can also be used to place confidence limits around predictions. The relationship between the two methods can be described by a regression analysis and used to predict laboratory results based on field screening measurements. The predicted values can then be located on a base map and contoured. These maps can be examined to evaluate the estimated extent of contamination and the adequacy of the sampling program.

Data Presentation and Analysis

Data presentation and analysis techniques can be used to compare analytical values, to evaluate numerical distribution of data, to determine and illustrate the location of hot spots and the extent of contamination across a site, and to assess the need for removal of contaminated soil with concentrations at or near the action level. Data presentation and analysis methods include:

- Data posting -- Data posting, the placement of sample values on a site basemap, is useful for displaying the spatial distribution of sample values to visually depict extent of contamination and to locate hot spots.

- Geologic graphics -- Geologic graphics include cross-sections and fence diagrams, two- and three-dimensional depictions, respectively, of soils and strata to a given depth beneath the site. These types of graphics are useful for posting

subsurface analytical data, for interpreting subsurface geology and contaminant migration, and for placing monitoring wells.

- Contour mapping -- After depicting sample values on a basemap with data posting, contour lines (or isopleths) can be drawn at a specified contour interval. Interpolating values between sample points and drawing contour lines is done manually or by using computer contouring software. Contour maps are useful for depicting soil and groundwater contaminant concentration values across a site.

- Statistical graphics -- The histogram is a statistical bar graph which displays the distribution of a data set. A normal distribution of data is a bell-shaped curve, with the mean and median close together about halfway between the maximum and minimum values. A probability plot depicts cumulative percent against the concentration of the contaminant of concern. A normally distributed data set plotted as a probability plot would appear as a straight line. A histogram or probability plot show trends and anomalies in the data prior to conducting more rigorous forms of statistical analysis. Common statistical analyses such as the t-test and the regression analysis rely on normally distributed data. The distribution or spread of the data set is important in determining which statistical techniques to use.

- Geostatistics -- A geostatistical analysis can be broken down into two phases. First, a model is developed that describes the spatial relationship between sample locations on the basis of a plot of spatial variance versus the distance between pairs of samples. This plot is called a variogram. Second, the spatial relationship modeled by the variogram is used to compute a weighted-average interpolation of the data. The result of geostatistical mapping by data interpolation is a contour map that represents estimates of values across a site, and maps depicting potential error in the estimates. The error maps are useful for deciding if additional samples are needed and for calculating best or worst case scenarios for site cleanup.

The data interpretation method chosen depends on project-specific considerations, such as the number of sampling locations and their associated range in values. A site depicting extremely low soil data values (e.g., non-detects) with significantly higher values (e.g., 5,000 ppm) from neighboring hot spots with little or no concentration gradient in-between, does not lend itself to contouring and geostatistics, specifically the development of variograms. However, data posting would be useful at such a site to illustrate hot spot and clean areas. Conversely, geostatistics and contour mapping, as well as data posting,

can be applied to site data with a wide distribution of values (e.g., depicting a "bell shaped" curve) with beneficial results.

Incorporating Representative Sampling into the Removal Program

Although the principles discussed here are utilized in the Removal Program, there is no national consistency with how they are employed. The first step to *representative* sampling consistency in the Removal Program is the completion of guidance documents for each environmental medium. In order to keep the guidance documents current while sampling methodologies are evolving, EPA has placed the documents on a two-year update schedule.

The second component of incorporating the concept of representative sampling into the Removal Program is the development of a training program for site personnel, based on the guidance documents. The training course will introduce the concepts presented in the documents, structured around a realistic example site (an actual Superfund site). One common site is being incorporated into each document. This will facilitate the development of an integrated training program addressing all media.

To enhance the integration of representative sampling into the Removal Program, the guidance documents discuss computer software that assist in implementing the concepts presented in the documents. This includes the use of EPA's Geo-EAS program (Geostatistical Modeling Assessment Software) and its application to soil sampling in the soil document, and an evaluation of available air models to assist in sample design in the air document.

Finally, specific tools will be developed and incorporated into the documents as necessary. In the air document, an air sampling methods database has been developed to provide up-to-date information on sampling methods and compounds that can be sampled by those methods.

SUMMARY

The U.S. EPA Committee on Representative Sampling for the Removal Program is planning and developing guidance documents to assist Removal Program personnel in the collection of representative samples at removal sites. Five guidance documents, addressing soil, air, biota, waste, and groundwater/surface water/sediment sampling will be published in FY91 and FY92. Each document addresses considerations unique to its medium, but follows the overall objectives and recommendations for effective representative sampling. The documents address: assessing available information; selecting an appropriate sampling approach; properly selecting and utilizing sampling, field analytical screening, and geophysical equipment; utilizing proper sample preparation techniques; incorporating suitable types and numbers of QA/QC samples; and interpreting and presenting the resulting data.

35

PRELIMINARY FIELD AND LABORATORY EVALUATIONS AND THEIR ROLE IN AN ECOLOGICAL RISK ASSESSMENT FOR A WETLAND SUBJECT TO HEAVY METAL IMPACTS

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ABSTRACT

An integrated laboratory/field project was initiated by Environmental Protection Agency [US EPA] Region 8 as part of their ecological risk assessment for the Milltown Reservoir Superfund site located on the Clark Fork River in western Montana, six miles east of Missoula, Montana. Preliminary work supporting the ecological risk assessment included field studies completed at Milltown Reservoir, while laboratory work [biological testing and chemical analysis] was completed at the US EPA Environmental Research Laboratory-Corvallis [ERL-C], Corvallis, Oregon. For the wetlands evaluation at Milltown Reservoir, heavy metals appear the most critical contaminant which must be considered in the ecological assessment; those of primary interest include arsenic, zinc, copper, cadmium, and nickel as well as manganese and iron. Preliminary laboratory and field investigations evaluated the extent of contaminant and its impact on the indigenous wildlife and vegetation characteristic of the site. Field work included scoping activities; the identification of sampling units; preliminary sampling of surface water, soil, and sediment; and preliminary field screening tests. Results from the preliminary studies indicate ecological effects may be subtle in expression, and future work should focus upon current as well as historic sediment deposition areas in the reservoir and associated wetlands.

INTRODUCTION

Milltown Reservoir is located on the Clark Fork River in western Montana, six miles east of Missoula, Montana [US EPA Region 8]. The reservoir was formed in 1907 following the construction of a hydroelectric facility located on the Clark Fork River immediately downstream from its confluence with the Blackfoot River. Since construction of the dam, a wetland habitat has been created, but because of the upstream mining activities on the Clark Fork River, Milltown Reservoir has accumulated a large volume of heavy metal-contaminated sediment. The Milltown Reservoir wetland was initially identified under CERCLA in 1981 after community well-water samples were found to have arsenic levels that ranged from 0.22 to 0.51 mg/L; the EPA recommendation for potable water supplies suggested that arsenic not exceed 0.05 mg/L [Woessner, et al. 1984]. Within an ecological context, however, the impact of the contaminated sediments on the wetlands is unclear [Adamus and Brandt 1990; Tiner 1984].

The laboratory and field investigations completed during FY90 evaluated the extent of contaminant and its impact on the indigenous wildlife and vegetation characteristic of the site. During the preliminary season, field work was completed at Milltown Reservoir and supporting laboratory work [biological testing and chemical analysis] was completed at the Environmental Research Laboratory-Corvallis [ERL-C], Corvallis, Oregon. Preliminary field work included scoping activities, such as the identification of sampling units; preliminary sampling of surface water, soil, and sediment; and preliminary field screening tests [NSI 1989]. In addition to field methods [e.g., earthworm, seed, and amphibian evaluations] being used as part of the biological and ecological assessment, complementary laboratory evaluations were completed [Greene, et al. 1989]. Routine water quality measurements on surface water samples and soil measurements [e.g., texture analysis] were also collected as part of the preliminary field activities.

SYNOPSIS: PRELIMINARY FIELD AND LABORATORY ACTIVITIES

Sampling plan. Historic information regarding Milltown suggested that a preliminary field effort could well determine the extent of contamination, and definitive field operations planned for FY 91 could be focussed along habitat lines suggested by our preliminary field season. Clearly, the sedimentation problems of the reservoir would require those matrices being evaluated in our definitive studies, but little previous work had considered the impact of periodic inundations upon upland habitats. Accordingly, the sampling plan which guided our preliminary field season was designed within topographic and historic bounds and assured the definitive sampling and analysis plan guiding our FY 91 field season be developed on defensible empirical grounds. For the preliminary field effort, Milltown was stratified into sampling units based largely on topography, and line transects were established on each sampling unit. Each line transect was derived from an initial random vector, then defined along habitat gradients amenable to each of the evaluations being completed on the sample units; plant and earthworm methods were applied on the upland features, and amphibian methods were applied in emergent zones [Schweitzer and Santolucito 1984].

Laboratory and field testing: Vegetation evaluations. Within laboratory settings, critical developmental stages in plant life cycles were evaluated and physiological endpoints pertinent to ecological impact were measured [Linder, et al. 1990]. Seed germination evaluations were completed to evaluate soils directly in the laboratory without preparing eluates [Thomas and Cline 1985]; root elongation tests were completed on site-soil eluates [Greene, et al. 1989]. On-site seed germination evaluations also considered the germination endpoint, but were less time consuming, generally more cost-effective and minimized the manipulation of the site-soils, since tests were performed directly in the field [NSI 1989]. Data derived from on-site testing complemented terrestrial laboratory tests and chemical analysis of site samples. The on-site evaluations also addressed questions regarding lab-to-field extrapolation.

Earthworm testing. Integrated field and laboratory methods using earthworms contributed to soil evaluations and afforded a direct test of an environmental matrix which may greatly influence the impact of soil chemicals on indigenous macroinvertebrate communities [Rhett, et al. 1988; Marquenie, et al. 1987]. Adverse biological or ecological effects may be expressed owing to contaminant-related effects associated with anthropogenic chemicals. Or, physical alterations in habitat may effectively impact terrestrial or wetland systems through direct and indirect mechanisms. Within ecological evaluations for terrestrial and wetland habitats, then, biological and ecological measurements in general must assess and, if possible, distinguish between effects mediated by physical alterations in habitat and those effects mediated by anthropogenic chemicals or contaminants associated with human activities. Additionally, lab-to-field extrapolation bias was addressed through the integrated field and laboratory work completed with earthworms.

Amphibian testing. The integrated laboratory and in situ methods using amphibians contributed to an evaluation of the extent of contamination as well as lab-to-field extrapolation error. For the preliminary field season, in situ evaluations were completed at selected emergent zones at Milltown Reservoir and used field-collected eggs and early embryos of Rana catesbeiana [NSI 1989]. Grab samples of surface waters at Milltown Reservoir were also collected as part of the preliminary field season for the Milltown Reservoir endangerment assessment; laboratory evaluations using standardized amphibian methods [FETAX] were completed as parallel and complementary components to these in situ amphibian evaluations [ASTM 1991; Dawson, et al. 1988].

RESULTS AND DISCUSSION

From the preliminary field season completed at Milltown Reservoir:

+ There are no indications that acute effects are associated with any presumptive contaminant exposures on those areas surveyed and sampled during FY 90.

+ Occasionally, biological tests suggested that subacute or chronic effects may be expressed at some locations on the Milltown wetlands; these expressions of adverse biological effects appeared to be associated with deposition zones where sediments either currently or historically had accumulated as a function of changes in the Clark Fork channel or flow rates.

+ Samples characterized by adverse biological responses in laboratory or field exposures were frequently identified by more than one test method; adverse biological responses in laboratory tests should be evaluated for laboratory-related manipulation "effects," particularly when their field analogs yielded dissimilar endpoints.

+ Potential sample heterogeneity may be minimized by stratifying future sample plans along topographic boundaries determined by current or historic depositional areas on the Clark Fork.

+ The significance of Blackfoot River input at its confluence with the Clark Fork could not be determined from these preliminary studies.

+ Some soil and sediment samples from the Milltown wetlands, again in current or historic zones of deposition, presented metals concentrations which may be considered elevated [Beyer 1990].

+ Biological, and presumptively ecological, impacts associated with these elevated metal concentrations were not overtly expressed, and the biological information collected during the preliminary field season should be considered when interpreting these total metals concentrations.

Within an ecological context, these in situ and on-site biological methods have proven to be applicable to integrated field and laboratory studies that evaluate, not only the current status of the wetland, but also provide information which will contribute to future mitigation and restoration efforts.

SUMMARY

While the work completed in FY 90 represents preliminary efforts in evaluating ecological risks, the information garnered can focus future work for the Milltown Reservoir assessment. While overt expressions of toxicity are not expressed in the wetlands, these technical items were identified as significant considerations for discussion in designing field and laboratory evaluations that could contribute to future Milltown Reservoir work.

+ "Reference areas" must be defined for future work at Milltown; some comparative framework must be established, be that "site-equivalent areas," within-boundary reference locations or an adequate historical data base, for evaluating the information generated in the laboratory or field.

+ Within ecological contexts, the area being sampled must be extended to include the entire Clark Fork Arm and other upstream areas suspected of having more recently deposited and potentially heavy metal-contaminated sediments.

+ Sediment evaluations within the reservoir must be completed to adequately evaluate the wetland; these evaluations should consider metals concentrations in sediments, evaluations of sediment toxicity [including evaluations of its physicochemical properties], and a field survey which would yield ecologically

relevant information such as community structure.

+ Sediment evaluations should include invertebrate work [e.g., Timmermans and Walker 1989], and if possible, wetland plants [floating and emergent] should be evaluated for the potential adverse biological effects associated with sediment exposures [Federal Interagency Committee for Wetland Delineation 1989; Fleming, et al 1988; Reed 1988; Walsh, et al. 1990].

+ For more adequate site-specific evaluations regarding bioavailability of metals in soils and sediments, additional physicochemical characterizations may be advantageous; for example, to adequately evaluate vegetation responses, routine soil texture, nutrient [N-P-K] and total organic carbon [TOC] analysis may be beneficial [Chapman and Pratt 1961; SCS 1951; Vandecaveye 1948].

+ If total metals appear inadequate for evaluating metal bioavailability, speciation studies may be indicated; if such studies are anticipated, site samples targeted for these analyses should be selected after a thorough review of the current, as well as historic, geochemical information.

REFERENCES

Adamus, P.R., and K. Brandt. 1990. Impacts on quality of inland wetlands of the United States: a survey of indicators, techniques, and applications of community level biomonitoring data. [EPA/600/3-90/073]. U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon, 97333.

ASTM. 1991. Draft standard guide for conducting the frog embryo teratogenesis assay-Xenopus [FETAX]. American Society for Testing and Materials, ASTM Committee E-47 on Biological Effects and Environmental Fate, Philadelphia, PA.

Beyer, W.N. 1990. Evaluating soil contamination. U.S. Fish and Wildlife Service, Biol. Rep. 90[2]. 25pp.

Chapman, H. D. and P . F. Pratt. 1961. Methods for the analysis of soils, plants, and waters. Univ. of California, Division of Agricultural Sciences.

Dawson, D.A., E.F. Stebler, S.L. Burks, and J.A. Bantle. 1988. Evaluation of the developmental toxicity of metal-contaminated sediments using short-term fathead minnow and frog embryo-larval assays. Environ. Toxicol. Chem. 7[1]:27-34.

Federal Interagency Committee for Wetland Delineation. 1989. Federal manual for identifying and delineating jurisdictional wetlands. U.S. Army Corps of Engineers, U.S. Environmental Protection Agency, U.S. Fish and Wildlife

Service, and U.S.D.A. Soil Conservation Service, Washington, D.C. Cooperative technical publication. 76pp.

Fleming, W.J., J.J. Momot, and M.S. Ailstock. 1988. Bioassay for phytotoxicity of toxicant to sago pondweed. Chesapeake Res. Consort. Publication 129. pp. 431-440.

Greene, J.C., C. Bartels, W. Warren-Hicks, B. Parkhurst, G. Linder, S. Peterson, and W. Miller. 1989. Protocols for Short Term Toxicity Screening of Hazardous Waste Sites. US EPA Research Laboratory, Corvallis, OR. EPA/600/3-88/029.

Linder, Greg, J.C. Greene, H. Ratsch, J. Nwosu, S. Smith, and D. Wilborn. 1990. Seed germination and root elongation toxicity tests in hazardous waste site evaluation: methods development and applications. In Plants for Toxicity Assessment, ASTM STP 1091. W. Wang, J.W. Gorsuch, and W.R. Lower, Eds., American Society for Testing and Materials, Philadelphia, PA. Pp. 177-187.

Marquenie, J.M., J.W. Simmers, and S.H. Kay. 1987. Preliminary assessment of bioaccumulation of metals and organic contaminants at the Times Beach confined disposal site, Buffalo, N.Y. Miscellaneous Paper EL-87-6, Dept. of the Army, WES, Corp of Engineers, Vicksburg, MS, 67pp.

NSI Technology Services Corporation. 1989. FY 89 Report: Initial performance evaluation of three bioassays modified for direct in situ testing. Technical report submitted to Ecotoxicology Branch, Ecological Assessment Team, US EPA, Environmental Research Laboratory, Corvallis, OR.

Reed, P.B., Jr. 1988. National list of plant species that occur in wetlands: national summary. U.S. Fish Wildl. Serv. Biol. Rep. 88(24). 244pp.

Rhett, R.G., J.W. Simmers and C.R. Lee. 1988. Eisenia foetida used as a biomonitoring tool to predict the potential bioaccumulation of contaminants from contaminated dredged material. In Earthworms in Waste and Environmental Management. Eds: C.A. Edwards and E.F. Neuhauser. SPB Academic Publishing, The Hague, The Netherlands.

Schweitzer, G. E. and J. A. Santolucito. 1984. ACS Symposium Series 267: Environmental Sampling for Hazardous Waste. American Chemical Society, Washington, D.C.

Soil Conservation Service. 1951. Soil Survey Manual. U.S. Department of Agriculture Handbook No. 18. Washington, D.C. 503pp.

Thomas, J. M. and J. E. Cline. 1985. Modification of the Neubauer technique to assess toxicity of hazardous chemicals in soils. Environ. Toxicol. Chem. 4:201-207.

Timmermans, K.R., and P.A. Walker. 1989. The fate of trace metals during the metamorphosis of chironomids (Diptera, Chironomidae). Environ. Pollut. 62:73-85.

Tiner, Jr., R.W. 1984. Wetlands of the United States: Current status and recent trends. U.S. Fish and Wildlife Service, Habitat Resources, One Gateway Center, Newton, MA. 02158.

Vandecaveye, S. C. 1948. Biological methods of determining nutrients of soil. In: H.B. Kitchen [ed.], Diagnostic Techniques for Soil and Crops. American Potash Institute, Washington, D.C.

Walsh, G.E., D.E. Weber, T.L. Simon, L.K. Brashers, and J.C. Moore. 1990. Use of marsh plants for toxicity testing of water and sediments. Contribution No. 694, Environmental Research Laboratory, Gulf Breeze, Florida.

Woessner, W.W., J.N. Moore, C. Johns, M. Popoff, L. Sartor, and M. Sullivan. 1984. Final report: Arsenic source and water supply remedial action study. Prepared for Solid Waste Bureau, Montana Department of Health and Environmental Sciences, Helena, Montana.

36 **PAH Analyses: Rapid Screening Method for Remedial Design Program**

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The Iron Horse Park Superfund site (Billerica, MA) includes approximately 15 acres of lagoon area. Previous site investigations have demonstrated contamination by Polycyclic Aromatic Hydrocarbons(PAHs) and petroleum hydrocarbons. The US EPA record of decision and administrative order for the site stipulates stringent cleanup goals; all soil with Total PAH above 1 ppm or TPH above 100 ppm must be remediated.

As part of the pre-remedial design, iterative sampling was planned to tightly define the spatial limits of the contamination. The program required analytical support with rapid turn-around on high numbers of samples and action-level detection limits.

The method developed and validated to support this program has since proven to have wide applicability for site investigation and remediation. Analytical protocol will be presented with associated quality assurance/quality control data for samples from this site and a coal gasification waste site. The method includes sample extraction by sonication followed by direct analysis by GC/MS in the selected ion mode. Total analysis time per sample is under 30 minutes. Sixteen different PAH may be identified and quantified in samples, with individual PAH detection limits of 60 ppb. Comparison data from Method 8270 analysis for split samples will be presented.

A statistically-significant correlation at the 95% confidence level was found between total PAHs and Total Petroleum Hydrocarbons(TPH) at the Ironhorse Park site. Data for the regression analysis, which will be presented, were used to justify reliance on the PAH data alone for the remedial design.

37 EVALUATION OF HOUSEHOLD DUST COLLECTION METHODS FOR HUD NATIONAL SURVEY OF LEAD IN HOMES

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ABSTRACT

In conjunction with the National Survey of Lead-Based Paint in Housing conducted by the Department of Housing and Urban Development with the technical support from the Environmental Protection Agency, it became necessary to develop a method of collecting household dust samples for lead (Pb) analysis from a variety of surfaces. This sampling technique needed to be portable, simple to use, and applicable to surfaces ranging from window seats to baseboards to carpeted surfaces. In addition, because the field sampling crews would be intrusive into the occupied dwelling, it was desirable that adequate sample for analysis be collected in 5 to 10 minutes. Three pumps fitted with 0.8 micron membrane filters in cassette holders were evaluated at three flowrates (5, 20, and 100 l/min)/pressure heads (20, 60 and 125 mm Hg) specifications in combination with four different nozzle designs.

The results indicated the higher flowrate sampling pumps produced not only better collection efficiency in a shorter period of time, but also were more reproducible in their collection efficiency. The final system design adopted provides for better than 80% collection efficiency from a 4 sq. ft. area in less than 5 minutes. The system weighs less than 10 lbs and is usable with a minimum of training.

INTRODUCTION

While developing the design for the HUD National Survey, HUD carried out a pretest survey of several housing units in three counties of North Carolina (Boyle et al. 1989). HUD provided the data from this survey to EPA's Office of Toxic Substances to help select appropriate methods of sample collection and analysis. The analytical methods used, quality control samples, analytical results, and numbers of samples collected as part of the design were reviewed.

In the review of the data generated in HUD's pretest survey, it was noted that no data were presented on lead in household dust. However, a procedure was presented in the survey design for sampling and analyzing household dust (RTI Survey Design 1988). It was determined dust sampling had been carried out, but that none of the samples collected indicated lead above the method detection limit. It was decided to evaluate the pretest survey techniques to determine why the data were not consistent with previously observed results of lead in almost all dust samples (Bornschein et al. 1986). Studies by Bornschein and Clark at the University of Cincinnati showed that the majority of indoor dust had at least 100 $\mu g/g$ of lead. These concentration levels were predicted to be detectable by the AAS protocol, if sufficient sample mass was collected. Dust sample weights were not determined in the pretest survey to verify adequate sample mass had been collected. The lack of measurable lead levels suggests the sampling method did not collect a sufficient amount of sample for analysis. Therefore, a limited evaluation of the sampling technique was undertaken. The objective was to formulate a protocol to be used in the HUD National Survey of Lead in Homes.

Experimental Methods

The first step of the evaluation was to select a vacuum system adequate for dust collection from carpets, windowsills, and floors. (The criteria for selection of methods include: (1) less than 5 min to sample 4 ft^2 of sample area; (2) sampling apparatus weighs less than 10 lb; and (3) simplicity of operation.) The major problem with carrying out a systematic method comparison of indoor dust sampling techniques is the reproducible generation of representative dust samples on various substrates. Dust is a complex mixture of organic and inorganic particles of various shapes and sizes. Because no representative "standard" dusts were available due to time constraints and lack of commercial availability, the dust used throughout this evaluation was composited from dust collected in vacuum cleaner bags at a personal residence and from an MRI floor vacuum. Staff sieved the material to remove all particles greater than 250 microns and any extraneous carpet fibers. This produced a fine dust that appeared to settle in a pattern similar to that found in households.

Carpet represented a unique problem in carrying out a systematic evaluation. Staff used the percentage of weight of a representative dust sample as one of the criteria to evaluate collection efficiency. However, when vacuuming carpet, the vacuum picks up a large number of carpet fibers along with the dust. This prevents an accurate determination of the percentage of dust recovered from carpeted surfaces. For the National Survey in which the Pb in dust was determined as micrograms of Pb per square foot of sampled surface, this does not represent a major concern unless the carpet fibers contained significant amounts of Pb. However, in trying to assess the efficiency of a particular collection system, the weight of the fibers collected could significantly bias the results in a positive direction.

1. Method of Application to Surfaces

The method of application of dust samples to the surface areas needed to produce a fairly even distribution of a known amount of material. A fairly even distribution of dust over the surface would represent a typical field sampling situation. Static effects and non-retrievable dust in cracks or crevices in the natural dust settling patterns are more difficult to assess and were beyond the scope of this investigation. A child's toy flour sifter (Kitchen Play) was used to evenly apply the dust to the tested surfaces. Evaluation of the holdup of the dust in the sifter showed that greater than 90% of the dust reached the surface of the sample area (Table 1). The ability to reproducibly deliver greater than 90% of the dust over a dust burden range of 60 to 229 mg was considered adequate to proceed with this testing. The dust scattered fairly evenly over the templated area.

Table 1. Dust Recovery for Sifter

Weight of dust added to sifter (mg)	Weight of dust determined on surface (mg)	% recovery
112	102	91.1
59.6	57.0	95.6
229	220	96.1
78.2	70.8	90.5
		Avg = 93.3 ± 2.8%

2. Evaluation of Vacuum Collectors

Three vacuum pumps were evaluated, each with four different sample nozzle configurations. Table 2 lists the three pumps along with their pertinent specifications. The maximum flow rate for each pump was determined with a clean sampling cassette containing both filter and pad attached to a 4-ft section of 3/8-in heavy-wall Tygon tubing. The flow rate was measured using an NBS traceable anemometer.

Figure 1 illustrates the nozzle designs evaluated. Nozzle A, the design used in the HUD pretest study, attaches to a small sampling tube that is

connected to the small sample port on the cassette. Nozzles B and C are designs constructed at MRI for evaluation. The fourth option, Nozzle D, is the open end of the cassette used directly as a sampling port. Each of these nozzle designs was evaluated using each pump operating at its maximum flow rate. Nozzle designs B and C evolved during the investigation of sampling methods to meet the desired sampling time constraints and were not evaluated simultaneously with Nozzles A and D.

The efficiency of each dust collection method was evaluated by determining the weight of dust collected from a surface spiked with a known weight of household dust. In determining the amount of dust collected in each evaluation, a problem is the weight change in the cassette due to changes in the amount of moisture on the filter. This problem would be especially severe at high flow rates which could chill the filter with subsequent condensation. A preliminary evaluation, sampling just air for 5 min, showed very little change (< 5 mg) in a 2-L/min (SKC pump) system and larger changes (> 15 mg) in the higher flow systems (i.e., Gast pump). This problem was minimized by drying the cassettes at 80°C, removing them from the oven and immediately sampling, redrying for 5 min, and immediately weighing after removal. Weight gains associated with air sampling were less than 2 mg on cassettes after this treatment.

Table 2. Pumps Evaluated for Dust Collection

Manufacturer	Model	Flow rate specification (L/min)	Pressure head specification (mm Hg)	Weight (lb)
SKC	101-M	5	25	1.2
Gast	302-100	100	125	10.8
Fisher	A-20	20	60	7.2

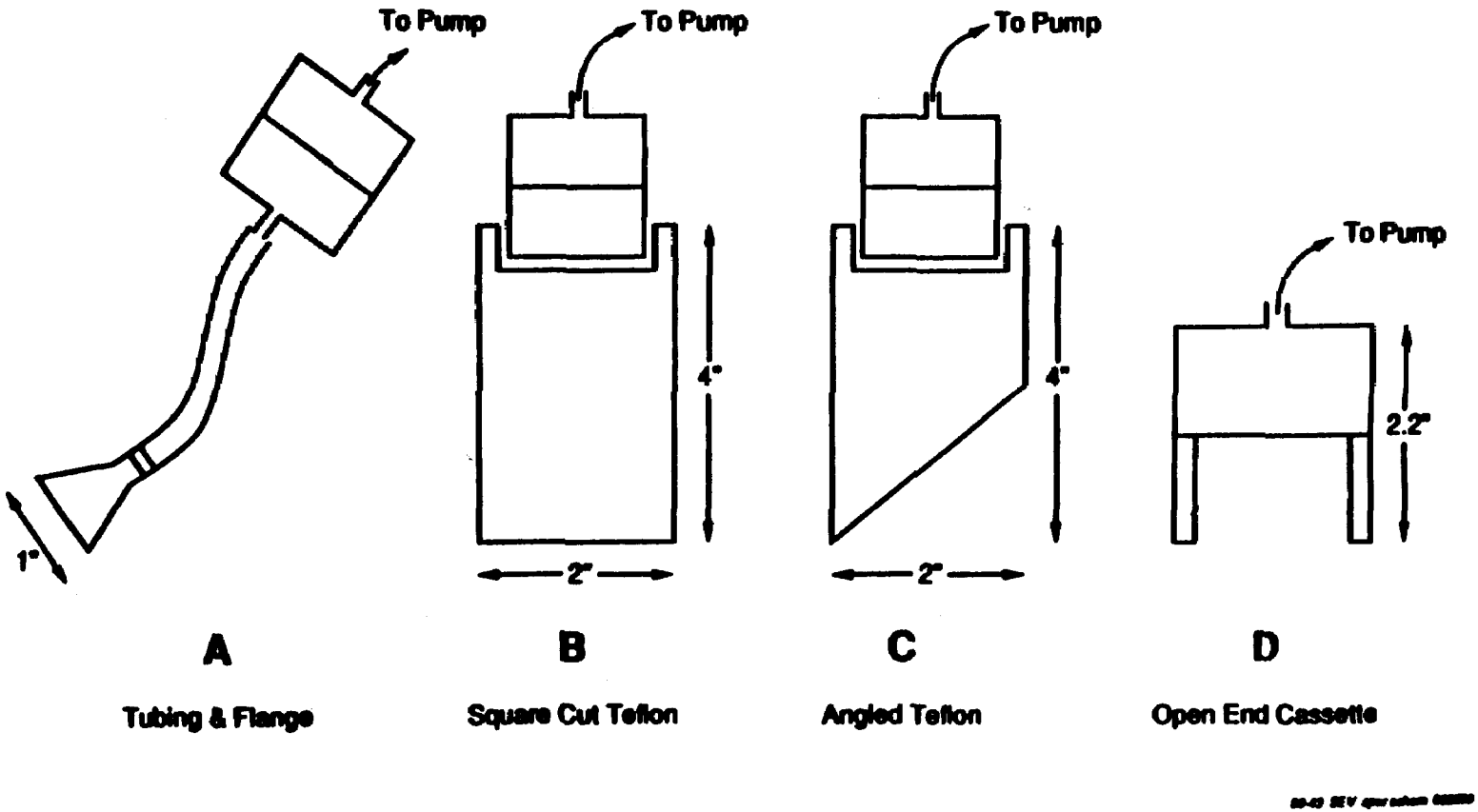

Figure 1. Nozzles evaluated in dust collection study.

Dust collection was determined on three different surfaces: (1) vinyl tile; (2) construction-grade plywood (unpainted); and (3) a piece of enamel-painted, construction-grade plywood. Table 3 shows the test matrix. Attempts at evaluating the collection efficiency from carpet were not successful due to continuing interferences from carpet fibers. These fibers did not allow for accurate dust weight determinations, and therefore resulted in artificially high recoveries.

Tables 4 and 5 show recovery results of the sampling evaluations. Each determination was made in duplicate, and average value reported. The procedure used to collect the dust involved 50% overlapping passes made on the surface from left to right and then top to bottom. Table 6 includes the approximate time to vacuum a 1-ft^2 area for each nozzle type and pump. The time difference to cover the specified area was significant, and this impacted the final selection between the systems. The early data on the time required to vacuum resulted in fabricating a larger vacuum nozzle for dust sampling (Nozzles B and C).

In evaluating the data in Tables 4 and 5, it is clear the larger flow rate pump is necessary to achieve high levels of dust recovery. This finding is contrary to reports by other researchers (Bornschein et al. 1985), who have previously reported > 80% recovery using the SKC 5-L/min pumps. This difference may be the result of sampling technique, time, or type of dust (i.e., particle size) sampled. Our finding, however, is consistent with the results reported in the HUD pretest survey. After considering the sampling efficiency (amount collected on filter) and sampling time, Nozzle C and the Gast pump operated at full capacity were selected to collect household dust in the HUD National Survey of Lead in Homes. Table 7 shows a summary recovery (%) performance of Gast pump/nozzle combination system.

It is clear significant research efforts in this area of dust sampling is warranted. Our efforts and decisions were based on an immediate need to meet the short-term deadlines required for the HUD national survey. EPA continues to investigate improved methods for household dust collection studies (Wilson et al. 1991).

REFERENCES

1. Bornschein, R.L.; Succop, P.A.; Krafft, K.M.; Clark, C.S.; Peace, B.; Hammond, P.B. (1987b) Exterior surface dust lead, interior house dust lead and childhood lead exposure in an urban environment. In: Hemphill, D.D., ed. Trace substances in environmental health - XX: proceedings of University of Missouri's 20th annual conference; June 1986; Columbia, MO. Columbia, MO: University of Missouri; pp. 322-332.

2. Boyle, K.E.; Gutknecht, W.F.; Neefus, J.D.; Stutts, E.S.; Williams, E.E.; Williams, S.R.; "Design A National Survey of Lead-Based Paint in Housing - Pretest Report". HUD Contract No. HC5796 (August 3, 1989).

3. Wilson, N.K.; Lewis, R.G.; Fortmann, R., et al.; "Evaluation of Methods for Measurement of Exposure of Young Children to Lead in Homes," to be presented at International Society of Exposure Analysis, Annual Meeting, Atlanta, Georgia, November 1991.

Table 3. Test Matrix for Vacuum Dust Collection

Pump (operating flow)	Surface type: Vinyl	unpainted plywood	Enamel plywood
SKC (2 L/min)	2[a]	2[a]	2[a]
Fisher (20 L/min)	2[a]	2[a]	2[a]
Gast (100 L/min)	2[a]	2[a]	2[a]

[a]Number of replicate collections carried out at each sample weight (50 mg and 150 mg).

Table 4. Recovery of Surface Dust Applied at 50 ± 10 mg/ft^2

Pump and nozzle	Average Recovery (%), $\bar{x}$ (RPD)*		
	Vinyl	Unpainted plywood	Enamel-painted plywood
SKC (2 L/min) + A	6.5(23.0)	2.0(100)	7.5(20)
SKC (2 L/min) + B	7.5(6.7)	3.0(33.3)	3.0(0.0)
SKC (2 L/min) + C	10.5(14.0)	12.0(25.0)	5.5(9.0)
SKC (2 L/min) + D	3.5(100)	19.5(79.5)	7.5(6.7)
Gast (100 L/min) + A	45.5(14)	46.5(3.2)	53.5(43.9)
Gast (100 L/min) + B	73.5(7.5)	85.5(6.4)	93.0(13.4)
Gast (100 L/min) + C	90.0(2.2)	92.0(5.4)	60.0(46.7)
Gast (100 L/min) + D	36.0(16.6)	25.5(37.2)	30.5(1.6)
Fisher (20 L/min) + A	12.0(0)	17.0(29.4)	35.0(67.9)
Fisher (20 L/min) + B	21.5(7.0)	28.0(10.7)	26.5(17.0)
Fisher (20 L/min) + C	27.0(7.4)	34.5(10.1)	51.0(11.8)
Fisher (20 L/min) + D	16.0(6.2)	15.5(100)	17.0(0)

*RPD = Relative percent deviation $\left|\frac{x-\bar{x}}{\bar{x}}\right| \times 100$

Table 5. Recovery of Surface Dust Applied at 150 ± 25 mg/ft^2

Pump and nozzle	Average Recovery (%), $\bar{x}$ (RPD)		
	Vinyl	Unpainted plywood	Enamel-painted plywood
SKC (2 L/min) + A	19.0(10.5)	10.0(20.0)	21.5(25.6)
SKC (2 L/min) + B	2.0(100)	4.5(55.5)	3.5(100)
SKC (2 L/min) + C	6.0(50)	7.0(71.4)	8.0(12.5)
SKC (2 L/min) + D	16.5(30.3)	6.0(16.7)	14.0(7.1)
Gast (100 L/min) + A	41.0(87.8)	38.5(13.0)	37.5(4.0)
Gast (100 L/min) + B	69.5(20.9)	82.5(4.2)	77.5(3.2)
Gast (100 L/min) + C	85.0(1.2)	94.5(2.6)	98.5(8.6)
Gast (100 L/min) + D	35.0(14.2)	35.0(2.9)	25.5(37.2)
Fisher (20 L/min) + A	22.5(28.9)	16.0(6.3)	21.0(4.8)
Fisher (20 L/min) + B	43.0(9.3)	42.0(11.9)	29.0(44.8)
Fisher (20 L/min) + C	68.0(48.5)	50.5(16.8)	53.5(12.1)
Fisher (20 L/min) + D	17.0(0)	10.5(100)	23.5(17.5)

Table 6. Time to Vacuum Surface

Nozzle	Time to cover area of 4 ft^2 (min)[a]
A	24
B	5
C	5
D	32

[a]Time to execute 50% overlapping passes as specified in the text. Visual inspection of collection efficiency not used for this evaluation.

Table 7. Summary Recovery (%) Performance of Selected Pump/Nozzle Combinations (Gast(100 l/min) + C)

	Average Recovery (%), $\bar{x}$ (RPD)		
Dust Loading	Vinyl	Unpainted plywood	Enamel-painted plywood
50 ± 10 mg/ft^2	90.0(2.2)	92.0(5.4)	60.0(46.7)
150 ± 25 mg/ft^2	85.0(1.2)	94.5(2.6)	98.5(8.6)

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FIELD DEPLOYMENT OF A GC/ION TRAP MASS SPECTROMETER FOR TRACE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

Field analytical support can directly impact the expense of environmental clean-up by reducing the cost-per-analysis. Cost for sample packaging, shipment, receiving and management are eliminated if analyses are performed on site. Field analytical support improves the chances that schedules and monetary constraints associated with remedial activities are met.

To reduce the cost associated with environmental clean-up we have developed a purge and trap/GC/Ion Trap Detector (ITD) at Los Alamos National Laboratory for the identification and quantification of volatile organic compounds present at chemical waste sites. A custom purge and trap/GC sampling system was integrated with a modified ITD to achieve instrument operation consistent with field activities.

The instrumentation and associated methods parallel those outlined in method 8260, SW-846. Qualitative and quantitative analysis for the 68 target compounds and the associated internal standards and surrogates is completed in an automated sequence that is executed every 25 minutes. Sample purging, analysis, data reduction, and preliminary report generation proceeds automatically. The instrument can be operated in a

continuous mode, pausing only for sample loading and data file specification. All data are archived on floppy disk for subsequent review by a skilled analyst. Part-per-trillion detection limits can be attained for many compounds from either 5 gram soil or 5 milliliter water samples.

The GC/ITD is being deployed in a mobile laboratory which has been designed to support volatile organic analysis. The use of the transportable GC/ITD for support of environmental surveillance and the characterization/clean-up of hazardous waste sites is being evaluated. We will discuss field activities completed to date and the evolution of field operation plans and field documentation. Additionally, we will discuss the quality control we have implemented for field analysis using the GC/ITD. Results obtained from blind quality control samples will be presented.

One purpose of the presentation will be to examine problems encountered with field analyses using the GC/ITD and to discuss any actions taken to address those problems. Notably, we will discuss how small quantities of water introduced into the ITD from the purge and trap sampling system negatively impact quantitation and the steps we have taken to mitigate those problems.

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ACCURATE, ON-SITE ANALYSIS OF PCBs IN SOIL -- A LOW COST APPROACH

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ABSTRACT

Polychlorinated Biphenyls (PCBs) are very stable materials of low flammability used as insulating materials in electrical capacitors and transformers, plasticizers in waxes, in paper manufacturing, and for a variety of other industrial purposes.

There are many PCB transformers and capacitors still in service throughout the United States today. The Environmental Protection Agency estimates that there are 121,000 (askarel) PCB transformers, 20 million PCB contaminated mineral oil transformers and 2.8 million large PCB capacitors currently in use. A certain percentage of this equipment will leak, fail or rupture and spill PCB into the environment each year (1).

Because of equipment leakage and widespread industrial dumping, PCBs have appeared as ubiquitous contaminants of soil and water. Chemical analysis for PCBs has been almost exclusively performed by gas chromatography. Other analytical techniques such as nuclear magnetic resonance (NMR) and liquid chromatography with UV detection are alternative methods for PCB analysis but can only be successfully applied where the suspected concentration level of PCB is greater than 1000 ppm.

A new instrumental method has been developed to analyze for PCB content using electrochemical methodology and a chloride specific electrode to measure quantitatively the amount of chloride. The instrument converts the chloride concentration into a PCB equivalent amount of PCB in an oil or soil sample and gives a direct readout in parts per million of PCB. The preparation steps involve extracting the PCBs from the soil (not necessary for oil samples) and reacting the sample with a sodium reagent to transform the PCBs into chloride which can be subsequently quantified by the instrument. Oil samples take about 5 minutes to prepare and soils about 10 minutes. One operator can complete about 150 oil tests or 100 soil tests in an eight hour day.

Although this paper will concentrate on the results of soil samples obtained from a Superfund site analyzed electrochemically and by gas chromatography, it demonstrates the accuracy and economic advantage of employing the electrochemical procedure in analyzing both oil and soil samples.

INTRODUCTION

PCBs were first formulated as far back as 1881. Although they were known to exist in the late 1800s, manufacturing on a commercial scale did not start until 1929. It was not until 1977 when all U.S. PCB production was halted.

In the late 1960s, PCBs were recognized as a potential environmental problem, which was probably due to the unregulated maintenance and handling of PCB-containing equipment. A series of studies has been done to identify and quantify the distribution of PCBs in the U.S. The overall distribution is shown in figure (1).

The wide use of PCBs was due to their non-flammable characteristics as well as their thermal and chemical stability, low vapor pressures at atmospheric temperature and high dielectric constants. Although the use of PCBs has been banned in most applications, they are still being used in vacuum pumps and gas-transmission turbines. PCBs have been used as plasticizers in synthetic resins, in hydraulic fluids, adhesives, heat transformer systems, lubricants, cutting oils and in many other applications.

The EPA currently recommends two PCB specific methods of analysis; the GC/MS Method 680 for quantitating PCB isomer class totals and the GC/ECD Method 8080 for quantitating Aroclors. Over the past decade, the use of these instrumental methods has increased dramatically and it is the purpose of this paper to provide an example of one type of non-specific analysis of PCBs where simple inexpensive chemical procedures can in fact, under certain circumstances, be a preferable alternative to chromatographic methods.

The examples chosen in this paper are the analyses of PCBs in transformer oil and soil. The tests involve measurements of PCB concentration down to a few parts per million where, as a result of extensive legislation, inaccurate results would likely evoke expensive litigation and heavy fines. The different methodology and apparatus will be described, the accuracy and precision of each method discussed, and the costs of each analysis reported.

METHOD FOR THE ELECTROCHEMICAL DETERMINATION OF PCB IN OILS AND SOIL

This procedure utilizes sodium metal to remove chlorine from any PCB present in the sample. The concentration of chloride contained in the final aqueous extract can be determined electrometrically by means of a chloride specific electrode. By immersing a chloride specific electrode in the aqueous extract and measuring the EMF produced, the chloride concentration and thus, the PCB content can be estimated. The chloride concentration is exponentially related to the electrode EMF and thus with a suitable electronic circuit design the results can be presented digitally in ppm of the selected PCB on an appropriate meter.

This is a non-specific method, testing for the presence of chlorine in the sample being examined. As a result, other chlorinated compounds will cause a false positive result because the analysis method reads all chlorinated compounds as PCB. False negative results should no occur, however, because if no chlorine is present, PCBs cannot be present.

SAMPLE PREPARATION

1/Oil Samples

0.2 ml of a solution of naphthalene in diglyme is added to 5 ml of oil sample. To this mixture is added 0.4 ml of a dispersion of metallic sodium in mineral oil and the mixture shaken for one minute. 5 ml of buffer is then added to neutralize the excess sodium and to adjust the pH to 2.0 to ensure the pH of the mixture is within the operating range of the electrode. 5 ml of the aqueous layer is then carefully decanted into a suitable vessel.

2/Soil Samples

10 g of the sample of soil is extracted by shaking for one minute with 12 ml of solvent containing 2 ml of distilled water in 10 ml of an immiscible hydrocarbon. The soil is then allowed to settle and the supernatant liquid filtered through a column containing Florisil to remove any moisture and inorganic chloride. 5 ml of the dry filtrate is then treated with 0.2 ml of a solution containing naphthalene in diglyme, followed by 0.4 ml of a dispersion of metallic sodium in mineral oil and shaken for 1 minute. 5 ml of buffer solution is then added and the aqueous layer allowed to separate. 5 ml of the aqueous layer is then decanted into a suitable vessel.

ANALYTICAL METHOD

The measuring instrument (Dexsil L2000™, Hamden, CT) is fitted with temperature compensation as the output of the chloride specific electrode varies with temperature. Initially the temperature compensation adjustment is set to the sample/electrode temperature. The electronic measuring device is then calibrated employing a solution containing chloride equivalent to 50 ppm. The electrode is immersed in 5 ml of the calibration solution and appropriate adjustments made to the calibration control to provide an output on the digital meter of 50 ppm of chloride.

After rinsing and drying, the chloride specific electrode is immersed into the 5 ml sample, gently stirred for 5 seconds and allowed to stand for 30 seconds. The concentration of PCB in ppm is then read directly from the digital output meter. The dynamic range of this analytical procedure is from 5 to 2000 ppm. The precision varies with the concentration. At concentrations between 50 and 2000 ppm, it is +/- 10%. Between 5 and 50 ppm it is about +/- 2 ppm.

ANALYTICAL TESTS, RESULTS AND DISCUSSION

Oil Samples

In general, PCB specific methods are more accurate than the non-specific methods, but they are also more expensive, more lengthy to run, and less portable. The L2000™ PCB analyzer provides accurate analysis of PCB concentration in oil by testing for the total amount of chlorine that is present in the sample.

The PCB concentration is calculated from the chloride concentration using a conversion factor based on the Aroclor present in the sample. If the specific Aroclor is not known, then the most conservative estimate results from assuming that the PCB present is Aroclor 1242. Aroclor 1242 contains the lowest percentage of chlorine of the commercially produced PCB mixtures.

The 1260 setting is used when a sample contains Aroclor 1260, but not the associated trichlorobenzene.

The Askarel setting is used for samples that contain Aroclor 1260 and associated trichlorobenzene. Askarel accounts for the majority of contaminated transformer oil samples and therefore this setting will usually supply the most accurate results; however, if a 1242 contaminated sample is tested on the askarel setting, a false negative will result if the sample contains between 50 and 120 ppm.

Tables (1) and (2) show comparison results of transformer oils contaminated with 1242 and 1260 (as Askarel) respectively, analyzed by the PCB specific GC method versus the L2000™. The GC method used to analyze the transformer oils in this study is EPA 600/4-81-045.

It is seen that accurate and precise results are obtained over a wide concentration range of PCBs and although false positives can cause unnecessary secondary testing, this method can be very economical when used on transformer oil, which contains few sources of chlorine other than PCB. Used crankcase and cutting oils, however, always contain some chlorinated paraffins and almost always give false positive results with non-specific testing. More expensive gas chromatographic analysis is required when testing for regulated levels of PCB in these matrices

Soil Samples

The EPA Spill Cleanup Policy stipulates that a PCB spill, once detected, must be cleaned up within 48 hours.(3) The EPA mandates that cleanup actions are taken in this short time frame in order to minimize the risk of human and environmental exposure to the spilled PCB. In addition to the many PCB Superfund sites, there are still many other PCB spill sites that have not made the National Priorities List that still must be cleaned up.

One of the most time consuming steps in laboratory soil analysis is the drying time. When a soil sample is received for GC analysis by ASTM D3304, the sample is dried for 24 hours. The sample is then weighed and placed in a soxhlet extractor and allowed to cycle for 8 hours. The sample must be completely dry, since the extraction solvent (usually hexane or isooctane) is immiscible with water. Extraction of a wet sample would yield a low result since the solvent cannot fully interact with the soil to extract the PCBs. Typically, 90% of soil samples received for laboratory analysis by GC require drying prior to extraction. With a 48 hour cleanup policy, twenty-four hours of drying time could be a substantial set-back. The content of the spilled material must ideally be determined at once and the cleanup procedures begun immediately. The L2000™ allows the operator to respond immediately and to make a quick evaluation of the concentration of PCB at the site. At an excavation site where soil analysis is being performed, the decision can be made immediately if more soil needs to be removed or if the excavation has been carried far enough.

The results of soils obtained from a Superfund site and analyzed by GC and the L2000™ are compared in Table (3). Since gas chromatography can quantitate each Aroclor present, the GC results are presented for each Aroclor actually detected in the soil samples. The corresponding L2000™ results for that particular sample are seen on the same line. These results are listed according to each setting available to the analyst. The L2000™ does not have the capability to quantitate each Aroclor; instead, all the chloride present is interpreted according to the Aroclor setting being used. For samples contaminated with an unknown Aroclor, the prudent analyst would use the 1242 conversion to provide the most conservative estimate.

Using the L2000™ as a screening method, the samples are evaluated according to column 4 interpreting chloride as 1242. For the ten samples analyzed, samples 2, 3, 4 and 6 would be considered as below the Code of Federal Regulations limit of 10 ppm set by the EPA. Since this is a site remediation, the results would indicate that these areas can be considered "clean" and would not need further treatment. If active clean-up were underway, these samples would indicate that the excavation has gone far enough in that area.

The remaining samples indicate that there is still possible contamination above the 10 pm level. This would result in further excavation being required to reach safe levels. If active excavation is not underway then the samples can be further analyzed to determine the specific Aroclor content. Whether the samples are further analyzed or excavation is continued based on the 1242 estimate will depend on the cost consideration of waiting for lab results while paying for an idle excavation team and remediation equipment, or excavating excess material while the crew and equipment are still on site.

From the GC analysis it was determined that only two of the six "positives" were "false positives" in that the total chlorine indicated an equivalent of PCB above the regulatory 10 ppm limit whereas GC analysis of those samples showed an actual level below 10 ppm.

The problem of contamination with chlorinated solvents is exemplified by sample 1 where the L2000™ result is considerably higher than the GC results. This high reading is again an over estimation of the PCB present and would result in a conservative action being taken such as retesting using GC or further excavation.

To make a systematic comparison of the GC results which quantify each Aroclor separately, to the L2000™ results, an equivalent amount of a single Aroclor must be calculated from the sum of all Aroclors detected. For the results given in this paper Aroclor 1242 was chosen as the basis for equating the L2000™ results with the GC results. The equivalent L2000™ reading, which converts the chloride concentration to PCB using a single Aroclor conversion factor, can then be calculated. The direct conversion of ppm 1260 by GC to its equivalent in ppm 1242 is based on the percent chlorine difference of 1242, 42%, versus 1260, 60%, according to the equation:

$$\text{L2000 equivalent ppm 1242} = (X)\ (60/42)$$

where: X = ppm 1260 by GC

60/42 = ratio of percentage chlorine

For example, the GC results for the first soil sample shown in Table (3) of 11.59 ppm 1242 and 2.24 ppm 1260 should theoretically read 14.79 on the L2000's 1242 setting. The value of 14.79 is attained by converting the GC 1260 value to 1242 according to the equation above, and adding it to the GC value for 1242. The actual reading on the L2000 1242 setting was 25.0 ppm, which is significantly higher than the theoretical prediction. The false high reading can probably be attributed to other chlorinated compounds being present in the soil that the GC does not detect. Nevertheless, from a regulatory point of view a false positive is preferable. A more realisitc and expected result is seen from the results for the seventh soil analysis shown in Table (3), and the once again a theoretical concentration of 1242 can be predicted from the conversion equation. The GC result for that sample was 92.66 ppm 1242 and 15.08 ppm 1260. 15.08 ppm 1260 converts to 21.54 ppm 1242, which when added to 92.66 ppm 1242 gives a theoretical projection of 114.2 ppm 1242 as the L2000 result. The actual 1242 result given by the L2000 was 122.7, which is within the +/- 10% accuracy level accepted for GC analysis.

Table (4) shows a comparison of results from soil samples obtained from a PCB spill site.

Like the oil samples, soil sample concentration of PCBs are also based on the detection of chlorine; however, it is only chlorine present from an organic source that would cause a false positive, as seen in the first example above, rather than an inorganic source such as road salt or sea salt. Some possible sources of chlorine contamination are pesticides and solvents.

One benefit to the laboratory personnel analyzing soils is that using the L2000™ first to screen PCB content allows the GC chemist to make an accurate dilution right away. The appropriate dilution is to 1 ppm and one chromatographic analysis is approximately 40 minutes long. The analysis time can certainly add up with trial-and-error dilutions being made, especially if there are many samples waiting to be analyzed. Knowing the right dilution also prevents overloading the column with PCB contamination.

The L2000™ system can analyze to fewer than 5 ppm in oil and soil, can be used in the field by non-technical personnel, and requires less than 10 minutes to run an analysis. These attributes make the instrument an excellent alternative to gas chromatographic analysis, especially for soil samples.

Although this new technique does not replace gas chromatography, it can significantly reduce the number of samples requiring GC analysis, and therefore allow a greater amount of samples to be run at a lower cost.

REFERENCES

1./Environmental Progress and Challenges: EPA's Update. United States Environmental Protection Agency. EPA-230-07-033. August 1988.

2./Finch, S.R., Lavigne, D.A., Scott, R.P.W. "One Example Where Chromatography May Not Necessarily Be the Best Analytical Method." Journal of Chromatographic Science. July 1990. pp.351-356.

3./40 CFR 761.125. Office of the Federal Register. Rev. July 1, 1989.

4./PCB Equipment, Operations and Management Reference Manual. SCS Engineers, Inc.

FIGURE 1

U.S. Distribution of PCBs (4)

Presently in use	750 million pounds	60%
In landfills and dumps	290 million pounds	23%
Released to environment	150 million pounds	12%
Destroyed	55 million pounds	5%
Total production	1,245 million pounds	100%

TABLE 1

RESULTS OF GC ANALYSIS OF PCBs (1242) IN TRANSFORMER OIL
vs
RESULTS OF L2000 ANALYSIS

Standard (ppm 1242)	Results from GC Analysis (ppm 1242)	Results from L2000 Analysis (ppm 1242)
0	None Detected (< 2 ppm)	0.6
	None Detected (< 2 ppm)	0.9
	None Detected (< 2 ppm)	1.5
		MEAN 1.0
		STD. DEV. 0.4
10	10.0	9.7
	10.8	9.3
	10.4	9.7
	MEAN 10.4	MEAN 9.6
	STD. DEV. 0.4	STD. DEV. 0.2
50	51.6	50.7
	52.3	46.2
	50.3	51.4
	MEAN 51.4	MEAN 49.4
	STD. DEV. 1.0	STD. DEV. 2.8
100	96.8	104.9
	95.8	95.2
	94.2	95.4
	MEAN 95.6	MEAN 98.5
	STD. DEV. 1.3	STD. DEV. 5.5
500	474.0	522.0
	482.2	492.0
	497.0	470.0
	MEAN 484.4	MEAN 494.0
	STD. DEV. 11.7	STD. DEV. 26.1

TABLE 2

COMPARISON OF RESULTS FROM THE ANALYSES
OF OIL SAMPLES CONTAINING AROCLOR 1260 (ASKAREL A):
GAS CHROMATOGRAPHY vs L2000

Standard (ppm 1260)		GC Analysis Results (ppm 1260)		L2000 Analysis Results (ppm 1260)
10		9.482		9.2
		9.241		9.5
		9.186		10.6
	MEAN	9.303	MEAN	9.8
	STD.DEV.	0.129	STD.DEV.	0.6
50		50.923		53.7
		48.409		48.6
		51.883		50.8
	MEAN	50.405	MEAN	51.0
	STD.DEV.	1.465	STD.DEV.	2.1
250		233.911		255
		232.007		262
		230.215		261
	MEAN	232.044	MEAN	259
	STD.DEV.	1.509	STD.DEV.	3.8
500		493.232		530
		486.400		519
		472.423		510
	MEAN	484.018	MEAN	520
	STD.DEV.	8.661	STD.DEV.	10.0

TABLE 3

COMPARISON OF SUPERFUND SITE SOIL ANALYSES:
GAS CHROMATOGRAPHY vs L2000 READINGS

GC RESULTS			L2000 RESULTS (read as)		
1242	1254	1260	1242	1260	ASKAREL
11.59 ppm		2.24 ppm	25.0 ppm	17.5 ppm	10.6 ppm
0.32 ppm		0.25 ppm	0.9 ppm	0.6 ppm	0.4 ppm
	2.64 ppm	1.78 ppm	7.9 ppm	5.5 ppm	3.3 ppm
0.33 ppm		0.20 ppm	2.8 ppm	2.1 ppm	1.4 ppm
5.00 ppm		2.53 ppm	10.6 ppm	7.5 ppm	4.6 ppm
0.77 ppm	0.80 ppm	0.35 ppm	7.5 ppm	5.3 ppm	3.2 ppm
92.66 ppm		15.08 ppm	122.7 ppm	85.8 ppm	51.7 ppm
7.18 ppm	1.54 ppm	0.08 ppm	11.5 ppm	8.1 ppm	4.9 ppm
7.87 ppm	3.25 ppm	0.30 ppm	13.0 ppm	9.2 ppm	5.6 ppm
		9.43 ppm	16.2 ppm	11.4 ppm	6.9 ppm

TABLE 4

COMPARISON OF PCB SPILL SITE SOIL ANALYSES:
GAS CHROMATOGRAPHY vs L2000

GC RESULTS			L2000 RESULTS (read as)		
1242	1254	1260	1242	1260	ASKAREL
.30 ppm		6.09 ppm	10.8 ppm	7.5 ppm	4.5 ppm
.10 ppm		41.59 ppm	62.5 ppm	43.8 ppm	26.4 ppm
.97 ppm		0.40 ppm	5.7 ppm	4.0 ppm	2.4 ppm
.38 ppm		0.05 ppm	6.1 ppm	4.3 ppm	2.6 ppm
.68 ppm		6.67 ppm	14.8 ppm	10.3 ppm	6.2 ppm
		4.42 ppm	7.3 ppm	5.1 ppm	3.1 ppm
		206.0 ppm	404.0 ppm	281.0 ppm	167.5 ppm
		1699.0 ppm	>2000 ppm	1642.0 ppm	996.0 ppm

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HOW GOOD ARE FIELD MEASUREMENTS?

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Abstract

Quick! Cheap! High throughput! We have all heard these words associated with field measurement methods. But what does the record show with respect to the application of these new technologies and the quality, acceptability, and usability of data produced in the field. Are the touted advantages of field screening methods and field analytical methods being fully realized to measure, monitor, or characterize waste sites or waste streams? Highlights will be presented from the Second International Symposium on Field Screening Methods that was conducted earlier this year. Technologies presented ranged from simple chemical and immunochemical test kits to highly sophisticated fieldable instrumentation for analysis of toxic metals and organic chemicals in all environmental media. Case studies indicate the current utility of several key technologies for monitoring and site characterization. In addition, information will be furnished on field measurement technologies recently demonstrated under the Superfunds Innovative Technology Evaluation program. Some institutional inertia appears to hinder the broader acceptance of field-produced data. One thing remains clear; the new field technologies do not, nor should they be expected to, replace operator skill and judgement in generating environmental data. But they do constitute a battery of new and available tools that can improve the confidence of decisions based upon such data.

41 # ASSESSMENT OF POTENTIAL PCB CONTAMINATION INSIDE A BUILDING; A UNIQUE MULTI-MATRIX SAMPLING PLAN

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ABSTRACT

Characterization of potential PCB contamination inside a large, active market and restaurant area was required. There was the possibility for PCBs to have entered the facility as a result of construction/demolition activities taking place in the area above the market.

This case history describes a unique assessment approach, including a multi-matrix sampling procedure. A representative number of samples had to be collected from this facility which occupies approximately 175,000 $ft.^2$ in area. The sampling also had to be performed in a practical manner, with the least possible disruption of routine daily activities.

A visual inspection and reconnaissance of the market was first conducted in order to identify entry points for potential PCB-containing materials such as dust, water and debris. Six different matrices were identified for sampling, including air, dust, water and sediments. Wipe samples were also taken from non-porous surfaces such as counter tops and fixtures. Destructive (chip) samples were taken from porous solid surfaces such as wood and insulation materials. Composite samples were taken from some areas. Quality Control samples, including items such as duplicates and field blanks were also taken.

The sampling plan is discussed in detail, including equipment used, statistics, and the selection of random and biased sample locations. Analytical procedures are also reviewed, including extraction techniques and quantitation limits.

1. INTRODUCTION

Roy F. Weston, Inc. was retained by the Department of Health of a large Eastern United States city to collect and analyze environmental samples from within a large urban food market. The purpose of this investigation was to assess the extent of, or confirm the absence of, polychlorinated biphenyl (PCB) contamination.

Demolition activities, including PCB removal, had been on-going in the open shed which is located above the market. The shed is an elevated area with a roof, but is open at one end. The market is approximately 175,000 ft^2 in area, and the platform of the shed is supported by steel columns within the market area. The ceiling of the market is suspended from the shed steel structure, and consists of a wood layer, covered with roofing paper and sheet metal. The interstitial space between the market's wooden ceiling and the underside of the shed structure houses a combined support-beam and stormwater drainage system.

The market is primarily a varied food market with a major area devoted to restaurants of different types to serve the people from the office buildings surrounding the market. Concern had previously centered around the potential for PCB contamination entering the market by way of leaks through or around the ceiling structure from the demolition activities on-going in the shed above. This concern was accentuated when the extremely heavy rains of one day deluged the shed and resulted in severely heavy leaks into the market below.

This report summarizes the assessment carried out and environmental samples collected from surfaces within the market. Field sampling activities were conducted by Roy F. Weston, Inc. personnel on a Sunday, while the market was closed. All sampling was conducted in Level "D" personnel protection requirements except during dust sampling when Level "C" protection was used.

It should be noted that this sampling effort included 55 samples from a variety of matrices (e.g., sediments, solids, air, dust, wipes of surfaces, water). Although this is a relatively small number given the size of the market, it is considered representative of conditions at that time within the market regarding assessing potential PCB contamination. Roughly one-half of the samples were biased toward areas of higher probability for contamination (such as areas of leaks or visible staining) and one-half were random throughout the active, occupied areas of the market.

2. SCOPE OF WORK

The sampling team first performed a visual inspection of the market in order to identify potential entry points for air, dust, water, oil and/or debris from the shed above into the market and delineate initial sampling locations. These entry points, and potentially affected areas below these points, were candidates for sample collection. The visual inspection to identify potential entry points consisted of looking for areas with distinct discoloration/staining, water marks, rust, damaged roof structure, clogged drainages, or penetrations in the roof. The visual inspection was supplemented with data from previous reports of a testing effort designed to determine PCB contamination within the interstitial space. Sampling locations were also identified for the biased and unbiased samples.

The battery limits of this study were from the floor of the market to ceiling level and within the four walls.

The following types of samples were collected by the field sampling personnel:

1. Wipes - From non-porous surfaces such as metal poles/beams, counter tops and market furniture, fixtures, food handling/preparation equipment, and floor drains.

2. Destructive - From porous hard surfaces such as wood, pipe insulation and rusted pillars.

3. Sediment - Standing sediment/solids from drainage outfalls, or "catch" samples from plastic or metal covers over stalls.

4. Water - Drippings from plastic catch areas, roof leaks, drains, or standing water.

5. Dust - Primarily from floor sweepings and in corners.

6. Air - Continuous air samplers to sample the ambient air in the market.

The actual sampling activities took place three days after the initial reconnaissance visit.

3. SAMPLING STATISTICS

A total of 55 field samples (and 14 quality control samples) were collected. Table 1 gives the breakdown of the various types of samples collected. All the samples were preserved on

Table 1

Summary of Environmental Samples Taken at the Market

Type of Samples	Number of Samples for PCB Analysis				
	Test	Control	Duplicate	Field Blank	Total
Wipes	27	2	2	2	33
Destructive	3	--	1	--	4
Dust	7	--	1	--	8
Sediment/solids	6	--	1	1	8
Water					
a) Unfiltered	4	--	1	--	5
b) Filtered	4	--	1	--	5
Air	4	1	--	1	6
Totals	55	3	7	4	69

ice and transported to the Weston Analytics Laboratory following completion of sampling activities. The individual sampling procedures are discussed in subsequent sections.

4. SAMPLING PROCEDURES

4.1 Wipe Sampling

Wipe sampling was conducted on 27 non-porous surfaces within the market. Samples were collected from a variety of surfaces such as counter tops, eating tables, freezers, steel pillars, cooking range hoods, glass cases, and others. The sampling locations were spread out over the entire market in order to get representative coverage. See Appendix A for complete procedure.

The wipes were divided into 2 categories:

- Biased - discrete
- Random - composite or discrete

The biased samples were collected as discrete samples. These samples were collected where visual observation and review of previous reports suggested a potential for PCB contamination.

The random samples were collected at various locations distributed within the building. These samples were collected either as discrete or composite samples. The discrete samples were collected on structures such as pillars, food cabinets, and range hoods. Composite samples were generally collected on larger surfaces such as long counter tops.

The composite samples were collected by taking three separate hexane soaked gauze pads and wiping each pad in various locations over a given surface and then collecting them in one sample bottle. The sampling area for composite samples was three times as large as that for the discrete samples (300 cm^2 vs. 100 cm^2). The analytical results were then adjusted to consistent units of 100 cm^2 for all samples to facilitate data comparison.

A total of six additional wipe samples were collected as quality control (QC) samples. Of these, two were controls, two were duplicates, one equipment blank and one field blank.

The control samples were collected from surface areas within the market which suggested the least likelihood of being contaminated (such as inside a closed food cabinet.) The equipment blank sample was collected by wiping the aluminum foil covered template with the hexane soaked gauze and analyzing for PCBs. The field blank sample consisted of a laboratory prepared wipe sample gauze pad in the sample

container taken to the market and returned for analysis along with the other samples.

The samples were placed in 250 ml wide-mouth glass jars (soil sample type jars) and preserved at 4°C by ice.

4.2 DESTRUCTIVE (CHIP) SAMPLING

Three destructive samples were taken of hard porous surfaces. Three different porous mediums were selected. They were a piece of wood, rust from a pillar and wrapping from pipe insulation.

All the samples selected were biased samples from different areas of the market. The rust sample from a pillar was collected near the wood ceiling. The insulation wrapping sample was collected from a drain pipe which comes down from the shed. The wood sample was collected from a temporary wall which was erected adjacent to a pillar in a corner of the market. A duplicate sample of the wood was taken at the same location.

Samples were collected using a decontaminated stainless steel trowel or chisel. Samples were collected in a 250 ml wide-mouth jar with teflon-lined lid and preserved at 4°C using ice placed in an ice chest. See Appendix B for complete procedure.

4.3 DUST SAMPLING

The team collected eight dust samples including one duplicate. Dust samples were collected from a variety of surfaces and locations. Two samples were collected from floor sweepings of two aisles, one sample from on top of the men's room roof, one from the louvers of an air exchange unit, one from a wall fan, one from the cold storage room screen, and the last one from a pipe near the roof directly across from an air conditioning unit. All samples were preserved on ice as previously described.

4.4 SEDIMENT/SOLID SAMPLING

A total of six sediment samples were collected from the market. Additionally, one duplicate sample and a field blank were also taken. Four sediment samples were collected in separate locations from the plastic suspended from the ceiling to catch water and solids which had dripped or fallen in from the shed above. These plastic sheets are predominantly located along the perimeter of the market.

Except in one area, no water leaks were visually evident on the day of the sampling. The sediment and water collected on

the plastic was potentially an accumulation from prior infiltration. It should be noted that during the initial site visit these plastic sheets were filled with water and some were overflowing due to the severe rain storm. However, by the day on which the sampling took place, much of the standing water was absent. Moist sediment and some water remained.

Except for one sample which was from a floor drain, the other samples were from solids/sediments which apparently dropped from the ceiling level. All samples were preserved on ice as previously described.

4.5 WATER SAMPLING

Water samples were collected in areas where there was stagnant or standing water. These areas included canopies of some of the stores and the suspended plastic surrounding some of the roof leak areas. The water samples were collected in 950 ml amber glass jars with teflon-lined caps and preserved at 4°C.

Eight water samples were taken from four locations (two samples per location) plus two duplicates (one location). For each location, one of the two samples was filtered and then analyzed for PCBs while the other sample was not filtered prior to analysis. This protocol was used to assess if the PCBs in the sample, if any, were potentially associated with the water phase or the suspended sediment/solid phase.

The water samples collected were from roof leakage which either collected onto the plastic sheeting beneath the leak or from a bucket under the leak or from a trough at roof level.

4.6 AIR SAMPLING

Five air samples were taken at locations inside and immediately outside the market building. Four samples were collected at inside locations, two from diagonally opposite corners and two samples within the active space of the market. One sample was drawn from a location outside the building to serve as a control sample. One blank sample tube was also analyzed as a field blank.

Air samples were drawn over an eight-hour period to determine time weighted average concentrations and for ease of comparison to OSHA Permissible Exposure Limits (PEL) and Threshold Limit Values (TLV) as set by the ACGIH. Collection of the analyte was accomplished as outlined in the National Institute of Occupational Safety and Health (NIOSH) Method 5503 as modified by Versar, Inc. to provide for the sampling of a greater volume of air and to provide a lower limit of detection of the analyte. The analytical methods and detection limits are discussed in detail in Appendix C. The

control sample was collected from outside the building near the entrance to the market. This was accomplished by running the source tube outside while the sampler remained inside the market.

5. RESULTS AND CONCLUSIONS

The analytical results are confidential to the client, but, in summary, none of the active areas of the market were found to contain PCBs at levels above the analytical detection limits. This includes the air and wipe samples from the restaurant areas. Trace amounts of PCBs were found in a few of the sediment and chip samples from isolated perimeter areas of the facility. These appear to be the result of an accumulation of residues from various small leaks over a period of time, and can be removed by routine maintenance operations.

6. SUMMARY

This survey of the extent of potential PCB contamination in the air, dust, sediments, etc. and on various porous and non-porous surfaces within the market was completed within a week. This included one day for reconnaissance and identification of sample locations, one day of sampling, and production of validated analytical result within 72 hours by the laboratory.

The sampling scheme represented, both statistically and logistically, a good survey of various matrices within the market. The results indicating a lack of detectable quantities of PCBs in the active market and restaurant areas was important to the continued safe operation of these facilities.

APPENDIX A

Procedure for Wipe Sampling

1 Prior to field activities, 3"x3" gauze pads are soxhlet-extracted in the laboratory with hexane and placed in the laboratory-cleaned glass sample containers equipped with teflon-lined caps.

2 Bring dedicated, prepared gauze pads (secured in glass containers) to sample site. Select appropriate sample location and area. Photograph area to be sampled, if necessary.

3 Measure area to be wiped or use dedicated aluminum template to mark area. Generally, a 100 cm^2 area is sampled; however, a smaller or larger area may be wiped, depending on the degree of cleanliness encountered in the field. Record size of area to be sampled.

4 Put on a clean pair of surgical gloves.

5 Hold gauze pad with clean glove and initially wipe sample area in a horizontal direction using a forward and backward motion. Wipe sample area a second time with a clean portion of the same gauze pad in a vertical direction using a forward and backward motion.

6 After wiping, replace the gauze pad in the appropriate laboratory-prepared container and secure the teflon-lined lid on the sample container.

7 Duplicate wipe samples will be taken in an area directly adjacent to the original sample location.

8 Attach the sample label with the sample identification number and other appropriate sample information. Apply custody seals and place in a plastic self-sealing bag.

9 Record all pertinent information in the site log and, if appropriate, on the site map, and complete the sample analysis request form and chain-of-custody record.

10 Follow the sample documentation, packaging, shipment, and chain-of-custody procedures.

APPENDIX B

Procedure for Destructive/Chip Sampling

1 Select appropriate sample location and record/mark location and area. Photograph area to be sampled.

2 Put on a clean pair of surgical gloves.

3 Using a decontaminated chisel and hammer, proceed to chip material to a depth of less than 2 cm, taking care not to scatter pieces outside the marked area. Clean, dedicated, or decontaminated aluminum pans or dust pans may be used to shield the area to prevent pieces from scattering. Record area and depth of sample.

4 Using a dedicated brush and dust pan or tweezers, collect the sample and transfer to an appropriate laboratory-cleaned container and secure the teflon-lined lid on the container.

5 Duplicate samples will be taken by homogenizing the sample material by mixing in an aluminum container. The duplicate portion of the sample will be taken from the same container as the original sample.

6 Record all pertinent information in the site log and, if appropriate, on the site map, and complete the sample analysis request form and chain-of-custody record.

7 Follow the sample documentation, packaging, shipment, and chain-of-custody procedures.

Analytical Methods for PCBs

The WESTON Analytical Laboratory used the following methods for analysis of PCB samples. Method references are to **EPA SW-846 (Test Methods for Evaluating Solid Wastes).**

I Solid and Water Analysis

- **Analytical Method - EPA Method 8080**
  This is a gas chromatographic method for analysis of PCBs in various matrices. Prior to use of this method, appropriate sample extraction techniques, as described below, are employed.

- **Extraction Methods**
  Solids: Method 3540, Soxhlet Extraction
  Water: Method 3520, Liquid/Liquid Extraction

- **Detection Limits**
  Both the extraction methods and the analytical methods referenced from above will, in most instances, yield a detection limit of 0.1 ppm with acceptable accuracy. Some matrices, such as those with a high organic and/or bituminous content, can present interferences to achieving this low detection limit.

  Appropriate "cleanup" procedures, such as the florisil method (3620) are employed to eliminate the interferences, if necessary. However, there may be instances, such as PCBs on oil-based paint surfaces or PCBs on tar-based roofing materials, where precise analysis down to 0.1 ppm is not possible. Detection limits in these cases can be in the 0.5 ppm range.

  Detection limits for wipe samples are in the 0.2 to 1.0 ug/wipe (100 cm^2) range.

II Air Sample Analysis

- **Method: NIOSH 5503**

  This is the standard NIOSH method for analysis of Florisil sorbent samples. The normal working range for this procedure yields results with a detection limit of 10 ug/m^3. There is a modification employed by Versar, Inc., in New York, in which a larger Florisil sample tube and larger air volume are employed. This can generate accurate results in the 0.1 to 1 ug/m^3 range.

III Quality Control (QC)

All standard EPA and/or Contract Laboratory Program (CLP) laboratory and field QC protocols are followed by WESTON including use of blank samples and replicate samples. These QC samples are an integral part of the analytical scheme and are important in substantiating validity of the analytical data. All sample data and QC data is reviewed and validated prior to issuing a report.

42

COMPARISON OF THE HNU-HANBY FIELD TEST KIT PROCEDURE FOR SOIL ANALYSIS WITH A MODIFIED EPA SW-846 5030/8000 PROCEDURE

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ABSTRACT

A sample generation procedure for the preparation of gasoline in soil standards was developed to produce homogeneous blends of consistent concentration and stability. Three sets of these standards prepared at different concentrations were analyzed utilizing the HNU-Hanby Field test procedure for analysis of soils and a modified EPA SW-846, 5030/8000 GC procedure. The relatively high degree of consistency of the concentrations within each set of the gasoline/soil standards allowed a statistically meaningful comparison between the accuracy of the two methods.

INTRODUCTION

Concurrent with the development of methodologies for the chemical analysis of environmental samples has, perforce, been the search for representative analytical standards. This principle, of course, is "sine qua non" to accurate chemical analysis, but probably in no case is it more de rigueur than in the analysis of soils. Soil matrices vary from relatively simple configurations, e.g. quartz sand, to those hellish quagmires we call "toxic waste sites".

This investigation focuses on a problem of sufficient magnitude to be of large scale environmental concern yet still retain tractability in an analytical sense. Underground fuel tanks are generally bedded in sandy soil, primarily, because of structural concerns for tank and associated line integrity. A procedure was developed at HNU-Hanby Environmental Laboratories which facilitated the preparation, packaging, and analysis of gasoline contaminated sand samples which could produce fairly large numbers (100-200) of homogeneous blends of the mixture at different concentrations. Three different sets of the gasoline/sand standards were prepared and subjected to analysis using the HNU-Hanby field test kit extraction/colorimetric procedure and modified EPA SW-846 5030/8000 GC methods.

PROCEDURE

An alluvial sand from a Houston nursery, typical "river bank sand", was obtained in sufficient quantity to allow for the preparation of a large number of samples for this as well as subsequent investigations. First experiments with this soil in attempts to produce homogeneous mixtures of fuel contaminated aliquots were frustratingly unsuccessful. Microscopic examination of the soil revealed that it typically contained relatively large "chunks" of clay interspersed with the more abundant quartz sand. The obvious remedy for this problem was to wash the more water-dispersive (and much more organically sorbent) clays out of the soil matrix. This washing was performed with warm laboratory tap water on approximately 25 kilograms of the soil. Subsequent drying of batches of the soil was carried out, rather tediously, in a laboratory vacuum oven at approximately 80 C and 29" Hg. A corollary effect of this vigorous approach to the removal of the clay turned out to be the sterilization evidenced by the fact that subsequent washings of the soil in de-ionized water produced no biota on filter samples cultured on M-F endo broth media plates.

Thus treated, a 2 Kg. batch of the sand was introduced into a gallon, glass screw-capped jar and placed on a small ball mill roller device. A 25 ml solution of super unleaded gasoline in methanol of approximately 10% was prepared in a 60 cc plastic syringe fitted with a 26 guage needle. This solution was sprayed through a small hole, previously drilled in the cap, as the bottle turned on the roller device. The mixture was turned for several hours with occasional hand shaking of the jar and intermittent tapping with a small wooden mallet to dislodge sand which accumulated on the sides of the jar. Observation of this decreasing tendency of the sand to adhere to the glass was used as the indication of an appropriate end point for the procedure. That is, the mixture was tumbled for approximately one hour after cessation of appreciable adherence of the mixture. The jar was then removed from the ball mill roller, and, using a specially prepared dispenser rack, the sand was very rapidly transferred to 1 dram screw cap vials which were immediately capped and placed in refrigeration at 4 C. the dispenser rack was designed to hold 24 small plastic funnels positioned over 24 of the 1 dram glass vials so that rapid removal and capping of the full vials was facilitated. A vibrator was attached to the filling rack to promote rapid funneling and settling of the sand into the vials.

Three separate concentrations of the gasoline/sand mixtures were prepared, designed to give final concentrations of approximately 500, 200 and 50 mg/kg. Twenty samples from each set (approximately 100 in each set), were randomly selected for

analysis by each of the two methods. The average weight of sample in the 1 dram vials was 6 grams. Actual weights for each sample were utilized in the calculations of concentration (mg gasoline/kg sand).

The method utilized with the HNU-Hanby field test kit is as follows:

1. Empty sample vial into the 50 ml beaker.

2. Immediately snap one 10 ml solvent ampoule from the kit and empty into the beaker.

3. Stir the sample/solvent mixture with a spatula for three minutes.

4. Pour solvent from the beaker into one of the kit test tubes up to the mark (4.2 ml).

5. Add contents of one of the catalyst vials from the kit into the test tube.

6. Shake test tube vigorously for three minutes and observe developed color in the catalyst at the bottom of the tube.

Comparisons of the color with standard gasoline in soil photographs supplied with the kit as well as with photographs made specifically to provide matches with the standard soil concentrations obtained in this investigation were facilitated by juxtaposition of the two sets of pictures with the actual test tube results. Apparent differences in hue can be seen in the color photographs accompanying this paper. These hue differences can largely be accounted for because of variable composition in the make up of the gasoline used in the original kit supplied photographs and the gasoline used in this investigation. Use of black and white photography minimizes the bias that these hue differences can cause. A quotation from MIT Professor of Physics Phillip Morrison's book The Ring of Truth is appropriate here, "...spectral photos in black white...bear the full information of the spectrum." [1].

The GC methods utilized in this investigation are adapted from the EPA SW-846 manual, 5030/8000 and from a study conducted by the Midwest Research Institute for the U.S. Environmental Protection Agency's Office of Underground Storage Tanks.[2]. The method employed the following procedures and instrumental parameters:

1. 40 ml VOC vials were placed on a top loading balance and tared.

2. A sample soil vial was emptied into the voc vial. The weight of sample was recorded.

3. Immediately, de-ionized water was added to carefully bring the meniscus of water to slightly above the voc vial top. Another weighing was recorded after this step to determine the weight (volume) of water added.

4. The vials were placed in a Fisher Scientific Bransonic ultrasonic water bath for 15 minutes, then removed to and Eberbach shaker for 30 minutes on high speed.

5. The voc vials were then analyzed on an HNU Model 421 gas chromatograph equipped with a photoionization detector connected in series with a flame ionization detector. 5 ml of water was poured from the voc vial into a gas tight syringe. This was then connected to an O.I. Corporation Model 4460A sample concentrator. The sample was sparged with helium for 11 minutes at 25 C.

The trap was desorbed at 180 C for 4 minutes through a heated transfer line to the GC. GC conditions were: 25 meter Nordion fused silica .53 mm column with a 1.0 micrometer MB 30 coating. The temperature program employed was: initial temperature 45 C, 2 minutes, then 10 C/minute to 100 C, hold for 3 minutes. Data was sent to a Spectra Physics 4270 integrator. GC parameters were initiated via an IBM PS/2 Model 70 386 channeled through the 4270.

A standard solution for calibration of the GC runs was prepared composed of the gasoline plus added concentrations of 2-methyl pentane and 1,2,4-trimethylbenzene. The GC standard curve was prepared by analysis of various concentrations of the gasoline in methanol standards which were injected through the front of the 5.0 ml sample syringe using a 10 or 100 ul syringe. Using the protocol established in the MRI study peaks considered typical of the gasoline range organics elute inclusive of and between the 2-methyl pentane and the 1,2,4-trimethylbenzene peaks. Total area counts from the FID as integrated by the SP4270 were used in this investigation. Further studies utilizing these same standards are planned which will incorporate the data from the photoionization detector which will correspond to the SW-846 5030/8020 method. A separate series of GC data charts indicate relevant quality control methods for blanks, surrogates and spiked samples.

All stock solutions, standard dilutions, and prepared soil standards were stored at 2 -4 C in a walk-in refrigerator. A primary consideration in the design of this study was the determination of the temporal stability of the soil standards. The period involved in this investigation was approximately 8 weeks. That is, soil samples were analyzed by both methods (FTK and GC) over a period of some 56 days.

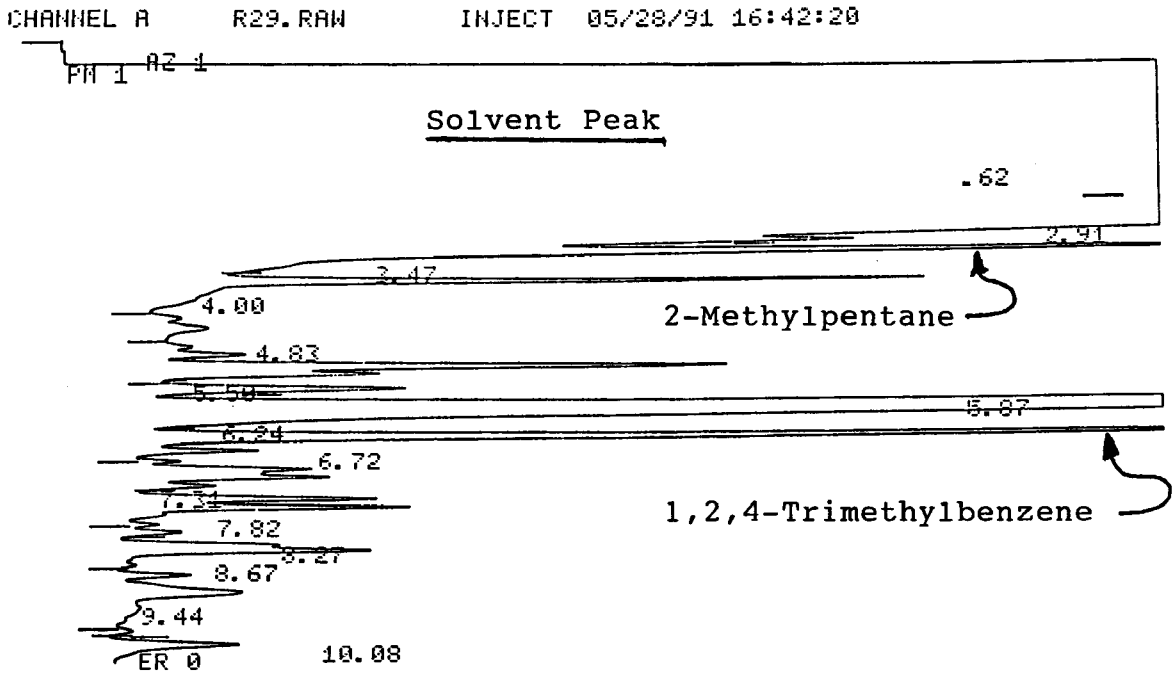
Figure 1 is a photograph of the HNU-Hanby Field Test Kit utilized in the investigation. The components pertinent to this study are the 50 ml beaker, the 10 ml solvent ampoules, the marked test tubes and the 1 dram vials of catalyst. Figure 2 is a chromatogram typical of the flame ionization detector peaks described in the report.

SUMMARY:

The utility of this method of preparation of consistently uniform samples of gasoline in soil is realized in the relatively small variability of the data obtained by both the HNU-Hanby Field Test Kit as well as the EPA purge and trap/GC methods of analysis. Correlation between the two methods themselves, in this visible comparison manner, is also evident. The gasoline range organic method of analysis as documented in the MRI study utilizing FID chromatographic detection gives consistent comparison to the test kit results even though GC method is essentially a total organic integration whereas the test kit is based on the colorimetric determination of the total aromatic components of the gasoline.

The utilization of photoionization detection being much more responsive to the aromatic components in gasoline will doubtless be even more closely correlative with this extraction/colorimetric technique. Investigations of this correlation are already underway as well as more elaborate techniques involving the utilization of reflectance spectrophotometry which, of course, will provide a means of obtaining data with the technique which will not be dependent on visual observation of relative color intensity. A study is also in process which will add a third dimension of analytical measurement, i.e., the utilization of a head space vapor technique.


HANDY ANALYTICAL LABORATORIES, INC. - FIELD TEST KIT
Aromatic Contamination in Water (PPM)*
Benzene
Toluene
Xylene
Ethyl Benzene
Gasoline
Total Volatile Gasoline
Diesel
Kerosene
Naphthalene
TOXIC
YOUR APPLICATION HERE
HANDY ANALYTICAL LABORATORIES, INC
HAL - 22B
HAL
WASTE BOTTLE
Field Measurements
Degreaser for Data Writers



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FILE 1. METHOD 0. RUN 33 INDEX 43

PEAK#	AREA%	RT	AREA	BC	
1	81.59	0.62	228452893	02	
2	7.61	2.91	21308942	02	Gasoline Range Peaks
3	1.027	3.47	2876678	02	
4	0.645	4.	1806063	02	
5	0.205	4.83	573927	02	
6	0.655	5.5	1834958	02	
7	0.17	5.87	476975	02	
8	6.17	6.24	17275023	02	
9	0.848	6.72	2373753	02	
10	0.303	7.31	847648	02	
11	0.323	7.82	905771	02	
12	0.044	8.27	122859	02	
13	0.214	8.67	599116	02	
14	0.195	9.44	544697	02	
15	0.001	10.08	2528	03	
TOTAL	100.		280001831		

1.A Sending Report...Done

Figure 2 Typical Chromatogram of Gasoline Range Organics

ACKNOWLEDGMENTS:

The authors are grateful to the U.S. EPA Office of Underground Storage Tanks and to the Midwest Research Institute, particularly Ms. Linda McConnell, for inviting this laboratory's participation in the round-robin study designed to produce a technically defensible Total Petroleum Hydrocarbon method of analysis of environmental samples.

REFERENCES:

1. Morrison, Phillip and Phylis, 1987, The Ring of Truth, Random House, Inc., New York, N.Y., p. 227.

2. Midwest Research Institute Draft Report, Nov., 1990, Evaluation of proposed analytical methods to determine total petroleum hydrocarbons in soil and groundwater, MRI, Falls Church, VA.

3. U.S. Environmental Protection Agency, SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition.

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FIELD TEST KIT FOR QUANITIFYING ORGANIC HALOGENS IN WATER AND SOIL

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ABSTRACT

In a continuing data-gathering program, the EPA monitors organic chemicals in the waters of the United States. The list of monitored chemicals includes both aliphatic and aromatic hydrocarbons, pesticides, industrial chemicals, plasticizers, and solvents. Many of these materials are halogenated, produced by chlorination of water during purification processes, through industrial and municipal runoff, natural sources, and sewage purification practices.

Chlorine is a contaminant often found in oils, soils, sludges, and organic liquids found at hazardous waste sites. Controlling wastewater discharges and landfilling of chlorinated compounds have become priority issues for EPA since the passage of the Hazardous and Solid Waste Amendments of 1984.

In response to toxicological and environmental concerns of trihalomethanes and other halogenated compounds present in water and soil, a quick, accurate, easy to use, portable field test kit has been developed for quantifying organic halogens. The analytical procedure requires an extraction with a suitable solvent, followed by colorimetric chemistry to quanitfy the organic halogens present.

This paper will detail field and laboratory results, limits of detection, matrix effects, and cost analysis.

INTRODUCTION

EPA regulation 40 CFR 261 establishes that any used or waste oil containing greater than 1000 ppm organic chloride may have to be classified as a hazardous waste. Chlorinated solvents are the primary contaminants found in waste oils and oily wastes.

Currently available instrumental methods of chlorine analysis (microcoulometric titration, X-ray fluorescence spectometry, oxygen bomb combustion and gas chromatography) are time consuming and must be performed in a laboratory by trained technicians. Foreseeing the additional testing that would be required under the new regulations, the EPA Region II contracted Dexsil Corporation to develop a field-portable test kit that could be used by untrained personnel. The result was two small, disposable test kits that require less than five minutes to determine chloride contamination in waste oil. The first method is a go/no-go test, indicating over or under 1000 ppm chloride. The second method is a quantitative analysis giving an amount of contamination between 200 - 4000 ppm.

These test kits were evaluated by Research Triangle Institute (Raleigh, NC) for EPA and were found to be acceptable methodology for chlorine detection. As a result, the kits were assigned EPA method 9077, to be published in the upcoming SW-846 manual. Interest has since increased in a test kit that would work on oil containing large quantities of water (oily waste) and, in light of the current regulations pertaining to leaking underground storage tanks, it would be useful to have a kit that would detect total organic halogens in soil. Two field-portable test procedures have been developed which address these issues of halogens in wastewater, oily waste, and soils.

The different methodology and apparatus will be described, the accuracy and precision of each method discussed and the costs of each method reported.

USED OIL CONTAMINATION

How do chlorinated solvents contaminate used oil? Chlorinated solvents are not ingredients of crankcase oil, but are indirectly introduced through careless management practices, such as pouring used degreasing and cleaning solvents into used oil storage drums. The most common solvents found in waste oils are dichlorodifluoromethane, trichlorotrifluoroethane, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene (1). Levels of contamination range from 100 ppm to thousands of ppm. The possible presence of chlorinated solvents can be flagged by checking total chlorine, an indicator of the potentially hazardous chlorinated substances present.

The EPA estimates that over 350 million gallons or about 30 percent of all used oil is landfilled or dumped annually. Approximately 160 million gallons comes from the "do-it-yourself" oil changers, who typically dispose of their oil by dumping it on the ground, in sewers, or in waterways, or by placing it with the household trash destined for a landfill that has not been lined to protect against soil and groundwater contamination. The remaining 190 million gallons is dumped or landfilled by automotive shops and industrial facilities. (2)

OILY WASTE SOURCES

Sources of oily waste include bilge and ballast, rain runoff, washings from cleaning vehicles and tanks, and cutting oils. All of these materials are predominantly water, containing from 0.1 to five or ten percent oil.

Bilge oil is a mixture of fuel oil, lubricating oil, and hydraulic oil dispersed in sea water along with dirt, rust, and bacterial sludge. Ballast oil composition depends on what is carried in the ballast tanks when the ship is not in ballast, usually fuel oil, crude oil, or petroleum products. The oil will usually exist as free oil droplets in the seawater, or as a sheen on the water surface.

Rain runoff that carries oil from contaminated areas often cannot be legally discharged to storm sewers. Trucks and fuel storage tanks are cleaned with water containing detergents. This produces oily water containing solids, emulsions, free oil, dissolved oil, and detergents. Metalworking fluids are used for both lubrication and cooling in various machinery processes such as cutting and grinding. Oily waste resulting from used oil mismanagement causes damage to streams, ground water, lakes, and the oceans. For instance, the Coast Guard estimates that sewage treatment plants discharge twice as much oil into coastal waters as do tanker accidents - 15 million gallons per year versus 7.5 million gallons from accidents. A major source of this pollution is dumping of oil by do-it-yourselfers into storm drains and sewers. A startling example of this has occurred in the Seattle area, where more than 40 percent of the water quality trouble calls received are related to used oil and other wastes dumped down storm drains, contaminating water bodies (3).

ENVIRONMENTAL IMPACT

Many contaminated sites containing oily wastes and oily waste sludges are now being cleaned up under authority of Superfund. The Superfund regulations affect the handling of oil wastes in the areas of spills and accidental releases, leaky storage tanks, and abandoned storage facilities. Oils from abandoned storage facilities fall into one of three catagories: Abandoned tank pumpings, abandoned drummed oils, or sludge pit residues (4).

The composition of the oils in each of these catagories can vary significantly from site to site. Over time, the oils in tanks and drums absorb material from the walls of the container. This process is exacerbated by corrosion due to seasonal temperature variations, rain, mechanical abrasion, and the like. The oils are usually significantly diluted by water infiltration. In order to fall under Superfund jurisdiction the sites must present a danger to the public or the environment. Thus the emphasis is on the quick and inexpensive analysis and disposal of the materials, rather than on recycling and reuse (5). Ideally, hazardous waste determinations, whenever possible, should be carried out in the field to quickly identify the extent and magnitude of the contamination. The advantages of alternative simple chemical tests have been foreseen by the EPA and some procedures have, in the face of alternative instrumental methods, been examined and subsequently become EPA approved.

A CHEMICAL METHOD FOR THE DETERMINATION OF ORGANIC HALOGENS IN WASTEWATER, OILY WASTES AND SOILS

This procedure requires an extraction with a suitable hydrocarbon solvent. Covalently bonded halogens present in the hydrocarbon solvent are then stripped from their solvent backbones by sodium metal according to the Wurtz reaction:

$$2Na + 2R\text{-}X \longrightarrow 2NaX + R\text{-}R$$

Any halogens that are present (now in ionic form) are extracted into an aqueous buffer, to which is added a color reagent to quantitate resulting chloride. A solution of mercuric nitrate is added dropwise until a color change from yellow to purple is realized, and the concentration (in ppm) is read directly off the dropper.

ANALYTICAL METHOD

1/Method for Samples Containing Water

10 ml of the liquid sample is extracted by shaking for one minute with 10 g of an immiscible hydrocarbon and 0.5 g of a (granular) emulsion breaking material. The sample is allowed to settle until it has separated into distinct phases (about three minutes). Approximately one-third of the top layer is dispensed into a vial containing a drying agent which will remove any moisture and inorganic chloride. The vial is shaken and the drying agent is allowed to settle. 0.34 g of the dried solvent is then treated with 1.5 ml of a solution of naphthalene in ethyl diglyme followed by 0.4 ml of organic dispersion and metallic sodium, and shaken for 1 minute. 7 ml of buffer solution is then added and the aqueous layeris separated and combined with 0.5 ml of a solution of s-diphenyl carbazone in alcohol. A solution of mercuric nitrate is added dropwise from a 1 ml microburette. When a true purple color is realized, the test is stopped and the chloride concentration of the original oil/water or wastewater sample is read directly off the microburette.

2/Method for Soil Samples

10 g of the soil sample is extracted by shaking for one minute with 12 ml of a mixture that contains 2 ml of distilled water and 10 ml of an immiscible hydrocarbon. The soil is then allowed to settle and the supernatent liquid filtered through a column containing florisil to remove any moisture and inorganic chloride. 0.34 g of the dry filtrate is then treated with 1.5 ml of a solution of naphthalene in ethyl diglyme followed by 0.4 ml of organic dispersion and metallic sodium, and shaken for 1 minute. 7 ml of buffer solution is then added and the aqueous layer is separated and combined with 0.5 ml of a solution of s-diphenyl carbazone in alcohol. A solution of mercuric nitrate is added dropwise from a 1 ml microburette. When a true purple color is realized, the test is stopped and the chloride concentration of the original soil sample is read directly off the microburette.

ANALYTICAL TESTS, RESULTS AND DISCUSSION

The samples chosen were both laboratory mixtures and Superfund samples containing a range of 125 ppm to 6500 ppm chloride. The procedures employed are the same as those previously described except a packed kit was used (HydroClor-Q™, Dexsil, Hamden CT). All reactions with this kit are carried out in sealed plastic tubes and all reagents are contained in crushable glass tubes to obviate any need to handle the reagents. This is advisable, as some of the reagents are hazardous to handle in the normal manner. The results obtained from the laboratory samples are shown in table (1) and table (2), and the results from the Superfund samples are shown in table (3). All three tables include results from the microcoulometric titration (EPA method 9076) of the same samples.

It is seen that the results from both the test kit and the microcoulometric titration of the samples agree very reasonably. It is also clearly demonstrated that no interference occurs in the presence of inorganic chloride. Laboratory soil samples were also tested in the same manner using an analytical kit (Dexsil, Hamden CT). This is a similar type of kit to the one used for liquids, but also provides a simple balance for weighing out the soil. The procedures previously described were used and the results obtained for wet and dry soils are shown in table (4) and the results for wet and dry sands are shown in table (5). Microcoulometric titration results of the same samples are shown in each table and it is seen that agreement is good between the two methods.

The cost of each kit is $10-13 and no capital investment in instruments is needed. The kits can readily and easily be used in the field and little skill is needed. The test takes about ten minutes. With increasing testing requirements, laboratory fees and laboratory turn-around times, the field-portable chemical test with colorimetric end-point would be the first choice for a suspect site or container, prior to laboratory analysis.

REFERENCES

1/Guide to Oil Waste Management Alternatives, Final Report, p. 4-15, Energy and Environmental Research Corporation, Irvine, CA, April, 1988.

2/Nolan, J.J., Harris, C., and Cavanaugh, P., Used Oil: Disposal Options, Management Practices and Potential Liability, 2nd Ed., p. 12, Government Institutes, Inc., Rockville, MD, 1989.

3/How to Set Up a Local Program to Recycle Used Oil, EPA Rept. No. 530-SW-89-039A, p. 1, U.S. EPA, Washington, D.C., May 1989.

4/Guide to Oil Waste Management Alternatives, p. 4-30.

5/Guide to Oil Waste Management Alternatives, p. 4-31.

TABLE 1

COMPARISON OF LABORATORY PREPARED SAMPLE ANALYSES:
MICROCOULOMETRIC TITRATION vs HYDROCLOR™

Sample	Hydroclor™	Microcoulometric Titration
2000 ppm Cl^- as $Cl_2C_2Cl_2$ in 1% oil in pond H_2O	2000 ppm 2500 ppm	1980 ppm 2460 ppm
2000 ppm Cl^- in previous matrix + dirt	2250 ppm 2275 ppm	2250 ppm 2210 ppm
1000 ppm Cl^- as $C_6H_3Cl_3$ in 1% oil in pond H_2O	900 ppm 1050 ppm	760 ppm 980 ppm
1000 ppm Cl^- in previous matrix + dirt	850 ppm 900 ppm	849 ppm 897 ppm
1000 ppm Cl^- as $CHCl_3$ in 1% oil in pond H_2O + 4000 ppm Cl^- as NaCl	900 ppm 975 ppm	996 ppm 959 ppm
1000 ppm Cl^- in previous matrix + dirt	1000 ppm 900 ppm	936 ppm 871 ppm

TABLE 2

COMPARISON OF LABORATORY PREPARED ANTIFREEZE SAMPLE ANALYSES: MICROCOULOMETRIC TITRATION vs HYDROCLOR™

Matrix	Microcoulometric Sample	Titration	HydroClor™
Tetrachloro-ethylene in antifreeze/H_2O	2740 ppm	2690 ppm	2900 ppm
	2670 ppm	2760 ppm	2850 ppm
Same	1230 ppm	1280 ppm	1200 ppm
	1140 ppm	1280 ppm	1350 ppm
Same	481 ppm	535 ppm	500 ppm
	444 ppm	548 ppm	500 ppm
Trichloro-ethylene in antifreeze/H_2O	3000 ppm	2810 ppm	3000 ppm
	3000 ppm	2800 ppm	3100 ppm
Same	1200 ppm	1120 ppm	1200 ppm
	1200 ppm	1160 ppm	1250 ppm
Same	451 ppm	509 ppm	600 ppm
	462 ppm	521 ppm	600 ppm
1,2-Dichloro-ethane in antifreeze/H_2O	2950 ppm	2820 ppm	3300 ppm
	2800 ppm	2800 ppm	3300 ppm
Same	1400 ppm	1370 ppm	1550 ppm
	1490 ppm	1410 ppm	1600 ppm
Same	697 ppm	693 ppm	800 ppm
	711 ppm	671 ppm	800 ppm
1,2,4-Trichloro-benzene in antifreeze/H_2O	3260 ppm	2880 ppm	2800 ppm
		2940 ppm	2800 ppm
Same	1400 ppm	1510 ppm	1500 ppm
	1640 ppm	1620 ppm	1500 ppm
Same	812 ppm	857 ppm	800 ppm
	791 ppm	856 ppm	825 ppm
Chloroform in antifreeze/H_2O	3090 ppm	2930 ppm	2900 ppm
	2930 ppm	2930 ppm	2800 ppm
Same	1300 ppm	1410 ppm	1400 ppm
	1310 ppm	1440 ppm	1350 ppm
Same	728 ppm	732 ppm	800 ppm
	718 ppm	730 ppm	725 ppm

TABLE 3

COMPARISON OF LIQUID SUPERFUND SAMPLE ANALYSES:
MICROCOULOMETRIC TITRATION vs HYDROCLOR™

Sample	Microcoulometric Titration	HydroClor™
TX - 563 ppm	230 ppm	200 ppm
TOX - 242 ppm	242 ppm	200 ppm
TX - 604 ppm	417 ppm	300 ppm
TOX - 315 ppm	396 ppm	350 ppm
TX - 2260 ppm	1187 ppm	1350 ppm
TOX - 1400 ppm	1425 ppm	1400 ppm
TX - 1910 ppm	1539 ppm	1600 ppm
TOX - 1690 ppm	1518 ppm	1700 ppm
TX - 6420 ppm	5750 ppm	5800 ppm
TOX - 5690 ppm	5900 ppm	5600 ppm
TX - 4940 ppm	3270 ppm	3600 ppm
TOX - 3980 ppm	3870 ppm	3400 ppm
TX - 1560 ppm	774 ppm	900 ppm
TOX - 712 ppm	748 ppm	800 ppm

TABLE 4

COMPARISON OF LABORATORY PREPARED SOIL SAMPLE ANALYSES:
MICROCOULOMETRIC TITRATION vs SOIL FIELD TEST KIT

Sample	Soil Kit	Microcoulometric Titration
500 ppm Cl^- in dry soil	600 ppm 500 ppm	515 ppm 509 ppm
600 ppm Cl^- in dry soil	650 ppm 650 ppm	635 ppm 624 ppm
700 ppm Cl^- in dry soil	850 ppm 650 ppm	700 ppm 727 ppm
800 ppm Cl^- in dry soil	800 ppm 800 ppm	784 ppm 790 ppm
900 ppm Cl^- in dry soil	950 ppm 900 ppm	931 ppm 948 ppm
1000 ppm Cl^- in dry soil	1000 ppm 950 ppm	960 ppm 979 ppm
1500 ppm Cl^- in dry soil	1500 ppm 1450 ppm	1450 ppm 1490 ppm
500 ppm Cl^- in wet soil	500 ppm 450 ppm	558 ppm 595 ppm
600 ppm Cl^- in wet soil	700 ppm 650 ppm	689 ppm 719 ppm
700 ppm Cl^- in wet soil	750 ppm 800 ppm	654 ppm 677 ppm
800 ppm Cl^- in wet soil	800 ppm 800 ppm	861 ppm 883 ppm
900 ppm Cl^- in wet soil	900 ppm 950 ppm	960 ppm 946 ppm
1000 ppm Cl^- in wet soil	1100 ppm 1000 ppm	1070 ppm 1080 ppm
1500 ppm Cl^- in wet soil	1600 ppm 1600 ppm	1520 ppm 1520 ppm
2000 ppm Cl^- in wet soil	2050 ppm 2000 ppm	1860 ppm 1910 ppm

TABLE 5

COMPARISON OF LABORATORY PREPARED SAND SAMPLE ANALYSES:
MICROCOULOMETRIC TITRATION vs SOIL FIELD TEST KIT

Sample	Soil Kit	Microcoulometric Titration
300 ppm Cl^- in wet sand	350 ppm 300 ppm	312 ppm 315 ppm
400 ppm Cl^- in wet sand	400 ppm 450 ppm	421 ppm 429 ppm
500 ppm Cl^- in wet sand	500 ppm 550 ppm	452 ppm 457 ppm
500 ppm Cl^- in dry sand	400 ppm	533 ppm 528 ppm
600 ppm Cl^- in wet sand	575 ppm 650 ppm	633 ppm 632 ppm
700 ppm Cl^- in wet sand	775 ppm	823 ppm 812 ppm
1000 ppm Cl^- in dry sand	1050 ppm 1050 ppm	1110 ppm
1186 ppm Cl^- in dry sand	1200 ppm 1250 ppm	1220 ppm
1200 ppm Cl^- in dry sand	1200 ppm	1200 ppm 1200 ppm
1500 ppm Cl^- in dry sand	1500 ppm 1550 ppm	1570 ppm 1510 ppm
2000 ppm Cl^- in dry sand	1800 ppm	1880 ppm