PROCEEDINGS

9th Annual
Solid Waste Testing
and
Quality Assurance Symposium

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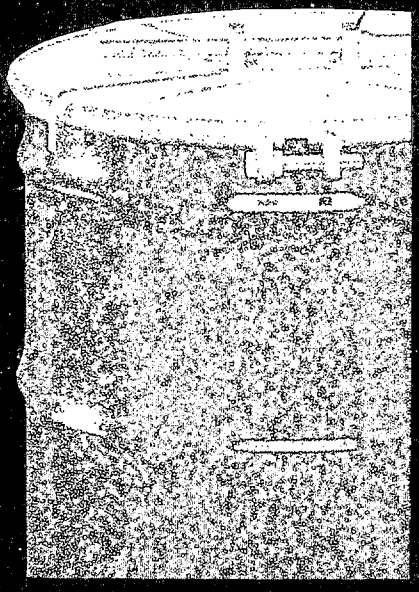
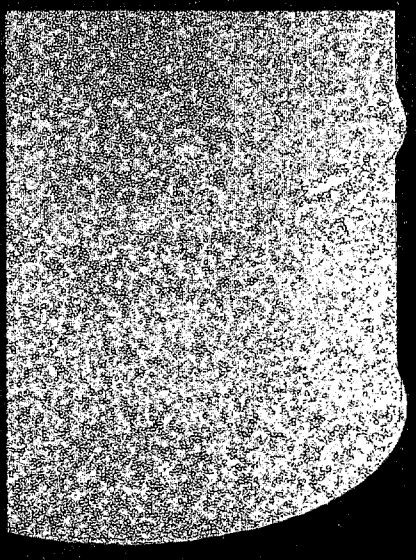


PROCEEDINGS

9TH ANNUAL WASTE TESTING & QUALITY ASSURANCE SYMPOSIUM



JULY 12–16, 1993
HYATT REGENCY CRYSTAL CITY
ARLINGTON, VA

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CURRENT TRENDS AND USES OF PERFORMANCE EVALUATION MATERIALS IN THE SUPERFUND CONTRACT LABORATORY PROGRAM

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Good day, I'm Jim Barron with the Analytical Operations Branch (AOB) of the Hazardous Site Evaluation Division. Our group manages some of the analytical services utilized by Superfund, including the contract laboratory program commonly known as the CLP. This includes a comprehensive Quality Assurance program. One facet of this program is ensuring an adequate variety of Performance Evaluation Materials (PEMs), also referred to as Performance Evaluation Samples (PES). Historically, PES have been used by government agencies for several purposes.

1. Multi-laboratory Validation Studies for validation of analytical methodology.

2. In the form of Blind PES for Laboratory Certification.

3. In an on-going Quality Assurance (QA) Program.

The CLP uses PES for all three purposes. PES are prepared to support inter-laboratory studies to validate CLP Statements of Work (SOWs). The Laboratories are required to participate in pre and post-award performance sample studies to maintain contract status, the so-called "de facto certification program." We consider number 3, the PES we provide for routine assessment of data, the most important part of our program. I'd like to discuss some of the trends we see in the use of these materials in environmental work, and some of the approaches we are taking in our program. We feel we have addressed on a smaller scale many of the questions EPA will to consider as it looks toward a national laboratory certification program.

The Analytical Operations Branch has established and operates a Superfund Performance Evaluation Sample Repository through it's Quality Assurance Technical Support Laboratory in Las Vegas. The Superfund Performance Evaluation Sample Repository was established in response to general and specific requests from Regions for an independent and relevant mechanism to monitor laboratory performance in the analysis of environmental samples from known and suspected hazardous waste sites. A wide range of performance evaluation samples is available at no cost to the Regions to support their needs for independent and external monitoring of laboratory performance in the analysis of environmental samples in the Superfund Program.

A key part of AOB's program is that it does not normally distribute standards or Laboratory Control Samples, it distributes PES materials to monitor analytical work where the government has a strong interest in determining the quality of the data it is paying for. Some exceptions are LCS'es such as the Interference Check Samples run to determine interferences in trace level metal analysis, and the multi-parameter LCS'es used in some Statements of Work.(24, 26) Available performance evaluation sample types are water and soils matrices. Performance evaluation samples for air analysis have been under development, but work has stopped due to lack of regional interest. Analytes incorporated into these samples include volatile and semi-volatile organic compounds, pesticides and PCBs, metals, anions, cyanide, and chlorinated dioxins and furans. Stability studies are run are archived on PES to ensure values are still within the statistical windows established for the particular PES. Regions select the type of performance evaluation samples

most suited to their needs from a widely distributed catalogue.(20)

Through the Superfund Performance Evaluation Sample Repository, the Analytical Operations Branch also provides related support services to the Regions. A PC-based tracking system PEACTOOLS has been developed, and is distributed to the Regions for use in assessing the analytical results for performance evaluation samples reported by laboratories. Using this system, Regional data reviewers evaluate laboratory performance on a particular set of environmental samples as soon as the data package is received. These evaluations also provide important documentation of data quality, when the PE sample is related to the site. Through the Superfund Performance Evaluation Sample Repository, Regions can also obtain assistance in establishing and operating their own performance sample repository which can serve regional needs in monitoring analytical work done for the Superfund Program.

AOB gets support and oversight from ORD at Las Vegas for it's program. In so far as possible we attempt to obtain real world materials from sites to prepare PEMs, however we also purchase neat materials and prepared sets from commercial vendors.

We prepare PES for contract compliance, in our quarterly blind program (Qbs) and for routine monitoring of data collection activities. In both types of samples, concentrations and recipes of the analytes support CLP, and other Superfund work. Our quarterly blind samples are the typical single blind PES supplied by most programs for certification. Some of our Qbs are solids, but several years ago we went from full-volume liquid samples to ampuled samples, because of problems in the samples, and to cut costs. It costs about 10 more to prepare full volume samples compared to ampulated samples. However AOB was aware of the pitfalls of ampulated PES already being used by other EPA certification programs. The first problem is the laboratories may run the ampuled sample concentrate undiluted, the second is calling around to compare answers, and third expending much more time and effort on these types of samples, then the laboratory would on a routine sample. Some parties have recently come out of the closet, admitting the excessive time spent on this type of sample, and possibly running the ampule straight ( ). The problem we found is the labs do not regard this as cheating,just an annoyance they must get through to stay certified. Calling around is probably more of a problem with government laboratories, where there is a more collegial atmosphere, than the commercial sector, where loss of certification by some laboratories, means more business for the successful labs.

What can be done about this problem? One answer is to give less importance to the do or die "Certification PES." Another is to send out different PESs to labs in the same study. However as noted we do not consider answer comparing a problem in the CLP, since we have companies with multiple laboratories, with one laboratory in the group failing a QB, while the rest pass. In any event we do not have sufficient Laboratories to use two sets, since our Qbs are scored on a statistical basis. A third approach AOB has completed is to develop indicator compounds that can be added to the ampulated PES samples.(1,2) This insures an aliquot will be removed from the ampule, diluted to the proper volume, and run according to the Statement of Work the laboratory is trying to be certified for. To be useful as indicator compounds, for contract compliance, analytes must possess these characteristics:

- Must be Stable in the test solution matrix
- Must be detectable by GC/MS when directly injected from ampule.
- Good Chromatography when directly injected and when run from normal extract
- Must be degraded or poorly recovered by the sample preparation technique used.
- Must be a clearly detectable difference in the results by direct injection and normal preparation.

Most of the people in our branch our experienced environmental chemists. While a preliminary study to pick candidate indicator compounds included VOCS, our experience we reasoned that probably no tries to run the ampule for VOCs, since this could produce a worse answer, that running it properly. This leaves Semi-volatiles, metals and pesticides. The first group picked were the semi-volatiles.

Chemical	CAS number
1-Hexanamine	111-26-2
Cyclohexalamine	108-91-8
2-Propenamide	79-06-1
1,3-Benzenediol	108-46-3
Phthalic Anhydride	85-44-9
Nicotine	54-11-5
Di-n-hexylamine	143-16-8
Simazine	122-34-9
Norflurazon	27314-13-2

The above are some of the materials we decided to test as indicators, that were selected from a larger list.(2) Our reports are available to parties who wish to design their own Indicator program. Since we now use continuous liquid -liquid extraction at a low Ph we narrowed the field quickly. Interestingly enough the compound we may use is nicotine. This was accomplished since the CLP requires identification of tentatively identified compounds (TICs). Since the laboratories did not identify all the materials, it was necessary to run tape audits on the raw data. EPA, EMSL-LV helped us with tapes for GC/MS Systems we did not have equipment for. There were other logistics involved, such as picking which internal standard to us with which indicator. The next group we are going to work on are the metals. The task will in effect reverse the work we did in developing interference check samples,(3,4)) by adding those interferents at levels that must be diluted to the proper volume, to be able to identify target analytes. At present the Pesticides offer no easy solution, since they are done by Gas Chromatography. The course we are following here is to build on work done by the Office of Drinking Water, in developing method 525, and try to achieve low enough quantitation limits, so all Target Compound list Pesticides could be run by GC/Mass Spectrometry. This would enable us to also develop indicator compounds for the Pesticides.(34) Indicator compounds are not an absolute determinant of fraud, but they are one more tool to ensure data integrity.

The CLP Quarterly Blind PE Sample Study data does have other uses besides contract compliance:

- **CLP Laboratory Performance Measurement** - This is the primary mission of the PE Study Program. All labs are measured against an independently prepared research mixture.

- **Surrogate Optimization**- Compounds added to the PES are checked for correlation to the Target Compound List, to find new surrogates which can give better analyte recovery information.

- **Feasibility of Target Compound List additions** - The QB studies have been used to determine how well SOW perform with new analytes which have become candidates for addition to the Target Compound List.

- **Method Performance Reports** - Because the QB samples are uniform samples which are sent to all laboratories, inter-laboratory precision and accuracy is determined.

- **Extraction Method Comparison** - QB sample results allowed a comparison between Separatory funnel versus continuous extraction techniques for semi-volatiles, which are now used exclusively in the CLP.
- **Laboratory Performance Database** - The QB results are part of a laboratory performance database to determine overall performance of a Contract Lab. (21)

Failure to analyze the Quarterly Blind sample correctly, results in suspension of the laboratory until a remedial PES is successfully analyzed. When statistically derived precision windows are used, as in this case, a certain percentage of laboratories in the study will fail. This does not mean the data previously produced by the laboratory is in question, unless the PES results show a trend of unacceptable performance.

In the near future the so-called national certification PES may not be that important to the CLP. CLP Routine Analytical Statements of Work (SOW), now being utilized, or in the testing phase (see table 1.) shows, are more specialized, and may only have one laboratory supplying that service. For these SOWs

Table I.
Performance Evaluation Sample Use.

	Types and Recommended Frequencies of PES		
Document/Reference number.	LCS (Zero-blind) (1)	Single or Double Blind (2)	Contract Action for Poor Performance on PES
CLP Low Concentration Water/22	by the Sample Delivery Group (SDG)	by the SDG	yes
CLP Quick-Turn-Around Methods/24	Special, multi-param		yes
CLP Dioxin Furan/23	by the SDG or use >	by the SDG	yes
CLP High Concentration Inorganic/28	by the SDG	by the SDG	yes
CLP High Concentration Organic/29	by the SDG	by the SDG	yes
CLP Low-Medium Inorganic/30	by the SDG		yes
CLP GeoTechnical/26	Special, multi-parameter PES		yes
CLP Water and Soil Characterizat./25	by the SDG	by the SDG	yes
CLP Quick Turnaround Dioxin/31		by the SDG	
CLP Air Toxics./27	inorg., by SDG	By the SDG, All Org. could be double-blind, on all types of samplers, i.e. Tedlar bags, PUFs.	yes

(1) All liquid samples are ampuled, all soils homogenized
(2) Single-blinds, all liquid samples are ampuled, all soils homogenized
Double-blinds, all liquids are full volume, soils are not homogenized

the project officer can have the laboratory run up to 5% PES.(35) He has the option of inserting them as double-blind, that is appearing to be a routine sample. However these "by the case" PES have their own set of problems as we are finding out with our Dioxin/Furan SOW. Our Dioxin/Furan PES were our best set of PEMs, all made from materials and hot spots obtained from Dioxin sites, with real world intereferents such as PCBs present. We've now gone through our entire set, and need to reblend the PES to produce new concentration levels. Recent catalogues received from commercial vendors indicate they are also addressing the problem of PES recognition.(32) Laboratories keep track of PES, and will compare old results with the latest PES.

This last problem pits two schools of thought on PES, used on a daily basis, or by the case, to assess the quality of environmental data. The first group seems to feel that PES should have extensive multi-laboratory validation, producing somewhat tight windows for bias and precision, resulting in fairly static recipes due to cost. The second, which AOB subscribes to, feels PES should be economical, readily available, and in a wide variety of realistic materials, representing the matrices and analytes being monitored. Recipes should be changed frequently. While the PES should evidence sufficient statistical control to assess the analytes of concern, it isn't necessary to have NIST grade materials.
As noted above, AOB distributes a variety of multi-Media PES For both CLP and non-CLP work. Initially PES are produced to support a proposed SOW. As is often stated PES should be similar to samples collected from a waste site, contain interferences relevant to the samples being analyzed, contain analytes, and concentrations approximate the range found in actual environmental samples. An initial workplan for concentrations and recipes of analytes expected to be monitored under the proposed SOW is prepared. For an interlaboratory study the PES are then made or purchased according to the workplan. These PES materials will continue to be made an utilized if the SOW goes into effect. The categories of PES AOB distributes or is working on include:

CATEGORIES OF PES DISTRIBUTED OR BEING DEVELOPED BY AOB
CLP Organic Low/Medium, Low Con., High Con, Target Compounds, and TICs
CLP Inorganic Low/Medium, Hicon, Target compounds
SITE-CHARACTERIZED PES, Analytes typical of the site
SITE CATEGORIZED (INDUSTRIALLY) PES, Analytes typical of that industry
DIOXIN/FURANS
QUICK TURN-AROUND PES, Really multi-parameter Laboratory Control Samples
GEOTECHNICAL PES, Really multi-parameter Laboratory Control Samples
FIELD ANALYTICAL METHODS

We don't plan to cover every type of PES that could be produced, for example a frequent Special Analytical Services request are the traditional water quality parameters. We wouldn't stock these since they have been available for a long time commercially, with good quality.

PESs are one of the few external QA/QC measures for independent monitoring of laboratory performance and demonstration of data comparability among laboratories. When the PE is site related, it documents the quality of analytical results generated in the Superfund program, for that site. Under the Superfund Accelerated Cleanup Model (SACM). the Office of Emergency and Remedial Response is attempting to reduce duplicative site investigations. However this may reduce the redundancy of data making an external QC indicator such as PE samples more important. Another Superfund initiative has been a change in the delivery of analytical services, with more analytical resources being placed in the region. With the increase in the use of non-CLP laboratories, field analytical procedures, and mobile laboratories, the availability of PES validated by fixed laboratory methods would allow for data

comparability.(36)

When we first set up our PES repository at Las Vegas, the philosophy was to have good range of PES in regard to matrices, analytes present, and concentration ranges. We set up a scoring program PEACTOOLS, which would score PES on a go/no basis. This was to be a fairly static operation. This is no longer viable, and we are now planning to shift recipes and concentrations on a regular basis, with more emphasis on site characterized PES.

Double-blind PES like site characterized or site specific materials, are the optimal type of PES, if available. They constitute a PES, which the laboratory feels is a routine sample, and does not put forth that extra effort associated with single-blind PES. Some matrices lend themselves to double-blinds better than other matrices. Solids are the most desirable matrix for double-blinds for Superfund, but they are also the most difficult to produce. Attempting to manufacture a solid where there is some statistical reliability of the concentrations of analytes invariably leads to homogenization, allowing the sample to be recognized as a PES.

There does not appear to be great difficulty in preparing water soluble analytes, so metal samples and the so-called Water Quality Parameters do not present a major problem. (7) More extensive stability studies are needed for this matrix to determine "shelf life." Some work has been done in the regions with Volatile Organic Compounds (VOCs). AOB is recommending the regions follow the work done by Oak Ridge National Labs in preparing double-blind VOC's in water.(14) AOB's QATS laboratory has recently been able to duplicate the results of work done by the US Army's CRREL group. This involves preparing VOCs on soil.(15,16) Because of the shelf life of these materials we are recommending they be prepared at the regional level, from materials in Regional PE repositories. One problem noted in preparing double-blinds using site-characterized materials for metals, was particle size. This was predicted from other work, but verified by analytical results. This has spun off another project to determine if sample sizes for metals should be changed of be more flexible. This work will also have application to field analytical procedures, where analytical results are also affected by particle size.

Air Samples lend themselves to double-blinds, as they are trapped in canisters, or bags or on solid matrices such as Poly-Urethane Foam (PUFs) or Tenax. In practice, real samples are indistinguishable from the PES. Again, a major need in this area is stability studies to determine shelf life. The only air parameter we get requests for are double-blinds prepared on PUFs for pesticides and Dioxin. Except in very specialized case we feel these types of PES should be prepared in the Regions.

The problem of double-blind solids PES is still difficult at this point. A sample that has been homogenized by particle size is immediately recognizable as a PE. Samples which have been thoroughly mixed, but not sized, require sample weights far above those specified in most methods to overcome the effects of particle size on concentration. The type of double-blind that seems to hold the most promise at this time are site characterized materials, mentioned below, that is materials that are obtained from a site, spiked and homogenized, but not sized, and returned to the site, to be submitted blind as part of the regular sample stream.

What has become apparent through workgroup meetings and conferences on PES and Site-characterized materials, is that environmental personnel are not concerned if they get a "NIST Grade" materials for this type of sample. The higher priority is being able to assess data quality in a timely manner at a reasonable cost, and realistic time frames.

An impediment to producing double-blind aqueous semi-volatile organic PES is more administrative than technical. As parties have commented, returning to one liter bottles instead of the two and four liter bottles commonly used, with rinsing of the container to collect materials that may have plated out on the glass,

would allow greater accuracy in determining this type of PES. As one commentator noted, this would also correct an obvious negative bias in real samples. Double-blinds should approximate the environmental sample in water color, and turbidity, or soil color, texture, particle size range and even % moisture. Containers should be the same as being used by the sampling team, and obtained from them in advance. The references, and anecdotal information indicate double-blind PES are being prepared and utilized on a more frequent basis than in the past.

We have done a study comparing our Contract Required Quantitation limits for target compounds against actual results in our analytical results database, and with values decided on in Records of decision, and the PRG cancer and non-cancer values for those analytes.(5) This has become part of our Pesticide task mentioned above, to see at what levels we can get good quantitation for important analytes, and has led us to re-evaluate our whole PES library. While we will probably not change our CLP CRQLs, the PES do support other Superfund work where lower quantitation levels are needed.(6) This latter work assignment actually complements our efforts to convert our CLP pesticides to GC/MS.(34)

Whether single or double-blind samples, we try to prepare site-oriented materials. AOB doesn't prepare site-specific materials per se, only when its a large enough project to a have a surplus as site-characterized materials. Before we get cited for not explaining sites, our perception of these materials is:

"SITE PES"
SITE SPECIFIC PES: materials obtained from "hot spots" at a waste site, possibly spiked with additional typical contaminants being found at that site.
Site Characterized PES: may be site specific materials, but the surplus can be used at sites with similar matrices.
SITE CATEGORIZED PES: Synthetic PES prepared using information obtained from CARD and the NPL databases, according to the industrial category of that site.

We think the Site Categorized PES is one of the more interesting projects we have worked on is our effort to develop industrially categorized site An other branches in our division has categorized waste sites on the NPL by the industrial category they fall under, i.e electroplating. Searching our databases we are able to identify the cases associated with those sites, and pull down the samples associated with those cases. From our CARD database we can get the sample results for the types of contaminants and their concentration ranges. This allows us to prepare synthetic single blind materials that are typical of waste sites, and in the absence of real world materials allows a project manager some means to assess the quality of a laboratories data. There are 45 categories, but we may find enough overlap in analytes lists between related categories, that we would only develop one set of PES to use for both sites.

Typical Information From the Databases for PES Design			
Industry	Sites on the NPL	Number of Cases	Number of Cases in CARD
Manufacturing, Gen.	683	286	59
Electro-plating	79	32	10
Fabricated Metal Products	136	53	14

A project we have provided assistance to in Region X, seems to indicate, at least for long term projects, site characterized materials can be prepared economically, and in a timely manner.(8) The advantage to the National Program Office, is that one of the hardest parts of the task is to persuade field personnel to fill up a few 55 gal barrels of dirt, from hot spots if possible, and ship them to the QATS Laboratory. However when working on a set of site-characterized PES, one can insist on a surplus of materials as quid pro quo.

A word of clarification is probably needed to differentiate site-characterized materials from blind spikes or matrix spikes. In spiking, one simply squirts some analytes of known concentration onto or into the sample. Site-characterized PES are made from the real world matrix, but a liquid recipe is mixed with a small volume of the soil, dried and blended with a larger portion of soil. Homogeneity is verified, concentration levels, and acceptance limits are validated by multi-laboratory analysis.

We developed approaches to preparing PES for Field Analytical Methods such as field X-ray Fluorescence, sometime ago, but with the renewed interest in Field Analytical Methods, we are going to implement the study. (36) A survey of the Regions indicated the most commonly requested PES was for VOCs in soil. As noted above we feel this type of PES can now be produced with some assurance of statistical control of the analytical results. Many of the types of specialized materials, such as wipe samples, are best prepared locally.

To summarize, we think the trend in Performance Evaluation Materials is toward:

- Away from "national certification" PES to "by the case" PES.
- More emphasis on PES tailored to specific waste sites, Site Specific, Site Characterized materials.
- Lower concentration levels, to approach as closely as possible, health effects criteria.
- "Recipes" changed more frequently to avoid PE recognition.
- Increased use of Double-blind PES.

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(24) Draft Statement of Work, "Quick Turn-Around Analysis"

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IMPROVED LABORATORY PERFORMANCE THROUGH MATRIX-ANALYTE SPECIFIC PROFICIENCY TESTING

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ABSTRACT

The New York State Dept. of Health's Environmental Laboratory Approval Program has been challenging its participating laboratories with proficiency tests since 1985. A review of the proficiency test data demonstrates a distinct improvement in laboratory performance, as measured by percent recovery, for analytes that have not been included in EPA's WP series. For example, the recovery for Non-potable Water phenol has improved from an average of 3.3% in 1987 to 45.1% in 1991. A similar improvement can be demonstrated for phenol in soil where first round testing yielded 30.7 % recovery and 1992 test data demonstrates an average recovery of 61.0%. The production of Solid Waste proficiency test samples, and laboratory performance in analyzing these samples is discussed. The data show clearly that the traditional practice of only challenging laboratories with sealed ampules containing analyte concentrates does not realistically assess their ability to analyze real solid waste samples.

INTRODUCTION

New York State's Environmental Laboratory Approval Program (ELAP) was established in the Fall of 1985 as a successor to and expansion of the state's Safe Drinking Water Act laboratory certification program. Initially, ELAP provided accreditation in the categories of Potable Water and Non-potable Water to approximately 600 laboratories. As originally structured, ELAP produced and distributed its own proficiency test samples for both chemistry and bacteriology. ELAP has since grown and now accredits over 900 laboratories in 30 other states and six foreign countries. Each of the certification categories, Potable Water, Non-potable Water, Solid and Hazardous Waste, and Air and Emissions, is proficiency tested twice yearly. In 1992, the program manufactured and distributed over 40,000 samples. These consisted of concentrates in sealed ampules for the water chemistry analytes, full-volume water bacteriology samples, air filter strips, and full-volume solid waste samples. A list of the program's proficiency test samples is given in Table 1.

The Solid and Hazardous Waste and Air and Emissions categories were added to the existing water categories early in 1987. Due to the rapid expansion of the program's breadth, ELAP initially accredited laboratories in the Solid and Hazardous Waste (SHW) category by requiring them to have and maintain accreditation for the same analytes in the Non-potable Water

category. This was based on the theory that both the Non-potable Water and Solid Waste methods are essentially the same. Thus accreditation for SHW could be granted by a combination of Non-potable Waster proficiency testing and on-site inspection of SHW preliminary extraction procedures. However, this did not take into account the reduced recoveries and errors that can be introduced during the additional extraction or matrix reduction processes required with a real-world solid waste sample (such as soil, sediment etc.). This paper will examine the improvement in laboratory performance that is seen through the use of proficiency test samples that closely mimic the real samples that are being analyzed routinely.

PRODUCTION OF SHW PROFICIENCY TEST SAMPLES

In 1988 ELAP started producing it own SHW proficiency test samples starting with metals in sludge. In general, production of other analyte-matrix samples (listed in Table 1) follows this same procedure.

Initially a bulk sample of apparently analyte-free sludge, sediment, silt, sand or soil is collected and oven-dried at 105° C overnight. This sample is then ground, sieved to 100 mesh and roller mixed. Sample aliquots are now randomly collected to determine background concentrations of the analytes of interest. The remaining dried sample is then weighed and sufficient appropriate solvent is added to create a slurry. Using a paddle blade mixer, the analytes of interest are spiked into the slurry at concentrations calculated to produce the selected dry-weight targets. The slurry is then air or oven dried (depending on the solvent used) and roller mixed. The dried powder is then dispensed into screw cap bottles. De-ionized water is next added to each bottle to produce a wet real-world consistency. The bottles are then capped and sealed with stretch tape. Several samples are collected from the beginning, middle and end of production and analyzed for product homogeneity. Additional samples are collected randomly and analyzed over time to determine product stability.

DISCUSSION

A question frequently asked of any laboratory certification program is: "How effective are you?". One way of demonstrating effectiveness is to show improvements in recoveries and interlaboratory precision. A cursory review of statistical summaries over the years demonstrates that improvement has been made in recovery and precision, especially for analytes not included in other performance testing schemes. However, because of the rapid growth of the Program and change in the nature of laboratories approved, from basically facility-types to basically full-service commercials, the improved statistics may be due to changes in laboratory type rather than laboratory ability. An in-depth study of the causes of apparent improved performance appeared appropriate.

The study protocol called for the selection of a set of laboratories (n ≈ 50) that participated in proficiency testing both in 1986 and the current rounds. As demonstrated in Table 2, for the analysis of water proficiency test ampules, the laboratories that analyzed for purgeable aromatics in 1986 had an average recovery of 97.1%. In the current round these laboratories had an average recovery of 100%, a marginal improvement. It is believed that since purgeable aromatics are commonly found in other performance evaluation schemes in which the laboratories may have participated, these laboratories were approaching their peak performance in 1986. Alternatively, if one examines laboratory performance, as measured by recovery, for phthalate esters, polynuclear aromatics and priority pollutant phenols a distinct improvement can be seen. Again, comparison was made using a set of laboratories participating in both the 1986 and current rounds. Average recoveries for phthalate esters, polynuclear aromatics and phenols went from 10.7% to 91.4%, 6.5% to 79.1% and 5.8% to 62.4% respectively.

The data presented in Table 3 reflect the improved performance of a set of laboratories (n ≈ 50) that initially participated in proficiency testing for metals or phenol in solid waste. The table also presents the same group's performance in an aqueous matrix for the same analytes. These laboratories were only able to produce an average recovery of 55.4% for cadmium, nickel and lead in a solid waste, while achieving an average recovery of 99.5% for these same metals in an aqueous matrix. However, through continuing proficiency testing the initial set of laboratories was able to improve their recovery of metals from solid waste to a current average of 95.8%. Similar improvement can be noted for phenol, with recovery going from 30.7% to 61.0%.

As illustrated in Table 4, improved recoveries were not the only benefits of continued matrix-specific proficiency testing. Interlaboratory precision for cadmium, nickel and lead markedly improved from an average relative standard deviation of 27.9% to 8.2%.

An additional factor to be considered is that several laboratories that initially applied for certification in the SHW category withdrew as soon as they were challenged with the full-volume samples. An obvious conclusion is that they doubted their ability to handle these samples and pass the test. However, if the program had continued to rely on sealed ampule concentrates to test these laboratories, they would have presumably continued to participate and been granted certification for Solid and Hazardous Waste analysis.

SUMMARY

The data leave little doubt that the traditional protocol of challenging laboratories with proficiency test samples consisting of concentrates in sealed ampules does not accurately assess their ability to analyze real-world solid waste samples. Considerable resources are being provided for the identification and clean-up of solid waste sites, and the additional expense of research, development and production of realistic proficiency test samples would seem to be easily justified.

Table 1

NYS ELAP: CURRENT PROFICIENCY TEST SAMPLE TYPES

Potable Water

Drinking Water Bacteriology:
- Total Coliform (& *E.coli*)
- Standard Plate Count

Analytes represenitive of:

Chlorinated Acids
Trihalomethanes
Microextractables
SDWA Metals
Methylcarbamate Pesticides
SDWA Minerals
Organohalide Pesticides
Volatile Aromatics
Volatile Halocarbons
Miscellaneous:
- Asbestos
- Semi-volatiles

Non-potable Water

Wastewater Bacteriology:
- Total coliform
- Fecal coliform

Analytes represenitive of:

Chlorinated Hydrocarbon Pesticides
Chlorinated Hydrocarbons
Atrazine and Carbaryl
Dioxins
Demand
Haloethers
Metals I:
- Ba, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag and Na

Metals II:
- Al, Sb, As, Be, Hg, Se, V and Zn

Metals III:
- Co, Mo, Tl and Ti

Nitroaromatics and Isophorone
Minerals
Miscellaneous:
- B, CN, Phenols, MBAS, TOC, pH and Oil & Grease

Nitrosoamines
Nutrients
Organophosphate Pesticides
Polynuclear Aromatics
Polychlorinated Biphenyls
Phthalate Esters
Priority Pollutant Phenols
Purgeable Aromatics
Purgeable Halocarbons
Residue

Solid and Hazardous Waste

Analytes represenitive of:

Chlorinated Hydrocarbon Pesticides
Metals I:
- Ba, Cd, Cr, Pb, Ni and Ag

Metals II:
- Sb, As, Hg and Se

Polynuclear Aromatic Hydrocarbons
Polychlorinated Biphenyls
Phthalate Esters

Priority Pollutant Phenols
Miscellaneous: Asbestos

Air and Emissions

Asbestos
Fibers
Formaldehyde
Lead
Nitrate

Table 2

IMPROVED RECOVERIES THROUGH PROFICIENCY TESTING

	1986			Current		
Analyte	Target	Mean	% Rec.	Target	Mean	% Rec.
Benzene	59.4	59.4	100.0	31.2	31.4	100.5
	127.3	119.7	94.0	50.2	49.9	99.4
Chlorobenzene	161.3	158.0	98.0	29.8	30.1	100.9
	69.9	67.3	96.3	47.7	47.5	99.5
Bis (2-ethyl-hexyl) phthalate	32.2	5.3	16.5	33.5	25.9	77.3
	85.8	8.1	9.4	83.8	67.3	80.3
Benzo butyl phthalate	64.5	6.8	10.5	28.4	28.4	100.0
	107.0	8.6	8.0	68.7	69.3	101.0
Dimethyl phthalate	94.7	7.4	7.8	59.9	56.9	95.0
	42.1	5.0	11.9	75.2	71.5	95.0
Phenol	81.9	3.54	4.3	105.0	47.7	45.4
	243.0	5.3	2.2	75.1	33.7	44.8
Pentachloro-phenol	75.2	7.0	9.2	79.6	64.0	80.4
	120.0	9.0	7.5	99.5	78.6	79.0
Benzo (b) fluoranthene	148.0	4.7	3.2	44.1	43.09	99.5
	63.4	4.0	6.3	118.0	97.3	82.5
Dibenzo (a,h) anthracene	38.6	3.5	9.0	30.3	20.7	68.3
	76.4	8.1	10.6	48.6	32.0	65.9

Table 3

MATRIX-SPECIFIC RECOVERY IMPROVEMENT

	1988			Current		
Analyte	Target	Mean	% Rec.	Target	Mean	% Rec.
Cadmium						
Water	33.0	33.2	100.6.	70.0	68.3	97.0
Solids	5.0	3.6	72.6	60.0	56.2	93.7
Nickel						
Water	170.0	168.8	99.3	400.0	394.7	98.8
Solids	40.0	17.6	43.9	401.0	403.3	100.6
Lead						
Water	220.0	217.1	98.7	250.0	246.9	98.8
Solids	113.0	56.2	49.8	184.0	171.4	93.2
Phenol						
Solids	183.0	56.2	30.7	333.0	203.0	61.0

Table 4

INTERLABORATORY PRECISION IMPROVEMENT

	1988			Current		
Analyte	Mean	δ	RSD	Mean	δ	RSD
Lead	56.2	9.8	17.4	314.0	28.1	8.9
Nickel	17.6	5.8	32.9	398.0	28.8	7.2
Cadmium	3.6	1.2	33.3	56.2	4.7	8.4

3 COMMERCIAL LABORATORY POSITION ON NATIONAL LABORATORY ACCREDITATION

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ABSTRACT

Environmental testing laboratories conduct sample analysis on soil, air, water, and other materials that may contain potentially hazardous substances. Services of the environmental testing industry are widely used by the U. S. Government, state governments, and private industry because almost every environmental decision is based on laboratory data. Reliable data are critical to protect the public health and the environment.

While the primary need for the data generated by these laboratories is to comply with federal environmental regulations, there is no national accreditation process to ensure uniform, rigorous standards. Environmental laboratories currently are accredited under a system of multiple state and private programs with varying quality assurance criteria and excessive processing costs. Implementation of a national accreditation program is a cost-effective method of ensuring data quality.

International Association of Environmental Testing Laboratories, Inc. (IAETL) has assembled a committee of its membership to discuss the effect and feasibility of a national program. IAETL represents over 150 commercial laboratories with an estimated 45 to 50 percent of the

commercial laboratory capacity. IAETL has adopted a position in support of national certification. IAETL's committee has reviewed various scenarios and implications of a national program including the recommendations of the Committee on National Accreditation of Environmental Laboratories (CNEAL) Report to EPA. IAETL's position supports the CNEAL recommendations and emphasizes the adoption of certain critical components: data assessment, onsite assessment, performance evaluation testing, a clearly defined process for both laboratories and accrediting organizations, and uniform, well-defined criteria.

The objective of our presentation is to share information on the implications of a national program and the specific recommendations we have developed on standards, organization, and enforcement to ensure that the national program will be effective.

INTRODUCTION

In late 1989, the International Association of Environmental Testing Laboratories (IAETL) recognized the critical need for national accreditation. The unwieldy, expensive, and time-consuming accreditation processes currently in place were adding considerable cost to environmental lab testing with little or no benefit to the users of laboratory services. IAETL formed a National Accreditation Committee to address the issues.

The National Accreditation Committee reviewed current federal programs, specifically the CLP program, USATHAMA, the Navy HAZWRAP, A2LA, AIHA, DOE, DOD, and the Drinking Water program. Major categories common to the programs were determined and a questionnaire was developed to survey current state programs.

At this point, mailings on the subject revealed a wider interest group than just environmental labs for a national accreditation program. Customers of the environmental laboratories such as engineering firms, various industries, and regulatory bodies also had a vested interest because of concerns about environmental data quality and prices. A new coalition was formed from the various interest groups called NELAC - the National Environmental Laboratory Accreditation Coalition.

NELAC used information from its participants along with the previously gathered information on federal and state programs on standard environmental laboratory practices and accreditation programs structures to formulate four options to be considered as possible models for a national accreditation program. After thoroughly examining and debating the various strengths and weaknesses of the four models, NELAC presented a single, comprehensive option.

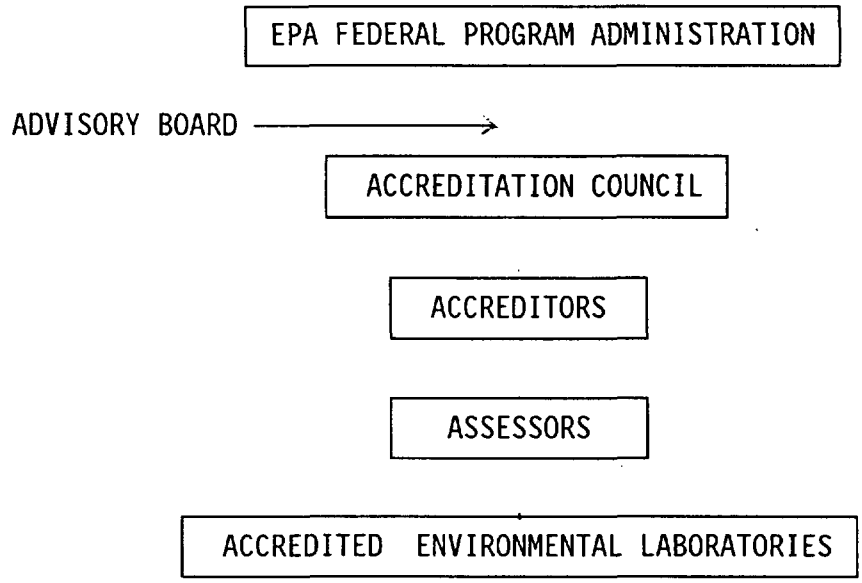
The advantages of the national accreditation program as described in the option developed by the IAETL/NELAC groups include:

- Self-sustaining structure
- Built-in controls to ensure continuing quality and uniformity of the program.
- Structures already in place (state agencies) may be used in the process.
- A mechanism for making necessary changes through the Advisory Board exists.
- Regulatory control is retained.
- Third-party administration is provided for.
- Funding requirements from regulatory agencies is minimized.
- States would be reimbursed for their participation.
- Higher standards of quality could be applied consistently to environmental data across the country.
- Duplication of efforts in accreditation could be minimized, particularly for audits, performance evaluation (PE) samples, and applications.
- QA requirements could be centralized within a structure similar to existing programs within the EPA. There would be a dynamic mechanism of input into these requirements through the Advisory Board.
- The EPA can influence states to adopt reciprocity as part of the acceptance criteria and through funding.

The key elements of this option were the accreditation process, the accreditation criteria, data assessment, onsite assessment, performance evaluation testing, accountability, and enforcement.

ACCREDITATION PROCESS

The accreditation process concurred upon can be diagramed as follows:



The EPA FEDERAL PROGRAM ADMINISTRATION is managed by a high-level EPA official who administers the Accreditation Council contracts.

The ADVISORY BOARD approves standards. Initially it would be made up of individuals from federal and state agencies, laboratories and data users appointed for two years from a volunteer list. In subsequent years, board members would be elected from nominated individuals.

The ACCREDITATION COUNCIL is an EPA contractor hired with a minimum contract of 3 to 5 years to administer the program, approve accrediting agencies, and maintain records.

The ACCREDITORS are state agencies, independent third-party organizations, and federal agencies that would accredit per the national program criteria. This would allow existing infrastructure in these organizations to remain intact and functional if they so desire.

The ASSESSORS are the trained individuals hired by the accreditors and required to undergo competency testing to perform data and site assessments.

ACCREDITATION CRITERIA

The program must consist of clearly established, uniform criteria. The laboratories must have detailed requirements that they are expected to meet to be accredited. Using these criteria, the laboratory may design the appropriate systems and the internal assessments to maintain these systems. The criteria must be clearly defined so that they can be applied uniformly from location to location by any accreditor. The accreditation council, the accreditors, and the assessors also must have uniform criteria by which the program is administered and by which accreditors and assessors are selected, trained, perform laboratory assessments, and document the accreditation process.

Accreditation Criteria for Laboratories

Uniform criteria for the laboratory will enhance a laboratory's ability to generate data of known and documented quality. A system must be established by which laboratories can be evaluated to determine if they are capable of performing competently and that their QA/QC programs are functioning to ensure the production of reliable and usable data. To this end, the criteria for evaluation of laboratories must address the following.

Organizational Structure and Staff

The organizational structure must be defined such that the technical functions can be performed adequately. The structure must not put undue pressure on staff to influence their judgment. The person responsible for Quality Assurance (QA) must report to senior management, and the QA role should be independent from the data generation process.

Staff must have adequate education, training, and experience for their assigned functions. Laboratory management should not rely on education and experience alone to ensure that technical assignments are completed properly. Therefore, the laboratory's training program must be comprehensive and documented. All employees should have a clear understanding of their job functions. Adequate supervision should be provided to ensure that work is properly completed.

Quality Systems

The criteria for accreditation should dictate the minimum requirements for documenting an internal quality system appropriate to the size of the facility and the scope of the analyses performed. The quality system should be well documented so that all staff understand its function and requirements. The accreditation program should provide enough direction to the laboratory to generate quality documents that

describe the management's policies and values, the laboratory's organization structure, responsibilities of management and staff, general QA procedures, detailed QC requirements, and corrective action processes for the systems described.

Facilities and Equipment

Minimum criteria for the physical plant are delineated to ensure that the environment does not adversely affect test results, that adequate security is available, that appropriate equipment is available and employed for the offered testing, and that appropriate health and safety programs are implemented.

Data Generation and Record Keeping

The accreditation criteria must address minimum requirements for documentation of the procedures used in the laboratory by requiring standard operating procedures, sufficient documentation of the analytical process to reconstruct the events, and adequate procedures for storage of these data for an appropriate period.

Accreditation Criteria for the Accrediting Council and Accreditors

The accrediting council, the accreditors, and the assessors must meet criteria similar to those as described above. The accreditation council (the administrative arm of the program/directed by the advisory board) and the accreditors (agencies providing accreditation under the direction of the accrediting council) must be clearly defined. The organizational structures must be known and provide for an environment in which the staff are free from compromising influences. Assessors (those people performing the data and site assessments hired by the accreditors) must have adequate education, training, and experience for their assigned functions.

Additionally, adequate training must be provided and documented to ensure that the assessors are competent to assess the laboratory and can provide uniform assessments to all laboratories that they visit. Each of these groups should abide by a documented quality program, including corrective action processes. The process by which the laboratory assessments take place, the reporting mechanism, and the maintenance of these records must be clearly defined.

DATA ASSESSMENT

Data assessment must be conducted as part of the quality assurance review of the laboratory operation. Data assessment can be conducted in two parts: (1) determination of the data acceptability relative to minimum data quality criteria established for nationally accredited laboratories and (2) determination of the data availability at the laboratory's site.

Data can be reviewed in advance of the onsite visit to determine problem areas that need to be investigated during the visit. The periodic onsite review process will determine if the laboratory's data assessment process includes data handling procedures, control criteria, and policies for data corrective actions.

The data assessment criteria should be defined clearly by the Advisory Board. These criteria will ensure that all data generated by a nationally accredited laboratory will meet a minimum data quality standard. Project- or regulatory-specific criteria still will be needed for more stringent data requirements; however, a national program will set minimum standards for data quality criteria.

Current data quality often is based on the contents of the data deliverable package. For example, data deliverables presented in CLP format are assumed to be of better quality than drinking water data presented as a single reported concentration. The data user assumes that quality control parameters for an application are within acceptable limits if the data are presented in CLP data deliverable format. The drinking water data assessment criteria are clearly stated for every primary drinking water parameter, and each must be met before reporting any data. The CLP data deliverables include documented data assessment criteria as part of the report. The question of data quality is not answered by how much of the data are presented and verified in the report; the question of data quality is answered only when the data are found to meet the acceptance criteria.

All data from a laboratory must be documented as to its quality. The data assessment verifies that data both meet the minimum data criteria and are well documented.

ONSITE ASSESSMENT

A single national program for accreditation of environmental laboratories must include the key element of an independent, onsite assessment as part of the accreditation process. This assessment, along with the data assessment described previously, should form the foundation to grant (or deny) accreditation to a laboratory. We have used the word "assess" to connote that the primary function of the assessment is to observe and evaluate, not to correct deficiencies or make recommendations.

The onsite assessment should address all aspects of the facility, staff, and systems to provide confidence that the laboratory is capable of providing the services for which accreditation is requested.

After the initial assessment, the accreditor should prepare a report that lists the findings and documents any deficiencies that must be corrected for the laboratory to obtain accreditation. The laboratory should be provided with an opportunity to remedy any deficiencies. If the assessment shows that accreditation is justified, the accrediting council then should issue a certificate authorizing the laboratory to provide data for the parameters included in the scope of accreditation. This information should be maintained by the accrediting council for dissemination to users of laboratory services. The accrediting council should establish a procedure by which laboratories can seek accreditation for additional tests.

The accreditation should be valid for 1 year. An annual reassessment must be performed by the accreditor that should address any changes in the laboratory based on information retrieval and the results on PE samples. Where concern is warranted, an onsite assessment may be performed. In any event, additional onsite assessments should be performed at least once every 2 years.

The assessment should address all aspects of the laboratory's facility, organization, quality systems, and record keeping. A critical element of this process is to determine if the laboratory personnel have the necessary education, training, technical knowledge, and experience to perform their assigned functions. It is the responsibility of laboratory management to ensure that laboratory personnel meet this requirement. A separate accreditation of analysts would not improve the process or add to the assurances already established by requiring comprehensive in-house training and documentation programs. The program could establish criteria relative to the expected education, experience, and knowledge for analysts.

Assessors must have a thorough knowledge of the accreditation elements, including detailed knowledge of the analytical procedures, and must act in an impartial manner. The accreditation system must establish procedures for ensuring the competency of assessors.

PERFORMANCE EVALUATION TESTING

Performance Evaluation or Proficiency Testing is a key element of the program in confirming the laboratory's capability to perform the methodology and identifying areas for improvement. A performance evaluation program is therefore a critical requirement of national laboratory accreditation.

The accreditation program will require completion of an initial series of PE samples representing the parameters and matrices in which the laboratory is seeking accreditation. The results of the PE samples will be compared to the certified values and the expected acceptable range for that parameter and matrix.

Because PE samples are not available for all parameters in all matrix types, the PE program must have a cross section of PE samples that covers representative parameters. For example, a volatiles PE may contain 5 to 8 compounds to represent the 20 to 30 volatiles normally analyzed in wastewater methods. Matrices evaluation may be limited to water, air, soil, and sludges for specific inorganics and organics, with other matrices available for only select items (PCBs in oil or mercury in fish for example). The areas of matrix accreditation must be clear to all participants and potential users of the national accreditation program. If, for instance, a PE for dioxins in fish does not exist, does the program accredit a laboratory for dioxins in fish if the laboratory is accredited in dioxins in water and soil; or should the approach simply be that unless covered by PEs, particular parameters in matrices will not be accredited.

The fee structure will depend on the type and number of PEs required by the laboratory. As new PEs or PEs in different matrices become available, previously accredited laboratories as well as new applicants will be encouraged to participate in these studies.

Only laboratories generating acceptable data will be accredited for a particular parameter or set of parameters for a matrix type by the method certified by the laboratory. For a laboratory failing a particular PE, the accrediting council will work with the laboratory to evaluate the program areas and needed changes. Laboratories, at their expense, have up to three chances in a 1-year period to perform a single PE successfully. After initial accreditation approval, the laboratory will be required to perform PEs annually to maintain accreditation for the designated PE parameter(s) in the matrix provided. Failing multiple PEs (two or more) by a laboratory will initiate a reassessment by the accrediting council.

A well-organized, broad-based PE program will be the heart of the national accreditation program to ensure continued proficiency of the member laboratories.

ACCOUNTABILITY AND ENFORCEMENT

A critical element of any accreditation program is accountability on the part of the accreditors as well as the laboratories being accredited. In addition, the accreditors must be in a position to enforce any and all accreditation and/or revocation of accreditation decisions that they make.

The accreditors will evaluate laboratories through a combination of onsite assessments, data assessments, and performance on proficiency test samples submitted to the laboratories. The onsite and data assessment activities will be used to grant or revoke accreditation for the laboratory. The accreditation must be specific for the areas of testing performed by the laboratory, to incorporate both parameters and matrix. As discussed previously, unacceptable performance in analysis of PE samples can result in loss of accreditation for a particular parameter. In this context, the accrediting council must be held accountable for developing the following:

- The accrediting council is accountable for providing requirements and standards for conducting onsite and data assessments. The accrediting council also is responsible for establishing a viable performance evaluation testing program.

- Once assessors are selected, the performance of each assessor must be evaluated annually, at a minimum, and allow for more frequent evaluation if their performance is questioned at any time. This review should be based on a combination of their accreditation record and evaluations from laboratories.

- A hearing process must be established to resolve disputes about assessor performance and laboratory performance issues. This process would provide all parties involved the opportunity to express their points of view before a final determination is made.

- Assessors who have demonstrated unacceptable performance must not be allowed to continue in that capacity once a determination has been made. The accrediting council would maintain an active list of acceptable accreditors and assessors.

- Laboratories that have demonstrated unacceptable performance must not be allowed to maintain an accredited status. The accrediting council would maintain an active list of accredited laboratories, along with the areas of accreditation.

Enforcement of decisions about acceptable laboratories, accreditors, and assessors would be controlled through the maintenance of the approved listings. A real-time listing of approved assessors and accredited laboratories could be maintained on a computerized bulletin board system.

CONCLUSION

Implementing a national accreditation program is a cost-effective vehicle for improving and maintaining data quality. Such a national program will help ensure that decision makers and the public receive accurate and reliable data to make cost-effective environmental decisions. Users of environmental testing services need an independent and comprehensive verification that laboratories have the capability to perform competently and that laboratory Quality Assurance/Quality Control programs are functioning to ensure the production of reliable and usable data. It is critically important that environmental monitoring data are reliable, reproducible, accurate, and defensible to support regulatory compliance and enforcement decisions made by the public and private sector.

A single, comprehensive national program for accreditation of environmental laboratories must establish:

1. Uniform, rigorous requirements for environmental testing laboratories to generate data of known and documented quality.

2. Uniform, rigorous standards under which accrediting organizations can oversee the program.

The accreditation process should be administered by a private/public partnership with federal oversight. Procedures would be developed by a governing board of representatives from the EPA and other interested federal parties, state agencies, the laboratory community, and users of environmental data.

A program designed and administered with these features would eliminate costly, redundant requirements while significantly increasing the accuracy, reliability, and timeliness of decisions that affect the quality of environmental cleanup and restoration efforts.

IAETL supports and continues to work toward a single, comprehensive national program that will provide an effective means of improving the consistent generation of high quality data to comply with environmental laws and to protect public health and safety.

REFERENCES

Jeanne Hankins, Final Report of the Committee on National Accreditation of Environmental Laboratories, United States Environmental Protection Agency, Washington, DC September, 1992.

4

COST EFFECTIVE PROJECT PLANNING: AN ALTERNATIVE APPROACH TO INITIAL RCRA FACILITY INVESTIGATIONS

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ABSTRACT

In a recent report by the General Accounting Office, the RCRA program is criticized for being "excessively slow in nearly all areas, and charges EPA with failing to develop a viable RCRA cleanup strategy."[1] It is the conduct of the large-scale multimedia RCRA Facility Investigations (RFIs) which this paper addresses. We propose an approach that combines stages in the RFI process and redefines the current phased approach to RFIs. This alternative approach can reduce the time and cost associated with the various RFI process stages and improve the responsiveness of determining appropriate corrective measures.

Project planning is an essential part of designing large-scale investigative programs. Although the initial planing process can be quite time consuming, it is vital in achieving data that are both scientifically sound and legally defensible to support corrective action decisions. However, many investigative programs have been delayed for years in the planning and negotiation stages. This delay is inefficient, costly, and can result in a continuing risk to public health and the environment.

A key element in the proposed approach is a Phase I scope that is defined through an iterative process with the regulatory agency, owner, and engineering and laboratory contractors. The scope is defined based on site-specific information (e.g., historical chemical and physical data, hydrogeological information), applicable and relevant or appropriate requirements (ARARs), health based criteria and other toxicological information. A site-specific sampling scheme and target compound list is defined. For example, if groundwater is not a relevant exposure pathway at the site, then groundwater samples would not need to be collected in the initial phase. Recommendations are made to base methodology on both health-based criteria and background levels of contaminants of potential concern. This approach allows for the controlled use of alternative methodologies (i.e., field techniques) that may have higher detection limits than standard methods but are acceptable to define the site conditions in reference to risk calculations. The initial object of the process would be to reduce risk, not to return the site to a "pristine" level.

This approach for RCRA sites is similar, in goals, to the Superfund Accelerated Cleanup Model (SACM). The use of a simpler approach and a narrower focus to the Phase I RFI allows for timelier risk reduction for people and the environment.

INTRODUCTION

RFI guidance defines the RCRA Corrective Action Process as having numerous stages. Generally, the approach to RCRA Facility Investigations (RFI) has included a large-scale sampling and analysis program (as Phase I of a phased strategy) encompassing a broad range of target compounds such as the full Appendix IX. As a result of the magnitude of the Phase I investigation (in terms of number of parameters, analytical methods, detection limits, etc.), the program details are so voluminous that the planning process can take years. Additionally, once the RFI is underway, several other stages in the RCRA process follow, including: review of the results by the regulatory agency based on health and environmental assessments; recommendations for interim corrective measures, and/or a Corrective Measures Study (CMS); implementation of the CMS; evaluation of the CMS; recommendations of appropriate corrective measures (actions), and Corrective Measures Implementation(CMI).

In a recent report by the General Accounting Office, the RCRA program is criticized for being "excessively slow in nearly all areas, and charges EPA with failing to develop a viable RCRA cleanup strategy."[1]

It is the conduct of the large-scale multimedia RCRA Facility Investigations (RFIs) which this paper addresses. We propose an approach that combines stages in the RFI process and redefines the current phased approach to RFIs. This alternative approach can reduce the time and cost associated with the various RFI process stages and improve the responsiveness of determining appropriate corrective measures.

OVERVIEW OF THE RCRA CORRECTIVE ACTION PROCESS

The RFI is carried out under either a permit or enforcement order. RFIs can range from limited investigations to large-scale investigations for a wide variety of target analytes and matrices. The RCRA Corrective Action Process has numerous stages. A RCRA Facility Assessment (RFA) should include a review of historical information at the site and a site inspection by the EPA, to identify solid waste management units (SWMUs), collect existing information on contaminant releases, and identify suspected releases needing further investigation. Depending on the results of the RFA, it is possible to either proceed with a RCRA Facility Investigation (RFI) or, in cases where public health or the environment is threatened, interim corrective measures may be required.

The owner or operator then performs the RFI to either verify the contaminant release, if required, or to characterize the nature, extent, and rate of migration of potential future releases. The results of this stage of the process are submitted to the regulatory agency for review. Further steps in the RCRA corrective action process include evaluation of the data generated from the RFI against established health and environmental criteria. At this stage, if further action is determined necessary, a corrective measures study (CMS) is performed which recommends appropriate measures to correct the release. Interim Corrective measures can be taken either prior to or during the CMS if a threat to health or the environment is identified during the RFI stage.

Finally, subsequent to the CMS, corrective measures are implemented (CMI). This includes design, construction, operation, and monitoring of the corrective measures decided upon by the regulatory agency.

ITERATIVE PROCESS IN DESIGNING THE PHASE 1 SCOPE

Evaluation of a RCRA site is extremely complex, and requires the application of a wide variety of scientific disciplines, and diverse technical and regulatory knowledge. During the course of an RFI, many individual contractors are hired to participate in the various phases of the project. The contractors can include engineers, field samplers, hydrogeologists, laboratory personnel, toxicologists, risk assessment specialists, and quality assurance consultants.

However, during the initial planning stages in which the Sampling and Analysis Plan (SAP) and Quality Assurance Project Plan (QAPP) are developed, the expertise of a number of these individuals is not utilized. For many programs, there is minimal communication between members of the "team." It is crucial to the success and expediency of the RFI process to assemble the entire project team to develop the work plan for the specific site that takes into account all of the necessary information required to generate valid data upon which to support corrective action decisions.

Project team members with risk assessment or toxicological expertise can influence the scope of the RI at the planning stage in order to avoid the low-level analysis of certain analytes that do not pose a threat to human health or in order to ensure low-level detection limits in cases of ecological risk. Additionally, these team members will help define the possible exposure pathways and media so that the SAP can be formulated to minimize the numbers and types of samples being collected and analyzed while maximizing the usable data generated. Also, this planning process can avoid costly resampling efforts due to omission of a significant media (e.g., air) or parameter type. At this stage, human-health based risk calculations can be performed using historical data, if available, as an estimate of the potential risks at the site. Health-based cleanup levels can also be estimated from these risk calculations to help clearly define the detection levels needed for the analytes of concern specific to the site.

Both the EPA and the site owner are in a position to require and facilitate working meetings during which an appropriate target analyte list is developed and associated required method detection limit are determined. This requires a commitment from both the regulatory agency and the site owner. From this information, methodology choice (in particular field vs. laboratory methods), data quality objectives, and a relevant sampling scope can be developed. Only from these criteria can a valid SAP and QAPP be developed. In terms of cost-effectiveness and timeliness it is crucial to evaluate field analytical methods (e.g., field gas chromatographic methods for analysis of volatile organic compounds, X-Ray Fluorescence techniques for the field analysis of metals, bioassay techniques for the field analysis of PCBs) as viable alternatives to laboratory analyses. Field method technology has become more sophisticated and rigorous and allows for the rapid analysis of constituents of concern on-site. In addition, laboratories can develop fast, cost-effective methodology when presented with a site-specific TAL and associated detection limits (e.g., "Soxtet" extraction, Solid Phase Extraction, GC-MS-SIM, GC-ITD). Therefore, decisions that are based on chemical information can be made more quickly - speeding up the RFI process.

The current RFI guidelines are certainly not in conflict with this recommended process. In fact, some of these activities are required. However, from experience (in both authoring and reviewing numerous Work Plans, SAPs, and QAPPs in various EPA Regions and states) it is evident that an organized, effective planning process rarely occurs. Much of the information which does exist about the site history, physical site conditions, and historical data is not taken into account during the planning phase or, if it is included in the Work Plan, is not included as relevant information upon which to define specific QA/QC criteria in the QAPP. This results in a program where the target analyte list and selected methodologies are inconsistent with the site history and expected contaminants and physical conditions at the site.

Coordination between the project team members needs to be maintained to generate a SAP and QAPP that the field personnel and laboratory personnel can follow as a protocol and that is sufficient to support usable data. However, the SAP and QAPP are often done as "boiler plate" documents with only minor changes due to site-specific information. This results in a waste of both cost and time when, for example, strict QA/QC criteria are required that are not relevant to the type of samples being collected or the expected chemical contamination. For example, a QAPP for a site in Louisiana required CLP-like quality control, DQOs, and detection limits for sludge samples that were known to be highly contaminated with organics and metals. The laboratory could not meet most of the QAPP required matrix QC or the detection limits stated because of the highly complex and contaminated matrix. The complex matrix and the level of contamination expected should have been taken into account during the generation of the QAPP. Less strict QC would not have compromised the usability of the data generated for this site due to the highly contaminated nature of the samples -- in other words, the relative extent of contamination and the order-of-magnitude were the necessary information. Lack of coordination between project team members caused an increase in cost (laboratories charge more for CLP-like QC than for more standard analyses) and time (CLP-like QC required more time to analyze and generate laboratory reports).

GUIDELINES FOR PHASE I OF RFI

The following steps are presented as guidelines for the coordinated project team approach in generation of the project QAPP, with specific emphasis on the usability of the chemical data. Similar team approaches would be required in generating the SAP and work plan and would bring together the engineering and field personnel with the laboratory and toxicologists and risk assessment specialists:

1. Determine Target Analyte List (TAL) based on Historical Site Activities & Data

The traditional approach in planning an RFI has been to analyze for the full Appendix IX list of compounds. However, many of the analytes included in Appendix IX may not be appropriate given the historical information which exists about operations at a particular facility and the results of previous sampling and analysis. The project team members involved in the initial planning need to have the site-specific information necessary to define the scope in terms of the target analyte list. A site-specific target analyte list must then be developed using this information. The expertise of both risk assessment and analytical chemistry personnel should be involved in defining the site-specific TAL. Without this information and coordination of project team members, the result may be inflated sampling and laboratory costs, and also higher costs

to validate data which is not of any particular use in the final determination of required corrective measures. In the Superfund Accelerated Cleanup Model (SACM), this problem is addressed:

> "Many, if not most of these assessments start from scratch, -- they do not necessarily take into consideration the information and data generated by the studies that preceded them. This happens not only because of the obvious financial incentives to the contractor community and the human inclination to distrust the work of others, but because each part of the program is gathering data to respond to its particular perceived need."[2]

In some cases, the directives to produce redundant data come directly from the regulatory authorities in an effort to restore the site to "pristine" conditions. However, the focus must shift from this effort to an effort of "worst first"[3] as described in the SACM model.

2. Define the Sampling and Analysis Procedures Based on Site Conditions, Historical Information, and Exposure Pathways

With the input of the engineering and risk assessment personnel, project costs and time-frames may be reduced, for example, by deciding that a portion of the soil and/or groundwater samples may be analyzed using field rather than laboratory methods. This would allow for less strict QA/QC, rapid generation of chemical results, and contribute to a more timely progression to the corrective measures process.

Often, the project personnel writing the QAPP are given instructions to "write a QAPP for the full Appendix IX list for water and soil samples." Although, for example, hydrogeological information about the site is used in defining the sampling plan, samples collected and analyzed from a crucial part of the site (e.g., a known hot spot or chemical release) are not treated differently than others in terms of defining DQOs, methods, quality control criteria, detection limits, and validation requirements. The same DQOs and detection limits are generally applied to all samples in this type of generic QAPP. By changing this approach, by generating a QAPP specific to the real needs of the program, usable data will be generated in a more cost-efficient approach.

3. Review SAP, QAPP, and Target Analyte List in Terms of Both Ecological and Human-Health Risk Potential

Once the site-specific TAL is identified for the site, risk assessment estimates (preliminary calculations based upon existing data from the site) must be taken into account to choose appropriate detection limits required for each of the compounds on the list.

Volumes of historical data on which risk calculations may be based exist for most sites which are in the RCRA corrective action process. However, risk assessment personnel are usually not brought into the RFI process until after the Work Plan, SAP, and QAPP have been developed, and after the analyses have been performed. The interactive process of the project team, to make decisions on detection limit requirements and methodologies, must occur prior to the development of these site documents that direct the activities for the RFI.

The input from risk assessment project team members is crucial in choosing appropriate methodologies, both conventional and alternative. This information is vital to adequately determine required quantitation levels and DQOs specific to the project. For example, recent RODs (1991) in both Region 1 and Region 5 have required targeted cleanup levels of 1 μg/L for vinyl chloride and 1,000 μg/L for toluene.[4] However, most QAPPs require a detection limit of 10 μg/L for both compounds and identical DQOs and QC criteria for both compounds. In this scenario, the toluene results were generated by the laboratory under far more stringent QC requirements than necessary to support the usability of the data in a cleanup level model. Conversely, any not detected vinyl chloride results generated at the 10 μg/L detection limit are not usable because these nondetects are reported at an order-of-magnitude higher level than the level of concern (cleanup level) for this compound.

If, at the planning stage, it is known that both toluene and vinyl chloride expected contaminants at the site, and that toluene is potentially highly contaminated (i.e., in the ppm range) as compared with vinyl chloride (i.e., in the low ppb range), methodology can be selected which will give relevant reporting limits for both compounds based on the targeted cleanup levels, as listed above.

However, if the historical information about toluene and vinyl chloride at the site were not reviewed, and the planning not performed as a project team process, the routine approach would be to define QAPP requirements to analyze for the Appendix IX Volatiles list by Method 8240. This would result in not detected vinyl chloride results reported at a high sample detection limit due to dilutions that would be required for high levels of toluene. With appropriate planning, incorporating the expertise of an analytical chemist and risk assessment personnel, a GC screening method for toluene could be defined for the project and a GC/MS method with strict QC (e.g., EPA method 524.2) could be defined for vinyl chloride so that the low-level detection limit needed for usability of the data could be achieved.

4. Establish A "Hot" List for Interim Corrective Measures

Interim Corrective Measures may be necessary at any point in the RFI process. During the RFI, sources can be identified as hot-spots as those regions of the site with the highest concentrations of contaminants. Once these hot spots have been identified, they should be evaluated against health-based criteria or cleanup level criteria, as appropriate. Field screening analytical techniques can be extremely useful in identification of hot spots and extent of contamination for rapid response. Interim corrective measures are appropriate at this stage.

SUMMARY

One of the crucial differences in the strategy which is recommended is evaluation of the historical data against both health-based criteria and estimated (or historical) cleanup goals at the initial planning stages of the RFI and prior to the formulation of the Work Plan, SAP, and QAPP. This evaluation should be the basis from which the target analyte list (TAL) is identified, the Sampling and Analysis Plan (SAP) and Quality Assurance Project Plan (QAPP) are written, and the basis from which the Data Quality Objectives (DQOs), including target quantitation limits and methodologies, are chosen. Without this step, many of the current RFI activities are superfluous in that methodology which is costly and time consuming is being used for analytes which are not

harmful to human health at the low detection levels required by the methods or not present at the site being investigated. This strains the budgets and timetables and results in taking resources away from remediation.

EPA is presently in the process of establishing requirements for RCRA corrective action. These rules are to address various parts of the RCRA corrective action process that are presently either not defined or subject to misinterpretation in implementation. These regulations will be published as Subpart S of 40 CFR Part 264 and are intended to address the following issues:

- Action levels based on health and environmental factors
  - Methods for development of action levels
  - Specific action levels for soil and surface water
  - Adjustment of action levels based on additive toxicity
  - Influence of quantitation limits on action levels
- Definition of "constituent"
- Definition of Solid Waste Management Unit (SWMU)
- Notification and reporting
- Semantics

The approach proposed in this paper was intended to address the issue of health-based action levels by involving risk and toxicology personnel up-front in the planning process. A key element in the proposed approach is a Phase I scope that is defined through an iterative process with the regulatory agency, owner, and engineering and laboratory contractors. The scope is defined based on site-specific information (e.g., historical chemical and physical data, hydrogeological information), applicable and relevant or appropriate requirements (ARARs), health-based criteria and other toxicological information. A site-specific sampling scheme and target compound list is defined. For example, if groundwater is not a relevant exposure pathway at the site, then groundwater samples would not need to be collected in the initial phase. Recommendations are made to base methodology on both health-based criteria and background levels of contaminants of potential concern. This approach allows for the controlled use of alternative methodologies (i.e., field techniques) that may have higher detection limits than standard methods but are acceptable to define the site conditions in reference to risk-based calculations for cleanup levels. The object of this phase of the RFI process would be to reduce risk, not to return the site to a "pristine" level.

This approach for RCRA sites is similar, in goals, to the Superfund Accelerated Cleanup Model (SACM). The use of a simpler approach and a narrower focus to the Phase I RFI allows for timelier risk reduction for people and the environment. Additionally, this approach focuses on one of the four primary goals set by EPA's Administrator, Carol M. Browner, to make permitting and other EPA decisions more prompt, fair, and definitive by using streamlined reviews and greater reliance upon state and local agencies.

FOOTNOTES

1 Energy & Environmental Document Service Catalog - First Quarter 1993.

2 Superfund Accelerated Cleanup Model (SACM), US EPA Office of Emergency and Remedial Response, Pub. 9203.1-01, March, 1992.

3 Ibid.

4 ROD Annual Report, April 1992, US EPA Office of Emergency & Remedial Response, Publication 9355.6-05-1.

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5

MATRIX SPIKES AND SURROGATES, DO WE NEED BOTH?

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The users of measurement data in environmental chemistry require specific knowledge of the quality of environmental measurements. Since samples are known to vary considerably in analytical difficulty, it is best to have estimates of precision and accuracy for each analysis. Conventional approaches, such as performing a replicate spiking study (e.g., standard additions) on each sample would be prohibitively expensive for the analysis of organic samples. By examining existing quality assurance data, we investigated the relative merits of two lower-cost alternatives. These include 1) spiking one sample from each batch of samples of the same matrix with a subset of the analyte list and performing duplicate analyses of this fortified sample, and 2) spiking every sample with a known quantity of surrogate compounds (substitute or isotopically labeled compounds). While either approach will yield estimates of precision and accuracy, we found better information in the estimates derived from surrogate analysis. Minor modification of the set of surrogate compounds would further enhance the quality of these estimates. Based on these results and on cost considerations, we recommend, contingent upon the execution of a properly designed confirmatory analytical experimental study, the use of surrogate recoveries in the estimation of precision and accuracy in each semi-volatile and pesticide analysis. The analytical design of the analysis for volatile compounds will require a new approach to obtain meaningful estimates of precision and accuracy.

NOTICE

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7 QUALITY ASSURANCE FOR ENVIRONMENTAL SAMPLING

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ABSTRACT

The concept of quality assurance (QA), in environmental sampling and analytical activities, is most often applied to the environmental laboratory. However, to ensure that data are both legally defensible and scientifically valid, the procedures, equipment, and personnel for the sampling portion of the environmental measurement process must meet requirements similar to those for the laboratory. They must also be reviewed with equal criticism, because the potential for error which can result in inadequate, biased, or invalid data is just as great during sampling operations as it is during laboratory analysis.

Though the QA requirements for field sampling are well documented in Environmental Protection Agency (EPA) references, they are often contained in documents where sampling is not the main focus, and are not always noted or understood. Therefore, much of what is known or practiced in QA for field sampling is obtained the hard way, through trial and error. It is essential that those performing the work have clear and specific guidance on QA procedures for the sampling portion of the environmental measurement process.

The QA activities associated with environmental sampling can be divided into three areas: pre-sampling preparation, collection of samples including quality control samples, and post-sampling preparation. This article will review these areas and provide recommendations on the specific steps needed to produce legally defensible and scientifically valid data.

PRESAMPLING ACTIVITIES

Presampling activities include both organizational and procedural planning. A project coordinator and an independent QA coordinator must be selected. Also, to ensure that the responsibilities for each different phase of the project are clear and that critical parts of the investigation are not be overlooked, a project organization chart must be written outlining the specific responsibilities of each project team member.

Once the project organization is clearly defined, a QA project plan (QAPP) must be written, which often happens in tandem with the writing of a work plan. Sometimes, the two plans are combined into one document. Required elements that must be included in the QAPP are listed in Figure 1. In addition, the workplan or combination QAPP/work plan should also include:

FIGURE 1. ELEMENTS OF THE QUALITY ASSURANCE PROJECT PLAN

1. Project Description and Purpose
2. Project Organization
3. Data Quality Objectives
4. Sampling Procedures
5. Sample Custody and Preservation
6. Calibration Procedures
7. Analytical Procedures
8. Data Reduction, Validation, and Reporting
9. Internal Quality Control
10. Systems and Performance Audits
11. Preventative Maintenance
12. Data Quality Assessment
13. Corrective Action
14. Quality Assurance Reporting

- a site specific sampling plan which is based on geostatistical or historic information about the site;

- standard operating procedures (SOPs) for sampling for every type of matrix involved including, groundwater, wastewater, soils, sludges, air, and composited samples;

- a summary of the tests to be performed based on historical data, the regulation of concern, and the data quality objectives; and,

- the number of samples, analytical methods, bottles, preservatives, and sample holding times for each sampling location;

The analytical laboratory should be selected prior to beginning the sampling phase of the project. The selection should be based on the laboratory's reputation for quality, the results of EPA performance evaluation (PE) sample studies, the analysis of PE samples for the specific tests to be performed, and an on-site laboratory audit. The laboratory should be kept fully informed of the anticipated sampling schedule, the number of samples to be taken, and the time the samples will arrive at the laboratory. This allows the laboratory to ensure that both holding and turnaround times can be met. Sending samples to a laboratory that is not informed and not prepared to receive them can result in the samples being given less attention or priority then samples which the laboratory had already accepted for analysis.

Sample bottles, preservatives, chain-of-custody records, custody seals, and other documentation should be acquired before going into the field. The sample shipping method also should also be determined beforehand. Proper planning can help eliminate common and detrimental sampling-related mistakes, such as the use of inappropriate sample containers, not preserving samples adequately, and not shipping the samples to the laboratory for several days because the laboratory or the method of shipment was unknown.

Project team members should be thoroughly trained for all equipment and procedures they will be expected to use during the sampling operation. They should also have been given a 40-hour hazardous waste training course as required in the Code of Federal Regulations (29 C.F.R. 1910.120) before entering potentially hazardous areas and collecting samples. This training should be documented in individual training records for each project team member. If the training documentation is procedure-specific and not project-specific, these training records can be used for future projects that involve the same procedures.

A project-specific safety plan must be written and an initial project meeting should be held to make certain that all project team members are familiar with the procedures to be

used. The project safety plan should outline the specific chemical and physical hazards expected to be encountered during the sampling operation, and provide measures for protection against those hazards. It is advisable, especially for larger projects, to select a project safety officer who is either an industrial safety or industrial hygiene professional to develop and implement the safety plan. It is also advisable to conduct personnel exposure monitoring and safety audits during the course of field operations.

The need to have quality considerations written into the formal plans before the actual operation begins is documented in the EPA's *Guidance on Remedial investigations Under CERCLA*: "Because the primary aim of the quality assurance/quality control program is to ensure that the data are reliable, rather than to ensure that a poorly conducted program is adequately documented, the QA/QC aspects should be planned in advance as an integral part of the investigation."

COLLECTION OF SAMPLES

Quality considerations in the collection of field samples include the use of sampling equipment and standard procedures, documentation of field activities, collection of field QA samples, and performance of field QA audits.

Standard cleaning procedures for sampling equipment should be used between samples to ensure that cross contamination does not occur. If historical data about the concentration levels of analytes of interest in the samples to be taken is available, it is often advisable to take the samples in order of increasing concentration to help prevent contamination of the sampling equipment after a high level sample is taken.

SOPs for use of sampling equipment, collection of samples, and the handling of samples after collection should be available in the field. Copies of the QAPP and/or workplan also should be available to project members in the field as reference. The most best-written QAPP and the most detailed SOPs can become ineffective if the sampling crew is not provided with copies.

Bound field notebooks should be used to record such items as the general sequence of events, the number of samples taken, any changes in sampling plans, geological observations, atmospheric conditions, difficulties in obtaining samples, and sample dates, times, locations, identifications, and descriptions (e.g., odors and colors). Any other unusual circumstances also should be recorded. For projects involving drilling operations, boring logs should be used.

Bottles, labels, preservatives, and chain-of-custody records should be prepared according to specific instructions before any samples are placed in the containers. Bottles should be washed and prepared using the appropriate EPA procedures, and they should be labeled with a sample identification that is traceable to field notebooks or to a master

sample-tracking log. The unique sample identifications, sampling location, date and time of sampling, sampler's name, tests to be performed on the sample, and the laboratory to which the sample is sent should be recorded in the field notebook or master tracking log should be . This process can be computerized in projects where computer capabilities are available; the sample information can be entered into the electronic logbook and sample labels and chain-of-custody records can be generated electronically.

QA samples, including trip blanks, equipment blanks, duplicates, PE samples and background samples, should be collected in the field. Consideration should also be given to the collection of additional sample volumes for laboratory duplicates and matrix spike analyses. To provide an independent check of the primary laboratory, a percentage of the samples can also be split and sent to two or more different laboratories. A summary of the types and recommended frequencies for field QA samples is presented in Table 1.

On-site sampling operation audits should be conducted and documented by the project QA coordinator to verify conformance with the QAPP and project SOPs, and to ensure that the field notebooks, chain-of-custody, and other documentation are complete. The representativeness of field and QA samples should also be monitored.

POST-SAMPLING ACTIVITIES

The first post-sampling activities include the decontamination of clothing, sampling equipment and the outside of sample containers. The decontamination procedures are outlined in the 40-hour hazardous waste training course. Care should be taken to ensure that the decontamination of the outside of sample containers does not affect sample results. For example, it would not be advisable to use benzene, toluene, or other solvents to clean the outside of a sample container holding sludge that will be analyzed for volatile organic compounds. All waste from the decontamination, including disposable clothing, should be disposed of using approved hazardous waste procedures.

Before leaving the sampling location, field logbooks and other documents should be rechecked to ensure that the information recorded is complete. Information that can be retrieved easily at this time may not be recoverable once the sampling crew has left the site, or once the site is altered in anyway after the sampling event (such as by earth moving equipment).

Samples that require cooling as part of the preservation should be placed in cold storage at 4°C as soon as possible after sample collection. It is important that containers be prepared adequately prior to shipment to ensure that the temperature is maintained until the samples arrive at the laboratory. Insulated coolers should be filled with sample containers and ice so as to prevent breakage of samples during shipment. Individual containers can be placed in plastic bags to avoid sample cross-contamination. Custody seals should be placed on the cap or lid of each container and on the lid of the shipping

TABLE 1. RECOMMENDED TYPES AND FREQUENCIES FOR FIELD QUALITY ASSURANCE SAMPLES

TYPE	PURPOSE	RECOMMENDED FREQUENCY
Field (Equipment) Blank	Measure background level in sampling equipment and containers	5% or one per sampling event
Trip Blank	Measures background level from sample transport and containers	One per sample shipment
Decontamination Blanks	Measures background level from field decontamination procedures	One per each decontamination procedure
Replicates	Measure variability in results from representative field locations or sampling procedures	5% or one per batch
Splits	Measure variability in results between laboratories	5% or one per sampling event
Field PE Samples	Measure accuracy of overall measurement system	One set per project

container to ensure that samples are not tampered with during shipment.

Unless circumstances prevent it, the samples should be shipped the same day they are taken, and should be received the following day at the laboratory. This helps to ensure that the samples reach the laboratory at the proper temperature, and that the laboratory has ample time to analyze the samples within the holding and turnaround times. If samples are not shipped immediately after sample collection, they should be put in secure storage areas that are accessible only by appropriate project personnel. Samples should never be left unattended. Before samples are shipped, it is advisable to record the airbill or shipping bill number on the chain-of-custody record. Chain-of-Custody, which must be completed before the sample is shipped, are placed in a sealed plastic bag inside of the shipping container. The chain-of-custody record should never be shipped separately.

CORRECTIVE ACTION AND DATA EVALUATION

Corrective action should be taken immediately for any deficiencies noted by a field sampling operations audit or field data evaluation. However, unlike laboratory QC samples, which are used as an ongoing control of the measurement process, field QA samples can only be used for assessing the quality of the data after they have been collected. Since this feedback is not immediate, the use of standard field QA procedures is the best way to minimize errors that can result in inadequate, biased, of invalid data. After the project is completed, the field documentation, results of field QA samples, and reports of sampling operations audits should be reviewed, along with the laboratory documentation and results, to determine if the requirements originally outlined in the QAPP have been met. A summary of this review should be included in any report written about the study, and where appropriate, the data should be qualified to indicate any
limitations there may be in fulfilling the original purpose of the study.

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AUTOMATED REAL-TIME PROJECT LEVEL LABORATORY QUALITY ASSURANCE

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ABSTRACT

Automated, real-time laboratory data management systems can be used in conjunction with Data Quality Objectives (DQO's) based on client needs, objectives and historical site information to design a relational database management system that provides control beyond the typical analysis and quality control database. With appropriate client/laboratory communication and interaction, such a system will provide clients with a complete project results database.

Curtis & Tompkins has designed a real-time laboratory data management system that acquires data directly from instruments and automatically checks data for batch quality control and calibration as well as consistency with historical project data. This system provides maximum automation without compromising data security yielding improved efficiency while minimizing response time in correcting errors. The system provides Real-Time Quality Control (RT-QC) at these levels:

- Data Generation
  - Calibration
  - Batch Quality Control
  - Completeness

- Monitoring
  - Current sampling event trends and anomalies
  - Historical trends and anomalies
  - RCRA statistical data reduction

Analytical applications of this system can also be automatically performed. Examples of this are anion/cation balances, ICP interfering element checks, BTEX ratios (found vs. theoretical), and carbon balance (BOD/COD/TOC).

Such a system has benefits not only for the laboratory but for the client as well, including:

- Real-time feedback on data anomalies,
- Reduced costs of QC compliance and data review,
- Automatic statistical data reduction and graphical reporting, and
- Timely delivery of complete and defensible monitoring data.

This system results in unprecedented improvements in efficiency, accuracy, and process control to the data generation phase of monitoring projects. Consultants using these data can be more confident in data quality and historical consistency. They are free to concentrate on higher tasks such as trends determination and environmental risk assessment.

INTRODUCTION

Why Real-Time Quality Control

There are many sources of data associated with environmental projects including sampling, geological, geographical, analytical, meteorological, analytical QA/QC and industrial hygiene, project data quality objectives and available historical data. Any of the elements available to laboratory personnel can be entered into the database management system and used in producing the client or project results database.

Using the Real-Time Quality Control (RT-QC) application of this system, we are able to provide a detailed review of summary and raw laboratory data including the evaluation of measurable data quality parameters such as holding times, instrument calibration and batch quality control (including blank, laboratory control sample, surrogate, matrix spike/matrix spike duplicate and sample/sample duplicate information). The data are assessed to ensure that the raw data do indeed reflect what has been presented in the summary format (such as CLP-type forms). The overall goal being a complete report on the overall usability of the laboratory data specific to a particular job or project. The benefits of this automated screening system are tremendous.

- Diskette deliverables are evaluated for compliance with the measurable parameters
- Data may be checked quickly and easily to ensure compliance with project-specific requirements
- A comprehensive and thorough data compliance report is generated
- Highly trained, experienced personnel are not required to perform this operation

There are parameters which cannot be checked using this system. These include pattern recognition of chromatograms (e.g., petroleum hydrocarbons and PCB's), mass spectral interpretation of TIC identity, ICP and AA spectral interferences, and masking interferences in the case of matrix interference (e.g., with surrogates). Therefore, the system cannot perform all functions and does have some drawbacks including:

- Complete data validation cannot be performed
- Many laboratories cannot produce diskette deliverables
- Many data users do not understand the technology

By utilizing the system fully, a long-term monitoring application can be applied which will evaluate historical data in relation to the most recent sampling event and provide trending data or anomalous data points.

Designing the System

Certainly, one of the core concepts driving C&T's LIMS project is the recognition that the screening of laboratory data is most effective and appropriate when performed at the point of data generation. However, this is only the first of many decisions in the LIMS development process. Concerns other than data quality control impact the design, development and implementation of RT-QC. The generation of technically and legally defensible data requires the collection of all the data, whether or not it is to be reported to the client, and the future accessibility of this data must be assured. A client may not want a data validation package today, but they may need it in the future and all the information necessary to generate the package must be retrievable. Laboratory size, capital available for improvements, software and hardware systems currently in use, and the complexity of client requirements faced by the laboratory were our major considerations. C&T's experience is used as an example to illustrate some of these points.

System Requirements

RT-QC requires the availability of LIMS throughout the lab at every instrument and workstation where data are generated. C&T has invested heavily in computer hardware and software to support our vision of easy data access throughout the lab. (See Figure 1). C&T's RT-QC system builds on top of the data sharing backbone, but only a few components are really critical for a basic implementation of Real-Time QC.

Instrument Interfacing: there must be a means of gathering analytical data electronically and "piping" it directly into the LIMS. The majority of instruments at C&T are connected to LIMS via serial, or "RS-232" lines. Other instruments (gas chromatographs, for example) that are controlled by PC's send their data into LIMS over the local area network.

Relational Database Management Software (RDBMS): in our opinion a relational database is crucial to flexibly manage the large data feeds generated by a typical lab. C&T uses Oracle but selection of the RDBMS should be based on the actual database structures required by the laboratory, size of the facility, and the dollars available to allocate to such a system.

Multi-processing Operating System: the basic LIMS operating system must be capable of processing many streams of data at once, in real-time. A robust, multi-user operating system such as UNIX or Novell Netware should be considered.

Software Toolkit: it is most prudent to begin by examining the LIMS presently in place in the laboratory to determine it's ability to proceed with development of RT-QC. C&T started with a LIMS package from Automated Compliance Systems, which provides much out-of-the-box LIMS functionality, as well as a toolkit for customizing the software according to the needs of a particular lab. C&T RT-QC system was built in-house using this toolkit.

People: RT-QC development requires a high level of understanding of RDBMS technology in order to design the database structures required to efficiently screen data and provide immediate feedback.

When selecting a programmer (either as an in-house hire or a contractor) particular attention should be paid to how the person will fit within the culture of the laboratory. The programmer must be capable of drawing information out of chemists and technicians regarding the processes they are running and introducing new technology and concepts.

To maximize the success of any LIMS project, you must get buy in from the analytical staff to answer the question, "What's in it for me?" They must be involved with the project from the initial planning stages and should clearly see the benefits of its complete implementation. Adequate training of all staff will require time and resources and must be included by management in any development schedule.

The C&T Scenario

C&T has completely automated the procedure for completing the screening of EPA CLP metals data. We selected this process for testing our RT-QC ideas because: no data system was in place, which eliminated the need to determine how to integrate it into RT-QC; the CLP graphite furnace requirements are complex and confusing which often result in errors requiring rework (and extensive analyst training); the short duration of the analysis means that immediate feedback will result in timely correction and prevent generation of unacceptable data; and we had an immediate need to improve the laboratory's ability to deliver the product in a timely manner.

RT-QC has completely automated the process of assuring that data which are in the final results database meet project-specific requirements (often requiring implementation of CLP SOW). The data are handled electronically from initial generation, and deliverables are automatically generated to paper or diskette. Diskette results invariably match the paper report because they are generated from the same database. (See Figure 2.)

From the graphite furnace analysts's standpoint, RT-QC provides the answer to the question, can I go on? It does this by reviewing the analytical result against all the criteria specified in the CLP SOW; calibrations, blanks, QC samples, post digestion spikes, duplicate burns, and all the other criteria for acceptable data. For example, suppose we've taken a GFAA reading whose injection RSD is > 20%, the SOW specified limit. About 5 seconds after the reading is taken, LIMS parses the data file and reports back to the analyst that they will need to complete another analysis of the sample (along with the reason why). The analyst completes the next run, to which the LIMS responds again: this time, noting that the data have been marked with the appropriate CLP RSD flag. The analyst then continues the analytical sequence using subsequent feedback in the same manner.

At this point, the data are ready to report. A full-screen reporting utility is used to queue up and generate client-ready reports in proper CLP format. Note that nowhere in this process were data typed in by hand. Note also that no runs had to be repeated unnecessarily; under RT-QC, the analyst knows immediately when QC criteria are out of specification, and can adjust or abort the run as needed. And only compliant data were stored in the final results database.

SUMMARY

Laboratory Benefits

The benefits of RT-QC and associated data screening and evaluation are reduced turnaround time, increased productivity (both through rapid feedback and reducing rework), and improved data quality. Real-Time Quality Control uses automation to complete the tasks which people find tedious and error prone thereby producing these benefits.

Although RT-QC is rapid, thorough and many times more complete than traditional manual method of "after the fact" compliance screening, it cannot replace aspects of laboratory data evaluation which require "intelligent" review such as spectral and chromatographic interpretations. These activities require analytical judgement based on experience which is most efficiently provided by a chemist. In an indirect manner RT-QC gives the chemist the time necessary to do thorough chromatographic interpretation, turning this limitation into an overall advantage.

Client Benefits

Regulatory requirements continue to drive the quality improvement process in environmental laboratories. Commercial environmental laboratories have another incentive - we have to do it faster, cheaper, and better to remain competitive. This scenario provides a bright and challenging future for RT-QC.

The CLP example presented here is a practical place for a commercial laboratory to begin developing RT-QC, but many possibilities exist. Projects which involve more stable, consistent sample types will encounter fewer obstacles in the development stage. It may be advantageous to begin by providing immediate feedback concerning compliance with NPDES specified methods. The laboratory could easily extend the advantages of RT-QC by developing client, site, and sample specific requirements. Data could be submitted for internal laboratory QC requirements designed in the same manner as the example provided above but tailored to the laboratory's own QA/QC plan. Data which meet laboratory requirements could then be fed into a statistics software package and screened for trending against historic data, regulatory limits, or client supplied data quality objectives. Reanalysis of outliers could be initiated immediately (literally within seconds of generating the outlier) which would reduce the possibility of reporting an error, such as a false positive, to a client. Client reports could automatically indicate if regulatory limits were exceeded. The possibilities for improving service to the client is tremendous.

RT-QC and the Future

At C&T we believe that RT-QC is a necessary step in meeting the challenges of the '90s for commercial environmental laboratories. In the future as more clients develop project-specific data quality objectives, require electronic deliverables, and push for ever more rapid turnaround times laboratories must respond by automating the data screening process. The water pollution control community will continue to feel detection limit pressure with ever increasing possibilities of false positives and associated costs. Data trending against historic data points will become increasingly important to your clients. Extensions of RT-QC will allow transfer of results directly into statistical analysis software and provide immediate feedback to the analyst regarding the status of the data point. Such advantages are going to be key in meeting the challenges of the future.

FIGURE 1.

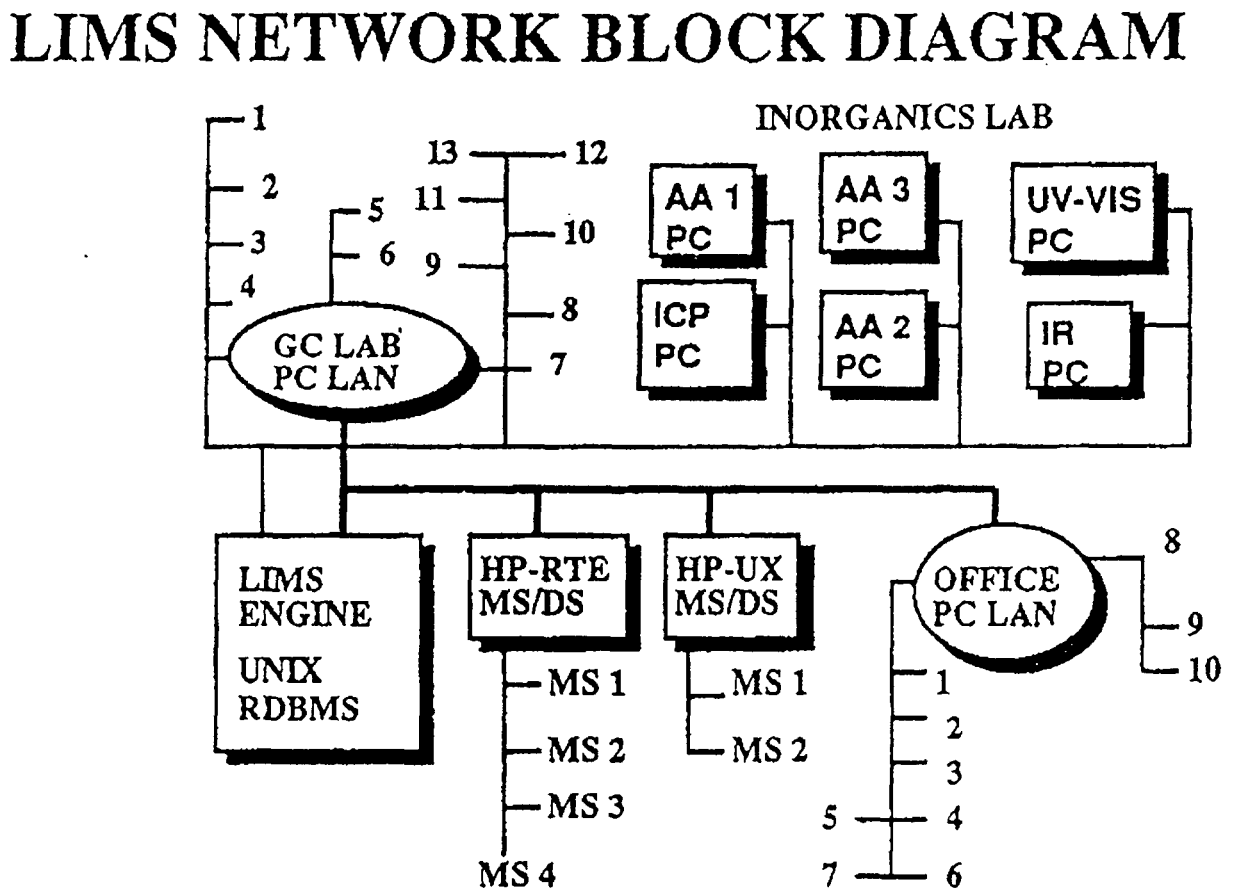

Figure 1: Complex multi-operating system computer network used to collect and evaluate data from instruments and data systems.

FIGURE 2.

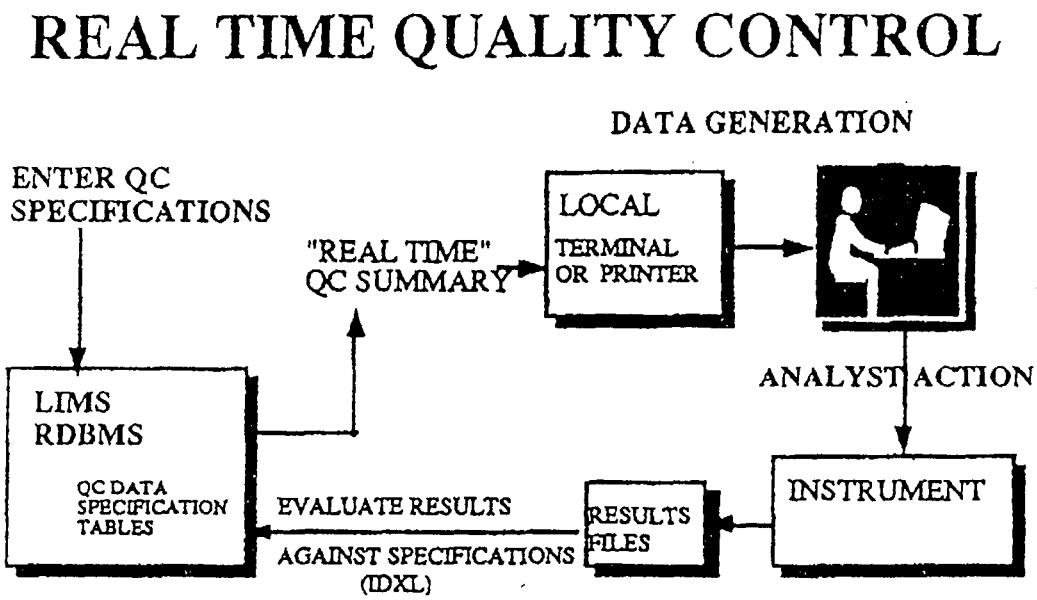

Figure 2: Process flow chart for real time QC. Data evaluated against QC specifications enetered into structures on LIMS file server are summarized directly to the analysts at their workstation within seconds of data generation.

9 FIELD AUDITING PROCEDURES FOR EPA CONTRACTOR PERSONNEL

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ABSTRACT

Traditionally, the major focus of quality assurance auditing in the hazardous waste remediation field has been directed at laboratory monitoring and performance. Field sampling and data collection activities have been identified as significant components in evaluating data validity and error. A comprehensive field auditing program should ensure that those who perform hazardous waste and environmental sampling are doing so in accordance with established Standard Operating Procedures (SOPs), Quality Assurance Objectives and site-specific scopes of work.

A procedure has been developed for performing internal audits of contractor performance at CERCLA Removal Actions within EPA Regions I through IV. This procedure is implemented through the use of a brief but thorough Site Audit Survey which directs the auditor's attention to all critical phases of hazardous waste site operations support. The prime focus areas include sampling methods including field screening (hazard categorization) techniques, use and calibration of direct-reading field monitoring instrumentation, site documentation, site data management, compliance with health and safety requirements, and adherence to specific contract requirements.

INTRODUCTION

For the Zone I Technical Assistance Team (TAT) contract, WESTON and its subcontractors employ over 200 multi-disciplinary environmental professionals in 11 office locations. These professionals provide technical and logistical support to the U.S. Environmental Protection Agency (EPA) at CERCLA emergency response and hazardous waste sites. The scope of work includes site assessment and evaluation, multi-media environmental sampling (including biota), treatment system design and evaluation, air monitoring, and general technical and engineering support within EPA Regions I through IV, ERT and Headquarters. All work assignments must be performed at the highest levels of professional quality and in accordance with the safety and health standards established by OSHA. Periodic visits from the regional and program management staff are necessary to ensure the quality of field work and client deliverables, and to identify procedural refinements to augment the quality of the TAT services. Audits of field/site operations are confined to the TAT contractor's scope of work and do not encompass any aspect of the EPA's decision-making process or management techniques.

DISCUSSION

Detailed Program Goals

The site audit format was designed and implemented as a positive and constructive means to 1) ensure adherence to EPA, TAT and WESTON quality assurance policies and procedures; 2) evaluate field screening and sampling capability and proficiency of field personnel; 3) identify regional and/or program-wide deficiencies or trends; 4) exchange innovative field techniques; and 5) obtain direct input from EPA On-Scene Coordinators and Site Managers regarding TAT contractor performance.

Program Preparation

The TAT auditing procedure required a strong commitment of both program and corporate resources. Initially, auditing objectives and protocols had to be developed and implemented which could evaluate and present an accurate picture of the proficiency and capability of personnel assigned to hazardous waste site operations and related support activities. WESTON chose to evaluate all aspects of field work, including technical, health and safety and administrative aspects. WESTON has embraced the concept of Total Quality Management (TQM) and therefore structured its auditing procedures to evaluate each component of a project and examine its performance and relationship to meeting the client's expectations.

Subsequently, qualified auditors were identified and trained. All participants were required to complete a 40-hour Hazardous Waste Site Worker Health and Safety Training Program required by OSHA in 29 CFR 1910.120. Completion of this training phase permits the auditors to freely move about hazardous waste sites to observe and evaluate worker compliance with specific sections of the site health and safety and QA sampling plans. Consistent with all other field personnel, the auditors are enrolled in a corporate medical monitoring program which evaluates and certifies each participant's physical ability to participate in site activities including the ability to use respiratory protective devices. Medical and respirator certifications enable the auditors to participate in site entry, sampling, and monitoring operations located in the hot zone.

Auditing Procedures

The centerpiece of the current site auditing program is the Site Audit Survey Form (Figures 1-1, 1-2 and 1-3). This form provides a framework for the site auditor including a brief listing of areas which should be examined during the auditing procedure. The following protocols are used as guidance when performing a site audit:

ZONE I
TECHNICAL ASSISTANCE TEAM (TAT)
SITE AUDIT SURVEY

SITE: _____ REGION: _____
LOCATION: _____ SITE LEAD: _____
SITE PHONE: _____ TATM ONSITE: _____
OSC: _____ _____

EVALUATION CRITERIA		COMMENTS
SCOPE OF WORK		
TDD is present in file	_____	_____
TAT is performing tasks requested	_____	_____
SITE DOCUMENTATION		
Site log is in proper format	_____	_____
Site files are organized	_____	_____
POLREPs are factual and regular	_____	_____
Personnel sign-in sheets are present	_____	_____
Site entry logs are maintained	_____	_____
Photographs are labeled and orderly	_____	_____
Off-site TAT costs are documented	_____	_____
COST TRACKING		
TAT costs are current	_____	_____
Project costs are current	_____	_____
RCMS is being used	_____	_____
EQUIPMENT USAGE		
TAT equipment is controlled	_____	_____
TAT personnel are trained in operation and maintenance of monitoring equipment	_____	_____
Instrumentation calibration and maintenance is documented	_____	_____

Y=Yes N=No M=Most of the Time O=Occasionally N=Never N/A=Not Applicable

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FIGURE 1-1

EVALUATION CRITERIA		COMMENTS
SITE MANAGEMENT (TAT)		
Site lead is designated		
Individual duties are assigned		
Morning safety meetings are held		
TECHNICAL INPUT		
TAT is monitoring removal		
TAT assisted with scope of work		
TAT performed spill containment		
Innovative treatment technologies were evaluated		
Disposal options were evaluated		
SAMPLING AND MONITORING		
Sampling plan is current		
Applicable SOPs are present and followed		
Sampling equipment is decontaminated properly		
Field screening is used appropriately		
Air monitoring is conducted as per SOPs		
Analytical Data is present		
Validation conducted by		
Funding source utilized		
HEALTH AND SAFETY		
Safety plan is complete to date and signed		
Directions to the hospital are present		
Emergency phone numbers are posted		
Site Emergency Plan exists		
Safety Plan has been implemented		
Site is controlled		
Decontamination systems are in place and effective		
Overall safety precautions are in effect		

Y=Yes N=No M=Most of the Time O=Occasionally N=Never N/A=Not Applicable

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FIGURE 1-2

9th Annual U.S. EPA Symposium on Solid Waste Testing and Quality Assurance - Proceedings July 12 - 16, 1993

OVERALL PERFORMANCE COMMENTS

Describe Site Conditions: _____

Describe Activities Observed: _____

EPA Performance Comments: _____

Other Comments: _____

TAT AUDITORS: _____ DATE: _____

_____ DATE: _____

C:\WP51\DOC\MISC_DOC\GERBO\TAT_SITE.AUD

FIGURE 1-3

9th Annual U.S. EPA Symposium on Solid Waste Testing and Quality Assurance - Proceedings July 12 - 16, 1993

1) If an audit is to be conducted by the TAT Zone Program Management Office (ZPMO), a member of the ZPMO contacts the appropriate TAT regional office manager to schedule a mutually agreeable date to perform the site audit. The office manager may designate himself/herself or a senior member of the regional management team to accompany the ZPMO representative to the site on the established date.

2) If the audit is to be performed solely by the regional TAT office, the office manager or selected senior regional management member is responsible for the completion of the audit and corresponding reporting procedure.

3) The EPA On-Scene Coordinator or Site Manager is notified by the TAT office manager of the pending audit at least 24 hours in advance. At this time, the EPA site manager may be requested not to inform the on-site contractor personnel of the upcoming audit.

4) Upon arriving on site, the auditor identifies himself/herself to the EPA and contractor personnel, produces an identification and health and safety certification card, completes the site sign-in sheet, reads/acknowledges the site safety plan, and briefs appropriate personnel on the purpose and procedures associated with the audit process.

5) The auditor evaluates site activities and records in a manner to minimize the interference with normal site activities. The auditor uses the Site Audit Survey Form to evaluate the following major areas as applicable to the site scope of work:

- Work assignment documentation
- Field and personal log books including supporting documentation
- Site QA sampling plan
- Site health and safety plan including amendments
- Equipment (monitoring instrumentation) use proficiency of field personnel
- Field calibration and maintenance logs for all field instrumentation
- Storage and maintenance of equipment,
- Site reports and client work product deliverables

6) A hot zone entry may be made by the auditor to observe site operations (e.g., soil sampling) and ensure adherence to relevant sections of the site scope of work, QA sampling plan and established EPA and TAT standard operating procedures. If properly trained, the auditor may participate in the respective site activity as a team member to more fully appreciate the actual working conditions and related operational and weather-related problems.

7) During a normal break period or after completion of the daily site activities, the auditor conducts a briefing with the contractor site lead to identify areas in need of

improvement; establishes a corrective actions plan to improve site operations; and reviews relevant program policies or procedures.

8) At the EPA Site Manager's convenience, the auditor solicits a candid evaluation of general contractor performance from the EPA manager. The auditor briefs the EPA Site Manager regarding the identified items to improve site operations and any technical advice.

9) The auditor subsequently drafts a report using a standardized outline (Figure 1-4) identifying the audit findings and corrective suggestions. This is sent to the EPA Site Manager and TAT regional manager for review and comment. After a ten day review period, the auditor initiates the final site report. These reports are then distributed to the TAT Zone Program Manager (ZPM), regional EPA Deputy Project Officer (DPO), and EPA Project Officer (PO) in Washington, DC.

Audit Frequency

The target frequency for regional field audits is three per quarter per each region. The ZPMO goal is to conduct three audits per quarter across the Zone.

SUMMARY

The current TAT site audit program has been in effect since June of 1989. Informal site auditing was performed using non-standardized formats prior to this time. A concerted effort was made to keep the Audit Survey Form brief despite the tendency to make continued revisions and lengthen the document. Finalized audit reports are typically from two to three pages in length. The simplicity of this auditing program is one of the primary causes for its longevity and acceptance by contractor and client personnel. Although the paperwork and personnel time commitments are minimal, this audit program has demonstrated its ability to maintain and improve the delivery of high quality services on a consistent basis. In terms of cost/benefit analysis, the return is significantly greater than the cost.

This auditing program has achieved numerous positive effects within the Zone I TAT contract including 1) the on-site evaluation of program field personnel; 2) the candid and timely feedback regarding contractor performance from the on-site EPA client; 3) the evaluation of the effectiveness and practicality of current standard operating procedures; and 4) the identification of regional or program-wide opportunities to improve training programs, purchase new field monitoring/support equipment, or revise standard operating procedures to accommodate new technologies.

Unanticipated benefits regarding this project are substantial. The on-site nature of this audit program requires the "hands-on" involvement of management, quality assurance and

Figure 1-4

SITE AUDIT REPORT OUTLINE

A. Introduction

1. Site Name
2. Location
3. Date of Audit
4. Auditors
5. Time Spent on site

B. Observations of Activities

1. Review assignment scope of work
2. Documentation
3. Equipment calibration, maintenance and use
4. Site management
5. Technical support
6. Health and Safety

C. Recommendations for Improvement

health and safety personnel. These individuals, many of whom had not performed actual site work for one or two years, regained their "real world" perspective on field work. This experience is extremely valuable to ensure that new or revised policies and procedures have a positive impact on field operations.

The technology transfer benefit of this auditing program also proved to be very beneficial. The auditors from the ZPMO were able to observe state-of-the-art techniques and innovative approaches to resolving unique site problems in a real world situation. Additionally, the auditors were able to participate in the assessment of the success or shortcomings of each application. Bimonthly program management meetings served as the forum to present these first hand observations to all the regional TAT office managers to augment their capabilities to serve their clients.

Another unplanned benefit was a marked improvement in the morale of field personnel including EPA Site Managers. The on-site presence of senior regional or program management auditors illustrated a commitment to field work and the front-line personnel. The site audit visit proved to be an excellent opportunity for field personnel to candidly interact with management to discuss issues and ideas in a non-office setting.

In conclusion, WESTON's audit program has been extremely effective during the execution of the Zone I TAT contract. It is our belief that this program can serve as a model for other hazardous waste site operations contracts.

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THE FIELD CHEMICAL DATA ACQUISITION PLAN: A DATA QUALITY OBJECTIVES APPROACH FOR THE USE OF REAL-TIME FIELD ANALYTICAL DATA IN ENVIRONMENTAL PROGRAMS

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ABSTRACT:

The acquisition and use of data from on site real-time sample analyses has conceptually always been the preferred approach for environmental programs. An examination of some field programs has shown that a full capability field analytical service yields a variety of project benefits including major decreases in project time; substantial cost savings in analytical services; increases in data quality; and decreases in health and safety concerns for sampling crews and nearby residents. Specialized vehicles for field analyses, e.g., vans and other mobile facilities, have been developed and manufactured. A variety of high quality portable and transportable analytical instruments have been developed to analyze soil, water, and air. Formalized research and developmental analytical programs exist in sensor technologies for industry and government. The question then arises, why are such field analytical services not routinely used? A possible explanation is in the lack of an up front planning guide for the acquisition of field chemical data. While the current data quality objective (DQO) guidelines present the up front planning framework for the entire remediation work plan process, the sampling and analysis plan has not fully explored the use of real-time field data. This oversight has restricted field analytical services. With the addition of a field chemical data acquisition plan to the work plan process, real-time field analytical data acquisition can assist in streamling the investigation and remediation process. This paper examines the state of environmental field analytical services today for the collection of real-time data and presents an approach using the current DQO methodology for preparing and implementation of a field data acquisition plan as part of the sampling and analysis plan.

This paper is the opinion of the authors. It does not reflect the current position/policy of the USEPA or USDOE. Any manufacturers noted are not recommendations of equipment but are examples of current equipment trends.

11

A NEW COST EFFECTIVE STRATEGY FOR ENVIRONMENTAL REPORTING SOFTWARE

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ABSTRACT

The prices for CLP reporting software have skyrocketed in the past year, reflecting the costs incurred by software vendors in attempting to stay current with the changing requirements and screening standards for CLP deliverables. The higher prices have put a new burden on environmental analysis laboratories, who are required to produce CLP and CLP-like computer generated reports. In an attempt to control the costs of environmental reporting software and reduce this burden on laboratories, TELECATION, INC. has spent the last year developing a new "software system", which takes advantage of efficient programming strategy to produce a variety of environmental deliverables at far less cost. In addition to the cost savings, the reporting options are more flexible, allowing both vendor and user to readily make sophisticated changes to address special variations in requirements. This approach has been used to generate reports modeled after the requirements of both CLP and RCRA/SW846, and other protocols are being examined. This paper will describe the techniques used to deliver both cost effectiveness and versatile software application for environmental reporting.

INTRODUCTION

The cost of computer software is controlled roughly by the ratio of the complexity of development to the market size. The market size for laboratory software applications is infinitesimally small compared to the general business software market place. This, along with the fact that many of the requirements of laboratory software make it inherently complex to develop, serve to inflate the final price of software designed specifically for laboratory use. The size of the market is a factor which cannot be controlled by a software vendor. However, the complexity of development can be controlled by applying large scale efficiencies in the process of software development.

Most laboratory software applications fall into the general categories of:

DATABASE APPLICATION - for data storage, retrieval, report generation, or;

SPREADSHEET APPLICATION - for calculations, data relationships, and graph generation

Since these are readily available tools, laboratories have always had the option of addressing their software needs by using one or more of the numerous, low cost generic database and spreadsheet products on the market and configuring the tools around each required application. Many laboratories, however, are not staffed with personnel who have the background, training, or time to configure and/or program the general purpose tools into a final application solution. Further, for laboratories who do have the programming resources, the additional costs of applying these resources to basic laboratory software needs largely offset the original cost savings realized in the general purpose software purchase.

A software vender who develops turnkey software solutions specifically for the laboratory market place must also incur these initial development costs. However, unlike the laboratory developing their own software, the software vendor can amortize the initial development cost over the entire client base for the product, providing a turnkey solution to a very specific task at a lower cost than it can be developed in-house, even if the programming resources exist. Even so, if each software application is developed from the "ground up" as a stand-alone product, the initial development cost for that product must be absorbed, only by the purchasers of that individual product. The next application will undergo a similar level of development, adding to the cost of that product, which again must be ultimately borne by the purchasers of that single product. The challenge for the software vendor seeking to reduce the prices of finished laboratory products is to address the repetitive nature of overhead development costs associated with each individual product.

A STRATEGY FOR PROGRAMMING EFFICIENCY

Approximately one year ago, TELECATION, INC., a company specializing in PC-based software for the laboratory, initiated a study into ways to dramatically increase the efficiencies of application programming with a corresponding reduction in development time and final software price. In doing so, TELECATION systematically analyzed the software needs of the laboratory community, looking for the software functions common to many different laboratory applications. The software company then embarked on a project to develop a base product which would contain most, if not all, of the software functions needed to implement almost any laboratory application. Additionally, the base product was specified to contain a variety of tools to give the user control over such things as database design, report definition, formula definition, etc. The goal for this product, in and unto itself, was that it should be the single-most powerful and flexible tool ever designed to specifically address laboratory software applications.

This product was to be different from the generic database and spreadsheet products on the market, in that it was to directly address specific laboratory needs. The system was designed to address general purpose laboratory data handling with little or no configuration by the final user of the product. Special laboratory-specific functions, like analytical quality control procedures, instrument interfacing, even export to LIMS, were part of the basic product.

To allow for extension of the capabilities of this product beyond the basic design, tools were provided for extensive tailoring for any specific task. A typical computer-oriented chemist could use the tools to automate very specific laboratory tasks, which could be routinely executed by anyone in the laboratory.

While user configurability of the system was to be a major feature of the software product, self-configuration of software solutions is, as previously stated, not necessarily in the best interest of every laboratory. Therefore, TELECATION expanded its strategy for the "universal" laboratory software tool to include its own, turnkeyed applications, running on the base software product. By using the configuration tools designed into the basic system, TELECATION did not have to design, code, test, validate and implement the basic functions, for which these processes had been previously conducted on the base product. In other words, the development overhead incurred in the base product, did not have to be repeated for each and every software solution operating on the basic system. TELECATION's goal of providing complete and specific software applications for the laboratory at breakthrough prices was, therefore, realized by implementing a systematic strategy for future software development, which dramatically reduces the product development overhead.

A block diagram of the concept is illustrated in Figure 1.

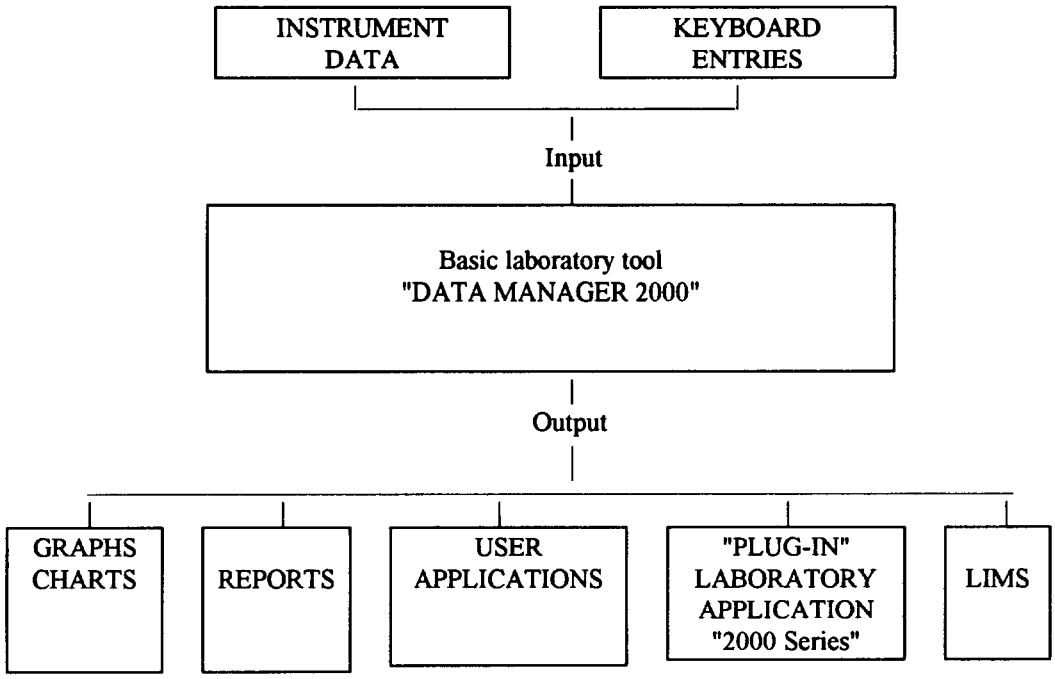

Figure 1. An Efficient Strategy for Laboratory Software Development

PLUG-IN APPLICATIONS FOR A GENERIC LABORATORY TOOL

The "base product" referred to above is called "DATA MANAGER 2000". The add-on applications, each of which takes advantage of the software development which went into DATA MANAGER 2000, are collectively referred to as "2000 Series Applications." All "2000 Series" applications literally "plug in" to DATA MANAGER 2000 through a series of program "hooks" designed to send and/or receive data from special data handling modules. The magnitude of effort which is required for each "2000 Series" application varies from literally a few hours for a simple application-specific database (like the Chemical Inventory Database) to many weeks for a more complicated application (CLP-like reporting), which may involve the automation of many relationships, calculations, and report formats. In all cases, the prices for "2000 Series" applications are far less than software products developed from the ground up with a specific purpose in mind.

A side by side comparison of software prices can be made in the case of CLP report generation software. TELECATION, INC. offers software products (the "ENVIROFORMS" ® product line) designed specifically to automate as much as possible the deliverable data requirements of the USEPA's Contract Laboratory Program (CLP). While the "2000 Series" products do not address all EPA-specific requirements with the same rigor as the "ENVIROFORMS" products, they provide an environmental deliverable which will meet the needs of most laboratories at a cost savings of approximately 85% compared to the CLP-specific alternative. Indeed, some of the price difference is associated with the development overhead associated with meeting EPA details in the "ENVIROFORMS" products, but much of the difference accrues from the programming efficiencies associated with the "2000 Series"

concept. (NOTE: TELECATION, INC. continues to offer and update the "ENVIROFORMS" software products for strict CLP applications, as well as the "2000 Series" products for those desiring to produce CLP-like deliverables at reduced prices.)

Table I lists the "2000 Series" applications currently available or under development. Given the company's extensive history with environmental software and the variety of environmental reporting protocols which have been promulgated, it is not surprising that many of these packages address environmental issues. However, of the current and planned applications, many address other laboratory tasks, as well. Specifically, a series of ISO 9000 and "Good Automated Laboratory Practices" (GALP) oriented tools are currently available and many more are under development.

Table I

EXAMPLES OF "2000 SERIES" PLUG-IN SOFTWARE APPLICATIONS

- CLP-like reporting for Inorganics, VOA, BNA, PEST
- RCRA/SW846 reporting for Inorganics, VOA, BNA, PEST
- Chemical Inventory System
- Hazardous Waste Disposal Tracking System
- Detection Limit Calculator & Reporter
- SOP Filing System
- Personnel Training Log
- R-Bar Chart
- Standards/Reference Material Log
- Computer Hardware/Revision Log
- Instrument Usage, Calibration & Maintenance Log
- Raw Data Archive Log
- Multi-Phasic TCLP/Inorganic Reporting System
- Storm Water Discharge Monitoring

ADDITIONAL BENEFITS OF THE STRATEGY

It was previously stated that market size, in addition to development complexity, plays a significant role in software pricing. In a very real sense, the product strategy described above increases the market size while reducing development complexity. Since each plug-in application uses the same base product, the development costs of the base product can be amortized over the market for all compatible products, which is significantly larger than for any single product. In this way, the development strategy is controlling both factors which affect software prices.

Price is not the only benefit from the strategy, however. Personnel training is a major concern and expense for a laboratory. In today's laboratory, a major portion of the training dollar goes toward training software operators. Since all applications in the "2000 Series" product line operate through a common base product, the learning process is greatly simplified. Once a user learns to use one application, they already have the background to use any other. The strategy thereby maximizes a laboratory's return on personnel training, by applying the experience gained with one application to all other system-compatible applications.

SUMMARY

Software prices for laboratory applications have traditionally been high due the small market size and complexity of development. Software prices can be significantly reduced through a software development strategy based on plug-in, application-specific routines which depend on the functions of a common base product for operation. In this way, the development effort which went into the base product can be used over and over again, thereby reducing the effort required to develop each compatible product. Additionally, the costs of the basic product can be amortized over the market size for all compatible products, which is significantly larger than that for any single product.

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Local Area Network Data Validation Software System

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ABSTRACT

The extensive data validation procedures required to review Contract Laboratory Program (CLP) data packages generated for both regulatory and private parties environmental investigations are extremely labor intensive and usually do not consider previous investigation data. To address these concerns, we have developed DataVal, a data validation software that reduces the review effort and enables the validators to access the full investigative database. DataVal translates CLP diskette deliverable formats (DDF) and automates validation procedures. DataVal enables the validation specialists to concentrate their review efforts in the interpretive areas of the data package. Using this software's capabilities to access the database generated over the entire course of a large investigation, the validation specialists and data users can better interpret the viability and usability of the analytical program results.

The DataVal software is a Client/Server application implemented on Windows™ based personal computers accessing a Relational Data Base Management System (RDBMS) that is a part of a Local Area Network (LAN). The Client component was developed using Visual Basic™ and the RDBMS component chosen was SQL Server. The software itself is modular in design, permitting the validators the flexibility to choose a "path" through the validation protocols. These "paths" allow assessment of complex data relationships and hierarchical review. The modular software design lets the validator set separate criteria for regional data validation modifications or set criteria for previous or future data validation requirements. The ability to access the previously validated database in the SQL Server allows validators to evaluate individual data sets in relation to the historical data.

Our company's project management system allows the transfer of laboratory information management system (LIMS) data directly into a larger project management historical database. DataVal is being integrated into this project management system. Upon completion of data validation, the data qualifiers are electronically transferred into the project management historical database, ensuring consistency of data qualification. The integration of DataVal into the project management data system combines a powerful data interpretation tool with a high capacity database management system. The data users are supplied with a a project database that is better evaluated, cost effective, and highly accurate.

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QUALITY ASSURANCE AND QUALITY CONTROL MEASURES FOR THE DETERMINATION OF HEXAVALENT CHROMIUM FROM STATIONARY SOURCES

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ABSTRACT

Midwest Research Institute has been collecting and analyzing stack gas samples for hexavalent chromium for the last 4 years utilizing the method from the Methods Manual for Compliance with BIF Regulations (EPA/530-SW-91-010). MRI has enhanced the methodology with the addition of matrix spikes, audit samples, reporting limit procedures, and validation of the integrity of sample preservation. This paper discusses these enhancements and associated data quality objectives plus the results from quality control samples.

In addition to performing hexavalent chromium analyses, MRI has also reviewed numerous trial burn plans and trial burn results under contract to the EPA. Through this experience, MRI has found that some firms conducting trial burns do not fully characterize the sample results in terms of the quality of the data. Problems include the contamination of collection reagent with hexavalent chromium, the lack of key information on the integrity of the collection media following sample collection and the lack of precision and accuracy data for the analysis results. These difficulties have resulted in trial burn plans which were deficient and trial burn results which could not be validated. This paper also addresses these issues.

1.0 INTRODUCTION AND BACKGROUND

1.1 Introduction

Midwest Research Institute (MRI) has been collecting and analyzing stack gas samples for hexavalent chromium for the last 4 years utilizing the method from the Methods Manual for Compliance with BIF Regulations (EPA/530-SW-91-010). In addition to performing hexavalent chromium analyses, MRI has also reviewed numerous trial burn plans and trial burn results under contract to the EPA. Through this experience, MRI has found that the method as written does not fully characterize the quality of sample results in regards to the

accuracy of the determinations, the detection limit and the validation of sampling activities. These difficulties have resulted in trial burn plans which were deficient and/or trial burn results which could not be validated due to a lack of information.

1.2 Background

Besides the typical Method 5 quality control (QC) procedures (e.g. calibrations, leak checks, etc.) the method for hexavalent chromium has 5 major quality control procedures:

1. Sampling Train Validation: Hexavalent chromium is an analyte which is very subject to reduction since it is a good oxidizer. To prevent loss of Cr^{+6} the pH of sampling train media (aqueous potassium hydroxide) must be maintained above 8.5, the train must be purged with nitrogen following sampling and the contents of the impingers must be filtered immediately following recovery.

2. Instrument Calibration: The instrument must be calibrated with at least four standards over one order of magnitude. A curve is run before and after samples and the relative percent difference (RPD) of the instrument response for the two analyses must be less than 10 %. In addition, the calibration standards must exhibit a relative accuracy of 93 to 107 % when calculated versus the linear regression curve.

3. Duplicate Analysis: Each sample must be analyzed in duplicate and the RPD of the instrument response must be less than 10 %. If RPD is not less than 10 %, the samples are reanalyzed until this criteria can be met.

4. Audit Sample: An EPA audit sample must be analyzed as an independent check on the accuracy of the determinations.

5. Blanks: Field blanks must be analyzed and can be used to correct emission data for blank contributions.

The method does not address the following three quality control subjects:

1. Sample Holding Times: Holding times are not given in the method. The only applicable RCRA holding time currently available indicates a 24 hour holding time (Chapter 2, SW-846, Revision 2, 11/90), but does not

require preservation at a pH above 8.5.

2. Accuracy: The method does not require any determination of the accuracy of the analysis as it pertains to the stack gas matrix (i.e. spikes).

3. Detection Limits: The method does not address detection limits or give a procedure for determining them.

The remainder of this paper will discuss some results for the method specified QC procedures and MRI's additional QC measures.

2.0 QUALITY CONTROL PROCEDURES AND RESULTS

2.1 Holding Times and Validation of Sampling

As previously indicated, holding times are not specified in the BIF method. The most current available RCRA holding time is 24 hours (Chapter 2 SW-846). However, most firms use a 14 or 28 day holding time with preservation requiring a pH greater than 8.5 and a temperature of 4 °C. The EPA/ASTM method for hexavalent chromium in water indicates a holding time of 24 hours with preservation at pH 9 to 9.5 and a temperature of 4 °C ("Determination of Dissolved Hexavalent Chromium in Drinking Water, Ground Water and Industrial Wastewater Effluents by Ion Chromatography: Collaborative Study" K. Edgell, et. al., Bionetics Corporation, April 6, 1992.) This document also indicates that dilute standards should be prepared daily but that stock standard solutions are stable for at least 3 months.

In planning trial burns or stack testing, it is best to be conservative and use the minimum acceptable holding time. Most EPA regions and states will approve a 14 to 28 day holding time with preservation at a pH greater than 8.5 and a temperature of 4 °C. The MRI field sampling and analysis team uses a 14 day holding time and preservation as indicated. However, when sampling is not performed by MRI, the laboratory meets a 14 day holding time from laboratory receipt.

During reviews of trial burn plans and reports, it has been noted that some researchers are not aware of holding times and preservation considerations for these samples. The following table gives results for the same samples, from the same stack, analyzed 6 and 19 days from receipt.

Table 1 * Results for Hexavalent Chromium Determinations in Stack Samples Analyzed 6 and 19 Days from Laboratory Receipt

Sample	pH	Result (ug/L) 6 Days From Receipt	Result (ug/L) 19 Days From Receipt	% Loss of Analyte From 6 to 19 Days
1	14	7.8	3.4	56
2	14	10.6	3.0	72
3	14	3.7	2.0	46
4	13	2.3	0.74	68
5	13	15.3	8.1	47

These results are only indicative of hexavalent chromium stability in impingers from that specific stack. It is interesting to note that the average loss is 58 % with a standard deviation of 12 indicating good agreement for the stability data despite the varying concentrations of the samples. These data clearly indicate that holding times are an issue and sample results can drop within the time frame accepted by regulatory agencies.

The BIF method has three validation steps which are specific to Cr^{+6} (as opposed to Method 5 requirements). These are a nitrogen purge of the train following sampling, the filtering of the samples following train takedown and each impinger must have a pH greater than 8.5 at the end of an analysis run. Many Quality Assurance Project Plans (QAPjP) for trial burns give descriptions of the sampling procedures but do not address these quality control measures. They should be discussed in the QAPjP and compliance must be documented during sampling to validate the collection and preservation of the samples.

Of critical importance is the pH of the impinger solutions. Many trial burn plans and reports do not address this topic. Some field sampling crews have adopted the practice of testing the stack before the trial burn and increasing the normality of the potassium hydroxide solution if needed for highly acidic stack gases to maintain a high pH. In addition, a significant number of trial burn reports and associated raw data do not have the pH documented in the field at the conclusion of sampling or upon receipt at the laboratory. Without evidence of a pH greater than 8.5, the

hexavalent chromium results cannot be validated.

Some permit applicants challenge the rejection of hexavalent chromium results in the absence of a pH check, and insist that the check was done even if it was not documented. MRI tracks the pH of samples received for hexavalent chromium analysis and in the past year about 10 % of the samples had a pH less than 8.5. The pH ranged from 5 to 7, and only one of these low pH samples had Cr^{+6} above the detection limit. (All samples collected by MRI personnel met the pH requirement.) Without documentation of sample preservation, the sample results can not be validated.

MRI measures the pH of all Cr^{+6} samples before analysis and reports the pH with the sample results in a manner similar to inorganic, volatile and cyanide samples which also require pH adjustment for preservation. Accreditation organizations, customers and regulators should demand that sampling firms document the pH of the impingers in the field and the pH should also be verified by the laboratory. Laboratories should not report Cr^{+6} results without also reporting the pH of the sample.

2.2 Precision Determinations

The method requires that each sample be analyzed in duplicate and that the RPD of the instrument response must be less than 10 %. If RPD is not less than 10 %, the samples are reanalyzed until this criterion can be met. There are three reasons why this is not a very practical way to handle precision. First, this requirement does not take into account the decrease in precision as the response approaches the instrument detection limit. Second, without a technical reason, the first analyses that do not meet 10 % RPD cannot be validly rejected and should be included in an average result. Third, this requirement assumes manual injection allowing for a repeat of analysis until the criteria is met. This is labor intensive and not practical given the availability of autosamplers.

MRI usually uses an autosampler for unattended, overnight analysis and injects all samples in duplicate. The precision criteria is rarely exceeded (<5 % of all analyses). In the cases where there are problems, it is usually due to the response being at the detection limit or there is significant interference from the stack gas matrix which is evident in the chromatogram (e.g. extraneous peaks.) If manual injections are made, the RPD is tracked and if samples do not meet the criterion it is analyzed a

third time and the average of all three analyses is reported.

In reviewing trial burn data for various EPA regions and states, MRI has noted that precision data are often not reported with trial burn results. Some laboratory reports do not address precision at all and others indicate only single analysis of each sample. These samples do not have any preparation beside filtering; therefore duplicate analysis is the only measurement of precision. The chromatograms are relatively short (<10 minutes) and duplicate analysis is not a burden. Permit writers need to be aware of this issue in reviewing trial burn plans and results.

2.3 Instrument Calibration

The method requires that the instrument be calibrated with at least four standards over a concentration range of one order of magnitude. All standards are run before and after samples and the relative percent difference (RPD) of the instrument response for the two analyses must be less than 10 %. In addition, the average of the calibration standards, analyzed before and after samples, must exhibit a relative accuracy of 93 to 107 % when calculated versus the linear regression curve. The calibration curve is verified with an EPA audit sample.

This method of calibration is not amenable to automation and routine analysis of large groups of samples. Since the standards are run before and after samples, the success or failure of calibration cannot be determined until after samples are analyzed. This not very practical. Instrument drift is usually negligible, however the relative accuracy of 93 to 107 % is sometimes hard to achieve with standards being run before and after samples. In addition, a curve of one order of magnitude covers a relatively small concentration range. Calibration criteria can be met with a 25-fold range and with a slight relaxation of criteria (i.e. 90 to 110 % relative accuracy) can be extended over a 100-fold range.

Currently MRI's clients want the method followed exactly as written to provide defensible data without any method modifications. However, the method could be updated and made more suitable for routine analysis by incorporating the following changes:

- Do not limit the calibration range.

- Require a curve at the beginning but not at the end. Initial calibration criteria should be 90 to 110 % relative accuracy.
- Require continuing calibration standards which must meet a 10 % drift criteria (measured using instrument response.)

These changes will increase laboratory efficiency and make the analysis method more like other SW-846 methods. It is hard to control instrument calibration when the calibration occurs before and after sample analysis. If criteria are not met; all samples must be reanalyzed, however the modified calibration criteria will require reanalysis for only those samples analyzed after the last successful continuing calibration. Of course, using the average of the curve run before and after samples provides marginally better data, but if the calibration criteria are set appropriately, data quality will not be affected.

These changes will not significantly affect data quality. When put in the context of the data quality objectives of the trial burn and other measurements of equal importance (GC/MS criteria are significantly wider) these changes will not affect regulatory decisions.

2.4 EPA Audit Samples

The method requires an analysis of an EPA audit sample and results must be within 90 to 110 % of the true value. The purpose of this sample is to serve as an independent check on the accuracy of the analysis; however it is not currently available from the EPA. Therefore, some method of verification of the accuracy of sample analysis is needed. The analysis method does not require an independent standard for calibration verification, thus there is no verification of acceptable calibration. For VOST and SVOST there are EPA audit samples and for metals analysis there is a requirement for calibration verification with an independent standard.

At MRI, we have QA personnel prepare an independent audit sample that is submitted for analysis with each batch of samples. The sample is prepared from NIST reference material in dilute potassium hydroxide to mimic the collection reagent and provide stability. The concentration of this sample is not known by analysis personnel. The results of the analysis must be within 90 to 110 % of its true value. The results for about 6 months of audit samples is presented below in Table 2.

Table 2 * Accuracy of MRI Hexavalent Chromium Internal Audit Samples

Audit Sample True Concentration (ug/L)	% Accuracy
10.2	102
11.5	110
9.5	98
13.7	101
9.1	101
6.9	98
8.8	110
12	97
8.8	101
8.6	100
Average (standard deviation)	102 (5)

Currently most firms do not provide this independent check on the accuracy of sample data; however, a similar check can be done by field samplers by submitting a reference solution. The preparation of such a standard requires purchasing reference material and the time takes about 1.5 hours (solution standards are stable for at least 3 months). Permit writers and trial burn reviewers should be aware that some independent check on the accuracy is needed.

2.5 Spike Sample Analysis

The analytical method does not require spikes of samples to determine the accuracy of the analysis given the stack gas matrix. However SW-846 requires spike samples, and the previously mentioned study using the ASTM and EPA methods for hexavalent chromium in water also require matrix spikes. MRI requires a determination of the accuracy and precision of every analysis to be evaluated in terms of the sample matrix. MRI does at least one matrix spike and sometimes a duplicate matrix spike for a set of samples from an incinerator, boiler or industrial furnace.

To prepare spikes, an aliquot of the sample is fortified with a very small amount of a high concentration standard to

achieve a concentration level in the middle of our calibration curve. This takes about 15 minutes of a laboratory technician's time. Our objective is for recovery to be between 80 and 120 %; however other objectives for trial burns, such as GC/MS surrogate recovery, are as wide as 50 to 150 % recovery. The data for the past year is summarized in Table 3.

Table 3 * Recovery of Stack Gas Impingers Spiked with Hexavalent Chromium

Initial Sample Concentration (ug/L)[1]	Average % Recovery from Matrix Spike Duplicates	Relative Percent Difference Between Duplicate
13.1	101	NA[2]
6.39	109	16
5.96	104	4
7.08	40	4
7.29	61	2
3.81	85	3
<1.0	92	7
<1.0	92	3
<1.0	89	NA
1.93	94	NA
Overall Average (standard deviation)	84 (22)	NA

[1] Spike level was about 10 ug/L for all samples
[2] NA = Not applicable; a single spike was prepared instead of duplicate spikes.

The spike recovery data indicates that most samples give a recovery well within the 80 to 120 % range; and all but one sample was within 50 to 150 % recovery. The precision of the results is excellent. Even though recovery is generally good, these data indicate that recovery is variable and without any spike determinations, the accuracy of the emission measurement is unknown. Usually samples with lower recovery show poor peak symmetry or extraneous peaks in the chromatogram, and these difficulties are consistent for

duplicate analyses of the matrix spike and between matrix spike duplicates. This indicates a truly different matrix from calibration standards and supports the claim that low recovery is due to the sample matrix and not to laboratory operations. In addition, good results for the audit sample provides evidence that the recovery problem is due to matrix effects and not a problem with calibration.

What is the impact of this low recovery? That depends upon the emission results. For example, the apparent problem indicated by the low recovery (40 to 65 %) in the previous table did not translate into a regulatory problem. Stack emissions for hexavalent chromium were very low and if emission rates were adjusted for the low recovery, risk assessment indicated acceptable incinerator performance. However, in cases where the emission results are borderline, recovery data are needed to support the regulatory decision.

2.6 Detection Limit Determinations

The method does not specifically define detection limits nor require their derivation. MRI has done detection limit determinations using multiple analyses of low standards (0.5 ug/L) and determined a detection based upon precision of about 0.2 ug/L. This 0.2 ug/L level is only slightly above the 5 times signal to noise ratio for most samples.

In analyzing calibration curves, MRI has determined that there exists a small amount of Cr^{+6} as background in our standards. The amount of this background level is between 0.2 and 0.4 ug/L and is evident as a positive intercept in the calibration curve by linear regression. This background level is due to the potassium hydroxide (0.1N) used to prepare calibration standards, since 0.1N potassium hydroxide has an observable Cr^{+6} peak and straight deionized water does not have any observable Cr^{+6}. However, this background is insignificant when compared to stack gas samples and the levels of regulatory interest. In addition, this background level is lower than or equal to that found in field blanks of collection reagent.

Due to this background, MRI has adopted a calibration curve that extends down to 1 ug/L and uses this level as a reporting limit. Since regulatory use of the data often employs the detection limit to prove low or no risk to the environment when the analyte is not detected, the use of the lowest calibration standard provides a conservative reporting limit. However, in reviewing trial burn plans and reports, MRI has noted that many firms doing these analyses

present detection limits without describing the derivation of the limit. In most cases this is not a difficulty due to the presence of hexavalent chromium in the samples, but in cases where the analyte is not detected, and emissions rates are based upon the detection limit, the detection limit must be supported with a technical justification.

2.7 Blank Correction

The method allows for correction of emission data by subtracting the amount found in the blank; however, a statistical justification for blank correction is not required. For example, to blank correct VOST results, the permit applicant must prove that the blanks are statistically different from the sample results. In reviewing trial burn reports, the blank correction option is often employed; however, its use is neither statistically justified nor is its impact upon the regulatory decision discussed. Often this blank correction comes from the analysis of a single field blank. In one case, the blank correction lowered emission levels by 25 to 50 %.

The general policy for blank correction in trial burns presented in Handbook of QA/QC Procedures in Hazardous Waste Incineration (EPA/625/6-89/023, January 1990) is to provide a statistical justification of the blank correction and to present emission data both corrected and uncorrected. Given the high toxicity of hexavalent chromium, this policy should be incorporated in future revisions of the method. In addition, permit writers have considerable latitude in requiring trial burn information, and they should accept blank corrected emissions only with clear justification and the emission rates presented as corrected and uncorrected.

3.0 CONCLUSION

The hexavalent chromium analysis method is rigorous and produces relatively precise and accurate data suitable for regulatory decision making. However, it does have a few short-comings in QA/QC procedures for holding times, accuracy, detection limits and handling blank data. In addition, calibration and duplicate analysis requirements could be modified to allow a more cost effective automation of the analysis. It is hoped that the topics brought up in this paper will be used when the method is updated and that the enhancements will be required by trial burn plan reviewers to monitor and demonstrate the quality of the sample results.

14 DEVELOPMENT OF TECHNOLOGY PERFORMANCE SPECIFICATIONS FOR VOLATILE ORGANIC COMPOUNDS

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INTRODUCTION

The Office of Technology Development (OTD) within the Office of Environmental Restoration and Waste Management of the Department of Energy has a mission to *deliver* needed and usable technologies to its customers. The primary customers are individuals and organizations performing environmental characterization and remediation, waste cleanup, and pollution prevention at DOE sites. DOE faces a monumental task in cleaning up the dozen or so major sites and hundreds of smaller sites that were or are used to produce the U. S. nuclear weapons arsenal and to develop nuclear technologies for national defense and for peaceful puposes (1,2). Contaminants and waste materials include the radionuclides associated with nuclear weapons, such as plutonium and tritium, and more common pollutants and wastes of industrial activity such as chromium, chlorinated solvents, and polychlorinated biphenyls (PCBs). Quite frequently hazardous wastes regulated by the Environmental Protection Agency are co-mingled with radioactive wastes regulated by the Nuclear Regulatory Commission to yield a "mixed waste," which increases the cleanup challenges from several perspectives.

To help OTD and its investigators meet DOE's cleanup goal, technology performance specifications are being implemented for research and development and DT&E projects. Technology performance specifications or "performance goals" describe, quantitatively where possible, the technology development needs being addressed. These specifications are used to establish milestones, evaluate the status of ongoing projects, and determine the success of completed projects. All too common within proposals, statements of work, and project milestones is a vague statement that the technology being developed will be "better, faster, safer, cheaper." A comparison to available technologies and quantitative definitions of the anticipated improvements are frequently lacking in proposals. Program managers and customers have little indication of whether they are funding a needed improvement in measurement technologies until the technology is actually developed, commercialized, and implemented.

This pilot project has focused on chemical measurement technologies for volatile organic compounds (VOCs) in soil and ground water. The project team has developed a model for the development and implementation of performance specifications and has applied this model to VOCs. The customers and their needs define the problems to be solved, a review of relevant available technologies defines the baseline from which development must progress, and quantitative performance specifications are identified on the basis of unmet monitoring needs. These general performance specifications are then translated into project-specific performance specifications in consultation with the principal investigator.

PERFORMANCE SPECIFICATION APPROACH

The general approach is to *document* what currently exists or is nearing completion and *compare* that baseline to the customers' needs to identify the *unmet requirements*. These

unmet requirements then are the basis for the technology development needs by the investigators, to be addressed. The process needs to be *quantitative* where appropriate, to steer project goals away from vague generalities like "faster" and toward specifics like "reduction of labor requirements for Step A from 4 hr to 0.5 hr."

Performance specifications constitute a program management tool and must fit within an overall program management structure. During the planning phase of a program, performance specifications are needed to identify the research or demonstrations requiring support. During the execution phase, performance specifications can help in the evaluation of both proposals and ongoing projects. The success of completed projects can be evaluated against the established performance specifications to provide a basis for considerations about further funding, technology transfer, or implementation.

For an individual project, technology performance specifications will be used to establish milestones, evaluate the status of ongoing projects, and determine the success of completed projects. Preliminary performance specifications will be required in proposals and will be evaluated as part of the proposal evaluation.

I. PERFORMANCE SPECIFICATION PROCESS

A. Baseline Technologies for an Environmental Research or Waste Management Need

1. *State the need* of the customer. What problems need to be solved? What are the boundaries of the need? (Limit the scope to a specific need to keep the process focused). What are the current deficiencies? What are needs versus desires? This information should be supplied in consultation with customers where possible; interactions need to both quantify the need and distinguish truly needed features and performance specifications from desired, but not required, properties.

   Discuss the potential impact of improved technologies. Where possible, quantitatively estimate what can be done better, faster, safer, or cheaper.

   This preliminary statement, prior to other work, is refined in Section I.

2. *Describe the relevant technologies* that can be applied to the customer's need. The focus is on the customers' need, not the technique, so address all viable alternatives, not only directly competing alternatives. (For example, characterization by gas chromatography/mass spectrometry, describe all VOC characterization technologies, not just the competing related technologies). In addition to available technologies, address current worldwide technology development and assess the probabilities of addressing unmet needs and the schedule for availability of the technology. For upcoming technologies, present only a brief overview of technologies that are still at the basic research stage, will not be available within the customer's time frame, or have a low probability of successful implementation. If no technologies currently exist to solve this problem state that.

   The text needs to include descriptions of technical alternatives, their status, their availability (with a list of vendors), and any barriers to implementation.

3. *Describe how the technology will be applied.* What are the conditions of the operating environment (environmental, space, health and safety, operational constraints)? What are the time requirements (setup time, measurement time, time to data availability, need for 24-hour operation.) What are the user attributes (education/training, number of operators).

4. *Tabulate quantitative performance specifications* for current technologies (including technologies under development that appear to be on a path toward successful and timely implementation and availability to DOE; i.e., don't fund new research and development if something is already in the pipeline). Since it is possible to consider specifications in dozens of areas (technical performance, cost considerations, applicability, availability, etc.), restrict the effort by limiting the list to the ten most important specifications, cost should be one of the ten.

5. *Document all* of the above and provide statements about the quality of the information (e.g., average of five vendors' specifications with similar applications to DOE needs versus educated guess with no firm information).

B. Customer Requirements

Revise and refine the customer need statement developed in Section I.A Address the following issues in more detail:

1. *Identify problems* that need to be solved. See Section I.A for more details.

2. *Identify the customer(s).* Name sites, sub organizations, individuals, operable units, etc. where available.

3. *Define quantitative requirements* (e.g., regulatory drivers for detection limits).

4. *Define functional and operating requirements .*

5. *Assess the priorities of* the need (e.g., critical versus desired for convenience).

6. *Assess the urgency* of the need (e.g., a start date for projects, by which commitments to technologies must be made).

7. *Document* all of the above.

C. Unmet Requirements

Compare baseline technologies versus customer needs and list unmet requirements.

D. Technology Development Needs

1. *Discuss the unmet requirements* that can realistically be met by the proposed technology; discuss the quantitative improvements that can be anticipated.

2. *Tabulate quantitative performance specifications* for the proposed technology (i.e., improvements over baseline).

3. *Assess the quality of estimates* (e.g., proven in other applications; within theoretical limits of techniques; best scientific judgment). Provide or reference documentation where available.

4. *Recommend priorities* where appropriate, for addressing requirements. These priorities should be based on the customers' priorities, the probability of success, and the time frame for completion. Discuss all considerations in the prioritization.

5. *Identify expertise* (organization, name, address, and phone) that can be tapped to confirm the validity of the effort.

After these steps, the needs baseline is established, and the performance specifications can be used as a program management tool to establish milestones, evaluate the status of ongoing projects, and determine the success of completed projects.

II. PERFORMANCE SPECIFICATION PROCEDURE

The development of performance specifications is a program management function. To minimize bias in their preparation, the specifications must be prepared by a disinterested individual(s); on the other hand, persons preparing performance specifications need good technical skills and current awareness in the area. These skills are precisely those needed by potential investigators, so conflicts are to be expected. After internal management review, the draft should be critiqued by selected principal investigators both to provide additional technical input and to educate the principal investigators on the process.

III. USE OF PERFORMANCE SPECIFICATIONS

1. The following guidelines should be applied to the use of performance specifications: The *principal investigator* should use the performance specifications as a goal in developing work plans, quality assurance project plans, and experimental plans and in assessing the progress of work.

2. The *program manager* should use the performance specifications as a criterion for evaluating progress on the project. This will be especially critical at reviews where decisions on continued funding are made.

   The program manager should also refer to the performance specifications in communications about the projected value of the technology to potential users.

3. *Customers* can use the performance specifications to assess the applicability of the technology to their needs and can plan to transfer the technology to their site application as it nears completion of development.

4. All involved parties (principal investigator, program manager, and customer) must remember that performance specifications are subject to change as new information becomes available (new research results, change in programmatic goals or changes in the customer's needs). All involved parties must initiate change whenever new information becomes available that will change the basis for the performance specifications.

Changes in performance specifications can constitute a change in the statement of work and thus necessitate a contractual change and possibly adjustments in cost and schedule.

IV. APPLICATION TO VOC MEASUREMENT

Reviews of currently available technologies and ongoing research projects were prepared on the following topics:

- Gas Chromatograhy
- Gas Chromatography/Mass Spectrometry (GC/MS)
- Electrochemical sensors
- Raman spectroscopy
- Infrared spectroscopy
- Fiber optics (ultraviolet, fluorescence, etc.)

As an example, the GC/MS review found the following:

Two manufacturers currently market field GC/MS instrumentation, Bruker and Viking. Both systems are capable of operation under either line or battery power. Both are relatively insensitive to environmental conditions, but neither is light enough to be carried by a person. VOCs can be introduced to the system by liquid injection, thermal desorption, direct air sampling (bypass GC), air sampling by trapping on sorbent thermal desorption and purging and trapping.

An older version of the Bruker instrument has been extensively used in the field for VOC analysis with results generally both more accurate and more precise than those from parallel fixed-base laboratory analysis, because loss of analyte during storage and transport is minimized. Substantial cost savings have been documented with field VOC analysis using field-portable GC/MS.

Current research on instrumentation focuses on developing a customized purge-and-trap/temperature-programmable GC for the instrument (Leibman et al. Los Alamos National Laboratory); development of a microprocessor to control the sampling system and software designed to integrate the sampling and ion trap functions (Hemberger et al. Los Alamos National Laboratory); and development of direct-sampling ion trap mass spectrometry technology by Guerin and co-workers at Oak Ridge National Laboratory. On the last project, no gas chromatography is provided for separation of compounds;

the mass spectral discrimination is judged sufficient. Sample introduction systems have been developed for air and water. The Los Alamos and Oak Ridge instruments have been field tested and are in various stages of commercialization. Additional work is being conducted on development of a person-portable (backpack) instrument by Meuzelaar and co-workers at the University of Utah.

Work is in progress to integrate the initial findings of the reviews and the customer needs to determine the unmet needs and thus the technology development requirements.

V. CONCLUSION

Performance specifications formalize an informal process to screen potential areas of research and match technology development with customers' needs. Although the steps outlined here may appear daunting, the process provides a structure for program management. The benefits include early development of a linkage between ongoing research and the customer's needs and also minimization of replication of research.

Much work remains on this project as we attempt to implement performance specifications on technology development for VOC measurement . Application of this methodology to other characterization technologies and remediation technologies is contemplated.

ACKNOWLEDGMENT

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THE QAPjP QUAGMIRE

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ABSTRACT

The Quality Assurance Project Plan (QAPjP) has become quicksand for environmental investigations. As a regulator, I reviewed them, as a contractor I wrote them, as a laboratory director I tried to comply with them. As a taxpayer I am appalled by how what was originally intended to be a document used to ensure that data of adequate quality is obtained has degenerated into a pound of paper that takes too long to write, review, and revise. This paper will present the sticky points in the writing of QAPjPs and how good science is sacrificed for ease of QAPjP approval. The substance of regulatory agency comments and concerns about QAPjP contents and how they can be addressed will be relayed via horror stories. The viewpoint of the laboratory and it's often lack of involvement in the QAPjP will be offered. The new industry of data validation will be reviewed and it's impact on the QAPjP assessed. Suggestions for a creative overhaul of the QAPjP elements themselves and ideas for streamlining the development and approval processes will be proposed.

INTRODUCTION

December 29, 1980 marked the birth of the term Quality Assurance Project Plan (QAPjP). The EPA Office of Monitoring Systems and Quality Assurance created QAMS-005/80 "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans". And, like so many other "guidance" documents, QAMS-005/80 soon became defacto regulation. All QAPjPs, if they are to be approved, must follow these specifications. Earlier, the EPA Administrator in May, 1979 required that "QA" must be done, smarting from the lessons learned at Love Canal. QAMS-005/80 prescribed that the primary way that QA was going to be assured for environmental measurements was through this QAPjP document. QAMS-005/80 painstakingly describes how to number the pages but glosses over how specifically to relay precision, accuracy, representativeness, comparability and completeness (PARCC) parameters and the mysterious process of data assessment. The QAPjP was originally intended to address both the laboratory and field activities as part of the Sampling and Analysis Plan (SAP). The field activities have since been segregated in a stand alone document, the Field Sampling Plan (FSP). Unfortunately, the PARCC parameters are not carried over into the FSP as they relate to the field investigation. Subsequent documents covering Data Quality Objectives (EPA-540/G-87-003) and Category IV QAPjPs (EPA-

600/8-91-006) were developed to provide additional aid. All of these documents are intended to help in the production of an "approvable" QAPjP so that the investigation can begin. The quest for the approval signatures requires some floundering in the quagmire.

WRITING THE QAPjP

Despite the fact that the format of the QAPjP is relatively rigid, some creative writing is required to get it through the approval process. Avoiding controversial points often results in good science being sacrificed for ease of approval. Specific target analytes or indicators are avoided because they are non-routine and often the project team settles for CLP Contract Required Quantitation Limits (CRQL) because it is easier than finding/validating a method with a lower detection limit. Use of an already approved QAPjP as a template with the names changed (project, organizational chart, laboratory) is helpful, but this practice perpetuates the QAPjP as a one-size-fits-all pantyhose exercise that is not tailored to the specific project needs.

The major issues that delay approval of the QAPjP are identifying non-CLP laboratories to conduct the analyses, and including non-routine analytes and/or methods. Any way that these issues can be presented to soften their deviation from the usual CLP boilerplate, such as citing other EPA accepted references and internal guidance, can aid in quicker approval.

To CLP or not to CLP

The Contract Laboratory Program (CLP), first implemented in 1980, was never intended to be the defacto "certification" for environmental laboratories that it has evolved into today. This "certification" perception was a major finding of the 1991 EPA management review of the CLP. The perception is that if a laboratory is participating in the CLP, it has jumped through enough documentation, facilities audits, and QC hoops to "guarantee" error free data. This perception is not only unfair to those laboratories that for economic reasons choose not to pursue CLP contracts, it is untrue. Granted, the data package documentation that has taken 13 years to refine has withstood legal and independent data validator scrutiny, however non-CLP laboratories are also capable of providing the same defensible data packages to meet requirements.

It appears that when a non-CLP laboratory is named in a QAPjP, the degree of scrutiny by the approving agency increases. An on-site audit is triggered and often blind performance evaluation (PE) samples will be sent prior to the on-site audit. It is ironic that despite this increased surveillance

of non-CLP labs cited in QAPjPs, only CLP labs have ever been suspended or disbarred by the EPA. The QAPjP author can help head off an unnecessary round of comments by supplying the following information in the first draft:

- Lab certifications/state approvals
- Dates of independent on-site audits
- Blind PE studies lab participates in
- Experience of lab with Level IV data packages

Offers to provide written audit reports from other state and/or federal agencies and results of the last blind PE study should be made at the pre-QAPjP meeting.

To SAS or not to SAS

Active CLP labs are not immune to scrutiny, especially if non-traditional methods (those not included in the CLP Statement of Work) or lower detection limits are needed for the project. These conditions require a Special Analytical Services (SAS) request if the project is under the auspices of an EPA contract. The SAS necessitates that the author supply a fully documented Standard Operating Procedure (SOP) with QC specifications for number, type, and limits of internal QC samples. This is usually a Catch 22 proposition, as the analysis is "special" because there is no SOP, let alone standardized limits. Even if the QAPjP is not for a federal lead project, the proposed laboratory must supply the details of what will constitute the analysis method and acceptance criteria.

It is imperative that the lab method SOP submitted for non-traditional analyses contain the following items, or an additional submittal will likely be requested:

- Method specific QC (frequency and limits)
- Basis for limit determination
- How detection limit was determined
- Supporting data for detection limit

One of the most frustrating issues in QAPjP authoring is centered around the SAS. Often, reviewers with little or no laboratory experience will be tasked with determining the appropriateness of the proposed SOP submitted. The shortage of bench chemists who desire to switch gears to review paperwork, and the dynamic nature of environmental analytical chemistry contribute to the lack of QAPjP reviewers with hands-on lab experience. The most successful tactic to deal with this is to ask to have access to the agency reviewer and agency lab staff set up a conference with the proposed lab's analytical team and draft an acceptable SOP together.

QAPjP REVIEW COMMENTS

Written comments are received from the agency reviewers and assessed by the project team for whether the QAPjP would need a substantive change affecting project scope, budget and/or schedule. Over the course of 13 years of authoring QAPjPs and responding to comments, I have compiled some requested revisions that illustrate the concept of losing the forest for the trees by focusing on minute technical details that do not make the project data more defensible:

The Case of the 5 Point Curve

The reviewer insisted on an initial 5 point curve for an indicator analyte that was expected at high concentrations. The lab SOP detailed a 4 point curve and an independent check standard at a fifth concentration analyzed every 20 samples. Heated 2 hour conference calls over the linearity of the curve near the detection limit and the semantics of the SW846 terminology of "minimum calibration" requirements against agency "requirements" ensued while leachate from the site ran into the river. The gap between this PRP QAPjP submittal and start of the field work was 15 months. The lab rolled over and rewrote their SOP to include an additional calibration curve concentration near the detection limit and dedicated a project "babysitter" to ensure that the analysts added the extra curve concentration. The detected concentrations in the samples were so high that a 3 point curve would have easily sufficed as the range component of the calibration function was the driving issue for the project data, not the sensitivity.

The Case of the Best Professional Judgement Holding Time

A SAS request was prepared using a USGS reference method. As no holding time was established by the USGS in their method, the agency reviewer disregarded the 28 day holding time suggested for the same analyte in an EPA method, and used "best professional judgement" to require that the sample be analyzed within 48 hours of collection. The process for SMO to solicit labs that would even bid on the work took months. After the project was finally underway, the analysis could not be consistently accomplished within the 48 hour constraints, and resampling was done. Out of intellectual curiosity, samples were analyzed again within 28 days and results were not significantly different. The mythical holding time cost the project 3 extra days field time at an estimated cost of $6,000 and delayed the project start by 2 months.

Top Secret SOPs

Some laboratories feel that their analytical SOPs are so revolutionary and innovative that they consider them confidential, proprietary business information. Evidently there are many complex nuances to these analyses that another lab learning a helpful hint would affect competitive pricing. As proprietary information, these labs will only submit their SOPs **directly** to the reviewing agency and **not** to the QAPjP author. The perception is that there is a lucrative black market for lab SOPs and the QAPjP author is selling them on the street corner to other labs too lazy to write their own, let alone follow the reference method. What is ironic is that for any federal lead project, a citizen can request all pertinent laboratory data and SOPs under the Freedom of Information Act. Being caught between the reviewing agency questioning the details of an SOP one is not allowed to see, yet being held responsible for revising the SOP and using to assess the project data for compliance is a dilemma for the QA professional.

QAPjP COMMENT HALL OF FAME

QAPjPs have been revised to satisfy the following "substantive" comments:

1. References to data or locations should be changed to read "in" Table X/Figure Y.

2. In the organizational chart, the line from the Project QA Officer to the Project Manager should be a dotted line, and the agency QA Officer box should be equal in size and location to the agency Project Manager's box.

3. The procedure for calibration and maintenance of the field trailer thermometer/barometer should be included.

4. Sample container cleaning protocols are not adequate to ensure contaminant-free bottles. (The SOP attached to the QAPjP was the agency's Scope of Work from it's currently awarded bottle contract, only retyped.)

Once a revision to a QAPjP is made and resubmitted for review, it is not unusual to have a different reviewer assigned to it and the "do not pass go, do not collect $200" review process starts all over again.

THE MISSING LINK

More often than not, the lab that must follow the QAPjP is left out of it's creation entirely, or consulted at the last

minute before submittal. An approval signature from the lab's QA and managerial personnel was never included in QAMS-005/80. For those QAPjPs involving the federal CLP lab pool, this would be burdensome, but for PRP and state lead projects, review and approval involvement is a necessity, especially if the QAPjP author is from an independent engineering firm. This review/approval also is necessary for the lab to appropriately price the analyses and advise whether they have the capacity to produce the deliverables in the turnaround time allotted in the project schedule.

Once a candidate lab is selected and preliminary contact is made, the QA representative from the lab should be involved in project scoping and DQO negotiations. Attendance at the pre-QAPjP meeting is usually invaluable. This time is not perceived as profitable as lab analyses in the bottom line, but the angst this upfront planning will save later is well worth it.

Being placed in the middle of philosophical arguments between the agency chemist/reviewer and the lab on issues like the real utility of matrix spikes and lab duplicate control statistics is not a pleasant experience. Trying to relay chemical "technospeak" is frustrating and direct contact between the factions with the QAPjP author as mediator is the most efficient way to resolve these issues to get the QAPjP written and submitted.

DATA VALIDATION

It is not enough to specify the methods, QC, calibration, reporting forms, analytical standards, and data package contents/order. The resultant data package must often be assessed by an "independent" data reviewer to look for analytical errors or take issue with "best professional judgement" calls. The new industry of data validation boomed after the reported discovery of fraud in several laboratories, yet it is doubtful that without an on-site inspection by a skilled computer guru and chemist with lab experience, that the anomalies would have been caught in data packages during independent validation.

Data validation itself is an inexact science. Most validators defer to the National Functional Guidelines, but even these documents allow for interpretive dancing by the validator in the areas of the effects of out of compliance calibration compounds, matrix spikes and field precision data. One of the most disconcerting positions to be in is to be the laboratory QA fall guy when the data validators assess the data using criteria you were never made aware of - and nonpayment of the analytical bill is threatened by the QAPjP author. The

criteria to be used in the validation process should be stated in the QAPjP, along with who/what firm will accomplish it. The validator's authority, responsibility, and communication protocols should be clearly defined to control requests to the lab for resubmissions and additional information. Data validators should be involved early in the project planning to become educated in the project goals and expected analytical challenges. Validating analytical data in a vacuum without regard to balance between the intended use of the data and definitive precision and accuracy of each number is only an exercise in accounting.

QAPjP MAKEOVER

The 16 element QAPjp contains at least 9 sections that have evolved into boilerplate. The meat of the QAPjP is the table of proposed samples, analytes and methods generally found in Section 5.0. Listed below is each section of the current QAPjP format and suggested changes to each to streamline the writing and approval processes:

Section 1.0 Title Page: Add provisions for signatures for Laboratory Director, Laboratory QA Manager, and data validation firm.

Section 2.0 Table of Contents: Change to reflect consolidated sections as described below.

Section 3.0 Project Description: Expend effort to organize clearly the available historical data and analytical methods used, indicate historical data quality assessment and issues.

Section 4.0 Project Organization and Responsibility: Add the authority and responsibility of the data validator including reporting, lines and methods of communication and the process for interaction with the laboratory.

Section 5.0 QA Objectives for Measurement Data in Terms of Precision, Accuracy, Representativeness, Comparability and Completeness: Reduce this section to the table of samples, analytes, methods and internal/external QC samples and limits. Highlight any special detection limits and/or method restrictions. Delete canned text boilerplate definitions of PARCC. The comparability descriptions and objectives are not quantifiable, and it remains to be seen what magic limit of percent completeness constitutes an acceptable level. The whole issue of field data quality objectives needs to be recognized and defined for the project in this section.

Section 6.0 Sampling Procedures: This section usually defers to a separate site specific sampling plan, which is generally

reviewed separately.. The sampling procedures, especially the proposed sample collection containers, volumes, and preservatives should be reviewed by the lab to ensure that the specifications are compatible with the lab analyses.

Section 7.0 Custody: No earth shattering revolutions in chain-of-custody protocols has transpired over the last 13 years. This section is filler boilerplate and can be handled by reference to the sample collection plan and laboratory custody SOP.

Section 8.0 Calibration Procedures and Frequency: This section usually refers to the specific lab methods and should be deleted and contained in section 9.0.

Section 9.0 Analytical Methods: Lab specific SOPs should be attached or the CLP SOW cited. Any known project specific deviations or contingencies should be mentioned.

Section 10.0 Data Reduction, Validation and Reporting: The data validation firm should supply their proposed SOP for validation and aid in the preparation of this section. The usual rehash of how to calculate RPD, % recovery, etc. is unnecessary filler.

Section 11.0 Internal QC Checks: This section is not needed as it should be included in the table of samples/analytes/methods/QC in section 5.0. Any lab specific terms used should have been defined in footnotes or text in section 5.0.

Section 12.0 Performance and Systems Audits: This section is more canned boilerplate unless a site specific field and/or lab audit is proposed. Delete this section and include in section 4.0.

Section 13.0 Preventive Maintenance: Delete this section as the analytical method or field SOP should cover it. Any field meter maintenance should be included in the field sampling plan.

Section 14.0 Specific Routine Procedures to Assess Data Precision, Accuracy, and Completeness: This section repeats the table in section 5.0 and generally contains pages of definitions and verbiage on how to calculate items such as mean and standard deviation. Back in 1980, QAMS-005/80 noted that "Recommended guidelines and procedures to assess data precision, accuracy and completeness are being developed." We're still waiting.

Section 15.0 Corrective Action: Who can stop/restart lab

analyses under what conditions is a major area of concern to project budgets and schedule. Section 4.0 could include the flow of action to out of control situations.

Section 16.0 QA Reports to Management: Usually an elegantly written section that says little, it should contain the specifics of the project QA summary and who will write it.

SUMMARY

In the current system, for less than a year approval time from QAPjP submittal to approval, authors should use an active, upstanding CLP lab to do only routine CLP SOW regulated analyses on nice clean soil and water samples. The utility of full Level IV data packages being reviewed by a third party data validator firm should be evaluated for the project.

An overhaul of the QAPjP purpose and process is needed. An injection of the lab personnel and data validators early in the project planning and evidence of their commitment by signatory approval of the QAPjP is critical to the success of the project. The perceived dismal record of Superfund investigations completed and Record of Decisions signed and cleanup accomplished is testimony to this need for change. A task force consisting of lab personnel, engineering firms, data validators and risk assessors should be initiated by the EPA Quality Assurance Management Staff. As Congress now calls for Superfund to be "fixed", the logical place to start is it's infrastructure, the QAPjP.

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EVALUATION OF METHODS FOR DETERMINATION OF INSTRUMENT DETECTION LIMITS

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ABSTRACT

Instrument detection limits (IDLs) that are used in the EPA Contract Laboratory Program (CLP) are defined in the current Statement of Work (SOW), and are reported by CLP laboratories each quarter. The SOW requires that CLP laboratories perform seven analyses for each analyte (except cyanide) on three nonconsecutive days; determine the standard deviation for the analyses on each of those days; and sum the three standard deviations. This procedure is labor-intensive, requiring a full week before results are obtained. Questions have been raised regarding applicability of the results over an entire quarter. In an effort to obtain more current IDL information, the authors evaluated the daily IDLs obtained over a 3-month period and compared their results to the contract required detection limit (CRDL) and the quarterly IDL. Using data submitted by CLP laboratories, IDLs were calculated using continuing calibration blanks (CCB) and standards at two times the CRDL (CRA for atomic absorption analytes and CRI for inductively coupled plasma analytes). The daily method calculates IDLs from existing QA/QC data and analyses dedicated to just IDL determinations are not necessary. We compare the results from the analyses using the alternate daily methods to results from the analyses using the quarterly method defined in the SOW. These data may be useful for determining the applicability of the SOW method of IDL calculation.

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TECHNICAL INFORMATION MANAGEMENT FOR THE PIT 9 PROJECT IDAHO NATIONAL ENGINEERING LABORATORY

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ABSTRACT

This paper describes the development of an access controlled data system that provides group-wide accessibility of laboratory and field information in support of the Pit 9 cleanup at the Idaho National Engineering Laboratory. Pit 9 was selected for remedial action in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) pursuant to the Idaho National Engineering Laboratory Federal Facility Agreement and Consent Order. Pit 9 contains approximately 150,000 ft^3 of buried waste, of which approximately 110,000 ft^3 of transuranic waste was generated at the Rocky Flats Plant.

The Pit 9 remedial action consists of three phases: (1) Proof-of-Process Test (POP), (2) Limited Production Test (LPT), and (3) Final remediation. Data produced during POP will be used to evaluate subcontractor's performance as part of the procurement process, and to provide the Environmental Protection Agency (EPA) and the Idaho Department of Health and Welfare (IDHW) with data justifying use of the proposed process for remediation of Pit 9. It is in the best interest of the subcontractors and EG&G Idaho that POP data be identified as reliable, accurate, and verifiable by the U.S. Department of Energy, EPA, and IDHW. The LPT phase would demonstrate that all integrated systems function as proposed to give a high degree of confidence that all systems are reliable before full-scale remediation would begin. The data generated during full remediation will be used as evidence that applicable or relevant and appropriate requirements described in the Pit 9 record of decision had been met.

EG&G Idaho feels the credibility and legitimacy of data produced during the remedial action can be greatly improved by independent data management. EG&G Idaho will provide another layer of data legitimacy through electronic links to subcontractor's laboratory instruments and by using an independent laboratory information management system (LIMS). EG&G Idaho will independently store the laboratory instrument signals, the signal processing software, and the quality assurance records/documentation associated with sampling and/or analysis to an optical disk for future analysis, if required, to verify objectives have been met.

Data and information that supports the 3 phases of the Pit 9 remedial action will be received in many forms such as photos, images, graphs, video-text, audio-text, field notebooks, and electronic media. The system was developed on a VAX/WMS using Standard Query Language (SQL) Multimedia for rdB/VMS which is a solution for manipulating, storing, and retrieving objects from client applications. Storing multimedia objects in a database provides data integrity, concurrent access, security, standard storage format, and the ability to share data across applications. The SQL/services provide the ability to interface to the following environments: VMS, MS-DOS, Microsoft Windows, and MacIntosh systems. The system will provide for storage on optical media using Write Once Read Many (WORM) technology to provide long term storage, and will provide the necessary tools for rapid manipulation of the data to controlled user community long term. Ultimately, the purpose of this system is to provide a secure, historical data repository for multimedia technical information for the Pit 9 project.

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QUALITY ASSURANCE PLANS FOR BASIC RESEARCH AND NEW CONCEPT STUDIES

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ABSTRACT

Writing quality assurance project plans (QAPjPs) for basic research and new concept studies presents a major challenge to scientists and engineers. Due to the nature of basic research studies, few functions are followed repetitively in exactly the same manner, at least in the initial stages of the study and sometimes throughout the study. This often precludes the use of standard methods, operating procedures, the ability to designate appropriate corrective action, even planning complementary quality control checks, and other topics usually addressed in a QAPjP. Recently we were challenged with writing just such a QAPjP for a set of studies. It was clear that we needed to maximize the flexibility of EPA QA requirements, and so we chose to try the Category IV guidelines prepared by Guy Simes of the Risk Reduction Engineering Laboratory in Cincinnati. Because the studies all fell into the realm of field screening methods involving proofs of principle and new concepts, we addressed them together in the first version of the QAPjP. We soon found that many of the QA topics in those guidelines were still difficult to address. We resolved that the QAPjP be written with statements of commitment that, as progress is made in the research studies, the "holes" in the QAPjP would be filled and eventually, as appropriate, the studies would be broken out into individual QAPjPs. We also put a major emphasis on recordkeeping in order to ensure that each experimental step, observation, thought, and action be recorded in such a way that the research can be thoroughly understood, reported, and repeated. The purpose of our poster presentation is to provide a detailed explanation of how we prepared the QAPjP discussed and to give examples of how other research studies can address QAPjP requirements.

INTRODUCTION

The Harry Reid Center for Environmental Studies (HRC) has a number of basic research and new concept studies, the sponsors of which include the U.S. Environmental Protection Agency (EPA) and the Advanced Research Projects Agency (ARPA). These require preparation of Quality Assurance Project Plans (QAPjPs). If the QA requirements are not

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specified, HRC still has a policy of the need to define data quality objectives (DQOs) for its research and new concepts studies. In the process of trying to meet standard QAPjP requirements (U.S. EPA, 1983) to these types of basic research and new concept studies, it was discovered that many questions and objectives could not be established beforehand; they could not necessarily be anticipated. The QAPjP requirements were difficult and in some instances not possible to apply to research studies. In searching for Agency-accepted QAPjP guidance, some of the clearest, most concise, reasonable guidance devised was discovered in the form of the graded approach (Simes, 1991) written by Guy Simes at the U.S. EPA Risk Reduction Engineering Laboratory. This groundbreaking set of guidance documents introduced the concepts that 1) not all projects can meet quality needs in the same manner, and 2) QAPjP requirements are more flexible and therefore more supportive of study objectives than often realized.

This paper describes HRC's adaptation of the graded approach of QAPjP requirements to basic proof-of-principle and new concept research studies. It is meant to provide a basic template to assist investigators in writing QAPjPs.

SUMMARY

The graded approach to composing QAPjPs has four levels of requirements based on the category of study or project represented. Level I requirements are the most rigorous because the projects they address are critical to Agency goals and must withstand legal challenge (Simes, 1991). In comparison, Level IV requirements, the least rigorous of the four levels, address studies whose results are used to assess suppositions (Simes,1991). A comparison of QAPjP requirements is listed.

Standard QAPjP requirements (U.S. EPA, 1983)	Level IV QAPjP requirements (Simes, 1991)
Project Description	Project Description
Organization and Responsibilities	
QA Objectives	QA Objectives
Site Selection and Sampling Procedures	
Sample Custody	
Calibration Procedures and Frequency	
Analytical Procedures	Sampling and Analytical
Data Reduction, Validation, and Reporting	
Internal QC Checks	Approach to QA
Performance and Systems Audits	
Preventive Maintenance	
Calculation of Data Quality Indicators	
Corrective Action	
Quality Control Reports to Management	
References	References
Other Items	Other Items

Difficulty in specifying QA Objectives, parts of the Project Description, and a complete Approach to QA/QC presents problems due to the unavailability of data in new concept

and basic research studies. The solution to this problem lies in the commitment of the research team to document requirements as answers are obtained and to state intents within the QAPjP. The attached EXHIBIT is a condensed version of how HRC met the Level IV QAPjP requirements for one set of basic research studies and commits to the requirements for which there currently are no answers. Hopefully, research investigators can benefit from the information and our experience.

EXHIBIT

For an explanation of what is needed for each requirement of a Level IV QAPjP, refer directly to Simes (1989) for guidance. Presented here is a description of how HRC composed the QAPjP entitled "Proof-of-Principle and New Concepts Studies in Chemical Sensors, Biosensors, and *In Situ* Methods for Field Screening." The italicized print indicates guidance and notes for consideration in composing the missing portions of the QAPjP.

SECTION 1.0

PROJECT DESCRIPTION

1.1 GENERAL OVERVIEW

Field screening methods for hazardous waste site investigations need to be rapid and low cost to support on-site monitoring and characterization activities. A variety of *in situ* and field portable analytical methods are needed for the analysis of contaminants in all types of environmental media. Needs for environmental sensors also go hand-in-hand with needs for sampling devices and methods. This project is meant to address these requirements.

There are major barriers which, if overcome, would provide new capabilities in selectivity and sensitivity of devices for field screening. This applies to both point and remote sensing applications. For example, the major technology barrier to the development of fiber optic and other sensors based on chemical/biochemical reactions and/or molecular association effects is the proper selection of the sensor coating materials. In most cases there is also a challenge to marry the chemistry to the particular device being used. There is a need to develop small and low power systems while maintaining selectivity and sensitivity. There are a variety of opportunities to exploit including the use of solid phase sensor chemical and biochemical coatings, self-indicating films, solid-state extraction disks in combination with spectroscopy, ion mobility spectrometry as an *in situ* well monitor, spectroelectrochemistry, and technology integration, to mention a few.

1.1.1 The Process

There are two parts to this project. The **first** involves performing applied research on field screening and measurement methods relevant to the type of pollutants most frequently encountered at hazardous waste sites. This is an investment for the long term and is meant to address the needs for basic information for proof-of-concepts. The **second** part is for the short term and involves integration of existing technologies in the search for new concepts. The strategy also includes reviewing emerging research and technology, and transferring appropriate aspects to development of methods for field screening.

Meeting field screening needs presents a major challenge because of the many scenarios which could be encountered involving any combination of air, water, or soil. In addition, the possible analytes, specifically their number and nature, can present a major challenge

even to the most experienced chemist. Organic chemicals alone - volatile, semi-volatile, and non-volatile - could range from several to hundreds in a particular sample.

Field screening systems, whether they use microelectronics, electrodes, or fiber optics as transducers, i.e., the physical probe, require chemistry to be worked out for the specific chemical or class of chemicals to be monitored and measured. Many times not only are there no guidelines for practitioners for a particular application, but there is also no information base on the fundamental chemistry. For example, major barriers still remaining to be solved in recognition coating selection and evaluation include:

- Lack of an information base on reactions and molecular association effects in vapor-solid and liquid-solid phases which can be drawn upon for development of sensor coatings.
- Lack of guidelines on choosing selective coatings for use in conjunction with sensors.
- Lack of standard or reference methods for screening and evaluating candidate coatings in sensor applications.

1.1.2 Statement of Project Objectives

The general objective of this project is to design and develop new field screening methods, including those based on *in situ* processes. Priority is given to systems which offer simplicity, selectivity, sensitivity, and low cost. One focus will be to overcome the technology barrier posed by nonselective recognition coatings in sensor monitoring and measurement needs. The output can be applied to a variety of sensors utilizing molecular recognition events based on reactions or molecular association effects. Another focus will be to integrate existing technologies toward the development of new concepts in field screening. Listed below are specific objectives for some of the studies under this project taken from research and study plans. New and updated project objectives will be documented in revisions of this QAPjP and/or in study-specific reports/plans as the objectives develop.

Potential Use of Ultrasound in Chemical Monitoring--(Research Plan, M.S. Thesis in Environmental Chemistry, University of Nevada, Las Vegas: Grazyna Orzechowska, November 1992)

The major objective of this study is to examine the potential of combining sonication with existing multiparameter monitors such as chloride specific electrodes in detecting organochlorine pollutants in water. This is an example of technology integration.

The approach in using sonication is obviously applicable to compounds other than organochlorine ones; these could contain inorganic elements (other halides, phosphorus, nitrogen, and sulfur). Anions specific to the inorganic components would be produced in sonication. Changes in anion concentrations before and after sonication would be used in monitoring for the pollutants. The choice of organochlorine compounds was made because these compounds are the most common pollutants found at hazardous waste sites. Success

with compounds such as trichloroethylene, chloroform, etc., will serve as proof-of-principle and form a base for expanding the research to other pollutant classes.

Surface Acoustic Wave (SAW) Biosensor for Detection of Environmental Pollutants: Kim Rogers, 1992

Objectives of this study are to: 1) demonstrate the feasibility of a receptor- or antibody-based biosensor which can detect a single compound or several classes of compounds of environmental concern; and 2) develop protocols which will explore and define the applicability (i.e., limits of detection, sample matrix and preparation requirements, etc.) of this biosensor for field assays. In this case the recognition coating may be a chemical one or a biologically-derived material.

1.2 EXPERIMENTAL DESIGN

Experimental designs for many of the studies under this project are under development and will be further documented in revisions of this QAPjP and/or in study-specific reports/plans (as the Project Manager deems necessary) and as the designs are finalized. Listed here for the benefit of the reader/reviewer are current approaches for the specific studies addressed in the project objectives section.

Potential Use of Ultrasound in Chemical Monitoring--(Research Plan, M.S. Thesis in Environmental Chemistry, University of Nevada, Las Vegas: Grazyna Orzechowska, November 1992)

As mentioned in the project objectives section, the study is meant to examine the potential of combining sonication with existing multiparameter monitors in detecting organochlorine pollutants in water. Success will establish a proof-of-principle for obtaining more detailed data and for using the concept with other organic pollutant classes. There are a number of factors which influence the effectiveness of sonication in a chemical reacting system. These will be taken into account in designing the experiments. Examples follow.

Choice of the solvent--Factors such as molecular cohesion and surface tension of the solvent can affect cavitation. There is no solvent choice in the proposed research since the application is in water. This will be the solvent.

Reaction temperature--It is common practice in sonochemistry to use the lowest possible reaction temperature consistent with reasonable reaction time. Keeping temperature low (thus reducing solvent vapor pressure) minimizes "cushioning" effects which could reduce the temperatures and pressures in cavitation. The temperature will be kept close to room temperature using a cooling bath.

Irradiation frequencies--Frequencies between 20 and 50 kHz are normally used in sonochemistry. A Branson Sonifier - Cell Disrupter model 101-063-200 with 20 kHz and an output power of 400 W will be used for this work.

Choice of disruptor horns--Disruptor horns (probes) transmit ultrasonic energy into a solution. The dimensions of the horn and the ultrasonic output power setting determine

the amount of amplitude (tip movement) and degree of ultrasonic activity in the liquid. Generally, the smaller the tip diameter, the higher the amplitude. Larger tip diameters have less amplitude but can accommodate larger volumes.

Three horns have been chosen for this work, a 3/4" diameter high gain horn with solid tip, a high intensity 1" diameter cup horn, and a tapered 1/8" diameter microtip horn. This will allow some flexibility in designing the experiments. The tapered microtip horn, for example, will have an amplitude three and a half times greater at its end than a standard horn. It can be used with small solution volumes (1-2 mL).

Other sonication equipment--A stainless steel continuous flow attachment with a water cooling jacket will be available for continuous processing of test solutions.

Though ultrasound is above the audible range of the human ear, mechanical noise occurs when liquids are treated ultrasonically. A soundproof box will be available to reduce this noise.

Surface Acoustic Wave (SAW) Biosensor for Detection of Environmental Pollutants--(2% Initiative Study Description: Kim Rogers, 1992)

A number of basic parameters will be considered in the research approach to develop sensor recognition coatings. These include choices of the coatings and the test beds.

Choice of candidate recognition coatings--Several considerations have to be taken into account when choosing a recognition coating for sensor applications. First, one must decide whether a reversible or irreversible effect is to be sought, then the chemistry of the coating has to be considered, for example:

- chemical reaction vs. molecular association mechanisms
- covalent bond formation vs. weak Van der Waals interaction
- hydrogen bond vs. charge-transfer vs. other donor-acceptor mechanism
- bimolecular vs. catalytic reaction mechanisms

The strategy for biosensors is to seek coatings based on known reaction chemistry that occurs in solution. However, a different approach may be needed for gas-solid and vapor-solid configurations in sensor reaction chemistry. Factors that may affect sensor performance include:

- coating adhesion to the surface
- mass vs. mechanical sensor coating mechanism
- surface vs. bulk coating sensor effects
- gain or loss in coating mass with analyte sorption
- boiling point of the coating material
- crystalline solids vs. amorphous

Factors such as solubility and molecular weight will be considered in selection of the candidate coating material. Though the physical and chemical properties of a coating may seem ideal, the material may not form a film conducive to sensor applications. Some experiments may need to be designed by trial and error.

Choice of test bed (physical transducer)--Test beds for examining the candidate recognition coatings will utilize SAW probes and quartz crystal microbalance (QCM) sensors. These devices monitor mass changes.

The equipment for measuring SAW sensor effects include a 158 MHz electronic system, a 4-channel SAW data acquisition system, and a VG-400 automatic vapor generation system. This sensor is able to detect low ppb levels with a selectivity of 1,000:1 or more. The QCM is 12 MHz and somewhat less sensitive. However, it is useful for preliminary experiments.

Temperature of the reaction--The test system will be maintained at constant temperature, close to ambient conditions for the initial experiments. Different temperatures using the same coating may be considered to increase selectivity.

Analytes to be tested--In the biosensor research organic analytes such as PCBs will be chosen. The results of the study with PCBs will be extended to other organic analytes. The biosensor study will address two main challenges: first, to immobilize an active receptor or antibodies to piezoelectric devices and, second, to develop methodology which will allow for sensitive and reversible detection of environmental pollutants.

1.3 SCHEDULE

The technology integration activity utilizing sonication is scheduled to run for two years with a goal to demonstrate proof-of-principle.

The biosensor effort is also a two-year effort with a goal in the first year to construct a flow cell and to develop assay protocols for detection of the target compounds. At the end of two years, it is expected that standard assay protocols will be established and detection limits determined for target analytes. Matrix effects and sample preparation requirements for "real world" samples will be determined.

1.4 PROJECT ORGANIZATION AND RESPONSIBILITIES

This subsection, since it is self-explanatory, is eliminated to save space in these proceedings.

SECTION 2.0

QUALITY ASSURANCE OBJECTIVES

2.1 QA OBJECTIVES

Project objectives have been discussed in Section 1.0. Because the research performed under this project is basic proof of principles and new concepts investigations, specific QA objectives are not specified at this time. Initially the data will be evaluated qualitatively or semi-quantitatively. The data will be used to make decisions whether to proceed further in evaluating the field screening methods developed by this project and to evaluate proofs and concepts. A future goal of the project *is* the development of complete

QA objectives for specific activities once proofs-of-principles have been determined and concept validation is initiated involving environmentally-related measurement data.

2.2 QUANTITATIVE QA OBJECTIVES: PRECISION, ACCURACY, METHOD DETECTION LIMIT, AND COMPLETENESS

See Section 2.1. Specific quantitative QA objectives are not specified at this time. As they are developed, they will be included in reports and/or revisions of this document. Listed below in italics are self-notes of intention and guidance to be considered when the answers are available. Much of this guidance has been taken verbatim from a Simes document (Simes, 1989, 1991).

2.2.1 Precision

It is believed that it is possible to estimate precision from duplicate determinations when the project gets to the stage where measurements are being made.

2.2.2 Accuracy

Likewise accuracy may be determined from measurements of a known. For example, if the field screening method is applied to an SRM and gets an 80% recovery, this is an indication of accuracy.

2.2.3 Method Detection Limit

2.2.4 Completeness (Simes, 1991)

In addition, it must be explained how the QA objectives are to be interpreted in a statistical sense. Often they are interpreted in a sense that ***all*** *data must fall within certain windows; for this type of specification, any data that fail to satisfy QA objectives are rejected and corrective action is taken. However, other interpretations are possible. For example, the requirements may be satisfied if the* ***average recovery*** *is within the objectives. This is where we describe how tabulated QA objectives will be interpreted.*

2.3 QUALITATIVE QA OBJECTIVES: COMPARABILITY AND REPRESENTATIVENESS

See Section 2.1.

2.3.1 Comparability

This is the degree to which one data set can be compared to another. For example, to evaluate a cleanup process, analyses of the feed and discharge streams must be comparable. Another example, to perform a nationwide environmental survey, methods used at different locations must be comparable, probably by the use of consistent methods and traceability of standards to the same or a reliable source (Simes, 1991),

I think that for this project, comparability would be achieved by use of the same evaluation methods for each test phase or mechanism. For example, comparability would be achieved by using the same analytical methods to evaluate each sensor coating.

2.3.2 Representativeness

This is the degree to which a sample or group of samples is indicative of the population being studied. An environmental sample is representative for a parameter of interest when the average value obtained from a group of such samples tends towards the true value of that parameter in the actual environment, as the number of representative samples is increased. Representativeness is normally achieved by collecting a sufficiently large number of unbiased samples (Simes, 1991).

Because this study does not involve a sampling exercise, I think that representativeness is associated with the applicability to the "real world" in two ways: 1) testing a field screening device on spiked water or sand is not as representative as testing it in a real field situation; and 2) approaching the true value of the parameter is gained by testing the device a sufficiently large number of times in a real field situation.

2.4 OTHER QA OBJECTIVES

Mass changes for SAW and QCM sensors for "screening experiments" are sought to be ± 10% based on frequency changes.

2.5 EFFECTS OF NOT MEETING QA OBJECTIVES

Not meeting QA objectives may give false indications as to the efficacy of candidate recognition coatings being screened.

SECTION 3.0

SAMPLING AND ANALYTICAL PROCEDURES

3.1 SAMPLING PROCEDURES

This requirement does not apply for proof-of-principle and new-concept studies. These will be developed as part of each activity.

3.2 PROCESS MEASUREMENTS

Manufacturers' instructions for any needed process instruments will be followed.

3.3 ANALYTICAL PROCEDURES AND CALIBRATION

3.3.1 EPA-Approved or Other Validated Standard Methods

This requirement does not apply for proof-of-principle and new-concept studies. Methods will be developed as part of each activity.

3.3.2 Nonstandard or Modified Methods

This requirement does not apply for proof-of-principle and new-concept studies. Methods will be developed as part of each activity.

3.3.3 Calibration Procedure and Frequency

Manufacturers' instructions for instruments will be followed as recommended and necessary. An example is the calibration protocol for the Microsensor Systems Inc. Vapor Generator (Appendix A).

SECTION 4.0

APPROACH TO QA/QC

4.1 DATA RECORDKEEPING

Due to the very basic nature of the research performed for this project, few functions will be followed repetitively in exactly the same manner, at least in the initial stages of the studies. Therefore, it is important that each experimental step, observation, thought, and action be recorded to document the entire study in such a way that it can be thoroughly understood, reported, and repeated. Accurate and legible records of the research are noted in permanently-bound scientific notebooks. The scientific notebooks are prepared, controlled, and reviewed using the HRC standard operating procedure, scientific notebooks (Appendix A).

4.2 CALCULATION OF RESULTS (Simes, 1991)

This section is primarily reserved to show how analytical results will be manipulated to prove or disprove a hypothesis. This section should provide formulas and summarize any statistical procedures for reducing the data, including units and definitions of terms. Also define procedures that will be employed for determining outliers or flagging data.

If mass balance calculations are required, provide exact formulas relating the mass balance to the individual measurements that will be made. Specify data reporting requirements or plans at this point. Indicate units, matrices, and wet or dry intentions, etc. List deliverables and data deliverables for the report. Will the data package include raw data? What type of QC data will be reported?

The final report should also include a summary of the original QA objectives and a statement of whether they were met or further developments in this arena. If project/QA objectives were not met, explain the effect on the study or project.

4.2 INTERNAL QUALITY CONTROL (Simes, 1991)

Describe the nature and frequency of all QC methods. The QC procedures should relate to the QA/project objectives. They should be designed to support the objectives. Examples of QC checks to consider follow:

- *Samples*

  Collocated, split, replicate

- *Spikes*

  Spiked and duplicate spiked samples
  Spiked blanks
  Surrogate spikes and internal standards

- *Blanks*

  Sampling, field, trip, method, reagent, instrument
  Zero and span gases

- *Others*

  Standard reference materials
  Mass tuning for mass analysis
  Confirmation by second column (for GC) or instrument
  Control charts
  Independent check standard
  Determinations for detection limits
  Calibration standards
  Proficiency testing of analysts
  Any additional checks required by special needs of study

The use of ambiguous terms is a common problem in this section. The terms "duplicate" and "replicate" are examples. Explain the exact point in the study where replication occurs. Does "replicate" refer to samples collected simultaneously or sequentially in the field; to samples collected at the same sampling point but at different times; to samples that are split upon receipt in the lab; or to samples collected under yet another splitting protocol?

Similarly, there are numerous types of blanks; the exact procedure for preparing these blanks must also be described.

4.3 CALCULATION OF DATA QUALITY INDICATORS

4.3.1 Precision - (Simes, 1989)

If calculated from duplicate measurements:

$$RPD = \frac{(C_1 - C_2)\ x\ 100}{(C_1 + C_2)/2} \quad ;$$

RPD = relative percent difference,
C_1 = larger of the two observed values, and
C_2 = smaller of the two observed values.

If calculated from three or more replicates, use relative standard deviation (RSD) rather than RPD:

$$RSD = (s/\bar{y})\ x\ 100 \quad ;$$

RSD = relative standard deviation,
s = standard deviation, and
$\bar{y}$ = mean of replicate analyses.

When s is defined as follows:

$$s = \sqrt{\sum_{i=1}^{n} \frac{(y_i - \bar{y})^2}{n-1}}$$

s = standard deviation,
y_i = measured value of the i-th replicate,
$\bar{y}$ = mean of replicate measurements, and
n = number of replicates.

4.3.2 Accuracy - (Simes, 1989)

For measurements where spikes are used:

$$\%R = 100\ x\ \left[\frac{S-U}{C_{sa}}\right] \quad ;$$

%R = percent recovery,
S = measured concentration in spiked aliquot,
U = measured concentration in unspiked aliquot, and
C_{sa} = actual concentration of spike added.

For situations where a standard reference material (SRM) is used instead of, or in addition to, spikes:

$$\%R = 100 \; x \left[\frac{C_m}{C_{srm}} \right] \; ;$$

%R = percent recovery,
C_m = measured concentration of SRM, and
C_{srm} = actual concentration of SRM.

4.3.3 Completeness (sampling and analytical) - (Simes, 1989)

$$\%C = 100 \; x \left[\frac{V}{T} \right] \; ;$$

%C = percent completeness,
V = number of measurements judged valid, and
T = total number of measurements.

(statistical) - (Simes, 1989)

Defined as follows for all measurements:

$$\%C = 100 \; x \left[\frac{V}{n} \right] \; ;$$

%C = percent completeness,
V = number of measurements judged valid, and
n = total number of measurements necessary to achieve a specified statistical level of confidence in decision making

4.3.4 Method Detection Limit (MDL)

Defined as follows for all measurements:

$$MDL = t_{n-1,\ 1-\alpha=0.99)} \times S$$

MDL = method detection limit

S = standard deviation of the replicate measurements

$t_{(n-1\ 1-\alpha=0.99)}$ = Students' t-value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

SECTION 5.0

REFERENCES

APPENDIX A

PROCEDURES

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19 DATA VALIDATION GUIDANCE FOR CONVENTIONAL WET CHEMISTRY ANALYSES

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Abstract: Data validation is the process of determining the compliance of analytical data with established method criteria and project specifications. The validation of environmental data assesses the quality of the data generated for environmental measurements and determines if the applicable analytical method requirements and project data quality objectives were met. This paper provides guidance for the validation of data for conventional parameters obtained by wet chemistry analysis methods. Summaries of method specified quality control (QC) criteria for select wet chemistry methods are provided, in addition to general recommended QC guidelines. Examples of data review checklists to use in conducting and documenting data validation are included. A standard approach is presented for the review and validation of data for environmental samples analyzed for conventional parameters by wet chemistry analysis methods.

INTRODUCTION

Analytical methods from the U.S.EPA, Standard Methods, and other sources are available for the determination of conventional parameters in various sample matrices by wet chemistry and instrumental techniques. Each method and associated QC sections define specific requirements associated with application of the method; additional requirements may be further specified by the governing regulatory agencies or defined in the quality assurance project plan and associated data quality objectives. Laboratory analysts and data reviewers need to be familiar with the requirements of the analytical methods that are routinely used in order to ensure that the appropriate procedures are followed and that the required criteria are achieved. While the available methods for organic and inorganic environmental analyses provide detailed and extensive specifications on QC and other technical requirements, the wet chemistry methods do not always include the same level of detail or specifications. Relevant guidance for wet chemistry analyses is needed in order to validate data for conventional parameters.

Data validation activities determine if analytical data are in compliance with the analytical method requirements and project specifications. Data validation procedures developed by EPA for specific programs are used as standards for data validation.[1,2,3] A previous publication provided method comparisons and data validation guidance for EPA organic and inorganic analysis methods for the determination of volatiles, semivolatiles, pesticides/PCBs, and metals in ambient air, drinking water, wastewater, solid waste, and hazardous waste.[4] In this paper, an overview of QC requirements and recommended guidelines for select wet chemistry methods are provided. A standard approach to data validation is presented that can be applied to the validation of data for conventional parameters obtained from wet chemistry analysis methods.

The wet chemistry analyses covered include methods from EPA Methods for Chemical Analysis of Water and Wastes, EPA SW-846 Solid Waste methods, EPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganic Analysis, and Standard Methods for the Examination of Water and Wastewater where EPA methods are not specified. The conventional

parameters covered include inorganic and organic non-metallics analyzed by colorimetric, gravimetric, titrimetric, turbidimetric, spectrophotometric, and other instrumental techniques.

DATA VALIDATION DEFINITION

Data validation has been defined by EPA as a systematic process, consisting of data editing, screening, checking, auditing, verification, certification, and review in order to provide assurance that data are adequate for their intended use.[5] Data validation can be considered a question and answer process to determine if the data meet both the analytical method requirements and the associated project specifications. The four major questions to assess in validating data are the following: (1) were the required technical and QC analyses performed, (2) were they included at the required frequency, (3) were the required acceptance criteria met, and (4) were the project specifications or data quality objectives met.

DATA VALIDATION PROCESS

The data validation process follows a step by step procedure for reviewing the data for completeness, correctness, and acceptability. Specific procedures for data validation may be found in EPA data validation documents or project specified data validation procedures. Presented here is a generalized procedure for the data validation process as applied to wet chemistry analyses. After defining the project requirements and obtaining the data package, the first step in the data validation process should be a data completeness check to determine if all of the required data and documentation are present. If any of the required data or documentation are missing, then the needed information should be obtained, if possible, before conducting the data validation. The next recommended step in the process is a review of the QC data associated with the analysis of the sample batch, referred to here as method QC. Next is a review of the sample data and related QC information for each sample, followed by an overall review of all of the data and associated documentation. Any data that does not meet the method requirements or project specifications at any of these steps should be qualified appropriately. The final step should be the preparation and distribution of a data validation report. A recommended sequence for the data validation process that includes each of these steps is provided in Figure 1.

DATA COMPLETENESS CHECK

In the first step of the data validation process, the data package should be reviewed to determine if all of the required data and associated documentation are present. This check should include a review of the analysis specifications to ensure that the required method, target analytes and their reporting limits, and data quality objectives are defined. The next step should be a review of the documentation on sample custody and condition in order to determine if custody was maintained and if the sample was received and maintained in the proper condition. The data report, QC results, and associated raw data for each analytical parameter should be reviewed to ensure that all required information is present. Documentation for sample preparation, standards preparation, standards and sample analysis, data interpretation and calculations, and correspondence should be reviewed to ensure that all of the required information is present. An example checklist to use for performing the data completeness check is provided in Figure 2.

DATA VALIDATION APPROACH

The recommended approach for performing data validation is to first summarize the analytical method requirements, associated reference QC requirements, and the project specifications. Summaries of the QC and other technical requirements are prepared for reviewing and validating data for each target analyte. An example of a summary chart comparing the QC requirements for select cyanide analysis methods is provided in Table 1. The data validation process proceeds by following closely to the sequence of the analysis and the procedures established by EPA for data validation. Data generated from any of the specified methods are reviewed for compliance with each requirement and applicable criteria using general or method specific data review checklists. Examples of a general checklist for wet chemistry analyses and a method specific checklist for cyanide analysis by the EPA CLP SOW for Inorganic Analysis are provided in Figures 3 and 4, respectively. Using summary charts that provide the required criteria and checklists that record compliance with the applicable criteria, a standard approach to data validation can be performed effectively and efficiently for wet chemistry analysis methods.

QUALITY CONTROL REVIEW

The types of analyses that are subjected to data validation are method specified quality control and sample specific quality control. Method quality control refers to the analyses that are necessary for initiating sample analyses and that are common to the sample analysis batch. This includes instrument calibration, calibration verification standards, blanks, laboratory control standards, spikes, and duplicates. Also included in method QC are other analyses that are necessary to assess the field and laboratory procedures related to the sample data. This includes container certifications, field blanks, field replicates, detection limit determinations, precision and accuracy determinations, and performance evaluation analyses. Sample quality control refers to the criteria that are specific to each sample. This includes holding times, sample preparation and analysis, and the identification and quantitation of target analytes.

The following section provides a summary of items to review during the validation of wet chemistry data. Comparisons of the QC requirements for cyanide analysis methods and summaries of the method specified QC requirements for other wet chemistry analyses are provided in Tables 1 and 2, respectively. Because QC requirements for wet chemistry analyses are often undefined or not specified, general QC guidelines are provided in Table 3 that may be considered when method or project specified criteria are not available. These general QC guidelines are not intended as a replacement for specific requirements defined in the reference method or project specifications, but are presented as guidelines for performing data validation when QC requirements are not specified. Further details on QC requirements are provided in the reference methods and EPA or project specific data validation procedures.

Instrument Calibration. Instrument calibration data are evaluated to ensure that the analysis and the associated instrument were set up properly and that acceptable quantitative and qualitative data were generated at the beginning of the analysis. Initial calibration data are reviewed for the analysis of the required analytes, at the required number of levels and concentrations, at the required frequency, and within the required or recommended acceptance criteria (i.e., a linear calibration curve with a correlation coefficient of ≥ 0.995).

Calibration Verification. Calibration verification analyses are evaluated to ensure that acceptable quantitative and qualitative data were generated during the course of and at the end of the analytical run. Initial and continuing calibration verification data are reviewed for the analysis of the required analytes, from the correct source, at the required concentrations, at the required frequency, and within the required acceptance criteria (i.e., % recovery).

Blanks. Data for calibration blanks and preparation blanks are evaluated to check the background from the analysis and preparation procedures, respectively. Blank data are reviewed for the analysis of the correct source of material, at the required frequency, and within the acceptable background levels for the target analytes.

Laboratory Control Standards (LCS). LCS analyses are evaluated to check the overall performance of the laboratory, including both sample preparation and analysis procedures, on each method utilized. LCS data are reviewed for the analysis of the correct type of standard, at the required frequency, and within the required acceptance criteria (i.e., % recovery).

Spikes. Data for spikes are evaluated to check if the analytical performance was within the accuracy specifications that have been established for the method. Blank spikes determine the laboratory performance for recovery of analytes in blank matrices and matrix spikes assess the effect of the sample matrix on analyte recovery. Spike data are reviewed for analysis of the correct type of spike (blank or matrix spike and pre-preparation or post-preparation), at the required frequency, with the correct analytes at the required concentration, and within the required acceptance criteria (i.e., % recovery).

Duplicates. Data for duplicates are evaluated to check if the analytical performance was within the precision specifications that have been established for the method. Duplicate sample data are reviewed for analysis of the correct type of duplicate (sample duplicate or matrix spike duplicate), at the required frequency, and within the required acceptance criteria for relative percent difference or other specified duplicate evaluation criteria.

Other Quality Control. Other quality control refers to additional analyses associated with evaluation of the acceptability of the sampling and analysis procedures. Quality control measures associated with sampling include the evaluation of field blanks and replicate samples to determine background contamination and sampling precision, respectively. Other laboratory quality control measures include instrument detection limit determinations and performance evaluation analyses. Data for each quality control analysis are reviewed to determine if the required analyses were performed at the required frequency and if the results were within the required acceptance criteria.

Sample Quality Control. Sample data are evaluated to ensure that holding times were met, that preparation and analysis procedures were performed correctly, that the analytes were reported correctly (both identification and quantitation), and that reported values were within the calibration range or linear range. The adherence to holding times should be reviewed for each parameter as holding times are variable and depend upon the analyte and method specification. Raw data for all samples should be reviewed and recalculated to determine if the reported results correlate with the raw data.

DATA VALIDATION DOCUMENTATION

Data validation procedures should be documented on standardized forms such as the example data review checklists provided in Figures 3 and 4. The checklist or other form should report the adherence or lack of adherence to each of the method requirements or project specifications. The agreement of the raw data and the data report should be determined and documented. Any major or minor deficiencies identified should be documented in a data validation report describing each deficiency and its potential impact on the sample results. Qualifiers used for data in question should be in accordance with the project specifications and they should be clearly defined. Examples of qualifiers used in EPA data validation procedures are: (R), the results are rejected due to serious deficiencies in quality control criteria; (J), the associated numerical value is an estimated quantity because certain quality control criteria were not met; (N), presumptive evidence of presence of material; (U) the material was analyzed for but not detected; and (UJ), a combination of U and J.[1] The data validation report should include an overall assessment of the data, in addition to any recommendations for further action.

SUMMARY

Data validation is an integral part of the environmental data generation process and in order to be efficient and effective, the data validation process must be versatile and widely applicable. With the large number of analytical methods that are available for environmental sample analyses, laboratory analysts and data reviewers must be familiar with the QC requirements for each method and project. The information provided in this paper summarizes the QC requirements for several wet chemistry analysis methods and provides general QC guidelines when method specifications are not available. Data validation guidance, including example checklists for performing and documenting data validation, is provided so the data reviewer can use a standard approach when validating data from various analytical methods. This guidance provides an effective and efficient approach for addressing the specific requirements of each method utilized and for determining if the applicable QC specifications were met. This information is not intended as a replacement for the analytical methods or EPA data validation procedures, but is a guide on QC requirements and data validation for wet chemistry analyses.

REFERENCES

1. U.S.EPA Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures, EPA 540-G-90 004, April 1990.

2. U.S.EPA Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses, 1988.

3. U.S.EPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 1991.

4. A.E.Rosecrance, "Data Validation Guidance for EPA Organic and Inorganic Analytical Methods", Proceedings of the EPA Eighth Annual Waste Testing and Quality Assurance Symposium, Arlington, VA, July 1992.

5. U.S.EPA Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005-80, December 1980.

Figure 1. DATA VALIDATION PROCESS

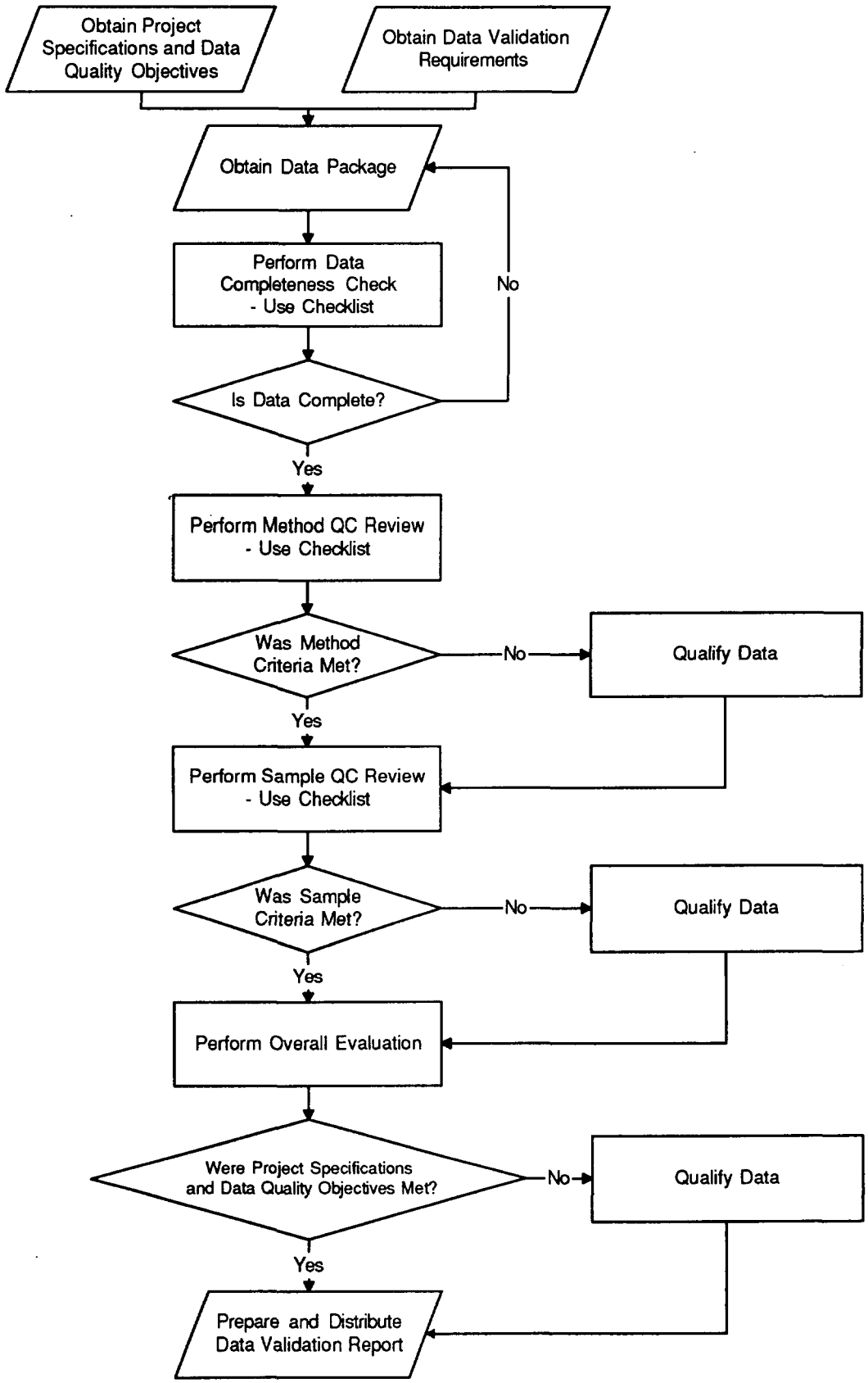

Figure 2. Data Package Checklist

REVIEW ITEM	INCLUDED	NOT INCLUDED	NA	COMMENTS
ANALYSIS SPECIFICATIONS				
Project Specifications				
Method Reference				
Target Analytes and DL/QL Specifications				
SAMPLE CONDITION / CUSTODY				
Chain of Custody Records				
Sample Receipt/Log-In Records				
DATA REPORT				
Case Narrative				
Client ID/Lab ID				
Parameters				
Matrices				
Dates of Preparation and Analysis				
Method Reference				
Required Forms				
Sample Results/DLs				
QC Results				
RAW DATA				
Organic				
Metals				
Wet Chemistry				
Radiochemistry				
Other				
LOGS / RECORDS				
Sample Preparation				
Sample Analysis/Run Logs				
Standards Preparation				
Calculations				
Correspondence				

OTHER

Figure 3. Wet Chemistry Data Review Checklist

REQUIREMENT	YES	NO	NA	COMMENTS
A. CALIBRATION CURVE				
1. Frequency: Daily?				
2. Levels: Blank + ≥ 3 or _____ standards?				
3. Range: Appropriate?				
4. Correlation coefficient: ≥ 0.995?				
B. LABORATORY CONTROL STANDARD				
1. Frequency: Each batch?				
2. Source: Independent?				
3. Reference: Certified?				
4. % Recovery: 90-110% or _____?				
C. BLANK				
1. Frequency: Each batch?				
2. Matrix: Matrix specific?				
3. Preparation: Entire procedure?				
4. Analytes concentration: <DL/QL?				
D. SPIKE				
1. Frequency: Each batch?				
2. Matrix: Matrix specific?				
3. Preparation: Entire procedure?				
4. % Recovery: 80-120% or _____?				
E. DUPLICATE				
1. Frequency: Each batch?				
2. Matrix: Matrix specific?				
3. Preparation: Entire procedure?				
4. % RPD: <20% or _____?				
F. SAMPLE ANALYSIS				
1. Holding times: Met?				
2. Results: a. Calculated correctly? b. Within calibration curve? c. Dilution factors (included)? d. Rounding/significant figures acceptable? e. Detection limit sample specific?				
3. Report: a. Agrees with raw data? b. Complete? c. Correct?				

ADDITIONAL COMMENTS:

Figure 4. DATA REVIEW CHECKLIST FOR CYANIDE ANALYSIS DATA BY EPA CLP SOW

REQUIREMENT	YES	NO	NA	COMMENTS
A. CALIBRATION				
1. Frequency: Daily?				
2. Levels/Range: Blank + 3 stds (1 at CRDL)?				
3. Correlation coefficient: ≥ 0.995?				
B. CONTINUING CALIBRATION				
1. Frequency: Beginning/end/every 10 samples-2 hrs?				
2. Level: Mid-range for CCV?				
3. % Recovery: 85-115%?				
C. OTHER STANDARDS (DISTILLED)				
1. Frequency: 1 per batch?				
2. Level: Mid-range?				
3. %Recovery: 85-115%?				
D. CALIBRATION BLANK				
1. Frequency: Beginning/end/every 10 samples-2 hrs?				
2. Analyte concentration: ≤CRDL?				
E. PREPARATION BLANK				
1. Frequency: 1 per batch?				
2. Analyte concentration: ≤CRDL?				
F. LABORATORY CONTROL STANDARD				
1. Frequency: Each batch?				
2. Source: Distilled ICV standard?				
3. % Recovery: 85-115%?				
G. SPIKE				
1. Frequency: 1/matrix/concentration/batch?				
2. % Recovery: 75-125%?				
H. DUPLICATE				
1. Frequency: 1/matrix/concentration/batch?				
2. % RPD: ≤20% or ±1x CRDL if ≤5x CRDL?				
I. SAMPLE ANALYSIS				
1. Holding times met?				
2. Sample pH ≥12?				
3. Checked for oxidizing agents and sulfides?				
4. Distillation procedure performed?				
5. Results within calibration range?				
6. Reported results agrees with raw data?				

Table I. Comparison of QC Requirements for EPA Cyanide Analysis Methods

Requirement	Water and Wastewater Analysis Method 335.2	RCRA Solid Waste Analysis Methods 9010/9010A	Superfund Hazardous Waste Analysis CLP SOW ILM03.0
Method Detection Limit	Titration: 1mg/L Colorimetric: 0.02 mg/L	Titration: 0.1 mg/L Colorimetric: 0.02 mg/L	CRDL: 10µg/L
Holding Time	14 days (24 hours when sulfide is present)	14 days	12 days from sample receipt
Initial Calibration[1]	6 standards and a blank	6 standards and a blank	3 standards and a blank (one standard at the CRDL)
Frequency	Daily	Daily	Daily
Calibration Verification[2]	NS	Mid-range standard	CCV: Mid-range standard
Frequency	NS	Every 15 samples	Beginning, end, and every 10 samples or 2 hours
Criteria	NS	85-115% Recovery	85-115% Recovery
Other Standards (Distilled)	High and low standard	High and low standard	Mid-level standard
Frequency	1 each per batch	1 each per batch	1 per batch
Criteria	90-110% Recovery	90-110% Recovery	85-115% Recovery
Calibration Blanks			
Frequency	Colorimetric: 1 per batch	Colorimetric: 1 per batch	Colorimetric: Beginning, end and every 10 samples or 2 hours
Criteria	Use in initial calibration	Use in initial calibration	≤ CRDL
Preparation Blanks			
Frequency	Titration: 1 per batch Colorimetric: Not specified	Titration: 1 per batch Colorimetric: Not specified	Titration: 1 per batch Colorimetric: 1 per batch
Criteria	Titration: Use in calculation Colorimetric: Not specified	Titration: Use in calculation Colorimetric: Not specified	Titration: Use in calculation Colorimetric: ≤ CRDL
Laboratory Control Standard	NS	Independent check standard	Distilled independent standard (ICV)
Frequency	NS	1 per batch	1 per batch
Criteria	NS	85-115% Recovery	85-115% Recovery
Matrix Spike Samples			
Frequency	1 per batch to check distillation efficiency	Matrix spike and matrix spike duplicate per batch	1 per matrix per concentration level per batch
Criteria	NS	NS	75-125% Recovery
Duplicate Samples			
Frequency	NS	1 matrix spike duplicate per batch	1 per matrix per concentration level per batch
Criteria	NS	NS	≤ 20% RPD for values > 5x CRDL
Other Method Criteria	Verify sample pH ≥ 12; Check for oxidizing agents and sulfides	Verify sample pH ≥ 12; Check for oxidizing agents and sulfides	Verify sample pH ≥ 12; Check for oxidizing agents and sulfides

(1) Calibration standards must be distilled for EPA Methods 335.2 and 9010/9010A when sulfides are present in the samples.
(2) CLP SOW specifies that the initial calibration verification standard (ICV) be distilled and analyzed as the laboratory control standard (LCS).
For complete information, refer to the method reference.

Acronym Definitions

CCV = continuing calibration verification
CRDL = contract required detection limit
ICV = initial calibration verification
LCS = laboratory control standard
NS = not specified
RPD = relative percent difference

Table II. METHOD SPECIFIED QUALITY CONTROL FOR WET CHEMISTRY ANALYSES

PARAMETER (METHOD NO.)	CALIBRATION CURVE		BLANKS		SPIKES		DUPLICATES		OTHER		
	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Type	Frequency	Acceptance Criteria
Acidity (305.1)[1]	pH Calib. Daily/2	pH Meter Specification							pH Check	1/Batch	± 0.05 of True Value
Alkalinity (310.1)[1]	pH Calib. Daily/2	pH Meter Specification							pH Check	1/Batch	± 0.05 of True Value
Anions (300.0)[1] by ion chromatography	Daily	± 10% of True Value	1/Batch	<Detection Limit	10% or 1/Batch	Not Specified					
BOD and CBOD (405.1)[1] by electrode (5210 B)[2]	Daily	DO Meter Specification	1/Batch	≤ 0.2 mg/L			10% or 1/Batch	See Table 1020:I[2]	G/G Std.; Seed Control; LCS	2/Batch; 2/Batch; Daily	198 ± 30.5 mg/L; 0.6-1.0 mg/L; 90-110%
Boron (4500-B)[2] by colorimetry	Daily	Linear	1/Batch	Zero Instrument	5% or 1/Batch	80-120%	5% or 1/Batch	See Table 1020:I[2]	LCS	1/Batch	90-110%
Bromide (320.1)[1] by titration			1/Batch	Blank Correcting							
Carbon (TOC) (415.1)[1] by combustion or oxidation	Daily	Instrument Specification	1/Batch	<Detection Limit							
Chloride (325.3)[1] by $Hg(NO_3)_2$ titration			1/Batch	Blank Correcting							
Chloride (9252)[3] by $Hg(NO_3)_2$ titration			1/Batch	Blank Correcting	5% or 1/Batch	Not Specified	10% or 1/Batch	Not Specified	LCS	Every 15 Samples	Not Specified
Chloride (4500E-Cl^- B)[2] by $AgNO_3$ titration			1/Batch	Blank Correcting	5% or 1/Batch	80-120%	5% or 1/Batch	See Table 1020:I[2]	LCS	1/Batch	90-110%
COD (HACH 8000)[4] by colorimetry	Daily/ Range	Instrument Specification	1/Batch	Zero Instrument							
COD (Mid-level) (410.1)[1] by titration			1/Batch	Blank Correcting							
COD (Low Level) (410.2)[1] by titration			1/Batch	Blank Correcting							
Color (110.2)[1] by platinum-cobalt			1/Batch	<Detection Limit							
Corrosivity (1110)[3] toward steel			1/Batch	Blank Correcting			5% or 1/Batch	Not Specified			

Table II. METHOD SPECIFIED QUALITY CONTROL FOR WET CHEMISTRY ANALYSES (continued)

PARAMETER (METHOD NO.)	CALIBRATION CURVE		BLANKS		SPIKES		DUPLICATES		OTHER		
	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Type	Frequency	Acceptance Criteria
Phenol (9065)[3] by spectrophotometry	Daily	Linear	1/Batch	<Detection Limit	10% or 1/Batch	Not Specified			LCS	Every 15 Samples	Not Specified
Phenol (420.1)[1] by spectrophotometry	Daily	Linear	1/Batch	Zero Instrument							
Phenol (420.2)[1] by automated 4-AAP	Daily	Linear	1/Batch	Establish Baseline							
Phos. Total & Ortho (365.2)[1] ascorbic acid, single reagent	Daily	± 2% of True Value	1/Batch	Zero Instrument							
Phos. Total & Ortho (365.3)[1] ascorbic acid, two reagent	Daily	Linear	1/Batch	Zero Instrument							
Sulfate (375.4)[1] by turbidimetry	Daily	Linear	1/Batch	Zero Instrument					LCS	Every 3 or 4 Samples	Not Specified
Sulfide (376.2)[1] by colorimetry	Daily	Linear	1/Batch	Use in Calibration							
Sulfite (377.1)[1] by titration			1/Batch	Blank Correcting							
Surfactants, Anionic (425.1)[1] as MBAS (5540C)[2]	Daily	Linear	1/Batch	Use in Calibration	5% or 1/Batch	80-120%	5% or 1/Batch	See Table 1020:I[2]	LCS	1/Batch	90-110%
Total Petroleum (418.1)[1] Hydrocarbons (TPH) by IR	Daily	Linear	Solvent Blank: 1/Batch	Zero Instrument							
Turbidity (180.1)[1]	Daily	Instrument Specification							Check Standard	1/Batch per Range	Instrument Specification

CCV Continuing Calibration Verification G/G Glucose/Glutamic Acid Standard LCS Laboratory Control Standard RPD Relative Percent Difference

[1] Methods for Chemical Analysis of Waster and Wastes, EPA-600/4-79-020, U.S. EPA, Cincinnati, Revised March 1983.

[2] Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 17th. Edition, 1989.

[3] Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, U.S. EPA, Washington D.C., Third Edition, September 1986.

[4] Gibbs, C. R., "Introduction to Chemical Oxygen Demand", HACH Company, Technical Information Series-Booklet No. 8, 1992.

[5] Statement of Work for Inorganics Analysis, Multi-Media Multi-Concentration, U.S. EPA Contract Laboratory Program, ILM03.0.

[6] D93-80, "Test Methods for Flash Point by Pensky-Martens Closed Tester", American Society for Testing and Materials, Philadelphia.

Table II. METHOD SPECIFIED QUALITY CONTROL FOR WET CHEMISTRY ANALYSES (continued)

PARAMETER (METHOD NO.)	CALIBRATION CURVE		BLANKS		SPIKES		DUPLICATES		OTHER		
	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Type	Frequency	Acceptance Criteria
Hexavalent Cr (7197)[3] by chelation and FLAA	Daily	Linear	1/Batch	<Detection Limit	10% or 1/Batch	85-115%	5% or 1/Batch	Not Specified	LCS; Method of Standard Addition	15%; All EP Tox Extracts	Not Specified; Linear Curve
Iodide (345.1)[1] by titration			1/Batch	<Detection Limit							
Nitrogen - Ammonia (350.1)[1] by automated colorimetry	Daily	Linear	1/Batch	Establish Baseline							
Nitrogen - Ammonia (350.2)[1] by colorimetry	Daily	Linear	1/Batch	Zero Instrument					Distilled Standards	High & Low/Batch	Comparable to Undistilled Standards
Nitrogen - Ammonia (350.2)[1] (350.3)[1] by ion electrode	Daily	Instrument Specification	1/Batch	<Detection Limit					Distilled Standards	High & Low/Batch	Comparable to Undistilled Standards
Nitrogen - Nitrate (352.1)[1] by colorimetry	Daily	Linear	1/Batch	Zero Instrument							
Nitrogen - Nitrite (354.1)[1] by colorimetry	Daily	Linear	1/Batch	Zero Instrument							
Nitrogen - Nitrate & Nitrite by hydrazine reduction (353.1)[1]	Daily	Linear	1/Batch	Establish Baseline					Efficiency Check	1/Batch	100% Reduction
Nitrogen - Nitrate & Nitrite by auto. Cd reduction (353.2)[1]	Daily	Linear	1/Batch	Establish Baseline					Efficiency Check	1/Batch	100% Reduction
Nitrogen - TKN (351.3)[1] by titration			1/Batch	Blank Correcting					Distilled Standards	High & Low/Batch	Comparable to Undistilled Standards
Oil and Grease (413.2)[1] by IR	Daily	Linear	Solvent Blank: 1/Batch	Zero Instrument							
Oil and Grease (413.1)[1] by gravimetry			Solvent Blank: 1/Batch	Blank Correcting							
pH in Soil (9045)[3]	pH Calib. Daily/2	pH Meter Specification					5% or 1/Batch	Not Specified	Check Standard	1/Batch	Not Specified
pH in Water (150.1)[1]	pH Calib. Daily/2	± 0.05 of True Value					Every Sample	± 0.01 pH units	pH Check	1/Batch	± 0.05 of True Value

Table II. METHOD SPECIFIED QUALITY CONTROL FOR WET CHEMISTRY ANALYSES (continued)

PARAMETER (METHOD NO.)	CALIBRATION CURVE		BLANKS		SPIKES		DUPLICATES		OTHER		
	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	Acceptance Criteria	Type	Frequency	Acceptance Criteria
Cyanide, Total (335.2)[1] by titration			1/Batch	Blank Correcting	1/Batch	Distillation Check			Distilled Standards	High & Low/Batch	90-110%
Cyanide, Total (335.2 CLP-M)[5] by titration			1/Batch	Blank Correcting	5% or 1/Batch	75-125%	5% or 1/Batch	≤ 20%RPD	LCS; Distilled Standard	1/Batch; 1/Batch	85-115%; 85-115%
Cyanide, Total (335.2)[1] by colorimetry	Daily	Linear	1/Batch	Use in Calibration	1/Batch	Distillation Check			Distilled Standards	High & Low/Batch	90-110%
Cyanide, Total (335.2 CLP-M)[5] by colorimetry	Daily	Linear	1/Batch	≤Contract Required Detection Limit	5% or 1/Batch	75-125%	5% or 1/Batch	≤ 20%RPD	LCS; CCV; Distilled Standard	1/Batch; 10%; 1/Batch	85-115%; 85-115%; 85-115%
Cyanide, Total (335.3)[1] by automated UV	Daily	Linear	1/Batch	Use in Calibration							
Cyanide, Total (335.2 CLP-M)[5] by semi-automation	Daily	Linear	1/Batch	≤Contract Required Detection Limit	5% or 1/Batch	75-125%	5% or 1/Batch	≤ 20%RPD	LCS; CCV; Distilled Standard	1/Batch; 10%; 1/Batch	85-115%; 85-115%; 85-115%
Flash Point (1010)[5] (D93)[6] by Pensky-Marten Closed Cup									p-Xylene Standard	1/Batch	81 ± 2°F
Fluoride (340.2)[1] by ion electrode	Daily	Instrument Specification	1/Batch	<Detection Limit							
Fluoride (340.3)[1] by automated colorimetry	Daily	Linear	1/Batch	Establish Baseline							
Halides (TOX) (9020)[3]	Daily in Duplicate	± 3% of True Value	1/Batch	<Detection Limit	10% or 1/Batch	Not Specified	Every Sample	Not Specified	LCS; Nitrate Blank; Efficiency Check Standard	15%; Every 8 Samples; 1/Batch	Not Specified; Blank Correcting; ±5% of True Value
Hardness (130.2)[1] by titration			1/Batch	<Detection Limit							
Hexavalent Cr (218.4)[1] by chelation and FLAA	Daily	Linear	1/Batch	<Detection Limit			Aspirate Samples in Duplicate	Report Average			

Table III. General QC Guidelines for Wet Chemistry Parameters*

	Type	Freqency	Criteria
Calibration	Multiple standards + blank	Daily	r > 0.995
QC Check Sample/LCS	Independent source	Batch	90 - 110% recovery
Blank	Preparation blank	Batch	≤ DL
Spike	Matrix spike, pre-digestion	5 - 10%	75 - 125% recovery
Duplicate	Sample duplicate, pre-digestion	5 - 10%	≤ 20% RPD for values > 5 x DL; ± 1 x DL for values < 5 x DL

* *Recommended guidelines for QC analyses where method QC requirements are not available. Refer to the method reference for method specific requirements.*

Acronym Definitions

DL = detection limit
LCS = laboratory control standard
RPD = relative percent difference

20 DEVELOPING A PERFORMANCE-BASED APPROACH TO ENVIRONMENTAL ANALYTICAL TESTING

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ABSTRACT

Documented analytical methods are prescriptive. However, they can be generated, selected, or modified based upon performance criteria. Freedom to select and use methods based on performance criteria allows laboratories flexibility to generate data that meet well-defined data quality objectives (DQOs) cost effectively.

To support the U.S. Department of Energy Waste Management and Environmental Restoration (DOE-EM) programs, we suggest using DQOs and a performance-based approach for selecting methods to analyze environmental and waste samples. Over the long-term, a performance based approach is viewed as a generally cost-effective approach for producing analytical data of the needed quality. Adopting such an approach will encourage development of innovative and efficient analytical technologies that address the complexities of waste and environmental characterization at DOE sites while ensuring comparable data are produced among the many laboratories supporting DOE-EM programs.

A primary mission of DOE is the environmental restoration of its waste sites. Accomplishing this mission will require that a vast number of environmental and waste samples be analyzed for the presence of inorganic, organic, and radionuclide constituents. Many of the needed analyses cannot be performed according to existing published methods (e.g., ASTM or EPA) because of constraints that accompany sample characterization in radiological environments. Selecting and applying analytical methods within the framework of a performance-based program would improve effectiveness of DOE analytical support programs.

A guidance document, DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods), is being developed in support of DOE-EM programs. This document contains general guidance for characterization of contaminants in radioactive waste and environmental samples as well as recommended analytical methods necessary to meet the broad range of analytical characterization needs existing across the DOE complex. DOE Methods and other recognized documents (e.g., EPA's SW-846) should be consulted when selecting methods to perform analyses in support of DOE-EM programs; however, these methods may be modified as long as the modified methods are demonstrated to meet DQOs. In addition, alternate sources of methods may be used if those methods are cost-effective and again, are demonstrated to meet project DQOs.

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INTRODUCTION

This paper presents concepts associated with implementing a performance-based approach to waste and environmental analytical testing within United States Department of Energy (DOE) programs. The approach employs a data quality objectives (DQO) process that leads to the establishment of project specific DQOs, rather than imposing prescriptive analytical method requirements on analytical laboratories to meet program goals. For the purposes of this paper, we define DQOs as statements that define the analytical-testing-method-performance requirements for a program based upon a consensus that is reached by the regulatory community, DOE Program Management, and analytical laboratory management and staff (EPA 1986).

This paper describes 1) the basic elements of the approach, 2) strengths versus perceived weaknesses in applying a performance-based approach to analytical testing, and 3) arguments that implementing such an approach over the long-term will reduce costs and improve analytical data quality. The goal is to stimulate responsible debate regarding the adoption of a performance-based approach to analytical testing.

BACKGROUND

Currently, analytical testing in support of environmental monitoring, restoration, and waste management programs is based upon required laboratory implementation of standard, usually promulgated, analytical methods. Thus, laboratory personnel responsible for supplying data in support of these programs are required to adhere strictly to analytical methods specified in program specific plans. This approach is prescriptive in nature; laboratory personnel are given very little flexibility to perform analytical testing according to methods they believe would best meet project specific DQOs or to deal with problems associated with highly complex sample matrices. Many problems associated with characterization of DOE environmental and waste sample matrices are not addressed by promulgated methods.

As a framework for the performance-based approach, the DQO process converges the thoughts of interested parties (i.e., program managers, analysts, regulators, clients) toward a consensus opinion regarding project goals, DQOs to meet project goals, and analytical methods to be used. A decision to use promulgated methods, unpromulgated methods, or some combination of both to meet DQOs will be a product of this DQO process.

ELEMENTS OF A PERFORMANCE-BASED APPROACH

Once an analytical method has been selected through the DQO process, responsibility for documenting validation of the method lies with the organization that will be implementing the method, the analytical laboratory. Validation is the process of establishing the suitability of a method for authorized use in the laboratory (Dux, 1990). Guidance can be found (Dux 1990; ASTM 1986) relating to the validation process. One aspect of the validation process consists of demonstrating method performance using relevant sample matrices and addressing sample logistics (e.g., manipulation of samples containing high levels of radioactivity in a hot cell or glovebox). The following quality control documentation should accompany validation of an analytical method.

- The method's bias and precision should be documented by analyzing spiked and replicate samples of the matrix of interest. When it is not possible to perform this

test on a portion of the actual sample matrix, the test should be performed using a matrix that exhibits as many of the physical and chemical characteristics of the actual sample matrix as possible. When applicable, test data can be used to develop method warning and control limits.

- Analysis of method and matrix blanks should be documented.

- The working range of the method should be documented. Parameters for which calculated data should be provided include minimum detection limit, limit of detection, and limit of quantitation.

- The ruggedness of the method should be documented. Youden presents information relating to ruggedness testing (Youden and Steiner, 1975).

- Method interferences and limitations as they apply to the matrix in question should be identified and documented.

- The method should be controlled so that changes to the method subsequent to its selection and validation are documented and receive concurrence from the appropriate regulators and DOE project management.

- Method comparability tests should be documented. Where applicable, the analytical laboratory should consider documenting comparability of the selected method with a standard, published method to obtain data credibility with peers. "Round robin" interlaboratory comparison studies can be helpful in demonstrating that a method produces comparable data. Periodic requalification of validated methods should be performed by laboratories using those methods.

STRENGTHS OF A PERFORMANCE-BASED APPROACH--COST AND DATA QUALITY BENEFITS

The most important strengths of a performance-based approach to analytical testing of waste and environmental samples fall into two broad categories: improved cost and improved data quality over time.

- Cost--A performance-based approach allows methods that are tailored to provide data of the quality needed to meet program objectives (part of the DQO process decision) to be selected. The performance-based approach makes a larger pool of analytical methods available for consideration during the DQO process. Design of the most effective analysis program may be based upon cost, as long as assurances are made that DQOs will be met. For example, analytical data generated from standard methods are often based upon minimum detection limits (MDLs), limits of detection (LODs), or limits of quantitation (LOQs) that are, in general, lower than those required to meet project DQOs. In contrast, the performance-based approach allows the flexibility to adapt or chose alternative analytical methods that provide data of only the quality needed, while minimizing additional costs associated with methods that produce data of higher quality than project DQOs require. In evaluating cost, factors to consider include time required to perform the method, equipment and facilities required to assure worker safety, training of analysts, and waste minimization and disposal.

In applying the DQO process within the performance-based approach, analytical methods can be selected that are tailored to the resources available (e.g., personnel and equipment) rather than requiring purchase of additional equipment, making expensive modifications to existing facilities, or hiring specialized personnel to perform the analytical testing according to standard/promulgated methods.

- Data Quality--A performance-based approach to analytical testing offers a means to ensure enhanced data quality by selection/application of the best available analytical methodology. In doing so, weaknesses associated with standard methods can be avoided. Currently, methods accepted for use in support of regulatory requirements present a very conservative approach to laboratory analysis. Little room for adoption of innovative approaches exists in the current prescriptive environment. This prescriptive approach has the effect of stifling creativity in analytical testing methodology.

  Standard methods, such as those published in SW-846, were not developed to accommodate the variety of complex sample matrices encountered in DOE programs and frequently cannot be easily adapted to such matrices. In a program requiring prescriptive methods, the process of data production can over shadow the data upon which decisions are based. In this situation, the process can become more important than the product. This can be dangerous because data quality may be compromised to comply with standard methods. Such situations may be avoided using a performance-based approach.

PERCEIVED WEAKNESSES OF A PERFORMANCE-BASED APPROACH

The following are perceived as weaknesses of the performance-based approach:

- Approach Acceptance--The performance-based approach is currently untested. Historically, promulgated methods are adopted to secure regulatory "buy-in" by offering some assurance that data of high quality are produced and are defensible in the event that they are introduced into litigation. Because of entrenched habits, it will take time for regulators and the regulated community to accept a performance-based approach to analytical testing. After the performance-based approach achieves success, the rigid, conservative approach to method selection will yield to the more flexible performance-based approach.

- Cost of Documentation--Implementing a performance-based approach to environmental and waste analysis could require a greater "up front" investment of time and dollars to gain acceptance. Method validation by a laboratory could require that more quality control data be generated and documented in the near-term than might be required to support standard/promulgated methods. These added "up front" costs could create cash flow problems for small laboratories. However, the QC data produced will be more pertinent to program DQOs and to the matrix of interest. Data will, therefore, be more meaningful.

- Training Costs--The flexibility built into a performance-based approach places greater responsibility for management of unpromulgated or modified promulgated methods (i.e., selection, validation and application) on laboratory personnel. The additional technical responsibility could lead to the need for more education and training for laboratory analysts and managers to assure they are able to make sound

scientific judgments during the method selection and application process. This increased training for laboratory analysts and managers should, however, improve the quality of the data.

Similarly, auditors providing program oversight might need more extensive training to effectively audit programs developed according to a performance-based approach. The emphasis in auditing prescriptive-based programs is placed on monitoring for compliance to program requirements. "Monitoring for compliance type auditing" is generally thought to be much simpler (i.e., requiring less extensive training) than monitoring a performance-based program for its effectiveness. However, this change in emphasis of the auditing process should produce value added over time.

- Contractual Costs--More planning could be required for acquiring and monitoring subcontracts for analytical services in programs developed according to a performance-based approach. The flexibility inherent in the performance-based approach could require DOE to spend more time preparing a request for proposal and the subcontracted organization to spend more time preparing the proposal than might be required using the more traditional approach that requires the use of standard/promulgated analytical methods. However, the resulting proposal is more likely to better meet the needs of the program.

CONCLUSION

A primary mission of DOE is the environmental restoration of its waste sites. Decisions regarding site remediation require the use of legally defensible data of high quality. Because projected costs associated with remediation efforts are so high, DOE, the regulatory community, and analytical laboratory staff need to consider how best to reduce analytical costs while still providing sound data to serve as the bases for decisions.

The DOE is endeavoring to create an environment where continuous improvement is fostered. This continuous improvement atmosphere extends to organizations outside DOE that have been contracted to provide analytical testing support for DOE programs. A performance-based approach to analytical testing allows the flexibility to implement the continuous improvement philosophy by allowing the DQO process to drive the selection of sampling and analytical methods.

Standard/promulgated methods currently available for analytical testing do not address the problems associated with measuring analytes in complex waste and environmental matrices found at DOE sites, nor do they provide the data quality required for sound site remediation and waste management decisions.

To bridge this gap, the Laboratory Management Division of DOE is supporting development of DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods). DOE Methods contains guidance and methods that are not currently provided by existing guidance manuals for DOE and DOE contractor laboratories to use for radioactive waste and environmental sampling and analysis at DOE sites. DOE Methods recommends that analytical methods contained within the document be considered, through the DQO process, for use in support of DOE programs. However, encouragement is given to use alternate methods if they can be demonstrated to provide a

cost effective alternative to methods published in DOE Methods or other recognized methods documents (Goheen et al. 1992)

This paper describes the elements of a performance-based approach to analytical testing and the strengths and weaknesses of the approach compared to a strictly prescriptive approach. Readers of this paper are encouraged to provide constructive comments on the performance-based approach that incorporates the DQO process. All feedback will be given serious consideration as this subject is addressed in forthcoming revisions of DOE Methods. All comments should be addressed to Dr. Steven C. Goheen, at Pacific Northwest Laboratory, P.O. Box 999, MS P8-08, Richland, WA 99352.

ACKNOWLEDGMENT

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21 QUALITY ASSURANCE AND DATA COLLECTION: ELECTRONIC DATA TRANSFER

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ABSTRACT

The Radiological Environmental Monitoring (REM) group at the Fernald Environmental Management Project is involved in an Electronic Data Transfer practice that will result in the improved quality assurance of collected data. This practice focuses on electronic data transfer from the recording instrument to reduce the manpower normally required for manual data entry and improve the quality of the data transferred.

The application of this practice can enhance any data collection program where instruments with electronic memories and a signal output are utilized. Organizations employing this practice can strengthen the quality and efficiency of their data collection program. The use of these practices can assist in complying with Quality Assurance requirements under ASME NQA-1, RCRA, CERCLA, and DOE Order activities.

Data from Pylon AB-5 instrumentation is typically configured to print data to a tape. The REM group has developed a process to electronically transfer stored data. The data are sent from the Pylon AB-5 field instrument to a Hewlett-Packard portable hand computer, model HP95LX. Data are recorded and stored on a 128 K-byte RAM card and later transferred to a PC database as an electronic file for analysis. The advantage of this system is twofold: (1) Data entry errors are eliminated and (2) considerable data collection and entry time is eliminated. Checks can then be conducted for data validity between recorded intervals due to light leaks etc. and the detection of outliers.

This paper/presentation will discuss the interface and connector components that allow this transfer of data from the Pylon to the PC to take place and the process to perform that activity.

INTRODUCTION

Fifteen continuous radon monitors have been installed at the DOE Fernald Environmental Monitoring Project (FEMP) at both on-site and off-site locations to measure what, if any, contribution to the natural radon background is made by sources of radon located on the Fernald project. On-site outdoor locations for each of the samplers have been selected to provide representative measurements of radon that are either close to the sources of emission (K-65 silos that contain concentrated radium byproducts) or near buildings and areas where production occurred. Several monitors have measured radon at the FEMP fenceline and from two background locations a minimum of 13 miles from the project including one located in the opposite direction of the prevailing wind.

Each monitor prints the results of hourly measurements and also stores the

data in the instrument computer memory. Each result consists of four fields of data: sequence number, hour (24 hour clock), instrument response (counts/hour), and radon concentration (pCi/l). Data is retrieved from each instrument by environmental data collection personnel on a weekly basis. Data collection personnel initial each data paper tape and reset the instrument sequence number to initiate another run. An identification number, calibration factors, and other data constants are printed on the data tape whenever the instrument is reset. Data are also collected/transferred electronically onto a hand held computer at each location. The instrument response is also conducted using a check source on a weekly/monthly basis per established protocol.

The radon collection instruments are housed in environmental enclosures to protect them from the direct adverse effects of the environment but are not heated or sealed in any manner. They operate 24-hours a day and are expected to function properly in all types of weather and generate 168 hourly readings each week. The instruments sample radon in the ambient air based upon the diffusion principle and, thus, have no moving parts or pumps. Other than weekly inspection by the data collection personnel to retrieve data, reset the instrument, and insure that the instrument is still operating, no other operator attention is provided or required. Instrument re-calibration is scheduled on an annual basis contingent upon the satisfactory instrument source check results.

OVERVIEW

Collection of data, albeit an important function, comprises only half of the environmental monitoring activity. Sometimes it can be just as cumbersome to appropriately deal with the data that has been collected, as it can be to collect the data. The Radiological Environmental Monitoring group at the DOE FEMP facility has identified a solution, to at least take some of the dread and monotony out of the voluminous environmental data reduction and reporting activity, without sacrificing quality.

OBJECTIVE

Obtaining a workable electronic file for generating reports from data tapes requires considerable labor intense quality assurance activities. These steps are depicted in Figure 1. To relieve the burden of work related to the data collection and reporting, a method has been devised to transfer the data electronically. These steps are depicted in Figure 2.

There are essentially two steps in the electronic data transfer process. The first step is the transfer of an electronic data file from the Pylon AB-5 unit to RAM card on a handheld computer in the field. The second step is the transfer of field data from the RAM card to an electronic data file back at the office on the hard drive of a PC.

This data is then transferred via disk along with the hard copy data tape of the Pylon AB-5 data to a data previewer, and then to an independent group that produces the environmental reports. This activity should eliminate data errors and data entry form.

MATERIALS NEEDED

The following is a list of equipment that is needed to complete the electronic data transfer from the AB-5 Pylon to a personal IBM disk operating system computer.

- Pylon AB-5 Radon Monitor
- Pylon Model PPT-1 Printer
- Pylon Model CI-55 Computer Interface
- CPRD (radon detector) or a 300A Lucas cell
- DB15 Female A/B Switch Box
- DB15 3 foot M.M. Transfer Cable
- DB15 3 foot M.F. Transfer Cable
- DB25/9 M.M. Gender Changer
- DB15 M.M. Gender Changer
- HP95LX Computer
- HP F1001A Connectivity Pack
- HP F1002A 128 K-byte RAM card
- 128 K-byte RAM card drive linked to PC

METHODOLOGY

Data collection personnel have procedures for performing instrument checks and retrieving data from each of the instruments. They observe instrument operation and determine that the data output tape appears normal. They also initial the data tape, electronically transfer the data, and reset the instrument. Should the instrument appear to be malfunctioning, they will notify management and initiate a service request from the instrumentation group. Periodically, after electronically transferring and collecting the data, the data collection personnel perform an instrument response check by removing the radon sampler and attaching a check source. Following the performance check, the data collection personnel re-attach the radon sampler to the monitor, and reset the instrument.

The following are the steps that are needed to transfer the electronic data file from the Pylon AB-5 unit to a personal IBM disk operating system computer. Each step of transfer will be presented in detail in the Appendix.

QUALITY ASSURANCE OF TRANSFERRED DATA

To ensure that the data are successfully transferred from the Pylon AB-5 to the RAM card, a quality control check is performed each week. During the weekly inspection one data tape from those collected is randomly selected and 10% of the data points are randomly chosen and compared to the same data points on the electronic file. Once each quarter, one data tape is randomly selected and all data tape data points are compared with the electronic file data points.

SUMMARY

Using the electronic data transfer scheme described in this paper, radon data can be easily converted into an electronic file for further processing. Once the data are transferred to a disk, the data can be previewed by the individual assigned the task of quality assurance and data validation. It

will be necessary to parse the data using a Lotus function to be able to work with each of the columns. This data translation process would also be required if other software programs (any software capable of handling ASCII) were used in the transfer process. A check of data will then need to be conducted to confirm that the data was correctly transferred and that all data points were valid observations.

By utilizing the electronic transfer of data, considerable time can be saved in both the areas of manual data entry, and the checks that are required to ensure that the data is correct. Activities that had previously taken more than a day can be performed in much less than a day without sacrificing data quality.

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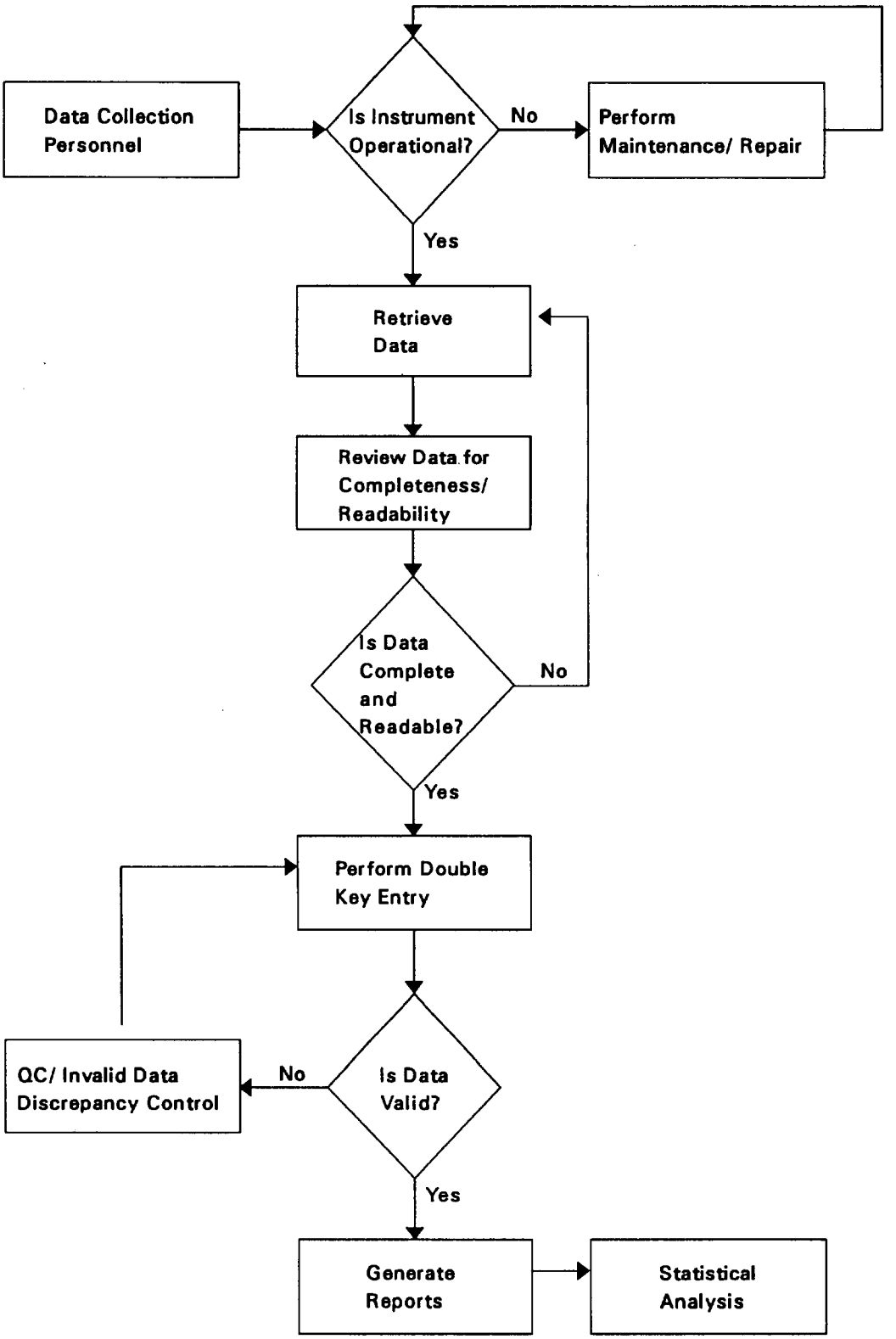

FIGURE 1

Manual Data Collection and Data Entry

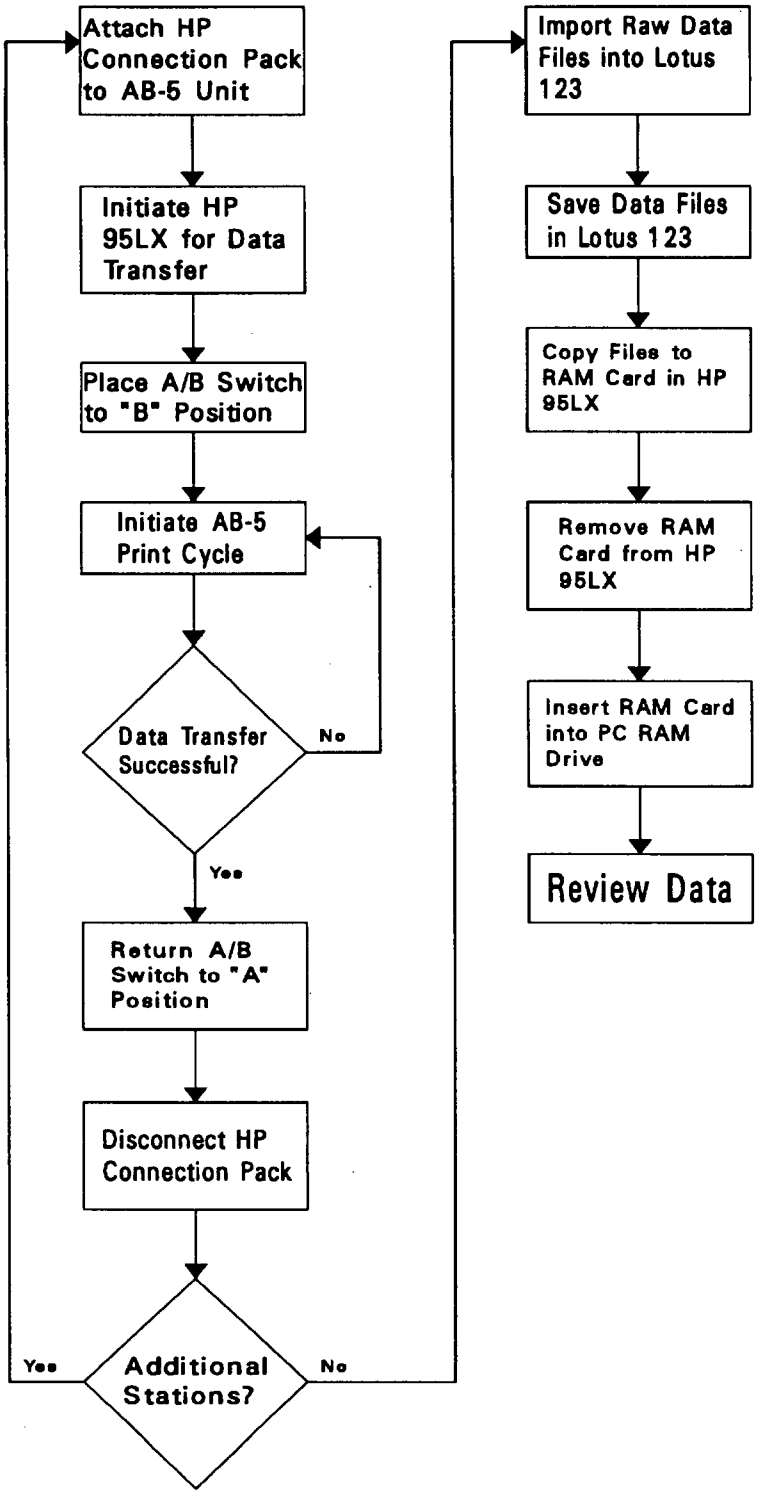

FIGURE 2

Data Transfer from AB-5 to HP 95LX
Data Transfer from HP 95LX to PC

APPENDIX

TRANSFERRING DATA FROM THE PYLON MONITOR TO THE HP95LX COMPUTER

1) Hook up the HPF100A1 Connectivity Pack to the HP95LX and the CI-55 Computer Interface
   Connect the CI-55 to a DB-15 M.M. Transfer Cable.

2) Prepare the HP95LX for use

   Turn on the HP95LX
   Press: **ON/OFF** key

   Press: **BLUE FILER** key
   Select PRN (DIR)
   Press: **CURSOR DOWN** key
   Note: Delete all PRN files to start off the day. This will ensure that sufficient memory will be available on the unit to collect the data.

   Press: **F9** key to tag the old file to be deleted

   Press: **F3** key
   Y key (to delete)
   MENU key

   Press: **Q** key to quit
   Press: **COMM** key
   Press: **MENU** key
   Press **S** key for **SETTINGS** selection
   Press: **U** key for **USE** selection

   Press:Cursor Arrow ---> key over to File (PYL.DCF)
   Press: **ENTER** key
   Check the following setup information:

   Port:
   Inter. 1
   Baud 3
   Stop 1
   Parity none
   Char 8

   Dial:
   Type Pulse

   Press: **Q** key for **QUIT** selection

   Hold **CTRL** key and **press** F-5 key simultaneously

   Backspace to **DAT** and delete by using the <---(Break) key
   Type **PRN\name.prn**
   Press: **ENTER** key

Note: 8 characters max. name

Press: **MENU** key

Press: **C** key for **CONNECT** selection
(at this point set up the pylon to send data)

3) Transferring data from the pylon unit to the HP95LX:

Pylon Monitor
Press: **START/STOP** key to stop current run

Switch Box
Place **A/B** switch to **B** position

Pylon AB-5 unit
Press: **RECALL** key

Press: **PROG STEP** key, this will show the most current run.
If it is necessary to collect a different run use the **PUMP** key to change the first digit and the **START/STOP** key to change the second digit. After the **RUN** is selected press the **PROG/STEP** key 3 times.

Press and hold: **STATUS** key
Display will show the run, cycle, and interval.

Press: **PROG/STEP key** while holding the **STATUS** key
This will start the data transfer.

Release: **PROG/STEP** and **STATUS** key.
When the data transfer is complete the Pylon AB-5 display will display the word "ready" .

Switch Box
Reposition **A/B switch** to the **A** position
Disconnect CI-55 Computer Interface cable from transfer cable on switch box.

HP96LX Computer
Press: **MENU** key to exit program
Press: **Q** key for **QUIT** selection

4) Checking data transfer
Press: **FILER** key
Select the **PRN (dir) ENTER** key
(check if file and data exists)

Press: **MENU** key
Press: **Q** key for **QUIT** selection
Turn off instrument
Press: **ON/OFF** key
Note: Prepare for next station. At the next location it is not necessary to repeat step #2, but step #1, the hookup is still applicable.

DATA TRANSFER FROM THE INTERNAL DRIVE OF THE HP95LX TO THE RAM CARD

1) Transfer data from the HP95LX capture file to the HP95LX Lotus 123 Directory on the RAM Card
   - Turn on the HP95LX
   - Press: **OFF/ON** key
   - Press: **LOTUS 123** key
   - Press: **MENU** key
   - Press: **F** key for **FILE** selection
     I key for **IMPORT** selection
     T key for **TEXT** selection
   - Arrow to ---> **_PRN** enter
   - Search for file of interest
     - Press: **ENTER** key

2) Saving the file
   - Press: **MENU** key
     F key for **FILE** selection
     S key for **SAVE** selection
   - Press **ESC** key two times
   - Type in A:\file name
   - Press: **ENTER** key
   - Press: **R** key for **REPLACE** selection if necessary to write over previous data
   - Press: **ENTER** key
     - Repeat this step to transfer the files to the LOTUS (dir Drive A RAM card)
   - Transfer data from the 128 K-byte RAM Card to the PC via the RAM Card Drive
   - Press: **MENU** key
   - Press: **Q** for **QUIT** selection
   - Press: **Y** for **YES** selection
   - Turn off the HP95LX
     - Press: **ON/OFF** key

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22

AN INTEGRATED APPROACH TO MAINTAINING QUALITY ASSURANCE DURING THE RI/FS PROCESS

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Abstract

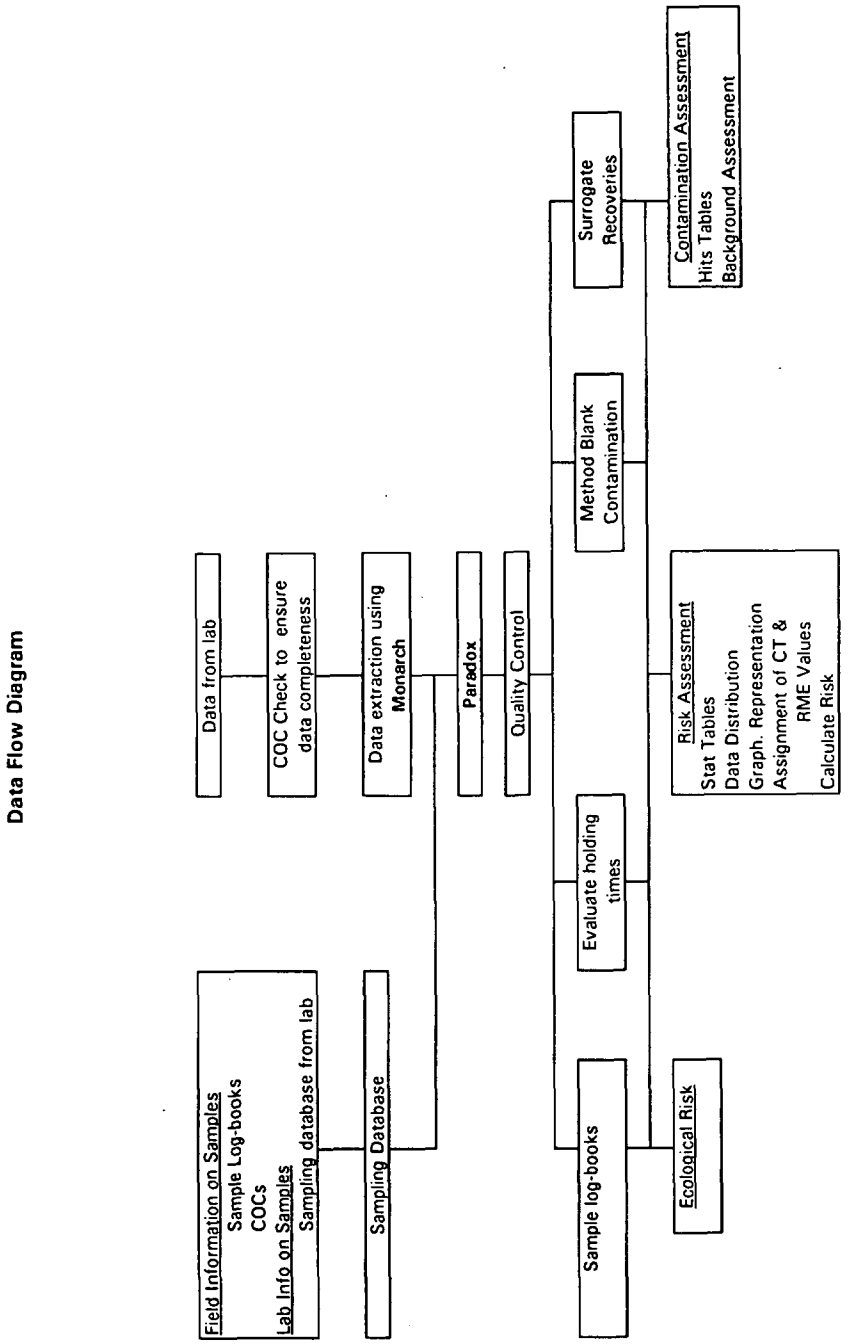
Recently much attention has been given to the applications and requirements of Laboratory Information Management Systems (LIMS), including maintenance of data integrity, implementation of automated scripts for the processing and reporting of data and data security. However, data management and tracking during the field investigation phase of a project have not received the same scrutiny. The case study described in this paper focuses on two potential problem areas in the data collection/reduction process: the standardization and documentation of sample tracking, numbering, and the collection process; and the automation of electronic data transfer, analysis and review.

Introduction

Interest in the project began when an unusual number of cases of Hodgkin's disease were reported in the area of a former army hospital. Public concern over a biomedical waste incinerator operated at the army hospital prompted the U.S. Army Corps of Engineers (USACOE) to launch a site investigation. The purpose of the site investigation was to provide a baseline risk assessment, a contamination assessment and an ecological risk assessment for the areas of concern. Due in part to the high risk of litigation, Woodward-Clyde Federal Services (WCFS) augmented its existing sample tracking program and implemented strict sample handling and documentation procedures. This system was designed to track all samples from collection through the reporting and data analysis phases with a high degree of confidence. All samples were systematically numbered and logged upon collection. The analytical laboratories supplied documentation detailing sample receipt and status in the analytical process at specified time intervals. Both analytical results and supporting QA/QC information were uploaded into a WCFS database using a data-parsing program that converts ASCII text files into database format.

Once the data from the analytical laboratories was uploaded into the WCFS database, programs were developed to compile statistical information in support of the on-going human and ecological risk assessments. Programs were also developed to review and qualify data, and provide output suitable for the final report. By training the field team and maintaining strict documentation, samples could be accurately tracked from the field through the lab until results were reported. By utilizing data-parsing programs along with batch processing to automatically upload data to the database system, WCFS eliminated manual entry of data without having to write complex computer programs that could not offer the flexibility required by the data analysis. A diagram that outlines the

flow of data during the project and some of the deliverables produced is presented in the following section:



Roughly 520,000 records were manipulated in support of this project, and every milestone for deliverables was met on time. Through documentation and automation, WCFS was able to maintain the integrity of the data during the course of the project. This presentation will discuss the systematized methods used to manage data and their impact on the successful completion of the project.

Systematic Numbering Procedure

In order to glean as much information as possible from the sampling event, all sample numbers were coded to provide information about the date of sampling, the sample matrix, whether the sample was a QC sample, etc. To make the numbering system as simple as possible, the date was used as a key element of the sample number. The site identification or spatial location were not part of the coded sample number because all of the sites would have to be selected and coded for sampling well in advance of the sampling event. The basic format of the sample number was:

AAYYMMDD-##XX
where **AA** refers to the installation or site code
YYMMDD is the date (in the format year-month-day)
is the number of the sample collected for that day
and **XX** is an extension that tells the matrix being sampled whether the sample is a QC sample.

This method of coding information into the sample numbers provided field personnel with a fairly simple method of numbering the environmental samples in a systematic fashion. It also provided the staff members checking the sampling data with additional information that allowed for further QC of the dataset.

Field Sampling Documentation

Sample documentation was another key element in the quality control of the RI: chains of custody were used to document sample transport, but a sample log-book, along with extended documentation provided from the laboratory, made it easier to track and QC samples from collection to analysis and invoicing. Chains of custody were sequentially numbered in the same fashion as bank checks. If a COC was voided, it was retained to ensure that all COCs were accounted for.

The sample log-book contained the coded field sample number, the sample's spatial location and depth, the analyses requested, the COC number used to document sample transport and the initials of the individuals performing the sampling. The labs were required to confirm receipt of samples by a written statement listing the WCFS field sample number, the corresponding lab sample number, the analyses requested for that

sample and a copy of the chain of custody for those samples. Every two weeks the labs were required to submit a status report listing all samples still within the analytical process at the laboratory as well as their status within the lab (logged, prepped, analysis complete, etc.)

At major milestones in the project the lab was required to submit an ASCII file correlating WCFS field sample numbers with lab sample numbers. This allowed a check of the WCFS sample log-book and all of the information provided by the lab, data upload and analysis could begin.

Data Extraction from Diskette Deliverables

Contract Laboratory Protocol (CLP) was used as the primary analytical methodology for the RI/FS (herbicides and dioxins were analyzed using SW-846 methods). This protocol is characterized by very specific quality control, documentation, and deliverables. The CLP diskette contains a wealth of information seldom used in its entirety. However, by using data-parsing and pattern-scanning programs, WCFS was able to extract both the analytical results and all of the supporting quality control information that allowed WCFS to perform an automated data review.

Templates to extract data from diskette deliverables were developed using Monarch, a data-parsing program. This program allows the user to read ASCII files, define traps that key on selection criteria to determine which records to extract, name and format all fields for export into a database format. Templates could be developed in roughly a half-day, and then all data could be extracted without any data entry. Gawk, a pattern-scanning language originally developed for the UNIX operating system, was used to create the batch files that would run Monarch. It was used to extract the information from the diskettes for roughly 150 separate sample delivery groups. This totaled nearly 520,000 records for six different analytical methodologies.

Quality Control

Master database files were created for each of the six analytical methods. This was done by appending individual data files, and the files were then checked against the information contained in the sample log-book to ensure that all samples were accounted for and that the proper analysis had been performed and reported. A percentage of the results in the database were checked against hard copies supplied by the lab and no errors were found. For the entire project, only three errors were found in the entire data set, and all were attributable to data entry errors at the lab.

Once the content of the database files had been checked to ensure accurate upload had been performed, results were qualified by the chemistry staff. Queries were created to evaluate hold times, method blank contamination, and surrogate recoveries for all samples.

Sample results whose hold times had been exceeded were qualified, and method blanks were correlated with their associated samples to perform a blank evaluation.

Under CLP methodology, the "B" flag is used to denote a compound which has been detected both in an environmental sample and its associated blanks. If there is a blank contamination, the EPA has issued guidance to qualify those results: for compounds that are considered common lab contaminants to be considered as detects (not artifacts of the sampling/analysis process), the concentration in the environmental sample must exceed ten times the concentration found in any associated blank for those compounds. For all other compounds (those not considered common lab contaminants), the concentration in the environmental sample must be five times greater than the concentration found in any associated blank. The table shown below lists the compounds found in method blanks:

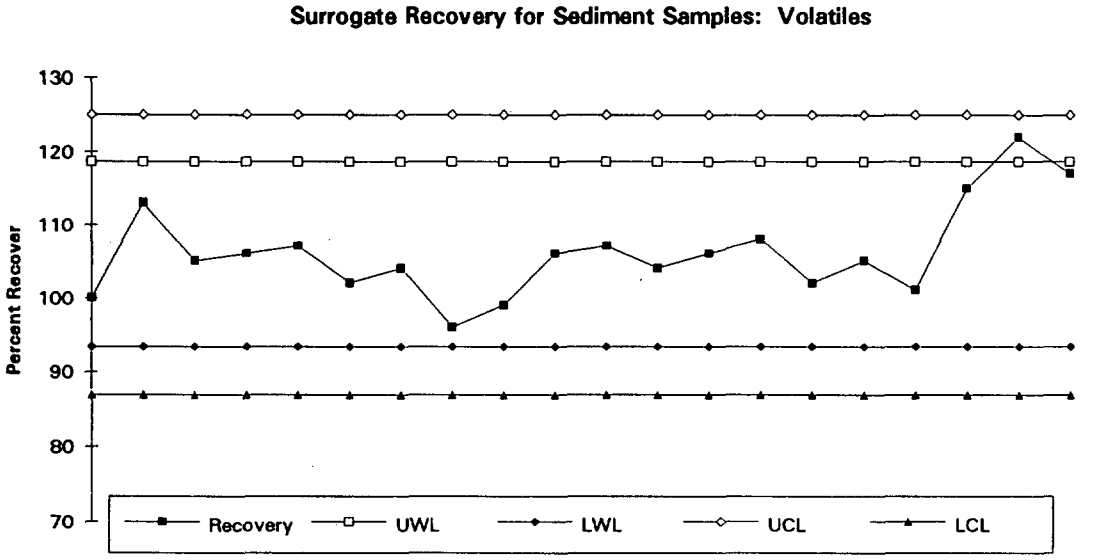
Lab Contaminants Found in Method Blanks

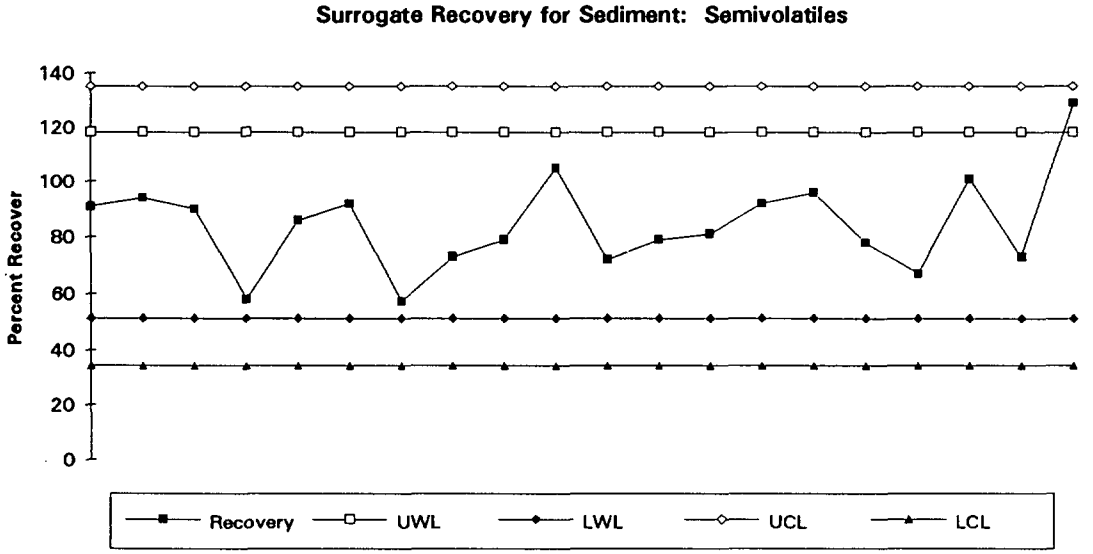
Compounds (Units are ug/L)	Avg. Value	Minimum Value	Maximum Value	No. of Detects	No. of Samples
Volatiles					
2-Hexanone	2.56	1.00	5.00	9	90
Acetone	7.26	3.00	18.00	46	90
Methy Ethyl Ketone	4.03	1.00	19.00	33	90
Methylene Chloride	1.91	1.00	14.00	35	90
Semivolatiles					
3-Nitroaniline	40.00	40.00	40.00	1	66
4-Nitroaniline	46.00	46.00	46.00	1	66
Carbazole	34.00	34.00	34.00	1	66
Di-n-Butylphthalate	40.50	1.00	80.00	10	66
Di-n-Octyl Phthalate	82.00	82.00	82.00	1	66
Diethylphthalate	3.00	3.00	3.00	1	66
Phenol	1200.00	1200.00	1200.00	1	66
bis(2-ethylhexyl) pthalate	203.09	1.00	580.00	11	66

Roughly 293 detects in environmental samples had the "B" flag as a qualifier: after blank assessment and qualification, only two detects with the "B" flag were considered actual detects and not artifacts of the sampling/analysis process.

Surrogates were analyzed using Shewart charting techniques commonly used for process control. Samples were grouped by matrix, analysis date, and sample delivery group to check for trends resulting from either matrix effects, or instrument or operator error. The standard deviation was calculated for each group of samples and warning and control limits were calculated by multiplying the standard deviation by a factor of two or three, respectively. The data for those samples with unacceptable surrogate recoveries

was reviewed, the chromatograms were analyzed and if necessary, the results were qualified. Some Shewart charts for sediment samples are shown on the following page:





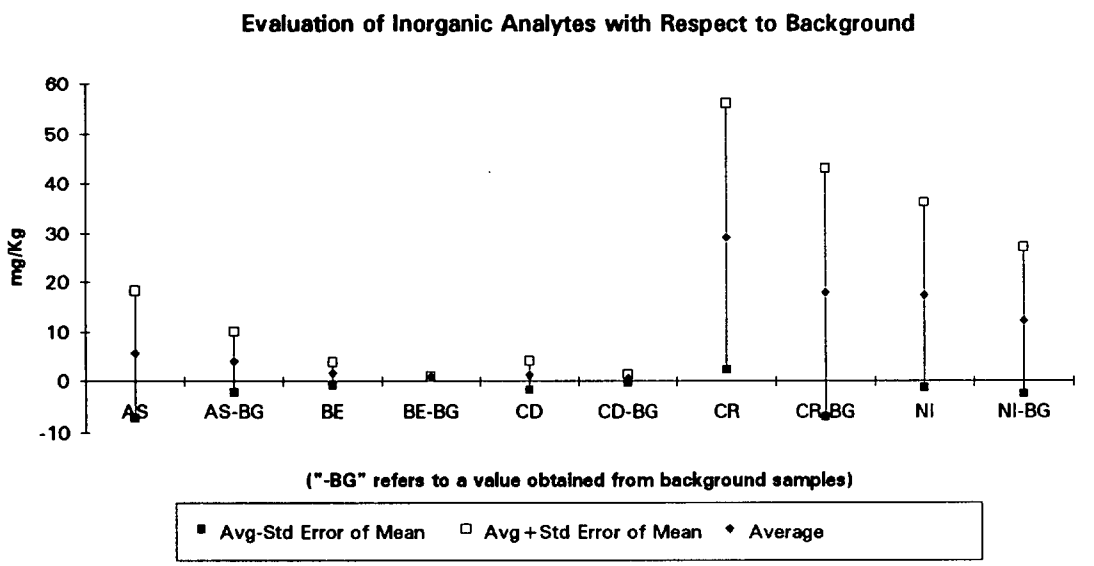
Both blind and designated duplicates were submitted to the lab. They were evaluated for the precision associated with both the sampling and preparation (sub-sampling) methods. For samples with detects above the contract-required detection or quantitation limits, the relative percent difference between a sample and its duplicate was typically below 20%. Matrix spike and matrix spike duplicate results were also evaluated and were found to have similar precision. Accuracy of the methods was evaluated using

matrix spike/matrix spike duplicate results, laboratory control samples, and surrogate recoveries.

Risk Assessment Calculations

In support of the risk assessment, samples were first grouped by exposure area for each group of receptors. The samples were further subdivided by matrix. Contaminants of concern were determined using automated queries to calculate minimum, maximum, minimum non-detect, maximum non-detect, average, standard deviation, and number of detects vs. number of samples for every chemical analysis by exposure area and media. Data was log-transformed and the process was repeated. Both normal and log-transformed data were evaluated with respect to background samples to determine if the data set being analyzed was statistically distinct from the background results. Based on that statistical information and frequency of detection, chemicals to be included in the risk assessment were selected.

Plots similar to the one shown below were used as a graphic means to determine if the background samples were part of an statistically distinct population as compared to on-site samples. The graph shows the average plus or minus the standard error of the mean (standard error of the mean=three times standard deviation) for arsenic (AS), beryllium (BE), cadmium (CD), chromium (CR), nickel (NI) and selenium (SE). On-site results for a particular element are designated by that element's symbol, while background results are shown as the symbol plus "-BG." Based on this technique, none of the elements shown have statistically distinct populations between on-site and background samples. It must be emphasized, however, that this test was merely one of several techniques used to evaluate the presence or absence of on-site contamination.



Once the chemicals of concern were selected, data distribution was evaluated to determine the proper treatment of the data for risk assessment purposes. For this site, calculations using log-transformed data proved to be more conservative, so the log-transformed version of the data was employed for all further risk assessment calculations.

A number of scenarios were established based primarily on the number of samples of a particular matrix for an exposure area. Those scenarios are listed below:

Scenario Summary for Risk Assessment Data

	Values used for RA	
	CT	RME
10 or more samples per matrix per exposure area		
UCL > max.	UCL	UCL
UCL > avg., UCL < max.	Average	UCL
Less than 10 samples per matrix per exposure area		
avg. < max.	Average	Maximum
max < avg.	Maximum	Maximum
No detects per matrix per exposure area		
	Omitted	Omitted

Note: Maximum indicates the maximum detected value
Average is the average of all samples
UCL is the log-normally distributed UCL95 value

Given the scenarios presented above, the data was uploaded into a spreadsheet application that had the compatibility to easily convert files from the database application. Three fields were added to each record; they included the name of the scenario for which the data belonged, and the Central Tendency (CT) and Reasonable Maximum Exposure (RME) values that should be used with that scenario. The CT and RME values were modified by uptake factors for the dermal and ingestion portions of the risk assessment. For well and surface water, the CT and RME values were modified by a value Kp, which is the permeability constant for dermal uptake of compounds from water. The CT and RME were multiplied by an absorption factor for dermal uptake of compounds in direct contact with the skin for all sediment, surface soil, and soil boring data. These calculations were again automated through the use of macros to only calculate if the situation was correct for that scenario. The final tables contained either the calculated value or an "NA" if the data should not be modified by an uptake factor.

Given the now reduced number of chemicals of concern with detects, the data was uploaded into the Woodward-Clyde Risk Assessment application, Assess, which was used to calculate risk. Following all calculations, the hard-copy reports generated were checked for validity against the spreadsheet tables and the source database files. The spreadsheet macros proved helpful in classifying the data into the correct scenario and then choosing the values to be used in the risk assessment.

Conclusion

Methods can be easily employed during the field investigation phase of a project to ensure levels of data integrity that are comparable to a Laboratory Information Management System. The first phase, which deals primarily with the sampling event, requires thorough planning, appropriate documentation and training of all field personnel. Planning provides a forum for all project staff to arrive at a workable solution and documentation provides a means of ensuring that sufficient information is gathered regardless of the individual performing the task. Typically, field personnel are typically given only the minimum training required by their job: proper training and complete involvement in the project allows the staff to realize the intended uses of the data. This translates into more accurate data collection.

The second phase of data management should be designed to minimize any manual entry of data and should also allow sufficient information to be uploaded into a database to permit automated review and analysis of all data. By using Monarch, a software that will extract of information from ASCII files, it was possible to make use of all of the information contained in a CLP diskette. By using a relational database, it was possible to easily perform the ad hoc queries required to track all samples from the time of collection and to provide output for analysis. This project made use of a variety of software packages, including spreadsheets and risk assessment programs to minimize the chance for human errors. These elements of WCFS' program allowed the staff to complete the RI/FS on-time and on-budget.

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EFFLUENT EMISSIONS MONITORING AT THE DOE HANFORD SITE

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ABSTRACT

There are numerous regulatory requirements controlling the effluent emissions monitoring at a U.S. Department of Energy site. This paper defines how these regulatory effluent emissions monitoring requirements and the Quality Assurance oversight of these requirements were implemented by Westinghouse Hanford Company, the operations contractor, at the DOE Hanford Site.

INTRODUCTION

Westinghouse Hanford Company (WHC) struggled with the implementation of DOE and other regulatory effluent monitoring Quality Assurance (QA) requirements. There was little guidance or direction provided on how this should be done. By using the QA organization from the earliest planning stages, a more effective compliant process has evolved.

These initial monitoring requirements were prescribed by the implementation of DOE Order 5400.1 which specified that the sites implement plans to monitor regulated hazardous and radioactive effluents by November 1, 1991. Included in this order were the environmental QA requirements to be used in this effort, but there was little direction given for their implementation.

The DOE environmental QA requirements are very similar to U.S. Environmental Protection Agency (EPA) Quality Assurance Management Staff (QAMS) requirements that WHC had been using for well sampling and analysis activities. These plans had been effective in monitoring well water so WHC decided to use these as guidance for preparing plans for the liquid effluents.

The radioactive air requirements from 40CFR61, Appendix B, Method 144, Section 4, include the DOE requirements plus specific items related directly to radioactive air measurements, items that would normally be considered Quality Control (QC) activities. It was decided to prepare a QA Program Plan (QAPP) in accordance with the EPA QAMS requirements and include the stack specific measurement requirements as appendices to this document.

These effluent monitoring activities are currently being performed with added enhancements as the effort continues.

HANFORD SITE

The Hanford Site covers approximately 560 mi^2 (1,450 km^2) of semiarid land that is owned by the U.S. Government and managed by the U.S. Department of Energy, Richland Operations Office (RL). In early 1943, the U.S. Army Corps of Engineers selected the Hanford Site as the location of reactor, chemical separation, and related activities for the production and purification of special nuclear materials and other nuclear activities. Since 1988, the mission of the Hanford Site has focused on environmental remediation and restoration.

Activities on the Hanford Site are centralized in numerically designated areas (see Figure 1). The reactors are located along the Columbia River in the 100 Areas. The reactor fuel processing units are in the 200 Areas, which are on a plateau approximately 7 mi (11 km) from the Columbia River. The 300 Area, located adjacent to and north of the City of Richland, contains the reactor fuel manufacturing plants and the research and development laboratories. The 400 Area, 5 mi (8 km) northwest of the 300 Area, contains the Fast Flux Test Facility that is used for testing liquid metal reactor systems. Other areas and buildings designated on the map are for administrative purposes and do not produce regulated effluents.

Hanford Site facilities are no longer producing nuclear materials for defense purposes, rather operations are continuing for cleanup purposes. The air and liquid effluent streams are being generated during maintenance or shutdown of existing facilities.

EFFLUENT MONITORING REGULATIONS AND QUALITY ASSURANCE REQUIREMENTS

Figure 2 depicts the roles of the DOE, EPA, Washington State Department of Ecology (Ecology), Washington State Department of Health (DOH), and the sources of the environmental QA requirements specified in the regulations. This paper is limited to major effluent monitoring efforts of the operating facilities that require regulatory control. The effluent monitoring environmental QA regulations are identified by the double-lined boxes on Figure 2. The RCRA/CERCLA efforts required for cleanup, waste analysis, and efforts specified only for DOE purposes are not included.

A major factor in almost all environmentally regulated activities at the Hanford Site is the *Hanford Federal Facility Agreement and Consent Order* more commonly referred to as the Tri-Party Agreement (Ecology, et.al. 1992). This agreement among DOE, EPA, and Ecology specifies requirements and schedules for most environmentally regulated monitoring, operating, and construction activities. As noted on Figure 2, the Tri-Party Agreement relies on the EPA QAMS documents for effluent environmental QA requirements.

The DOE effluent monitoring QA requirements, DOE Order 5400.1, General Environmental Protection Program, Chapter 4, Section 10, do not provide direction on implementation. WHC decided to use the QAMS requirements for all liquid effluent monitoring activities. These requirements specify similar requirements while providing implementation guidance.

The other sources of QA effluent monitoring requirements found were:

- *National Emission Standards for Hazardous Air Pollutants* (NESHAP), 40CFR61, Appendix B, Method 114, Section 4, QA Methods
- *National Pollutant Discharge Elimination System* (NPDES), 40CFR122.44, Establishing Permit Conditions
- *Toxic Substance Control Act* (TSCA), 40CFR763.121, Appendix A, Quality Control Procedures, and Appendix B, Detailed Procedures for Asbestos Sampling and Analysis.

There is only one effluent stream, associated with the N Reactor, that has an NPDES permit. Since all monitoring activities are specified and controlled by this permit, the N Reactor stream will not be further addressed in this paper. The TSCA controls are also not addressed in this paper.

The remainder of this paper will discuss how the regulated liquid and radioactive air streams were identified and the environmental QA controls were applied.

INITIATION OF EFFLUENT MONITORING PROGRAM

Regulated effluent monitoring was instigated in response to DOE Order 5400.1, which required the preparation of effluent monitoring plans by November 1, 1991. The Order states that

> "An implementation plan shall be prepared for each facility or group of facilities, the purpose of which is to ... comply with environmental regulations and DOE policies."

WHC responded to this by preparing a management plan for facility effluent monitoring plan activities to direct the identification and implementation of these monitoring efforts. The management plan specified the regulatory criteria that would require monitoring, the facilities that would need to be addressed, the basic information needed in a Facility Effluent Monitoring Plan (FEMP), and the schedule for completing the determinations.

The criteria, as noted in the management plan are taken from the following regulatory requirements:

(1) For Radioactive Air Emissions, 40CFR61.93, "Radioactive emission measurements ... shall be made at all release points which have a

potential to discharge radionuclides into the air ... in excess of 1% of the standard." As the EPA allowable dosage is 10 mrem/yr all facilities that could cause radiation doses in excess of 0.1 mrem/yr to the maximally exposed member of the public must be monitored.

(2) For discharges of nonradioactive materials, monitoring is required of all facilities with the potential to release quantities of hazardous materials exceeding the reportable quantities listed in 40CFR302.4, "Designation of Hazardous Substances."

(3) All potential radioactive discharges to the ground must be monitored.

The plan preparation required that all facilities be reviewed to determine if any of the above requirements had been exceeded and thus require monitoring.

FACILITY EFFLUENT MONITORING PLAN DETERMINATIONS

Each facility had to be thoroughly examined to identify each effluent, and an analysis was done on each stream to see if any of the above criteria were exceeded. The determinations of the streams and the preparation of the FEMPs took over one year to complete.

To put this in perspective, there were 17 geographical areas that included approximately 110 facilities. Of these, 15 facilities, with 22 hazardous and/or radioactive liquid streams and 7 radioactive emissions stacks, exceeded the criteria. Discussions are ongoing with the Washington Department of Health that may add other radioactive stacks to this program. There is also another ongoing program (Air Emissions Inventory) to identify the hazardous air emissions.

FACILITY EFFLUENT MONITORING PLANS

Each facility with a regulated stream(s) was required to prepare a FEMP to address the requirements specified in the management plan. To expedite this effort and to ensure consistency between facilities, a guide for preparing Hanford Site facility effluent monitoring plans was prepared. This document expanded on the management plan requirements with guidance on what to include in each of the following sections including:

- Purpose and scope
- Applicable regulations
- Facility/process description, source terms, release pathways
- Characterization of the airborne and liquid discharges to be monitored, providing potential effluent concentrations
- Characterization of effluent points, providing design criteria and technical specifications of monitoring/sampling systems

- Historical monitoring/sampling data and a comparison of normal and upset conditions
- Sample analysis and laboratory procedures
- Notification and reporting requirements
- Interface with operational reporting requirements
- QA Plan
- Internal and external plan review requirements
- Compliance assessment describing conclusions reached, if monitoring was required and will system need upgrading.

The fifteen FEMPs were prepared to these criteria with the appropriate reviews and approvals.

QUALITY ASSURANCE INVOLVEMENT

The QA organization was invited to join in this effort shortly after it was started when the developers encountered problems trying to implement the DOE Order 5400.1 QA requirements. The QA representative was familiar with the QAMS document with its defined method of implementation and this was used to implement the DOE requirements. The QA organization also reviewed the implementation documents to ensure that these were reviewed and controlled in accordance with DOE Order 5700.6C, *Quality Assurance*.

The facility effluent monitoring QA Project Plan that was prepared described the existing facility procedures and how they would be used to implement the QA requirements. However, this effort was not successful as the existing procedures did not have the needed custody or control checks required for regulatory environmental QA controls. In addition, each facility had their own procedures with little correlation between them. There was a need for some standard operating procedures (SOP) with the needed QA/QC controls.

The FEMP documentation provided the background information that was needed to prepare for monitoring the facilities, but other programs were used for QA verification. This was done through the implementation of two other regulatory requirements, the Liquid Effluent Characterization Program and National Emission Standards for Hazardous Air Pollutants (NESHAP).

LIQUID EFFLUENT CHARACTERIZATION PROGRAM

At the time of the signing of the Tri-Party Agreement, the DOE agreed to monitor and analyze 33 specified liquid streams, called the Liquid Effluent Study (LES), in accordance with the EPA QAMS QA criteria. There had been ongoing monitoring of these streams since 1985 in response to congressional requests and the regulators requested that this be continued and that EPA QA requirements be applied to the activities. These were the same streams as those identified in the FEMP determinations; except however, as the site continues to shut down facilities, some of the streams are no longer in use.

QUALITY ASSURANCE OVERSIGHT OF LIQUID EFFLUENT MONITORING ACTIVITIES

The initial LES sampling and analysis activity was done shortly after the signing of the Tri-Party Agreement in 1989 without QA support and with no QA/QC protocols. Since information could not be verified or validated it was not acceptable to Ecology. After this was completed, the QA organization was asked to perform a post-completion surveillance of the sampling and analysis activities. The intent was to verify the implementation of the required EPA QAMS requirements. After finding this uncontrolled situation, the QA organization was invited to be an integral part in setting up the QA Program to ensure the validity of future data.

It was agreed initially that a QA Project Plan (QAPjP) would be prepared in accordance with the requirements of EPA QAMS-005/80. This was later expanded to include management control and changed to a QAPP. There was also consensus that all sampling and analysis activities could not be included in a single plan. Those activities that were common to all streams were included in the sitewide QAPP. Individual Sampling and Analysis Plans (SAP) were prepared for stream-specific information.

The QAPP provides the general framework for sample collection, laboratory analysis, and data reporting with the common QA requirements for the characterization of liquid effluent streams. These common QA requirements include program description, Data Quality Objectives (DQO), program organization, sample control, laboratory analysis, and data processing.

The SAPs are wastestream-specific documents that describe how QAPP requirements are implemented. The SAPs include a discussion of stream-specific DQOs, a description of the liquid effluent, and a justification for sample location and frequency. The SAPs also identify any stream-specific exceptions to the QAPP.

An effluent monitoring organization was responsible for identifying the regulatory requirements, preparing the QAPP, and specifying the implementing requirements and criteria to include in the SAPs. The SAPs format and content were based on *Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA* (EPA/540/G-89/004, October 1988) for a field sampling plan (FSP).

The SAPs are prepared by each facility with input from the common sampling organization. This coordination of sampling and analysis preparation provides the control needed to achieve environmental QA implementation.

The environmental and facility QA groups work together to perform the stream surveillances. The environmental QA group reviewed and approved the QAPP and SAPs. The QA group's familiarity with these documents allows them to prepare the stream surveillance plans. The facility QA personnel are familiar with the facility and thus better able to witness the field sampling activity. Environmental QA is responsible for the surveillance, but both groups coordinate and approve the surveillance findings.

RADIONUCLIDE AIR MONITORING

The Clean Air Act was amended in December 1989 to include 40CFR61, Subpart H, *National Emission Standards for Emissions of Radionuclides Other Than Radon from Department of Energy Facilities*. This subpart requires that a QAPP for radionuclide air monitoring be prepared in accordance with the requirements of 40CFR61, *National Emission Standards for Hazardous Air Pollutants* (NESHAP), Appendix B, Method 114, Section 4, QA Methods.

The Washington Department of Health was satisfied that the seven stacks required monitoring, but did not feel that the FEMPs adequately covered the continuous monitoring requirements. The DOH required that regulated stacks and analytical laboratories be Point by Point (PBP) compared to 40CFR61, Appendix B, Method 114 to be certain that all requirements were satisfied. This major PBP exercise compared the existing air monitoring equipment and program with that specified in the requirements, including Section 4, QA Methods.

It was decided to use the QAPP as the binding document to control the NESHAPs activities. All stack monitoring sampling and analytical requirements are included in the document.

NESHAPs QUALITY ASSURANCE PROGRAM PLAN (QAPP)

There was a concern as to how to address the QA requirements of Method 114 for all the various activities at the stacks. It was initially proposed that an overall QAPP be prepared with separate QAPjPs for each stack. It was finally agreed that a QAPP with the stack PBPs appended would address all QA program requirements.

The QAPP was prepared in accordance with the guidance provided by EPA QAMS-004/80 and is organized as shown on Figure 3, NESHAPs Table of Contents. The major responsibilities and actions needed to control the NESHAPs program are defined in Sections 3.0, 6.0, and the appendices.

Section 3.0, Quality Assurance Management, defines the various oversight organizations that are responsible to verify that the NESHAPs activities are being properly done. The body of the QAPP describes these various organizations and the procedures they use to perform these oversight activities. WHC is organized with a central QA group, Environmental Services Quality Assurance. This central group reviews and approves documentation and provides guidance to facility QA organizations, who assist with field overviews. The same relationship exists as in the liquid effluent monitoring where actions are combined, but the central environmental QA group is responsible for the surveillances.

Section 6.0, Radioactive Air Emissions Measurement Quality Assurance Project Implementation, specifies the organizations that are performing the NESHAPs activities. This section describes organizational responsibilities and interfaces. Included are responsibilities for specifying NESHAPs requirements, sampling and sample transport, laboratory

analysis, flow data information, systems calibration, regulatory reports, procedures preparation, and data verification. Section 6.0 was difficult to prepare but defining these responsibilities and organizing the activities was crucial to properly completing the NESHAPs activities. In preparing this document it was determined that some activities were not being properly addressed. These were corrected and included in the document.

The PBP comparisons for the seven stacks, appended to the QAPP, provide the total overall program control needed for NESHAPs activities. Items that are specific to a stack are included in the PBP, but standard operating procedures are included, or referenced, in the body of the QAPP. There is an added advantage to this in that if additional stacks have to be registered a stack-specific PBP can be prepared and appended to the existing QAPP. There will be no need to prepare a QA Plan for each added stack.

The QAPP provides the needed control of the NESHAPs activities but allows the flexibility to add regulated stacks as needed.

SUMMARY

The preparation and implementation of the QAPP was crucial to properly organizing the activities and obtaining verifiable data.

Both liquid and air monitoring started out without Environmental Services QA help and the responsible facilities were at a loss as to how to implement these new unique sampling and analysis requirements. The Environmental QA person was able to define what information was needed for the QAPPs and help the responsible organizations in their preparation and implementation.

It is important to have the implementing organizations prepare the plans. In the case of the FEMP activities, outside consultants prepared most of the documentation without facility input. The facilities were not aware of the commitments made and were hesitant to implement these. As noted in the document, the LES program is used to verify the control of liquid effluents.

In both the liquid and radioactive air monitoring existing facility procedures were initially used; however, it became imperative to prepare SOPs. In the FEMP program the existing procedures were not definitive enough nor did they have the needed QC controls. In the NESHAPs program it was determined that it would be easier to have common procedures and these have been prepared.

In closure, someone familiar with Environmental QA requirements, but not part of the assessment organization, should be a working partner with the implementing organizations in preparation and implementation of environmental QA requirements. This relationship will allow for compliance and will ensure that the data gathered is verifiable.

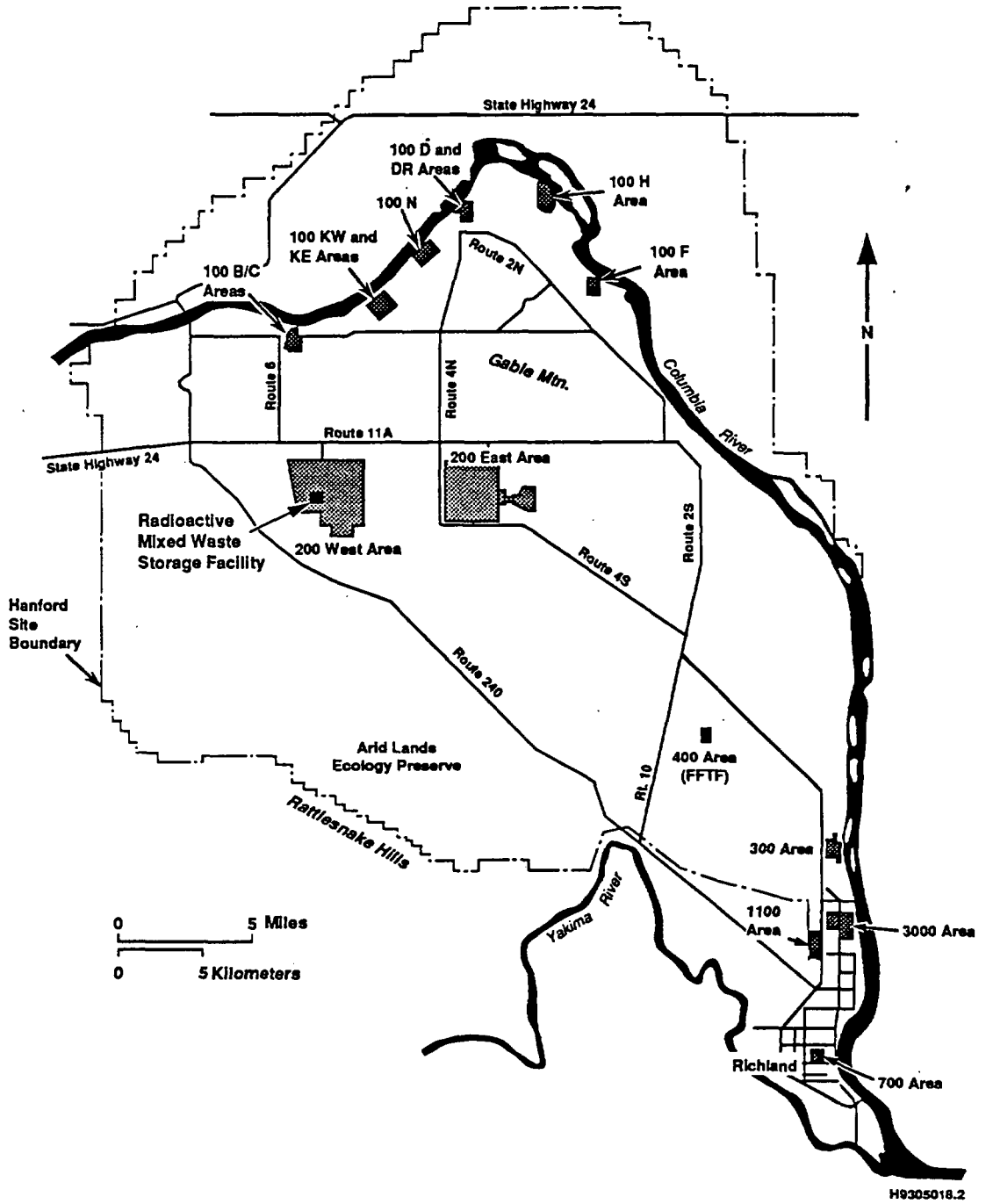
State Highway 24
100 D and DR Areas
100 H Area
100 N
100 KW and KE Areas
100 F Area
100 B/C Areas
Route 2N
N
Route 6
Route 4N
Gable Mtn.
Columbia River
Route 11A
State Highway 24
200 East Area
Radioactive Mixed Waste Storage Facility
200 West Area
Route 4S
Route 2S
Hanford Site Boundary
Route 24O
Arid Lands Ecology Preserve
400 Area (FFTF)
Rt. 10
Rattlesnake Hills
300 Area
Yakima River
1100 Area
3000 Area
0 5 Miles
0 5 Kilometers
Richland
700 Area
H9305018.2

Figure 1

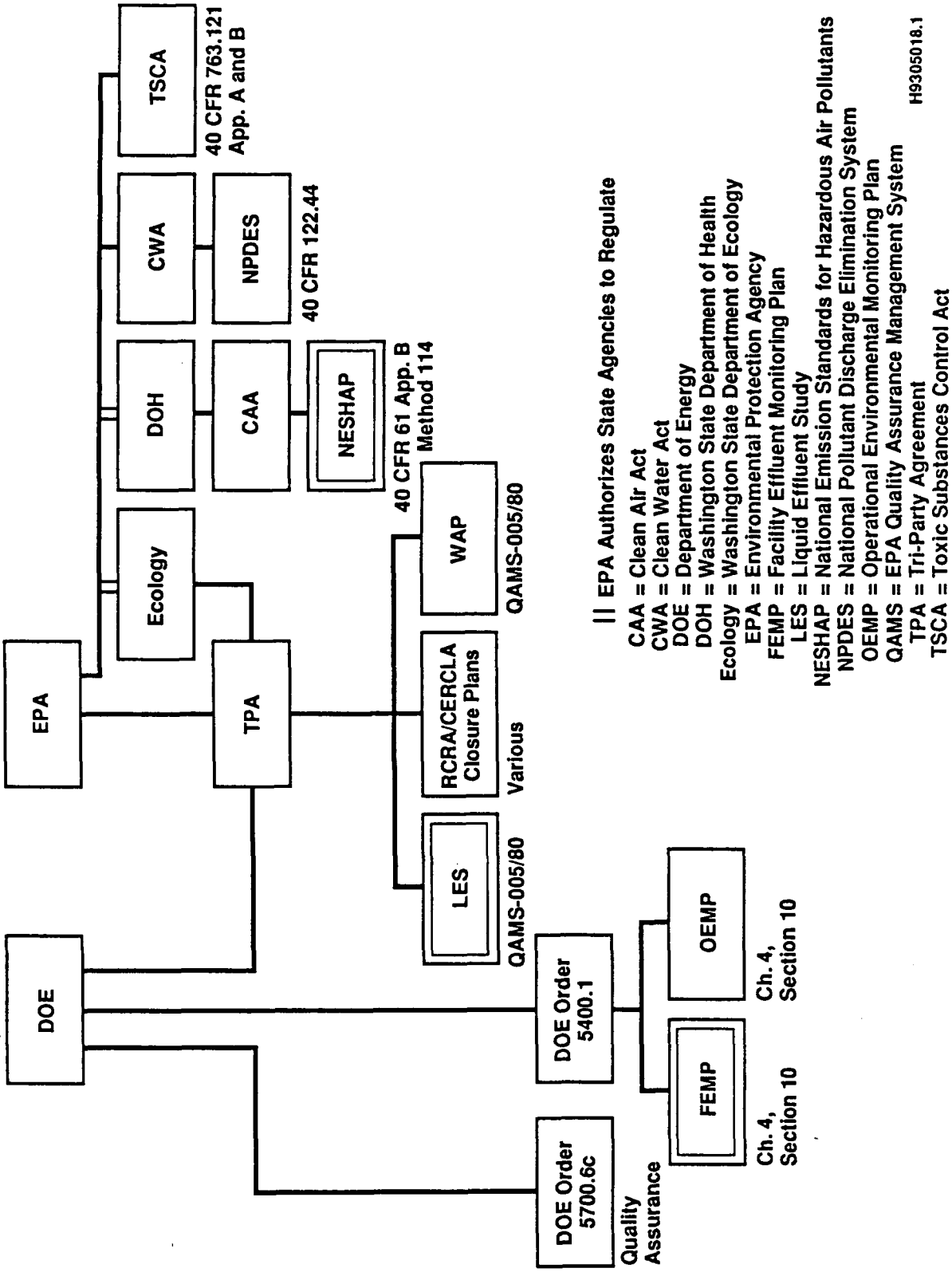
EPA
DOE
TPA
Ecology
DOH
CAA
CWA
TSCA
NESHAP
NPDES
40 CFR 763.121
App. A and B
40 CFR 122.44
40 CFR 61 App. B
Method 114
WAP
RCRA/CERCLA
Closure Plans
LES
QAMS-005/80
Various
QAMS-005/80
DOE Order
5400.1
DOE Order
5700.6c
Quality
Assurance
FEMP
OEMP
Ch. 4,
Section 10
Ch. 4,
Section 10
EPA Authorizes State Agencies to Regulate
CAA = Clean Air Act
CWA = Clean Water Act
DOE = Department of Energy
DOH = Washington State Department of Health
Ecology = Washington State Department of Ecology
EPA = Environmental Protection Agency
FEMP = Facility Effluent Monitoring Plan
LES = Liquid Effluent Study
NESHAP = National Emission Standards for Hazardous Air Pollutants
NPDES = National Pollutant Discharge Elimination System
OEMP = Operational Environmental Monitoring Plan
QAMS = EPA Quality Assurance Management System
TPA = Tri-Party Agreement
TSCA = Toxic Substances Control Act
WAP = Waste Analysis Plan
H9305018.1

Figure 2

Figure 3. National Emission Standards for Hazardous Air Pollutants Table of Contents.

CONTENTS

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QUALITY ASSURANCE AUDITS OF LABORATORIES

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ABSTRACT

Experience gained through audits of numerous laboratories across the United States has helped to focus on some common problems found in laboratories. Various regulatory requirements and programs help to complicate the audit process. Many laboratories are almost overwhelmed by the requirements, and the quantity and diversity of audits imposed upon them. Occasionally auditors add to this confusion as they sometimes arbitrarily require the laboratories to follow set protocols of documentation instead of focusing on the end products of the systems in place. Such actions can result in the laboratories developing multiple parallel systems to produce the same end results. This process of multiple systems can be very costly and a source of numerous errors within the laboratory. This presentation focuses on common pitfalls found within Laboratory Quality Assurance/Quality Control Systems and in the process of auditing such systems and their performance outcomes.

INTRODUCTION AND BACKGROUND

Requirements from numerous regulatory or governmental agencies seem never to stop growing and expanding in both scope and complexity. Guidance for interpretation and application of these requirements is not always clear or maybe even available. This can add more confusion as to exactly what is required and how to approach the various situations.

To compound these requirements, numerous companies, associations and boards publish or provide guidance and or requirements to be followed. Throughout the years, constant change and additions to requirements has produced a tremendous burden on both the laboratories and those auditing the laboratories. Even the terminology and approaches used to evaluate the laboratories has become very diversified and confusing. At present the author evaluates some laboratories within the DOE System and several Commercial Laboratories. Samples sent to these laboratories by Westinghouse Hanford Company may be analyzed under several different regulations.

Examples of these regulations are

- the Safe Drinking Water Act (SDWA)
- the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and it's Superfund Amendments and Reauthorization Act (SARA)
- the Resource Conservation and Recovery Act (RCRA) and it's Hazardous and Solid Waste Amendments (HSWA)
- the Clean Air Act (CAA) and the National Emission Standards for Hazardous Air Pollutants (NESHAP)
- the Clean Water Act (CWA) and the National Pollutant Discharge Elimination System (NPDES)
- the Water Quality Act of 1987 (WQA)
- the Toxic Substances Control Act (TSCA)
- the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), and
- the Solid Waste Act (SWA).

Sample types include:

- radiochemical
- mixed waste
- hazardous waste
- water quality
- air quality, and
- can consist of several matrixes.

These matrixes include:

- water
- air
- solid waste
- animal tissue, and
- vegetation.

These samples may or may not be subject to the Hanford Federal Facility Agreement and Consent Order of May 1989. This agreement is between the Washington State Department of Ecology, the United States Environmental Protection Agency and the United States Department of Energy. It is commonly referred to as the Hanford Tri-Party Agreement. Additional requirements from this agreement are contained in most of the Statements of Work (SOWs) to contract laboratories. It is extremely difficult to provide all exacting guidance in this fashion due to the enormous diversity of work.

A discussion of lessons learned and some common pitfalls will be presented. It is not the intent to single out laboratories or types of laboratories but to discuss things found throughout several laboratories in the nation. No attempt will be made to quantitate the extent of such problems or to statistically treat this subject.

AUDIT, SURVEILLANCE, ASSESSMENT OR INSPECTION?

In evaluating these laboratories each of these terms has been used in different notifications to laboratories about upcoming activities. Several laboratories have expressed concern about what to expect based on what term is used. EPA in general does different types of audits (system and performance as an example), whereas the NRC calls similar activities inspections. The DOE sometimes breaks these activities into surveillances, inspections, assessments and audits. In this paper, the term audit will be used to cover all these activities. Each agency can readily define what is meant by the terms it uses but often fails to do so in a clear way to the laboratories it associates with. What is important to the laboratory is to know the extent of the activity (audit); time required at the site; requirements for availability of personnel, the facility and records; what topics and areas will be covered; the focus of the audit in some detail.

The author's experience has shown that sharing the topics to be covered by the audit checklists with the laboratory, a few weeks before the audit has in general been very successful. This enables the laboratory to review requirements (often finding areas of miscommunication or incomplete understanding), allows time for the laboratory management to perform a focused self assessment (management audit), allows the laboratory time to gather the needed evidence and yes, even time to get everything caught up. The philosophy used here is a win-win approach.

A mistake auditors can make is to equate the success of an audit with the greater the number of findings, the better the audit. Large numbers of findings often result from poor communication and produce a lose-lose situation. If a company can correct mistakes before the audit, much time is saved in getting the laboratory into compliance. The audit trail is still there to show when the mistakes were corrected and the auditor should require the laboratory to still assess what potential impacts were to the data, and to correct or flag the affected data if needed. Much can be learned about the attitudes, philosophy and general operations of laboratories by this approach. When other purposes are paramount, checklist topics can be withheld from the laboratory.

REQUIREMENTS

Great care needs to be taken to identify and evaluate based on the established requirements. When auditing a laboratory's work done under specific regulatory requirements, those requirements need to be complied with unless a written waiver has been obtained from the applicable regulatory body(ies). Auditors sometime impose certain formats or requirements which are not based on the regulations or the contract with the laboratory. These are not enforceable and can be a source of both contention and loss of credibility.

Sometimes, laboratories sign contracts in which additional requirements have been imposed by the client. These laboratories sometimes try to hide

behind the fact that the area of noncompliance is not regulatory and therefore is not important. Any such written agreement may be just as important as the regulatory requirements to the client.

GIVE ME A CHECKLIST!

A critical mistake some companies make is to develop checklists to be used on audits and then send just anyone trained in auditing to perform the audit. First, of all, it is very difficult to produce a generic checklist that can be used in various laboratories. Second, the available of commercially generated checklists is decreasing as the industry reacts to suits or threatened suits from companies. These companies have used a generic checklist and have missed critical items that have resulted in heavy fines or loss of money from poor investments.

The most significant single point to be emphasized in this paper follows. The author fully believes that an auditor should be recognized as technically competent in the area of the audit being dealt with. This means that teams will often be used to perform the audit. The checklist is only a guide and a reference point and extensive knowledge of the subject can not be substituted for by making the checklist more extensive.

Knowledge gained through audits is vital to contracts and strong consideration should be given to who will conduct it. Auditors inexperienced in a given area tend to do one of two things. Either they don't act in areas of concern because they aren't sure of the situation, or they have multiple findings which are not valid. This misuses the laboratory's time and can cause needless confusion and conflict. Everyone makes mistakes but technically competent auditors tend to make fewer and less critical ones.

COMPLIANCE VERSUS PERFORMANCE

Significant confusion exists in both laboratories and with auditors as to what is the governing consideration between good performance and compliance to requirements. This is not an easy question to answer and the correct answer depends upon individual situations.

Some agencies have been more traditionally performance oriented whereas others have been more compliance oriented. All have incorporated both elements but have emphasized one to a greater degree. For example, EPA has Performance Evaluation (PE) and Round Robin Sample Programs in which it can be determined in a given matrix if the laboratory can produce results that meet certain accuracy, precision and detection requirements. Good scores on these samples are mandatory to receive work or to continue to receive work. On the other hand other agencies often have checklists based on compliance to very specific parts or steps of procedures and may or may not have quantitative means of assessing the final outcome.

The author, given the regulatory bodies that will assess the laboratory results in this case, takes the stance that both of these considerations

must be fully satisfied. Until all regulatory bodies who overview this work agree as to acceptance of a different approach, both considerations must be fully satisfied. An example is presented in the following discussion of the potential different approaches.

PROCEDURAL COMPLIANCE

A good example of the conflict between compliance versus performance comes in analytical procedural compliance. Some companies and auditors contend that regulatory procedures must always be exactly adhered to; while others say that, if the performance can be shown to be equivalent, a significantly modified procedure is acceptable. The author's experience has been that most companies take it for granted that all laboratories follow the approved procedures.

While performing audits, quite the opposite has been found in many cases. While reviewing RCRA water pH procedures of some 22 laboratories, the author found on his first visit that 21 out of 22 procedures were noncompliant in following the national standard procedure. A procedure found in SW-846 and one found in another approved Standard Method were the two procedures allowed to be used in these contracts. Both required that separate aliquots of the water sample be repeatedly measured until the pH measurement agreement was within 0.1 or 0.05 pH unit respectively. Twenty one of 22 laboratories were performing sample measurements on a single aliquot. Some laboratories had other nonconformances to the procedures also. To the author's knowledge all 22 laboratories's pH procedures are now compliant in this regard.

The point that is emphasized is that pH is a very straight forward measurement and if there is this much noncompliance to national procedures with the pH analysis, what about all the other analytical procedures. There are several significant noncompliances to regulatory procedures in well know laboratories today. Laboratories have the responsibility to report all potentially quality affecting modifications found in their procedures that are reported to be "equivalent to" or reformatted national standard procedures. Auditors can not afford to take quick looks at procedures if their contract requires compliance. Companies need to know if strict procedural compliance is mandatory on the samples submitted to laboratories and, if so, hold laboratories to the responsibility of being compliant.

The pH measurement example has been attempted to be refuted with the argument that through Performance Evaluation (PE) samples and other evidence that there is a sound scientific basis that the correct answer was obtained despite the nonconformance. This argument stands it's ground if performance alone is an acceptable end product. When the potential for litigation exists concerning the conclusions drawn based on these sample analyses, the question of procedural compliance becomes overpowering. The bottom line is to know the requirements for the samples in question and to have written waivers if necessary. In most cases such waivers are very hard to obtain and involve significant cost and time.

TRAINING

This is an area in which most laboratories have trouble understanding what is required and in presenting proper evidence. Training requirements will vary based on company, regulations and situations encountered. Some companies require less strict training documentation than those for which these audits were performed. The requirement categories presented here are:

- Qualification requirements including educational and training
- Job or position descriptions
- Evidence of training to policies and procedures
- On the job training or other performance indicators
- Documentation as to the required frequency of training for specific tasks
- Evidence of training and approval before sample analysis

Common deficiencies found include:

- Not having specific job descriptions
- Not having signed qualification statements listing specific qualifications required and demonstrated
- Procedural or policy reading lists that do not require training to revisions
- Training to revisions up to several months after put in use
- No indication if this item is a one time requirement or what the requalification period is
- Copies of test scores or QA sample results with no indication in writing what a passing score is and what happens if a person does not pass, or
- No record of what actions have been performed by the analyst before they are signed off as qualified.

A common mistake of auditors which causes laboratories time and financial burdens is to insist where or in what format this evidence is kept. What is needed is for the laboratory to be able to produce the documentation.

DOCUMENT CONTROL AND CHANGE CONTROL

The major aspects of document and change control that appear to be lacking in some laboratories will be discussed here. Laboratory personnel need to work to controlled copies of procedures. Controlled copies means that a system of accountability has issued and assigned specific procedures that:

- are identifiable as to review and signature responsibility
- are traceable to issue and effective date
- provide clear indication as to what types of samples, matrixes and analytes are covered
- reference standard procedures this procedure meets
- clearly indicate what QA/QC accompanies the procedure and that the copy is identifiable as a controlled copy.

The laboratory should develop a system to assure that when new revisions of procedures are issued, training documentation is in place before the procedure is used on client samples; that all copies of old revisions are removed from the work place; that the master copy of both old and new procedures are securely stored and maintained.

RECORDS MANAGEMENT AND SECURITY

Records must be stored in a certain manner to meet requirements. These are not universal requirements and potential laboratory shortcomings are offered as things to consider. Laboratories were required, by the contracts associated with these observations, to store records in the equivalent of an one hour lockable fire safe or cabinet. These containers needed to be either locked at all times when not in actual sight and use by the records custodian (or delegated representative) or they needed to be in a locked restricted access room to which only identified persons had access. Storage in two separate locations that meet other specific requirements could substitute for the fire safe requirement.

Even though several laboratories signed contracts with these requirements, it took several months to have most come into full compliance. Inexperience as well as incomplete checklists significantly contributed to the delay in compliance.

CORRECTIVE ACTION AND NONCONFORMANCES

Laboratories should have systems to identify nonconformances. They also need systems to identify, track, respond to, and correct conditions or items identified for corrective action. Nonconformances are conditions in which material or action does not match the requirements of procedures, contracts or policies. If such nonconformances are identified to be potentially quality affecting or violate the terms of a contract, they need to enter the corrective action system. The most common problems encountered in the audits of these laboratories ranged from not having systems in place to having systems that only partially addressed corrective actions.

Conditions were often found not to be formally addressed in the first and sometimes in follow up visits to laboratories, such as

- loss of temperature control
- missed holding times
- missed reporting times
- poor results on round robin or PE samples
- loss of document or change control
- loss of chain of custody or internal chain of custody control
- loss of or mishandled samples
- training noncompliances
- procedural nonconformances
- procurement noncompliances
- using standards or chemicals past their expiration date

- using noncompliant standards (or lack of documentation on standards)
- incomplete labeling of (standards, reagents or samples)
- problems with balances
- not maintaining proper calibration of instruments
- problems with water systems
- data calculation or reporting problems
- lack of proper control charting where applicable
- not meeting laboratory data specifications or contractual data quality objectives, and
- improper documentation of (standard, reagent or sample) make up.

The other common situation was to find that follow up and closure of identified conditions (especially internally identified conditions) were either not being done or were not being documented. Few laboratories had developed trending systems and a major weakness was that the effects of deficient conditions on past work were not being evaluated adequately.

INTERNAL CHAIN OF CUSTODY

The contracts audited against, required documented internal chain of custody. This meant that at any given time that the samples could be accounted for and could be traced to where they were. Personnel had to sign out the samples from storage areas, maintain custody requirements while they used the samples and signed unused portions back into storage. Several laboratories initially had difficulty in complying with this requirement. Once systems were developed the level of compliance dramatically increased.

PE AND ROUND ROBIN PROGRAMS

Most laboratories audited were participating in more than one PE and/or round robin program. Most laboratories fared satisfactorily to well in the programs. The major problem identified in this area was that many of the laboratories were not taking advantage of the information obtained from these studies. First, when passing scores were obtained, those areas in which the results were outside the control limits were not followed up on to identify whether a systems problem existed for that analyte. Second, samples that could have had incorrect results reported for a certain analyte as indicated by poor PE results were not checked to see if they were affected.

TEMPERATURE CONTROL

Refrigerator and freezer storage requirements for samples and standards were checked in the audits. Standard storage requirement differences for CERCLA and RCRA programs were not accounted for in many laboratories. The requirements for semi volatile organic compounds (semiVOAs) illustrates several points. The two cited programs require some of the standards to

be stored at different temperature ranges than for the other program. Most of the same standards for semiVOAs can be used for both programs.

The dilemma for the laboratory is to maintain two separate sets of standards in two different freezers or store the standards under the most stringent requirements and meet the intent of both programs. Here is where experience and knowledge are essential for the auditor. In the case of semiVOAs the critical factor is to prevent volatilization and escape of the analyte and no ill affects will be presented to the standards stored at the slightly lower temperature range of the more stringent program. The author's personal opinion and policy is to not present a finding if the laboratory takes this stance. It can be argued that this is not strict compliance and a slight possibility exists that the practice is quality affecting but the author stands by his opinion until directed otherwise.

The narrow storage range for inorganic samples is much more critical. If one stores at lower temperatures the possibility of freezing quickly increases. The freezing process can not be tolerated. Several laboratories were found to have informal temperature documentation programs during the first visit to them. Problem areas included the following:

- measurements done in air, not liquid, which caused frequent excursions from the acceptable temperature range,
- frequent excursions from acceptable ranges with no corrective action,
- no documentation as to which samples were associated with which refrigerators or freezers,
- incorrect postings on refrigerators and/or freezers as to temperature requirements,
- no procedure or policy as to how to handle temperature excursions,
- use of non-calibrated thermometers,
- use of calibrated thermometers passed their expiration date,
- not measuring and/or properly documenting measurements and not documenting temperatures of incoming samples.

Formal documentation and compliance improved after the first visit and with each subsequent visit. The most persistent problem remaining is the formal documentation of problems and addressing types of potential impacts to specific samples.

INTERNAL QA/QC PROGRAMS

The extent of the need for this program varies significantly with the needs of individual companies. Specific requirements were given to these laboratories in the regulations and with the contracts governing the work discussed here. Several laboratories did not meet the intent and requirements of this program until after the author's first audit. Some

then came into partial compliance and it was after the next audit that more progress was made.

Internal QA/QC is as much for the benefit of the laboratory as it is for the customer's benefit. Here is where a good idea of how the laboratory systems are functioning is obtained on a very frequent basis. Good programs are very cost effective and help avoid a lot of repeat work. Laboratories were encouraged to take full advantage of opportunities provided by internal QA/QC programs but were audited to the requirements set forth. Several root causes of types of deficiencies found were traced to not having an adequate internal QA/QC program.

INTERNAL LABORATORY AUDITS (SURVEILLANCES ETC.)

Internal audits of two types will be described. EPA considers audits as either system audits or performance audits. By system audit, it is meant to assess if all portions of a needed system or activity were developed and were auditable. Being auditable is defined here as being able to be traced to meeting requirements and in being adequately documented. Often the activities involve looking at documentation and handling much paperwork. Visual inspections of processes can also be included.

The term Performance Audit is commonly used in two different ways. First, this term is used to describe assessments of activities as they actually happen. The performance of processes or individuals is measured against procedural or contract requirements, in the real time mode. In this case, a system audit could also contain a performance portion. The second use, and the more common CERCLA or RCRA definition is to measure the performance outcomes against the requirements. For example is the required detection limit, accuracy, precision, holding times and completeness being obtained.

Either type of audit can range in scope from informal to formal, from minutes to several days or even weeks, from focused to a narrow scope to being very broad. The number of auditors can vary significantly also. The scope for external audits is even more variable. For example, external performance audits involving more than one laboratory may focus on shared Performance Evaluation (PE) and/or Round Robin samples, and on the results of split samples performed by all involved laboratories.

Few laboratories were meeting the internal audit requirements before this audit program was started. These requirements had been imposed by both the regulations and the contracts but were not fully understood by the laboratories and in most cases were being handled informally. The planning, scheduling, completion percentage, quality, quantity and scope of internal audit activity dramatically increased in most laboratories as audits continued.

LABORATORY MANAGEMENT ASSESSMENTS

These are activities that have met with varied requirements and success. The actual requirements are somewhat vague and as such a wide range of laboratory management assessment practices have been experienced.

The principal reasons for this process is to keep management in touch with what is actually happening in the laboratory and to provide an independent evaluation of the quality of work being done. Actually seeing and evaluating laboratory operations on a real time basis helps management to stop noncompliances and shortcut processes that may creep into laboratories. It is surprising how managers were sometimes not aware of current conditions in portions of their laboratories.

QUALITY CONTROL CHARTS

CERCLA type analyses do not specifically require control charts. Here the limits are preset and specific instructions are given as to what to do when the quality control limits are exceeded. Control charts can be used in CERCLA work for the purpose of trending data. For RCRA and most other work, control charts are necessary.

The three most common types of control charts are standard recovery charts that indicate the laboratory bias for that analyte, spike recovery control charts that demonstrate accuracy for a certain matrix for a specific analyte and duplicate or replicate control charts that demonstrate the precision for a certain analyte. Control charts need to be kept up at or near real time. Their use, besides defining working accuracy and precision limits, is for warning of marginal or unsatisfactory conditions needing immediate attention and which might lead to formal corrective action. They are also used for trending conditions. The most common problems encountered in this area were:

- not having control charts
- not having all three types of charts
- not keeping the charts on a real time or near real time basis
- not acting or documenting actions when limits were exceeded
- not tying noncompliances to specific samples, and
- not recognizing that seven consecutive data points on the same side of the mean constituted an out of control situation.

LABORATORY DATA SPECIFICATIONS VERSUS DATA QUALITY OBJECTIVES

Each laboratory needs to determine and provide to it's customers the laboratory data specifications. This helps the customer evaluate if the laboratory can meet the customer's needs. Accuracy, Precision, Detection Limits, Instrument Detection Limits, Quantitation limits (these are called by other names also), and other types of laboratory quality control parameters are these specifications.

Each customer needs to identify what it's data quality objectives (DQOs) are that apply to the laboratory analysis. Examples of these include:

- precision
- accuracy
- representativeness
- completeness and
- comparability (the PARCC parameters).

Specific method requirements, detection limits, instrument detection limits, quantitation limits and other types of laboratory quality control parameters are also specified.

The auditor needs to determine if the above specifications match. In the observations discussed in this paper, it was not possible to properly evaluate this information as it was not sufficiently available in most cases. It appears that some clean up projects are struggling to first develop adequate DQOs and then to properly pass those on to the laboratories. It also appears that the laboratories have in general not defined their data specification capability in enough detail to be fully auditable.

RADIOCHEMICAL PROCEDURES

The regulations and requirements for radiochemical and mixed waste samples are the most complex and incomplete of any involved. There are a few methods or procedures that have national recognition. It is this auditor's experience that compliance with these is less than with other procedures.

Several types of analysis have individual procedures that have been developed by various laboratories for their own use. These procedures often employ different separation and/or analysis techniques and are not easily comparable. In the contracts involved in these observations, multiple radiochemical laboratories were used.

A PE sample program is very difficult to develop for many of these analytes and the unavailability of this tool has severely handicapped evaluating the comparability of the results from these laboratories. Extensive work is needed in this area. A final observation regarding radiochemical laboratories is that in general they appear less focused on procedural compliance and on adapting to changes than do hazardous waste laboratories.

SUMMARY AND CONCLUSIONS

Requirements that laboratories must comply with are extremely complex and variable. These same requirements impose much difficulty to those who do audits (various types of assessments) of the laboratories. Clear direction as to how to interpret and impose these requirements is not always obtainable. There remains significant controversy even within

regulatory bodies as to how to apply some of these requirements. This situation adds stronger argument to the position that auditors need to be well informed both technically and with the quality assurance process.

Information obtained through performing audits of a variety of types of DOE System and Commercial Laboratories has been shared. No attempt has been made to identify these laboratories or to quantitate the problems involved. Examples of some types of problems encountered have been presented. It must also be recognized that this is a living system with constant change and audit programs must adapt to the changes as must the laboratories.

Repeat rounds of audits have been accomplished and compliance to requirements has been evaluated. It is concluded, that when requirements and failures to meet these requirements were documented in the audit process, the amount of time to come into compliance decreased. Increased frequency of audits from yearly to twice a year also sped up the compliance process. The amount of improvement has not been quantitated. If improvement in performance results can be tied to the audit process was not evaluated.

SAMPLING/FIELD

26 PRACTICAL SUGGESTIONS TO IMPROVE THE QUALITY OF FIELD WORK - SAMPLER'S PERSPECTIVE

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ABSTRACT

Before you attend another meeting on field sampling and quality assurance, consider the **sampler's** perspective on the work they perform.

Several conferences have been held recently to discuss the quality of environmental monitoring data. The discussions have expanded beyond an initial focus on laboratory analysis to include debates on the quality of field sample collection activities. Increasing emphasis is being put on assessing the errors associated with sample collection, which may be carried through the entire site evaluation process. In these discussions, samplers can provide a valuable perspective on improving the quality of field work. To date, their potential to contribute in this area has not been fully realized.

In this presentation, some of the root causes of problems in sample collection activities will be discussed from a sampler's point of view. Examples from actual field sampling projects will be used to illustrate some of these problems, which can occur in every stage of a project from planning to sample handling.

Common pitfalls to be avoided in the planning and scheduling stages will be highlighted, and workable solutions to these problems will be proposed. Other practical suggestions to improve the quality of field work will be presented in the form of "Simple Things You Can Do To Succeed in Sampling". Sampler training and certification will be discussed, and the benefits of cross-training of field and laboratory personnel will be emphasized. Lessons learned in the laboratory that can be applied to the field will be shared. The application of Total Quality Management principles to field work will also be discussed.

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EVALUATION OF THE HYDROPUNCH^{tm} TO ASSESS GROUNDWATER CONTAMINATION BY VOLATILE ORGANICS

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ABSTRACT

Hydrogeologic investigations have traditionally been performed with the use of monitor wells. Their disadvantages include the high cost to install, develop, sample and dispose of generated cuttings, development and purge water. Data is not available from a well until it has been installed, which can lead to numerous misplaced wells, providing useless data. This can lead to an investigation requiring months to complete, as the process is repeated, until wells are properly located to yield the required data.

The HydroPunch^{tm} II is a groundwater sampling tool developed for rapid and cost effective collection of groundwater samples from any depth in the saturated zone without the installation of a monitor well. The tool was evaluated to determine a cost effective decontamination procedure to prevent cross contamination between sample locations and if representative groundwater samples could be obtained when operating in the "hydrocarbon" sampling mode.

Decontamination procedures were tested on a HydroPunch^{tm} unit exposed to pure gasoline. After decontamination blank water was run through the tool and analyzed. The procedure which provided non-detects for the target analytes was: a soap and water wash (laboratory grade glassware detergent) followed by a steam wash and distilled/deionized water rinse.

Samples of groundwater were collected from the HydroPunch^{tm} II in the hydrocarbon sample mode and from stainless steel well points. The units were placed so the screen of each tool would sample the same cross sectional interval within a 5 foot radius of each other. Twenty two paired samples were collected and analyzed by EPA method 602 plus xylenes. Statistical results using a paired T-Test and the analysis of plots generated from logs of the sample concentrations indicate no significant differences between the tools and good correlation of data. This evaluation demonstrates the HydroPunch^{tm} II in the hydrocarbon mode will provide a representative sample of volatile organics in groundwater.

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AN INTEGRATED APPLICATION OF FIELD SCREENING TO ENVIRONMENTAL SITE INVESTIGATIONS: A CASE STUDY

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Abstract

A base in the Washington D.C. area was slated to undergo facility expansion. This expansion was to include construction of a commissary and parking lot, along with movement of an existing sports field and a playground to new areas. Immediately prior to the start of the construction, information became available which indicated that a landfill had existed in the general area slated for construction activities. The exact location and extent of the landfill were not known. Woodward-Clyde Federal Services (WCFS) was retained by the Baltimore District of the U. S. Army Corps of Engineers (COE) to perform an investigation of the area to determine the extent of the landfill and the health risk to construction workers and playground users. Due to the construction schedule, the project work had to be completed in an 8-week time period. Normally this type of project would require up to 6 months. In order to meet both time and budgetary constraints, an intensive field sampling effort was undertaken in conjunction with the use of field screening methods. Several field screening methodologies were employed to more fully characterize the site during the time between field sampling and lab analysis: 22 metals by portable X-Ray Fluorescence Spectrometry (XRF) and Polychlorinated Biphenyls (PCB) and Aromatic Hydrocarbons (AH) by immunoassay. The field screening was used to:

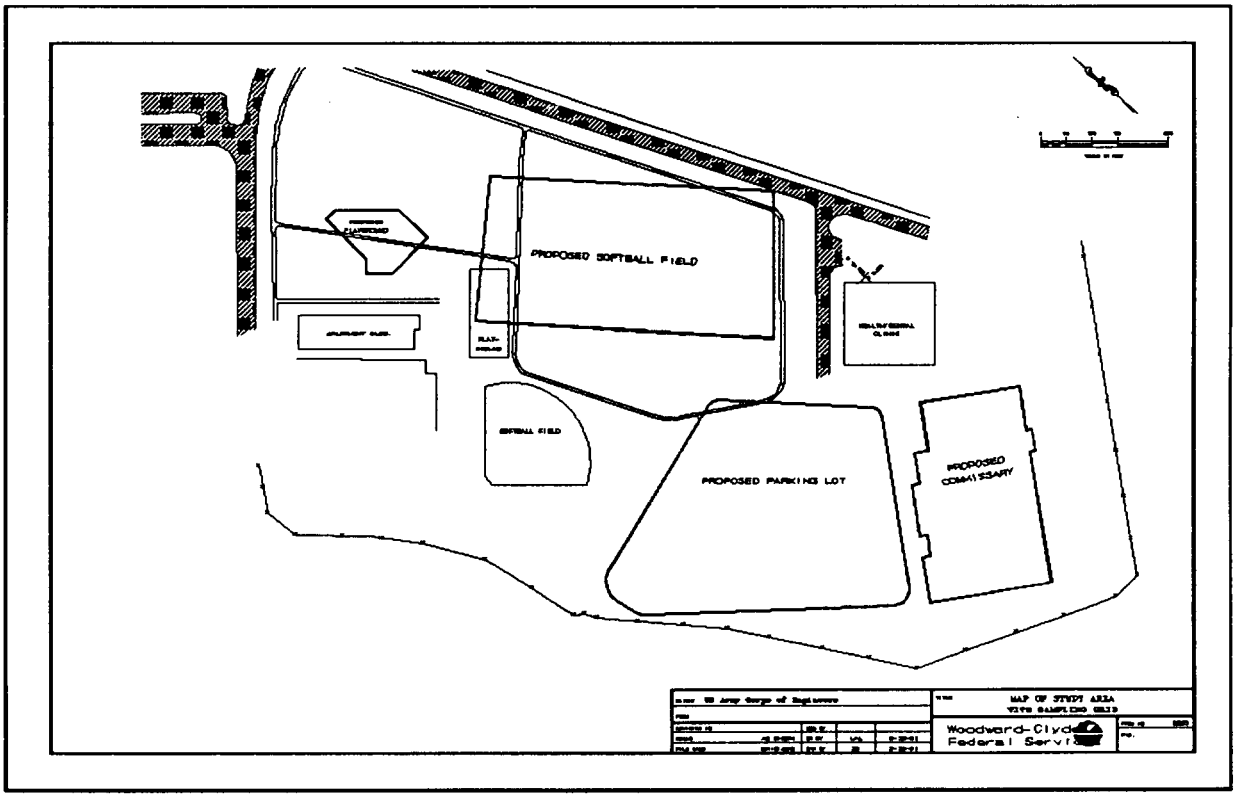
- direct field sampling efforts by delineating contaminated areas
- prioritize samples for laboratory analysis
- provide the laboratory with information on the expected range of contaminants

In total, approximately 130 samples were screened in the field and approximately 30 of those samples had results verified by lab analysis. The metals results for XRF and lab analysis generally corresponded to each other, provided samples were thoroughly homogenized. Although some false positives were observed by field screening for PCB and AH, no false negatives were observed. This presentation will discuss time and budgetary savings, QA/QC procedures and comparability of the field screening and lab results.

Introduction

Woodward-Clyde Federal Services (WCFS) was charged with the task of clearing a site for construction activities within 8 weeks while ensuring that sufficient samples had been taken to characterize the site and that those sample results were accurate. In addition to the historical information which indicated the presence of a landfill whose size and contents were unknown, there was the possibility that the landfill area contained burn pits where PCB transformer carcasses had been disposed. Some preliminary work indicated elevated levels of PCBs, miscellaneous other organics and metals in the areas where the present playground was located and where the athletic field was to be relocated (Figure 1).

Figure 1: Site Map Showing Proposed Construction



As a result of health and safety concerns for construction workers and future residents a site clearance was undertaken. Since the construction contract had already been awarded and the government would face penalties if construction was delayed the time frame available for the investigation was very short.

Lab analysis takes 3-4 weeks at normal turnaround times. Faster turnaround times are possible at premium rates but even the fastest analysis requires 24-48 hours before results can be reported. The approach that was developed for this project involved field screening and lab analysis with five day turnaround. Lab analysis was required to verify field screening results and to provide the quantitative information required for the health-based risk assessment samples. Field screening was performed on soil samples for PCB and aromatic hydrocarbons (the Petrorisc™ immunoassay which was chosen is designed to provide total petroleum hydrocarbon data but is very sensitive to bi and tri-cyclic polyaromatic hydrocarbons) using immunoassay technology, and 22 metals using a field portable X-Ray fluorescence (XRF) spectrometer. The field screening methods were used to prioritize samples for lab analysis, provide information to the lab on the approximate concentration range expected to minimize reanalysis and provide extent of contamination information for the areas being investigated.

Methods

Immunoassay technologies are well established within the medical lab industry where they have been used provide rapid, accurate test results for medical professionals. In recent years this technology has also started to emerge in the environmental analysis field. The two parameters analyzed by immunoassays for this project were PCB, using the Envirogard™ immunoassay by Millipore and aromatic hydrocarbons using Ensys' Petrorisc™ immunoassay kits. Soil samples were analyzed for 22 metals using the Spectrace 9000 field-portable XRF. The Spectrace 9000™ XRF uses a mercuric iodide (HgI_2) detector along with a fundamental parameters algorithm to qualitatively and quantitatively identify the metals.

A lab facility was set up on base for sample log-in and analysis. All samples were labeled, logged into a sample tracking system on and screened at this location. A portable computer was used for sample tracking as well as to store both the results and the spectra produced by the XRF. All immunoassay data, including balance calibration, extraction weight and the absorbencies of both the samples and standards were recorded in bound lab notebooks.

Immunoassays-General

As both immunoassay kits used methanol as their extraction solvent and immunoassay tests are quite specific for their target compound(s), one extraction was performed on each sample and the extract was refrigerated in a labeled screw-top vial. This ensured any re-analysis would be performed on the same aliquot of each environmental sample. The analysis reagents were added according to each manufacturer's instructions[1,2,3,4] and all samples were run immediately following calibration of the test kit. A spectrophotometer set to 450 nm was used to record the absorbencies of both the standards and samples.

Aromatic Hydrocarbons (AH)

For the Petrorisc™ immunoassays, sample absorbencies were determined relative to a low standard (0.7 ppm m-Xylene, which is equivalent to 100 ppm gasoline) which served as the threshold of detection. Two aliquots of the methanol extract were analyzed relative to this standard: the first represented the sample without any dilution and the second was the same extract at a ten-fold dilution. In this manner, approximate concentrations of petroleum constituents can be determined with relative ease. While the petroleum kits were calibrated using m-Xylene, they were sensitive to a variety of compounds found in petroleum products including bi- and tri-cyclic aromatics.[1,2] WCFS utilized the Petrorisc™ kits' sensitivity to aromatic hydrocarbons to indicate burn areas where these aromatic hydrocarbons remained as products of incomplete combustion. Because the Petrorisc™ kits are sensitive to a variety of compounds, the immunoassay results correlated well with the hot spots as defined by lab analysis. Data on the correlation between the two methods is shown in Table 1.

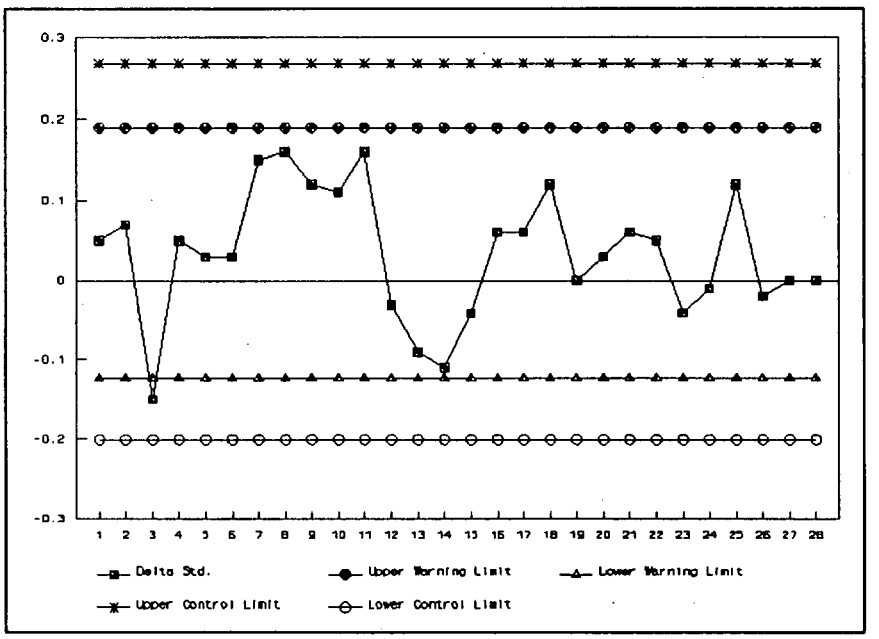
Table 1: Comparison of Lab and Field Values for Petrorisc[tm]

Sample Number	Petrorisc[tm] Value	Sum of PAH Values*
Sample 1	ND	ND
Sample 2	ND	ND
Sample 3	ND	ND
Sample 4	ND	ND
Sample 5	ND	ND
Sample 6	Detect	ND**
Sample 7	Detect	>1 ppm
Sample 8	ND	ND
Sample 9	Detect	ND
Sample 10	Detect	ND
Sample 11	Detect	ND
Sample 12	ND	ND
Sample 13	ND	ND
Sample 14	ND	ND
Sample 15	ND	ND
Sample 16	ND	ND
Sample 17	ND	ND
Sample 18	Detect	>1 ppm
Sample 19	ND	ND
Sample 20	ND	ND
Sample 21	ND	ND
Sample 22	ND	ND
Sample 23	ND	ND
Sample 24	Detect	>1 ppm
Sample 25	ND	ND
Sample 26	ND	ND
Sample 27	ND	ND
Sample 28	ND	ND
Sample 29	ND	ND

*Sum PAH=Sum of all detects for compounds listed in SW-846 Method 8100.
**Dilution at lab prevented proper quantitation.

The protocol for performing analysis dictated that the difference between duplicate standards (Delta Std) could not exceed 0.2 absorbance units (a.u.) or the calibration would be considered invalid and the samples would be re-analyzed. Although the precision data for the petroleum kits was acceptable, the use of a repeat pipettor rather than dropper bottles would have improved the precision. (All figures showing precision data are scaled to equal size, so a visual comparison may be made.) Ensys will supply the reagents either in dropper bottles or in bulk (for use with a pipettor), but for this project the dropper bottles were used. A Shewart plot of Delta Std for aromatic hydrocarbon analysis is shown in Figure 2.

Figure 2: Precision Data for Petrorisc[tm] Immunoassay



Polychlorinated Biphenyls (PCB)

For the PCB kits[3,4] (Envirogard[tm]), the concentration of the two calibration standards (2 and 10 ppm Aroclor 1248) were used and a linear dose-response was assumed between those two points in order to calculate an approximate Aroclor 1248 concentration. As Aroclor 1260 was the PCB found at the site, Aroclor 1248 concentrations were converted to Aroclor 1260 concentrations using relative response data for the two Aroclors provided by Millipore[3,4]. The PCB kits were used to delineate the volume of the burn pits being investigated and the samples taken for lab analysis in those areas was directed by the field screening results. Correlation data is presented in Table 2.

Table 2: Comparison of Lab and Field Values for PCB

Sample Number	Immunoassay Value	PCBs by Method 8080
Sample 1	ND	ND
Sample 2	ND	ND
Sample 3	ND	ND
Sample 4	ND	ND
Sample 5	Detect	ND
Sample 6	ND	ND
Sample 7	ND	ND
Sample 8	ND	ND
Sample 9	ND	ND
Sample 10	Detect	ND
Sample 11	ND	ND
Sample 12	ND	ND
Sample 13	ND	ND
Sample 14	ND	ND
Sample 15	Detect	ND*
Sample 16	Detect	ND
Sample 17	ND	ND
Sample 18	Detect	ND
Sample 19	ND	ND
Sample 20	ND	ND
Sample 21	Detect	ND
Sample 22	ND	ND
Sample 23	ND	ND
Sample 24	ND	ND
Sample 25	ND	ND
Sample 26	ND	ND
Sample 27	ND	ND
Sample 28	ND	ND
Sample 29	ND	ND
Sample 30	ND	ND
Sample 31	ND	ND
Sample 32	ND	ND

Sample Number	Immunoassay Value	PCBs by Method 8080
Sample 33	ND	ND
Sample 34	ND	ND
Sample 35	ND	ND
Sample 36	ND	ND
Sample 37	Detect	ND
Sample 38	ND	ND

*Dilution at lab prevented proper quantitation

Reagents were added using an Eppendorf repeat pipettor, which allowed for rapid analysis with good accuracy and precision. Typically a total of twenty tubes were analyzed per run: assuming analysis performed in duplicate, three standards and seven samples could be analyzed in one run. A Shewart plot (Delta Std) for both the low and high standards is provided in Figures 3 and 4.

Figure 3: Precision Data for PCB Low Std.

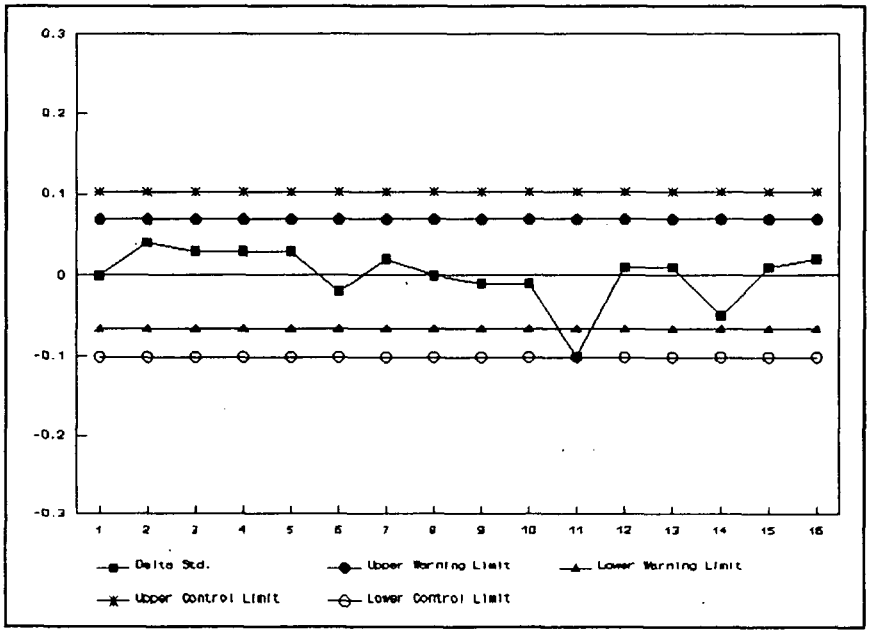
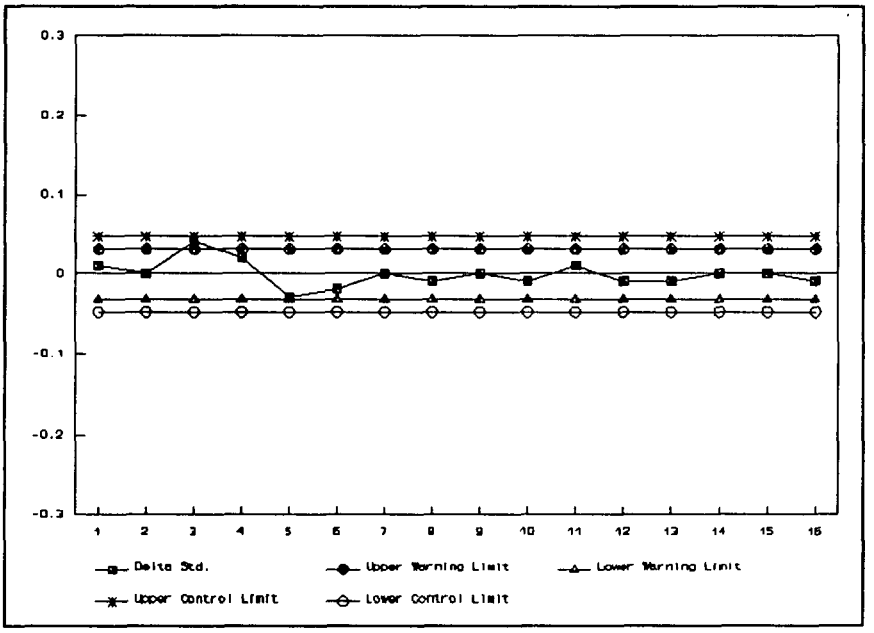


Figure 4: Precision Data for PCB High Std.



Field-Portable XRF

All samples were first air dried and sieved through a 10-mesh sieve and sample descriptions were recorded for all samples. If a significant amount of material would not pass through the sieve, the material remaining in the sieve was retained and labeled as the exclusion products of that environmental sample. The dried samples were then placed in 32mm sample cups and covered with Mylar film.[5,6] Each sample cup was labeled with the field sample number and retained for re-analysis, if necessary. At the end of each day, both the results and spectra were downloaded to a laptop computer for storage and data processing.

A mid-range standard reference material (SRM) and a quartz blank were run daily prior to any samples, after every 10 samples and at the end of the analytical run (10% frequency). This standard was an environmental sample which had been certified using traditional wet prep techniques followed by GFAA and ICP analysis. Both the SRM and blank were used to confirm instrument stability during the project. The standard was less homogeneous than was initially assumed at the start of the project: approximately a week after the XRF screening had begun, particles where discovered in the sample cup which would not have passed through a 10-mesh sieve. As there was a week of data on the standard it was not re-prepped. Particle-size effects from these large particles were believed to introduce some variability in the standard as illustrated in the Shewart plots for the standard. The samples were believed to be more homogeneous because all samples were dried and sieved prior to analysis. A plot of the Pb results (Pb was one of the elements which had poor precision relative to most of the analytes) for the standard over the course of the project is shown in Figure 5 and a table of the accuracy and precision data is shown in Table 3.

Figure 5: Precision Data for XRF Std (Pb)

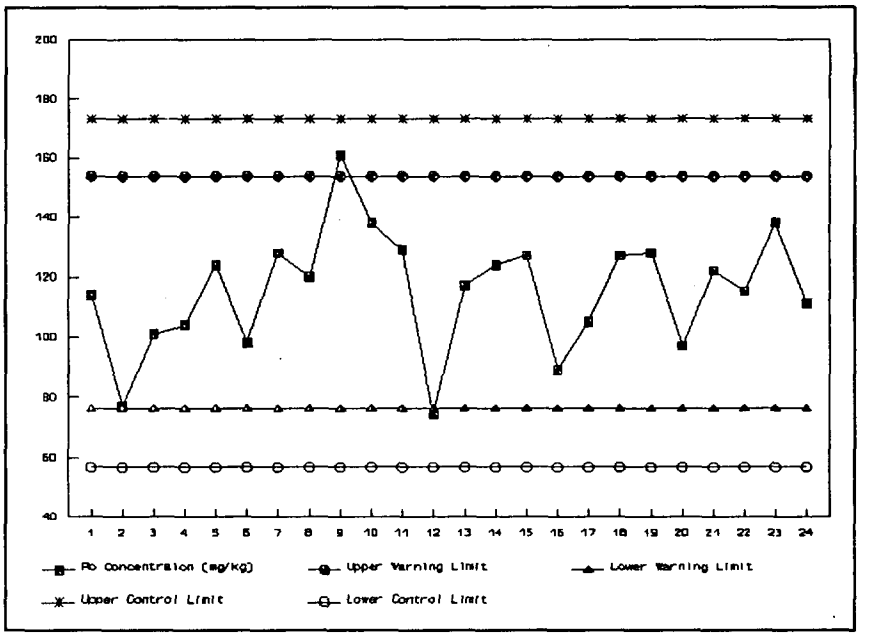


Table 3: Accuracy and Precision Data for XRF Standard Reference Material

	Cr	Ni	Cu	Pb	Cd
Average (mg/kg)	184170	16014	2787	115	387
True Value[1]	160287	13105	2946	141	292
Percent Recovery	114.9%	122.2%	94.6%	81.6%	132.6%
Std. Dev.	2263	423	144	19	65
Relative Std. Dev.	1.2%	2.6%	5.2%	16.9%	16.9%

[1]All true values obtained by acid digestion followed by GFAA/ICP analysis

Conclusion

Method-Specific: Immunoassay

The staff of two chemists performing analysis in the field lab was able to screen approximately 20 samples per day for metals, PCBs and aromatic hydrocarbons. The use of a repeat pipettor is recommended both to speed immunoassay analysis and to achieve better precision and accuracy. The correlation between lab and field data was good, but the difference in detection limits and sample heterogeneity sometimes make it difficult to directly compare immunoassay and lab data. However, the regions indicated as contaminated by field screening correlated very well with the areas indicated as contaminated by lab analysis, historical data, and PID/OVA results of samples taken in the field.

Method-Specific: XRF

The use of an independent standard which was certified by traditional metals techniques (GFAA/ICP) gave the data produced by the XRF an additional level of confidence. The instrument showed good stability over the course of the project and 16.9% was the worst relative standard deviation for any of the certified analytes (Cr, Ni, Cu, Pb, and Cd). Had the standard reference material been completely homogeneous, the standard deviation would probably have been considerably lower: Shewart plots showed only a few values which were close to the control limit (Average+/-[3*Std. Dev.]). If these values were considered outliers and removed, the standard deviation decreased markedly.XRF analysis of the standard reference material correlated very well with its certified values: the average percent recovery (defined as [XRF value/True Value]*100) was 109.2% with a high of 132.6% for Cd and a low of 81.6% for Pb.

QA/QC Issues

Field screening can provide either Level I or Level II data[9]: for this project the field screening data was regarded as Level I data and the laboratory analysis was used to make all final decisions regarding site contamination. Specific guidelines for producing Level II data may vary from site to site, and the sampling and analysis program must address the problems of sample heterogeneity, matrix effects, interfering compounds, and sample contamination as a result of improper handling or preparation[7].

Although field screening can present additional challenges to the field team, there are many instances where the additional data produced from the lower-cost field screening tests can significantly reduce the sampling error in site investigations. Analytical error (bias and variability introduced in the lab) typically accounts for only 15% of the total error introduced in the site investigation process. The remaining 85% of the error in site investigations results from insufficient samples or samples which do not accurately represent the contamination at the site[8]. Field screening allows for rapid analysis following sample collection, which reduces problems in sample handling, preservation and transport, and gives the field team the flexibility to employ an iterative sampling strategy to fully characterize the contamination.

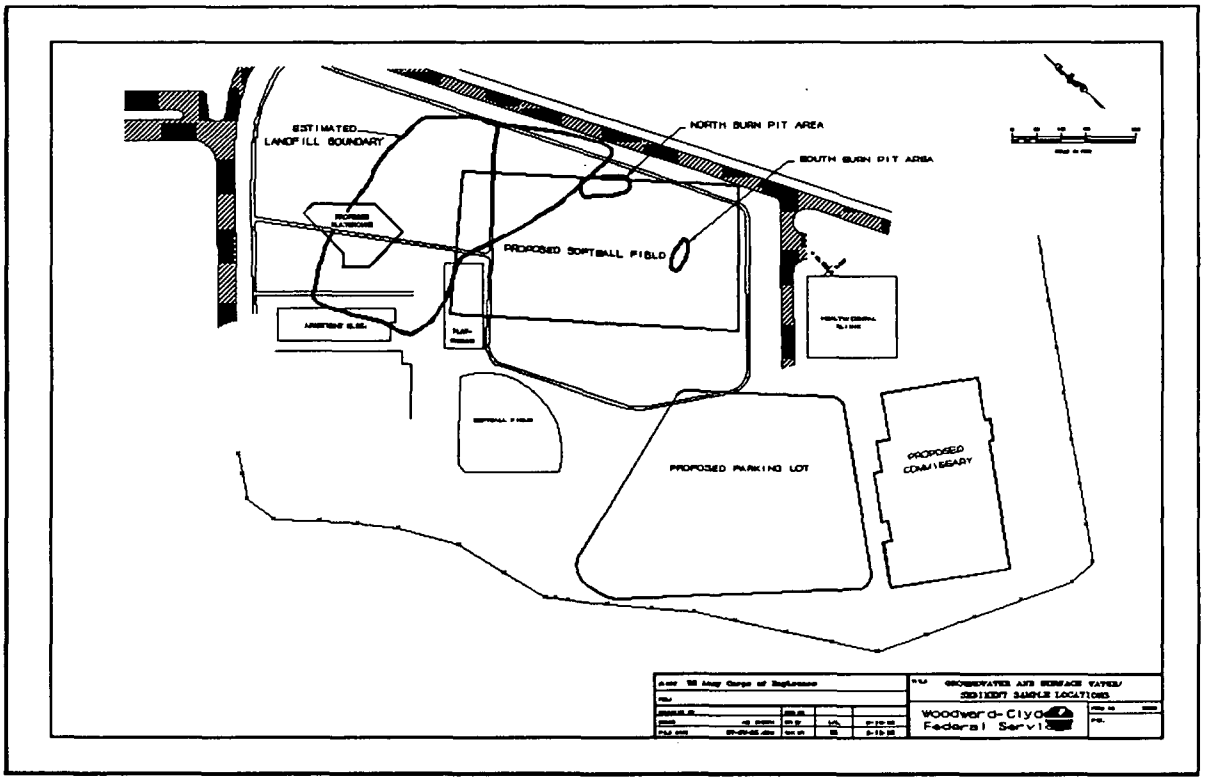
Effect on Sampling & Lab Analysis

Through the integrated use of field screening WCFS completed the site clearance on-time, better delineated the extent of contamination and helped to direct the activities of the field crew. In addition to the data provided by the lab, historical information such as aerial photos were used to identify the area occupied by the former landfill (Figure 6). While XRF has been used successfully in site investigations in the past, new advances in detector technology will provide field teams with an instrument which is both portable and sensitive. At the time of this project (April-May 1992), none of the immunoassay techniques had been recognized as methods by EPA. Subsequently EPA has granted SW-846 third update numbers of 4010 (pentachlorophenol), 4020 (PCB), and 4030 (Total Petroleum Hydrocarbons) for immunoassay screening techniques.

In keeping with the DQO development process defined by EPA[9], the project should be planned with field screening in mind from the outset, and a chemist familiar with the technology to be employed should be involved during the planning stage. The overall effectiveness of field screening will depend on project-specific needs. It is recommended that the actual screening analysis be carried out by, or under the supervision of, a qualified chemist to minimize resampling and reanalysis and to ensure that results are not used inappropriately. Both immunoassay and XRF are mature screening technologies, which, when used properly can be very cost-effective tools in the site investigation process.

Cost savings were realized in two ways on this project by utilizing field screening; 1) a reduced number of samples were analyzed by the laboratory since the field screening did not result in very many false negatives, and 2) contamination information was transferred to the project manager in a much faster manner than for a normal project where one has to wait 2 - 4 weeks for a lab result. This meant that the project could proceed with decisions in a faster manner.

Figure 6: Site Contamination as Delineated by Field Screening and Lab Results



References

[1]PETRO RISc[tm] User's Guide, Ensys Inc, 1992.

[2]"Soil Screening for Petroleum Hydrocarbons by Immunoassay," Draft Method 4030, USEPA SW-846 Third Update, July 1992.

[3]Envirogard Tests Kits User's Guide, Millipore Corporation, 1992.

[4]"Soil Screening for Polychlorinated Biphenyls by Immunoassay," Draft Method 4020, USEPA SW-846 Third Update, July 1992.

[5]Spectrace 9000 User's Guide, TN Technologies

[6]Donald E. Leyden, Fundamentals of X-Ray Spectrometry as Applied to Energy Dispersive Techniques; Tracor Xray, 1984.

[7]Kevin J. Nesbitt, "Application and QA/QC Guidance USEPA SW-846 Immunoassay-Based Field Methods 4010, 4020 & 4030;" Ensys Inc, 1992.

[8]Francis Pittard, Principles of Environmental Sampling: A Short Course Presented Prior to the 8th Annual Waste Testing & Quality Assurance Symposium, July 11-12, 1992.

[9]USEPA, Data Quality Objectives for Remedial Response Activities, EPA/540/G-87/003, March 1987.

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DIVERGENCE OF FIELD AND LAB RESULTS IN THE PONCA CITY INVESTIGATION

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ABSTRACT

This case study focuses on a Benzene-Toluene-Xylene (BTX) pollution of soils and water in a small hydrogeologically secluded pocket of Ponca City, Oklahoma. Despite complaint by the residents, State and Federal officials could not find significant levels of contamination at the site and recommended no action at this site. At the request of the State treasurer, an independent hydrogeological investigation was conducted by the author identifying high levels of BTX in the perched water table in an isolated pocket.

During an independent investigation, conducted by the author, very useful help was rendered by the community in data collection. Samples from the storm water runoff at the site produced flame for a very short duration when lighted. Other field tests, such as, oil emulsion/layering of the samples proved that the contamination was of significant level. Laboratory results, however, did not show very high levels of contamination. The hydrogeological information from the site uncovered the mystery behind this inordinately high levels of BTX in a pocket of the perched water table.

The feasibility of a commercial hydrocarbon recovery from the spillage has been looked into as a cleanup option. However, CONOCO has rehabilitated some of the residents from the site and started a cleanup action at this site in 1990 with full community cooperation. The divergence of the field and laboratory results during initial investigation at this site caused major problems and dissentment between the residents and the State. The results from this study call for emphasizing the need to rely upon field observations to locate and identify contamination and hazards associated with it.

INTRODUCTION

Ponca City is located in the north central part of Oklahoma. The CONOCO refinery borders southwest part of Ponca City. The site location is shown on Figure 1. The area of investigation for this assessment encompassed the boundaries of the CONOCO refinery in Ponca City and the Circle Drive area of south Ponca City adjacent to the eastern boundary of the refinery. The study area is bounded by South Avenue on the north, by Waverly Street on the west, by a county road on the south, and by State Highway 77 (14th Street) on the east. The horizontal extent of the study area is shown on Figure 2. Refinery area designations and the watershed boundary of the study area are also shown in this Figure. The Circle Drive portion of the study area extends from the eastern Refinery boundary formed by South Third Street, South Fourth Street, and Seneca Drive

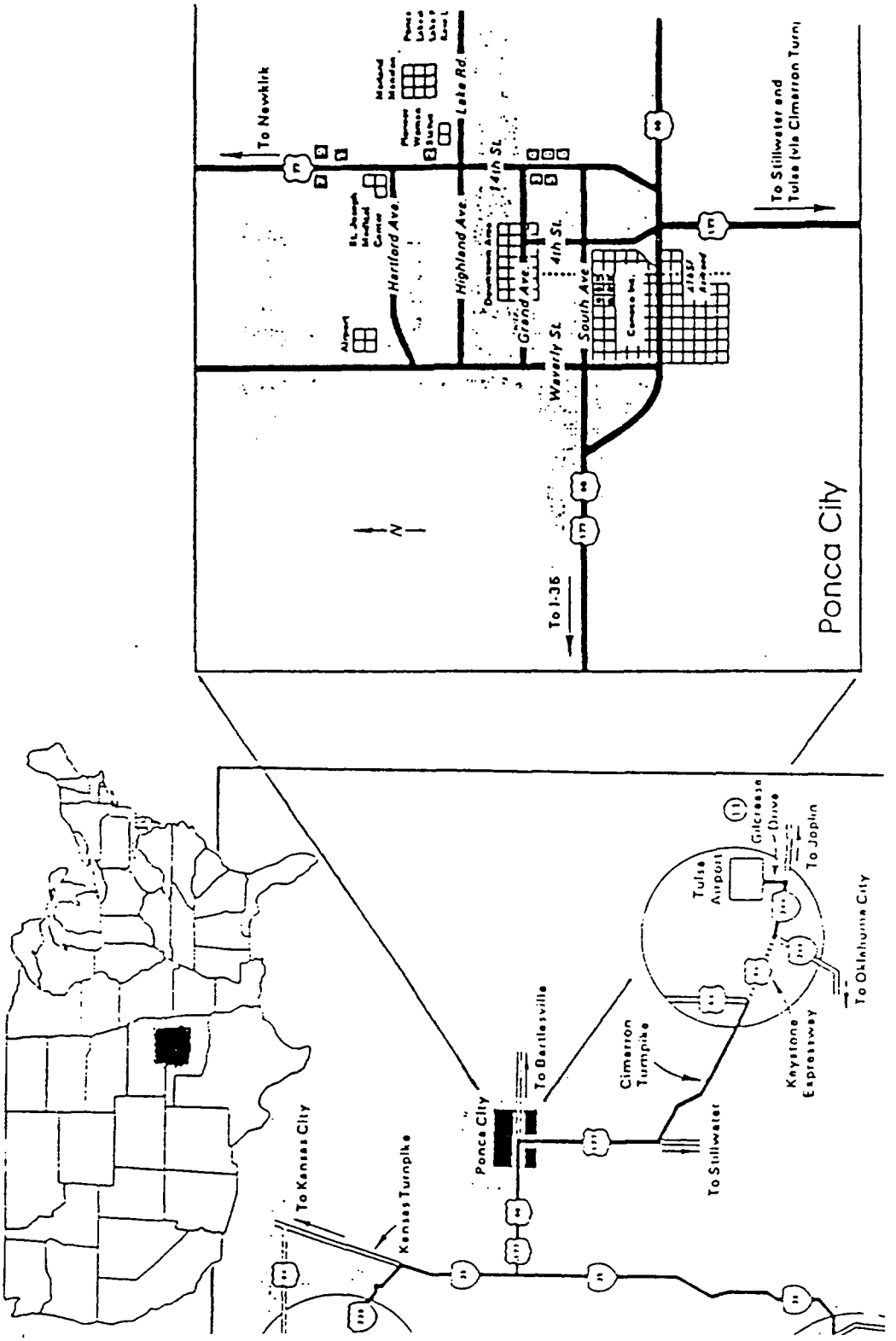

Figure 1 The Study Area in Ponca City, Oklahoma

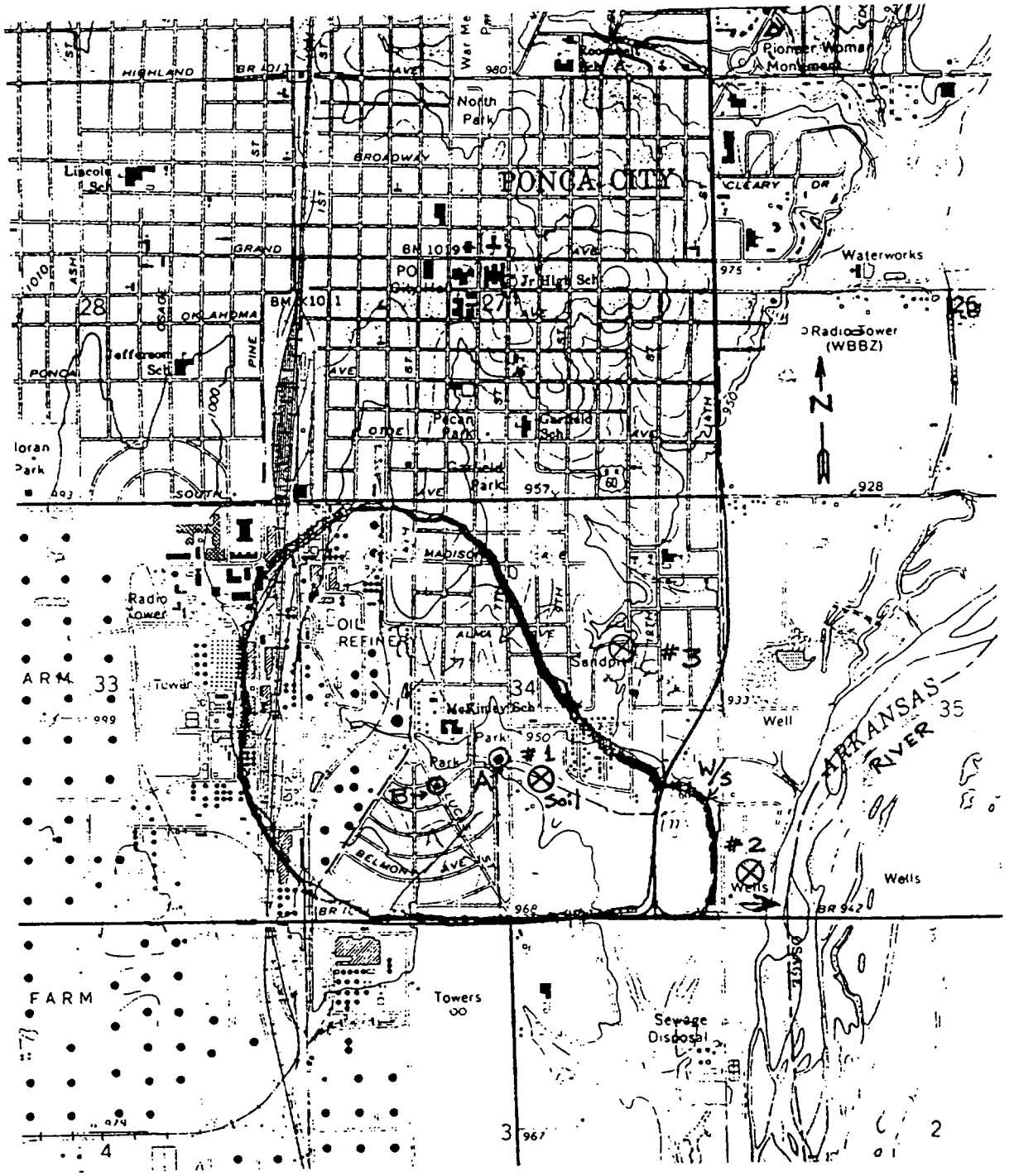

Figure 2 The Watershed Boundary and Sampling Locations in the Study Area

eastward to the 14th Street.

The vertical extent of the study area extends to the base of the uppermost aquifer underlying the study area. This alluvial aquifer ranges in depth from approximately 30 feet to 60 feet and is highly variable across the area thinning eastward towards the Arkansas River.

Ponca city refinery was developed in early 1900's. After sixty years there were reports of contamination of ground water. Hydrocarbon in ground water was observed in the 1950's and 1960's in the Circle Drive residential area of Ponca City adjacent to the east boundary of the Refinery. In 1968 the Oklahoma Corporation Commission received reports from two houses who had water with high hydrocarbon odor in their basements. Significant hydrocarbon accumulations have not occurred since the late-1960's when CONOCO, Cities Service, and Ponca City jointly installed and operated a hydrocarbon recovery well network across the East and South Refinery areas and the Circle Drive area of Ponca City. CONOCO has taken some measures to prevent and contain any potential releases which might migrate off-site.

Ground waters containing dilute concentrations of volatile organic petroleum hydrocarbons were detected seeping into Hoover Ditch from adjacent stream banks in late-1986 and early-1987. This seepage was a direct result of heavy rainfalls in excess of 20 inches which occurred in October and November 1986. The heavy rainfalls and accompanying recharge caused ground water elevations to rise to surface discharge points in the Circle Drive area of Ponca City. Due to serious public outcry, Mr. Ellis Edwards, state treasurer at that time, asked the author to conduct an independent hydrogeological investigation of the ponca city pollution problem.

The objectives of the independent hydrogeological investigation, conducted in August, 1988, were to:

(1) Define the sources and extent of hydrocarbon contamination in the area; and

(2) Develop recommendations for remedial actions for controlling and remediating the hydrocarbon contamination problem, taking all viable alternatives into consideration.

The scope of the investigation included:

- Study of the geological setting of the study area.
- Physical and chemical testing of water and water bearing formations/soils.

- Recommendation of possible steps to reduce severity of the problem.

- Recommendation of recovery of hydrocarbons from the contaminated water.

Nature and Extent of the Problem:

The initial assessment of the ground water and hydrocarbon conditions underlying the CONOCO's Ponca City Refinery and Circle Drive area indicates that there are two general types of hydrocarbon accumulations in the subsurface [1]:

(1) Free product - petroleum hydrocarbon mounds; and

(2) Low concentration, soil-absorbed hydrocarbon residuals from historical leaks and spills.

The initial study [1] determined that there were possibly four potential free product - hydrocarbon mounds which may exist under the CONOCO Refinery. Hydrocarbons in these areas are refined products, such as gasoline, kerosine, or heating oils, and can be chemically identified as such. Hydrocarbons observed in ground water seepage in the Circle Drive area are dissolved residuals and cannot be chemically characterized as a unique petroleum product. This hydrocarbon appears to be significantly older, as is indicated by the low concentrations of benzene, toluene, and xylene.

A major limitation of the study by Downs [1] was the lack of adequate ground water observation points, as well as concerns for the construction and completion history of old hydrocarbon monitoring wells from the late-1950's and 1960's. The 1987 field program for filling the information gaps identified in the initial study was implemented in the summer and fall of 1987. During this program, fifty-six (56) new cone penetrometer soil borings were constructed to develop detailed information on geological maps for the site. In addition, twenty-nine (29) new ground water/hydrocarbon monitoring wells were installed to develop new data on geology, ground water elevations, and potential hydrocarbon accumulations in the study area.

The hydrogeologic study [2] was focused on the quality and quantity of water in the surface and groundwater systems in the study area. The estimates were based upon the available information. A description of the baseline hydrologic conditions and a prediction of the effects on these baseline conditions in the study and adjacent area due to the pollution problem were amalgamated to form an integral part of the study.

The conclusion from the study [2] are based upon the available database and field measurements. Inadequate information on groundwater quality and quantity in the

adjacent area is a limiting factor in arriving at unequivocal conclusions concerning the groundwater of the adjacent area of the study.

The divergence of field observations and the laboratory results for the study area caused major problem in the hazard assessment for the site.

SUMMARY

The principal purpose of the study undertaken by the author was to assess the hydrogeological impact of an underground spillage problem on a tract of land located in Section 34-26N-2E of Indian Meridian in Kay County, Oklahoma. This pollution problem has surfaced near the Circle Drive area of Ponca City, Oklahoma.

The scope of the study also included investigation of the existing climatic and hydrogeological conditions prevailing in and around the study area.

Climate:

A humid climate prevails in the study area and its vicinity. Annual precipitation on the general area based on a 10-year average is found to be 32.34 inches. Seasonal precipitation is found to vary from 17% to 31% of 10-year average annual rainfall. Spring is the wettest season when 31% of the precipitation occurs from April through June. During the Fall season from October through December, minimum precipitation is observed to occur.

The total pan evaporation based on a 10-year average data is determined to be 56.2 inches. Some of the local meteorological parameters having effect on surface runoff, air quality, particulate transport, and intensity of photochemical smog were studied for a 10-year period.

Wind velocity varies considerably and can cause adverse effect due to increase local concentration of dust and other particulates. Prevailing wind direction is from south to north. The 10-year annual average wind velocity for the study area is 10.4 miles per hour per month with a standard deviation of 1.12 and a variance of 1.25 during the 12 month period. There are periods of prolonged wind movements up to 15-20 miles per hour.

The 10-year mean of annual temperature is found to be 60 degrees F. The minimum mean monthly temperature occurred in January, and the maximum mean monthly temperature was reached in the month of July. Drastic variations within a certain month are not uncommon.

The total pan evaporation is highest during June, July, and August, ranging from

8.23 inches to 9.35 inches per day. Mean annual evaporation is 56.3 inches.

Geology:

Geology of the Study Area [2]:

The pivotal area of study is section 34-T26N-R2E within the south and eastern city limits of Ponca City, Oklahoma. The area is between the Conoco Oil Refinery Plant on the west and the Arkansas River on the east. The general study area consist of nine sections being sections 2,3 and 4 T25N, R2E and sections 26, 27, 28, 33, 34, and 35 T26N, R2E in Kay County, Oklahoma. The area is covered on the Ponca City Quadrangle Oklahoma, 7.5 minute series, U.S. 6.5 Topographic map.

Topography:

The surface elevation varies from the highest point of 1020 feet in middle of section 27 to around 900 feet in the stream bed of the eastward flowing Arkansas River found in SW/4 of section 2, T25N, R2E. This is a north to south differences of 120 feet. Elevation differences from west to east of approximately 110 feet. In the area the surface slopes south and east and all surface water runoff is drained into the Arkansas River.

The study area sits atop of a portion of a northeast-southwest trending anticline. This anticline is expressed in the surface topography where the surface rocks dip slightly either eastward or to the west depending on the location of outcroppings. The anticlinal axis bisects section 34 slightly east of its northeast corner to the east of the southwest corner of section 34, T26N,R2E. The outcropping of strata from a regional aspect is characterized by broad expanses of strata of benches or alternating parallel escapements with abrupt slopes facing eastward. Older strata outcrops toward the east. The regional dip is to the west less than 50 feet per mile.

Stratigraphy and Lithology:

The surface rocks are sedimentary. With the exception of the terrace sands, the surface and the upper subsurface formations are of lower permian age. They embrace a approximately 300 feet of sediments and consists of four limestone formations alternating with same number of shale bud. Locally thin sandstones are present in the shale formations. The Permian and subsurface Pennsylvanian beds have been tilted gently westward, and subsequent erosion has beveled the section, exposing progressively older beds to the east. Resting unconformably on the truncated edges of the Permian sediments are local deposits of unconsolidated Quaternary alluvium and terrace materials that have been deposited by the Arkansas River and its tributaries as it slowly worked its way westward down the dip slopes of the limestone formations. The key beds of the study

area are listed in a descending order.

QUATERNARY- Alluvium and terrace deposits.
PERMIAN- System
LEONARD SERIES: Summer Group, Wellington shale
WOLFCAMP SERIES: Chase group of formations

Alluvium and Terrace Deposits:

Along both sides of the Arkansas River a considerable thickness of unconsolidated sands, slit, clay, and gravel occur overlaying the several Permian formations. Many of the alluvial and terrace deposits contain sand and gravel layers that are highly porous and permeable, and these deposits typically contain groundwater resources. Recharge areas for groundwater resources in alluvium and terrace deposits themselves become almost all ground water contained in these deposits as a result of downward percolation of water from the land surface.

Remedial Investigation:

As noted earlier, ground water seepage and the minor concentrations of organic and inorganic constituents that have been adsorbed and transported by rising ground water levels have discharged into various areas of Circle Drive. This includes natural ground water discharge into Hoover Ditch and surrounding ditches and natural ground water discharge into basements and foundation areas which intersect the rising ground water table. The manifestation of natural ground water seepage in the Circle Drive area has caused citizens to become concerned about both the occurrence of ground water seepage and what this ground water might be transporting. The hydrogeologic investigation conducted by the author involved soil and water sampling from the study area. Sampling locations are shown on Figure 2. Water samples were collected from locations A and B and soil borings were conducted at location #1, #2, and #3.

Testing of Soil & Water:

Chemical analyses were carried out on soil and water samples from the study area.

A columnar section of the alluvial formation from the study area is shown in Figure 3.

ZONE #	DEPTH	LITHOLOGIC DESCRIPTION
A.	6-8"	Topsoil
B.	9-45"	Grey, Sandy, Silty Loam (Highly Porous)
C.	46-80"	Reddish Brown Clay (Very tight)

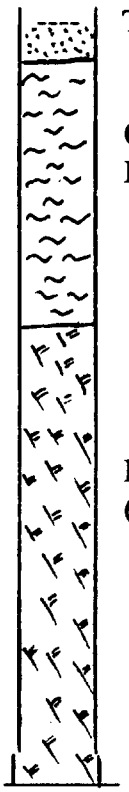

Figure 3 Columnar Section of the Alluvial Formation from the Study Area

Experiments were run to calculate porosity and permeability. A highly porous zone (#B) was present on top of a tight clay Zone (#C). Table 1 Shows the experimental results.

TABLE 1 EXPERIMENTAL RESULTS OF SOIL SAMPLES

ZONE #	Porosity (%)	Permeability (mD)	Dispersion Coefficient (sq. cm/sec.)	Sample#/Remarks
B	45	2000	0.037	# (1-2)/(2-2)
C	52	0.022	0.00	# (3-2B)

The grey alluvium soil containing 19% of moisture showed a porosity of 45% and a permeability of 2000 millidarcy. This zone was followed at the bottom by a tight clay having a permeability of 0.022 millidarcy. The Zone C thus served as a confining layer for the fluids to move through Zone B of in the study area.

The dispersion coefficient of the porous zone, as estimated roughly [3] , was found to be 0.037 sq. cm/sec. and the dispersion coefficient of the underlying clay zone was found to be 0.0 sq. cm./sec.

The result of the hydrogeologic investigation of the study area clearly identified a zone of high permeability sand channel at about 3-10 ft. from the ground which carried all the recharged water from the watershed which was contaminated with hydrocarbon. The very tight clay underneath the sand channel served as a confining layer.

Field Observations:

During an initial field visit in July 1988 the basements of two houses in the study area were visited. Very strong hydrocarbon odor was present in both the basements and oily liquids were visible. An oily surface discharge, oozing out of the ground, near the McInley School was also noticed. Hydrocarbon odor was also present at this location. The worst situation was observed where a 24" pipe was discharging high volume of water, with very strong odor of hydrocarbon, from underneath a road into the storm drainage system. The source of this water is from a subsurface system from the south side of the site. The discharge at this point could be visibly identified to carry hydrocarbon vapors.

A 1/2 gallon jar was filled up with this water and was taken to a dark room with the lid tightly closed. An open flame was introduced at the top of the jar upon immediate opening of the lid. Spontaneous blue flame was observed for a very short time at the mouth of the jar. This field test confirmed the presence of volatile hydrocarbon in the perched water table of the study area.

Lab Results:

Samples from the same discharge point (A) was analyzed in the lab which showed a flash point of 220° F and 100 ppm Benzene, 200 ppm Xylene, and 300 ppm of heavy hydrocarbons.

Samples from the basement of the house (B) showed 1.49 ppm toluene, and $<.0002$ ppm both benzene, and xylene. Faint smell of hydrocarbon was noted by the lab. These lab results were very similar to the earlier laboratory results as furnished in the following paragraphs.

An earlier report on Ponca City water analysis which was done on January 20, 1988 showed that the basement water had total hydrocarbon levels which ranged from 121 to 4,725 part per billion. The concurrent benzene levels in basement water ranged from 32 to 2,000 parts per billion. This water was not used for drinking or bathing. The results showed that there was volatilization potential for the various hydrocarbons contained in the basement water. The air samples taken at the time of water sampling were below 0.5 ppm for benzene using the dragger tube calorimetric technique.

The analysis by the Oklahoma State Department of Health Environmental Laboratory of basement water samples taken from 6 homes identified by the citizens as the "worst possible cases" in the Circle Drive Area of Ponca City indicated total hydrocarbon levels from 121 to 4,725 parts per billion. Of those total hydrocarbons, the concurrent benzene levels in basement waters ranged from 32 to 2,000 parts per billion.

These samples in and of themselves only address the potential for human exposure through direct contact with the basement water. This water was not used for drinking or bathing. These results do show that there was volatilization potential for the various hydrocarbons contained in the basement water. Entry surveillance air samples taken at the time of water sampling were below 0.5 ppm for benzene using the Dragger tube calorimetric technique.

The analysis by the Oklahoma State Department of Health Environmental Laboratory of drinking water samples taken at 8 sites in the Circle Drive neighborhood and adjacent areas indicated 1 sample with a level of 4 parts per billion of total hydrocarbon. The remainder of the drinking water samples were below the total hydrocarbon detection limit of less than 2 ppb. Additionally, none of the specific

hydrocarbons including benzene, xylene, or toluene were found in drinking water samples at the 1 ppb detection limit for specific hydrocarbons.

The drastic difference between the field observation and the laboratory results in this study could not be accounted towards any noticeable sampling or other procedural errors. High volatilization of the samples might have caused the discrepancy.

Conclusions and Recommendations:

The dispersion characteristic of the strata from the subject study area were investigated and the results show that the estimated dispersion coefficient of the highly permeable zone is very high compared to the dispersion coefficient of the underlying tight clay layer.

In this study the calculations of porosity and permeability of different layers show that a highly permeable zone lies between two clay layers in the affected area. This channeling effect of the highly permeable sand is partially responsible and may be considered as a natural calamity causing the seepage of the contaminated water into the basements of local residents. The recovery of free hydrocarbons from this porous zone could be done by using a pumping system. This will largely reduce the hydrocarbon percentage of the contaminated groundwater.

The chemical test report indicates that the concentration of Benzene, Toluene, and Xylene (BTX) is less then the standards set by Suggested No Adverse Response Levels (SNARL). However, when this discharge seeps through the basements of local residents, it creates uncomfortable and unhealthy living condition. The field observation from this study strongly supports the need for a remedial action at this site. On the contrary, the laboratory results do not call for such action. This divergence in the field and lab result is highly controversial, and more so in a residential area. The author recommends that an emphasis should be put on the field observations in such cases so that some remedial measures could be initiated at these sites. Also, it is recommended that some refinement in sampling and analytical procedures might be able to converge the differences between the field observations and laboratory results to an acceptable degree.

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FIELD SCREENING FOR HAZARDOUS MATERIALS IN SOIL AND GROUNDWATER AT A MAINTENANCE BUILDING

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ABSTRACT

A combination of field screening techniques were used to assess the nature and horizontal extent of hazardous materials in soil and groundwater at a maintenance building area at the Sierra Army Depot, California. Soil-gas surveys and groundwater sampling directly from a hollow-stem auger were employed to study a maintenance building area for which little information regarding past waste management handling and disposal practices was available. Although one maintenance building was identified as the potential source area for the generation of hazardous materials, eight other maintenance buildings and eleven warehouses in the area were discovered to be additional potential source areas of hazardous materials.

A series of field screening tools were used to design a cost-effective remedial investigation program and a groundwater monitoring network at this site. Since the use of solvents was documented, an extensive soil-gas survey program was designed to identify the potential horizontal extent of solvents in the soil and groundwater. A grid of 300 soil-gas sampling locations over 40 acres was established. The soil-boring and groundwater sampling program was focused in areas where soil-gas contaminant concentrations were highest. Since the groundwater gradient at the site was unknown, a series of piezometers were installed to serve as both groundwater level monitoring locations and as one-time groundwater sampling points. Additional one-time groundwater sampling points were determined on the basis of the groundwater gradient and on a preliminary estimate of the horizontal extent of any detected contamination, thereby allowing for monitoring wells to be installed down-gradient of detected contamination.

INTRODUCTION

Harding Lawson Associates (HLA) was contracted by the U. S. Army Environmental Center (USAEC), formerly the U. S. Army Toxic and Hazardous Materials Agency, to perform a Remedial Investigation and Feasibility Study (RI/FS) for nine of the twenty-two sites identified in the Sierra Army Depot (SIAD) Federal Facilities Site Remediation Agreement (FFSRA) between the State of California-Environmental Protection Agency (Cal-EPA) and SIAD. As a result of the Preliminary Assessment performed by the U.S. Army Hygiene Agency in 1987, the scope of work for the remedial investigation of these nine sites was referenced in the FFSRA. On the basis of initial site reconnaissance, the Field Sampling Design Plan (FSDP) and other associated work plans for the RI/FS were written with a two-stage field investigation to meet the scope of work requirements of the FFSRA and the overall objectives of the RI/FS in a cost-effective manner.

To facilitate this two-staged investigation, routine communication with Cal-EPA was required for FFSRA deadlines to be met and cost-savings to be realized. Upon completion of the first stage of the field investigation, sites were eliminated from further study while the scope of work for other sites was expanded. Data from the first stage of the RI allowed for data gaps to be identified and the scope of the

second stage of the RI to be determined. Through documented negotiations with Cal-EPA, the second stage of the RI was performed prior to the issue of a RI report. This allowed for the writing of an RI report that drew conclusions more meaningful than "that more data was needed." The staging of the field investigation and continuous communication with the Cal-EPA allowed for a flexible field screening program to be implemented resulting in significant cost savings for the field investigation at the Building 210 Area which is the topic of this paper.

SUMMARY

Stage one of the field program at the Building 210 Area included an extensive soil-gas survey and limited soil-boring sampling. Soil samples were obtained from areas where there were high detections of trichloroethene (TCE), freon-11, and trichloroethane (TCA) in the soil-gas. The results of soil samples from these areas revealed either very low or no detections of these compounds indicating that the groundwater was the likely source of the detections in the soil-gas although the depth to groundwater is in excess of 85 feet below the ground surface.

The stage two investigation designed for the Building 210 Area was a combination of soil-gas surveying[1] and Hydropunch®[2] sampling in conjunction with the installation of piezometers and groundwater monitoring wells. The objective of the stage two soil-gas survey was to reach an area west of the site where the soil-gas results were non-detections. It was important for an area of non-detections in the soil-gas data to be identified to verify that the source of TCE in the soil-gas was not from another site west of the Building 210 Area since groundwater flow direction was unknown and groundwater contamination approximately one-half mile from the Building 210 Area was documented.

The objective of the Hydropunch® sampling was to identify areas in the groundwater of both high contaminant levels and no contamination for the installation of groundwater monitoring wells. In addition, piezometers were installed prior to the Hydropunch® sampling to determine the local groundwater gradient. Piezometer locations were selected for their usefulness in determining the groundwater gradient and for verifying whether areas of suspected contamination were contaminated. Stage one soil-gas and soil boring data and stage two groundwater flow data from the piezometers were employed to determine optimal Hydropunch® locations.

Due to weather and geologic conditions, the field program was implemented differently than planned. Due to record snowfalls, the soil-gas survey and drilling efforts became out-of-phase and a local laboratory was contracted to do 24-hour turnaround organic screening via Environmental Protection Agency analytical method 624 (EPA Method 624) for the Hydropunch® groundwater samples. Another modification to the program was required when it was discovered at the first boring that the sands at the site were too dense for the Hydropunch® tool to penetrate. At that time it was determined that groundwater samples would be collected directly from the hollow-stem auger.

The hollow-stem auger was advanced five feet below the water table and a stainless steel bailer was used to obtain groundwater samples. There was concern that the aquifer would be disturbed and that the groundwater samples would not be representative. Table 1 presents a comparison of TCE in groundwater samples collected in the hollow-stem auger to samples obtained in colocated wells. The analytical results in Table 1 are reported in micrograms per liter (ug/l); analytical methods used were EPA Method 624 for the screening (bailed) samples and USATHAMA Method UM 20 for the well samples. The detection limit for Method UM 20 is 0.50 ug/l.

Table 1 Comparison of TCE Detections in Groundwater		
Sample Identification	Screening Results (ug/l)	Well Results (ug/l)
B21-3-MW	3400	3496
B21-4-MW	<1	0.75
B21-5-PZ	210	180
B21-6-MW	<1	<0.50

Figure 1 presents the locations where groundwater screening samples (noted by "HP" in the sample identification) were taken and where piezometers and monitoring wells were installed. Figure 1 also demonstrates how the screening data was used to outline potential contaminant plumes by contouring screening data concentrations. Table 1 and Figure 1 demonstrate one of the successes of this screening program, the close correlation between the groundwater screening data and the monitoring well data. One of the problems encountered implementing this program was the discovery of an extremely flat local and regional groundwater gradient and the project team's delayed ability to determine the local gradient due to fluctuations in the water table that were not stabilized until the wells and piezometers were developed. Once the groundwater gradient was determined, it was confirmed that contaminants had not only migrated to the northeast, as early field data supported, but that contaminants had also migrated to the southeast as the last field screening data set had indicated. Continued water level monitoring data showed that a groundwater mound, which was not anticipated, was present at this site.

In conclusion, the field screening techniques employed at the Building 210 Area met or exceeded their intended objectives although unanticipated groundwater conditions did not allow for all necessary field investigation activities required at this site to be performed during stages one and two.

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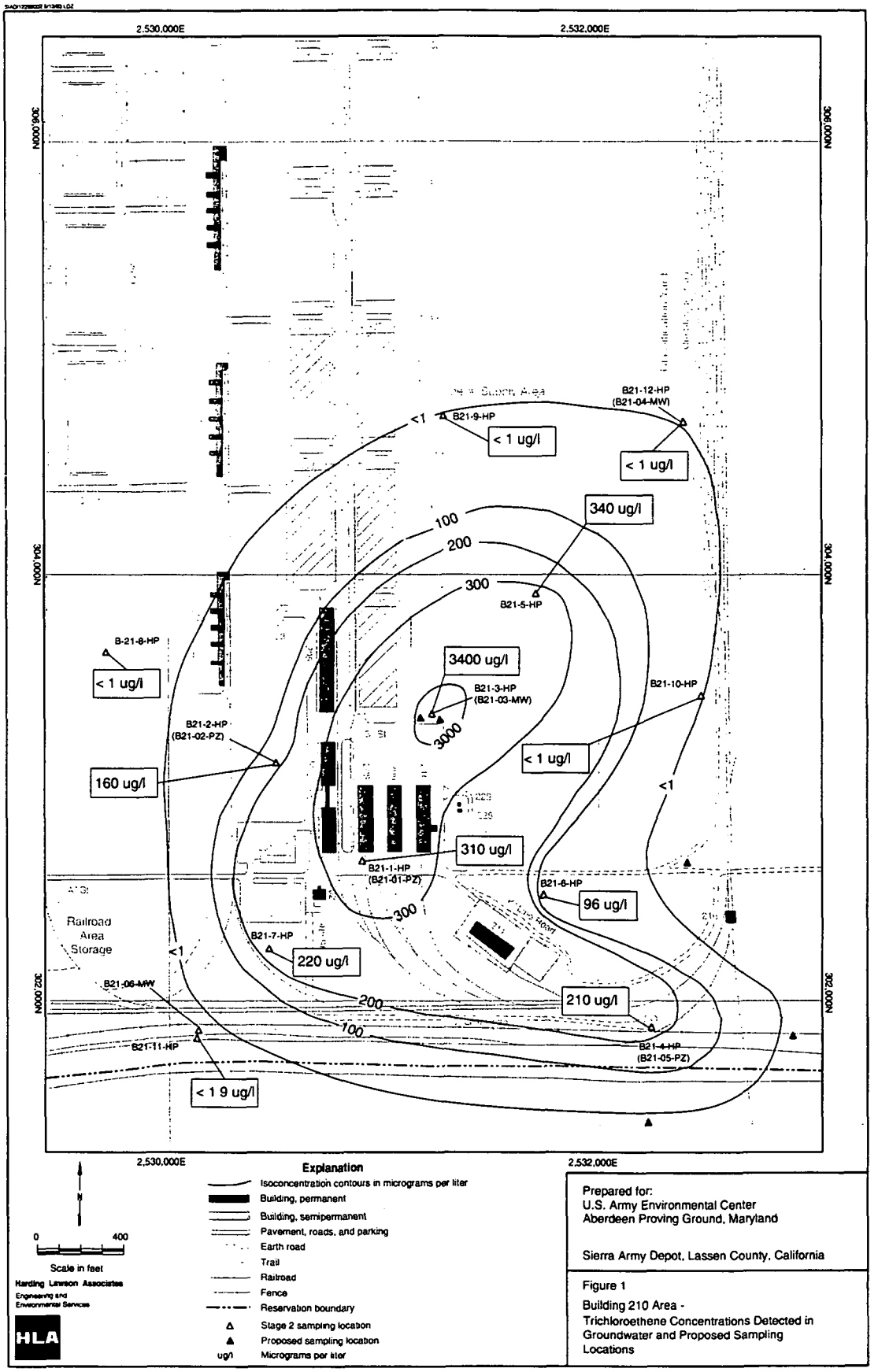
1. Soil-gas surveying is the collection and analysis of air from the vadose zone for the analysis of target analyses.

2. Hydropunch® sampling is a technique where a stainless steel probe is either driven into the soil or into an existing soil boring to collect groundwater.


2,530,000E
2,532,000E
306,000N
304,000N
302,000N
B21-12-HP
(B21-04-MW)
B21-9-HP
< 1 ug/l
< 1 ug/l
340 ug/l
100
200
300
B21-5-HP
B-21-8-HP
< 1 ug/l
3400 ug/l
B21-3-HP
(B21-03-MW)
B21-10-HP
B21-2-HP
(B21-02-PZ)
3000
< 1 ug/l
160 ug/l
<1
310 ug/l
B21-1-HP
(B21-01-PZ)
B21-8-HP
96 ug/l
300
Railroad
Area
Storage
B21-7-HP
220 ug/l
<1
B21-06-MW
200
210 ug/l
100
B21-11-HP
B21-4-HP
(B21-05-PZ)
< 1 9 ug/l
Explanation
Isoconcentration contours in micrograms per liter
Building, permanent
Building, semipermanent
Pavement, roads, and parking
Earth road
Trail
Railroad
Fence
Reservation boundary
Stage 2 sampling location
Proposed sampling location
ug/l
Micrograms per liter
N
0
400
Scale in feet
Harding Lawson Associates
Engineering and
Environmental Services
HLA
Prepared for:
U.S. Army Environmental Center
Aberdeen Proving Ground, Maryland
Sierra Army Depot, Lassen County, California
Figure 1
Building 210 Area -
Trichloroethene Concentrations Detected in
Groundwater and Proposed Sampling
Locations

31 FIELD AND LABORATORY METHODS IN ECOLOGICAL RISK ASSESSMENTS FOR WETLAND AND TERRESTRIAL HABITATS

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ABSTRACT

Field surveys are frequently included as part of an ecological assessment for hazardous waste sites. In addition, biological evaluations in both field and laboratory have increasingly been considered critical components in the ecological risk assessment process for Superfund. Depending upon habitat type, field methods have been developed which lend themselves directly to the Superfund ecological risk assessment process. Freshwater wetlands, for example, are frequently impacted by various anthropogenic chemicals, and field methods have been developed to help focus chemical and biological tests that have been identified for laboratory studies. Here, we compare and contrast the field methods used in evaluating wetlands that occurred in markedly different habitats and were impacted by two different, but relatively simple contaminant sources. Both field studies were completed as part of the baseline ecological risk assessment process. One site, located in western Montana on the Clark Fork River, was Milltown Reservoir wetlands, and had been impacted by heavy metals and sedimentation as a result of nearly ninety years of upstream mining activities. The other site occurred in the shrub-steppe of eastern Oregon, which had been a storage and disposal area for over 25,000 barrels of chlorophenoxy herbicides and chlorophenols. In both case studies, assessment methods had to be applied in lacustrine wetlands as well as the surrounding upland habitats. As part of the ecological assessment for each site, a variety of field methods [e.g., terrestrial and aquatic tests] were critical to the evaluation, yet despite differences in contaminant sources, each field site considered ecological effects potentially associated with:

- Preliminary food-web contamination;
- Phytotoxicity and contaminant uptake by plants;
- Adverse biological effects expressed by soil macroinvertebrates;
- Adverse biological effects expressed by sediment macroinvertebrates; and
- Adverse biological effects expressed by terrestrial and wetland vertebrates.

In conjunction with chemical analyses of soil, sediment, and water samples, these biological and ecological evaluations yielded an integrated evaluation of ecological effects and exposure for the baseline ecological risk assessments. Overall, the field activities at each site illustrate the role that preliminary field screening plays in the ecological assessment process.

INTRODUCTION

Ecological risk assessment has recently gained a more prominent role in hazardous waste site evaluations (US EPA 1991; Suter 1993), and this increased role has been reflected in technical guidance to assure that reliable, yet cost-effective methods are used in the process (Warren-Hicks, *et al.* 1989; US EPA 1991; Linder, *et al.* 1992). Field methods for chemical analysis, particularly for screening purposes, have been developed and are relatively routine in their application in waste site assessment (Fribush and Fisk 1991). But, biological methods are not nearly as widely used, despite biological tests and survey methods being readily available, well developed and standardized (Warren-Hicks, *et al.* 1989; ASTM 1992). As previously summarized, both chemically-based and toxicity-based approaches may make significant contributions to ecological assessments for hazardous waste sites (Parkhurst, *et al.* 1989). When used together, chemical and biological test and survey methods can directly evaluate ecological endpoints pertinent to risk assessment. From an ecotoxicological perspective, ecological effects and exposure assessments are complex interrelated functions which yield estimates of hazards, and potentially risks, associated with environmental contaminants in various matrices sampled at a waste site. Here, using two wetland habitats as examples, we illustrate an integrated approach to ecological risk assessment, and in particular we focus on field and laboratory activities that occurred early in the ecological risk assessment process.

Montana Field Site

Milltown Reservoir is on the Clark Fork River in western Montana, six miles east of Missoula, Montana. 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. Because of the upstream copper mining activities in the Clark Fork River watershed, Milltown Reservoir has accumulated a large volume of sediment enriched with heavy metals and metalloids, including arsenic, cadmium, copper, lead and zinc. The Milltown Reservoir wetland was initially identified under CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) 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. Within an ecological context, however, the impact of the contaminated wetland soils and sediments on the indigenous wildlife and vegetation characteristic of the site was unclear.

Oregon Field Site

Alkali Lake, Oregon is located in south central Oregon (elevation ca 1300m). When seasonally recharged or during wet years, Alkali Lake is characteristic of many Great Basin lakes, being relatively shallow and highly alkaline. During dry years, the lake recedes and the exposed lake bed presents extensive evaporative deposits of sodium carbonate. Between 1969 and 1971 over 25,000 drums containing herbicide formulations (primarily, 2,4-dichlorophenoxyacetic acid [2,4-D], MCPA [4-methyl-2-chlorophenoxyacetic acid], and related chlorophenoxy herbicides) were hauled from a Portland, Oregon production facility to a storage facility located immediately west of Alkali Lake. In November, 1976 the storage facility was converted to a disposal site, and the drums were placed into shallow (1 m), unlined trenches, crushed, and buried on the playa near Alkali Lake. Unfortunately, in addition to releasing the materials to the soil, groundwater contamination resulted from these disposal activities, since a relatively shallow aquifer (1 to 3 m below ground level) existed in the closed-basin around the Alkali Lake playa. Prior to these preliminary studies, the ecological effects associated with this contaminated soil and aquifer were poorly understood.

METHODS

As part of the ecological assessment at each site, a variety of terrestrial and aquatic laboratory tests or field survey methods were critical to each wetland evaluation (Table 1). While this overview must limit detailed descriptions of laboratory and field methods, those methods applied at each site reflected site-specific contingencies whenever possible. For example, amphibian work at the Montana site used standard methods (ASTM 1992), but also tested surrogate species (bull frog, Rana catesbeiana) that were more relevant to ecological interpretation (Linder, *et al.* 1991). In contrast, if amphibian work were identified as critical to the high desert site, an alternative surrogate (spadefoot toad, Scaphiopus intermontanus) would be appropriate. Despite differences in contaminant sources, each assessment considered ecological effects potentially associated with:

- phytotoxicity and contaminant uptake by plants;
- adverse biological effects expressed by soil macroinvertebrates;
- adverse biological effects expressed by sediment macroinvertebrates;
- adverse biological effects expressed by terrestrial and wetland vertebrates; and
- preliminary food-chain contamination.

Table 1. Summary of field survey and test methods used at study sites (from Linder, et al. 1994).

Ecological assessment component	Candidate field survey or test methods	Methods potentially applicable to Oregon field site, Alkali Lake disposal area	Methods potentially applicable to Montana field site, Milltown Reservoir wetlands
Phytotoxicity and contaminant uptake by terrestrial and wetland plants, and field surveys for in situ effects and vegetation communities	Standard laboratory phytotoxicity tests for seed germination, root elongation, and plant vigor	Seed germination, root elongation, and plant vigor tests with lettuce	Lettuce seed germination and root elongation; plant vigor tests with lettuce and Hydrilla verticillata
		Alternative site-specific tests species, including alkaline tolerant plants and native species such as Sacrobatus vermiculatus (greasewood)	Plant vigor tests using alternative species, including native species (Potamogeton pectinatus, or sago pondweed)
	Field tests for seed germination and plant vigor	Field testing limited in preliminary studies, and seed collections gathered for laboratory testing	In-field seed germination tests with standard laboratory test species and plant vigor tests using sago pondweed
	Field surveys for vegetation communities	Field surveys for evaluating in situ effects (e.g., plant health) and vegetation mapping for baseline evaluations	Wetlands delineation and survey of facultative and obligate wetland plants
	Field and laboratory measurements of soil physicochemical properties	Soil texture, organic matter, pH, cation exchange capacity, base saturation, extractable acidity, extractable nutrients, N-P, electrical conductivity, water retention, bulk density, infiltration capacity, hydraulic conductivity	Soil texture, organic matter, pH, cation exchange capacity, base saturation, extractable acidity, extractable nutrients, N-P, electrical conductivity, water retention, bulk density, infiltration capacity, hydraulic conductivity

Ecological assessment component	Candidate field survey or test methods	Methods potentially applicable to Oregon field site, Alkali Lake disposal area	Methods potentially applicable to Montana field site, Milltown Reservoir wetlands
Biological effects in soil macroinvertebrates, and field surveys of in situ effects and soil communities	Standard laboratory tests using earthworms, nematodes, ants, or isopods	Laboratory tests with nematodes, harvester ants or isopods; soil community tests (microbial or nematodes) using soil cores	Laboratory tests using nematodes or earthworms; soil community tests (microbial or nematode) using soil cores
	Field tests using earthworms, ants, or isopods	Field tests using harvester ants or isopods	In-field testing with earthworms
	Field surveys for soil communities	Field collections of frequently captured surface- and subsurface-dwelling invertebrates and vegetation-inhabiting invertebrates	Field collections of frequently captured surface-dwelling and vegetation-inhabiting invertebrates
Biological effects in sediment macroinvertebrates, and field surveys of in situ effects and benthic communities	Standard laboratory tests using benthic macroinvertebrates	Laboratory tests using alkaline tolerant sediment- or water column-dwelling invertebrate (e.g., brine shrimp)	Laboratory tests using Hyallela azteca and Chironomus riparius
	Field tests using benthic macroinvertbrates	No field tests currently available for alkaline sediments or surface water	In situ testing with aquatic macroinvertebrates such as Daphnia magna
	Field surveys for benthic communities residues evaluation	Field survey collections of sediment-dwelling larval invertebrates and brine shrimp community and contaminant	Field collections of benthic communities for sediment quality triad analysis

Ecological assessment component	Candidate field survey or test methods	Methods potentially applicable to Oregon field site, Alkali Lake disposal area	Methods potentially applicable to Montana field site, Milltown Reservoir wetlands
Biological effects in terrestrial and wetland vertebrates, and field surveys of *in situ* effects and wetland communities	Standard laboratory tests using small mammals, birds, or amphibians	Candidate methods include laboratory tests using small mammals, birds, or amphibians	Laboratory testing with amphibians (or terrestrial vertebrates)
	Field tests using terrestrial vertebrates	Candidate field methods using small mammals, birds, and amphibians	*In situ* testing with amphibians
	Field surveys for terrestrial vertebrate communities	Field surveys for small mammals and other terrestrial vertebrates; collection for analysis of gut contents	Terrestrial vertebrate surveys and collections for contaminant residues analysis
Preliminary food-chain contamination evaluation	Designed feeding trials using pertinent test species (e.g., terrestrial or wetland vertebrates)	Candidate studies address sediment-dwelling benthic invertebrate and shorebird food-chain contamination evaluation	Candidate studies address vegetation consumption by small mammalian herbivores

Overall, the field activities for the ecological assessment at each site illustrate the role that preliminary scoping activities play in the ecological assessment process.

Synopsis of Biological Methods at Montana Field Site

In the preliminary ecological survey for Milltown Reservoir wetlands, terrestrial vegetation assessments were accomplished through a wetlands delineation (Federal Interagency Committee 1989), and standard plant tests for soil contamination evaluations (seed germination, root elongation, and plant vigor; see Warren-Hicks, *et al.* 1989; Linder, *et al.* 1992). In emergent zone habitats, plant and animal tests were conducted in laboratory and field (Warren-Hicks, *et al.* 1989; Linder, *et al.* 1992; ASTM 1992). *In situ* tests were conducted using amphibians, and submerged aquatic vegetation was also evaluated in emergent zone habitats (Linder, *et al.* 1992). In upland areas earthworm and seed germination tests were completed on-site and in the laboratory. Root elongation tests using groundwater were also completed. Additionally, surface soils were sampled for metals analysis (US EPA 1986) and characterizations of soil quality (Page, *et al.* 1982). In order to determine food source contamination for site-specific receptors like small mammals, samples of native vegetation and terrestrial invertebrates were collected and analyzed for target analytes (cadmium, copper, zinc, lead, and arsenic). For aquatic food-chains, samples of aquatic biota, including fish, aquatic insects, and plants, were collected and analyzed for target analytes. Sediment samples were also collected from emergent zone habitats and analyzed to characterize the extent of metal contamination in depositional areas in the wetland.

Synopsis of Biological Methods at Oregon Field Site

As part of the preliminary ecological survey for Alkali Lake, terrestrial plants and invertebrates were sampled in various seasons. Aquatic invertebrates were also sampled at various times of the year, and representative species were identified and analyzed for tissue residues of target analytes (2,4-D and chlorophenols). Vegetation measurements taken during the survey determined cover and qualitative evaluations of plant health. In conjunction with survey samples for vegetation, terrestrial invertebrates were sampled using a combination of pit-fall traps and net surveys; for terrestrial vertebrates, small mammals were trapped and gut contents were analyzed to evaluate food sources. In addition to small mammal surveys, habitat use by birds was also noted; shore birds were surveyed and seasonal patterns in habitat use were recorded. With these preliminary field results target species were identified, and conceptual food-chain models were developed for risk assessments for terrestrial vertebrates. Vegetation patterns were also evaluated for their future role in long-term site monitoring.

SUMMARY

Montana field site. Milltown Reservoir wetlands represents a single operable unit within the Clark Fork River valley, but the wetlands must be viewed as a whole if they are to be considered within ecological contexts. Nonetheless, these preliminary studies have been incorporated into the baseline risk assessment being developed for the wetlands, and suggested future work in the continuing ecological risk assessment process. For example, soils and sediments at Milltown wetlands may be characterized as having greater metal loads than the surrounding watersheds, although the historic and current release and movement of metals may be quite dissimilar. At Milltown wetlands, the measures of exposure-point concentrations suggest that metals, and specifically target analytes -- arsenic, cadmium, copper, lead, and zinc -- occur at greatest concentrations in deposition zones located throughout Milltown wetlands. On the basis of total metal concentrations, it may be said that soils and sediments are both metal-enriched, though biological assessments suggest that only a small, and variable, fraction of that metal is biologically available and associated with subtle biological effects. Clearly, these deposition areas may warrant additional study, or at a minimum should be monitored to ensure that adverse effects do not develop with time.

As potential sources of metal, the soils and sediments, as well as the associated water column, must be considered in light of the potential biological and ecological receptors inhabiting Milltown wetlands. While diverse in their selection, the biological tests applied during the field and laboratory efforts at Milltown wetlands fall short of anticipating all the receptors potentially at risk. For example, while terrestrial vertebrates such as small mammals have been considered, the comparative-toxicity data base is clearly incomplete. Evaluations of vegetation completed at Milltown wetlands may have missed soil microbial effects. In summary, an understanding of the potential effects of metals on communities and populations at Milltown wetlands must be developed by inference, based upon these quantitative estimates of effects made during the ecological assessment.

The biological assessments at Milltown wetlands suggest that little, or no acute toxicity or adverse biological effects are occurring now. Consistently, and regardless of the field- or laboratory-test methods used, biological assessments at Milltown wetlands could not characterize acute toxicity; however, evidence of subtle biological effects was noted in samples collected from depositional areas. Future remediation plans should weigh the potential biological and ecological impacts associated with remediation efforts against of the current impacts associated with elevated metals in soils and sediments. While the current subtle effects and potential effects should not be understated in the risk-assessment, currently any widespread physical alteration of wetland habitats may not be justified on a technical basis. Future site monitoring should address problems that may occur with remediation at Milltown wetlands and at upstream operable units, and in particular should consider the long-term effects of metal exposures on vegetation in

depositional areas. Also, indirect effects associated with future management plans (e.g., habitat alterations associated with "no action" or sediment dredging alternatives) should be considered as a potential consequence of the metals that presently occur in the soils and sediments at Milltown wetlands.

The data gathered from laboratory and field work at Milltown wetlands has reduced the uncertainty associated with the baseline ecological risk assessment, and has suggested that biological and ecological effects, if present in the wetland, were subtle. The uncertainty associated with historic data or data collected in the current assessment at Milltown wetlands must be stressed, e.g, were surrogate test species (in either laboratory or field) sufficient for the biological assessment? Questions like these must be considered proximate sources of uncertainty in the ecological risk-assessment process at Milltown wetlands, and in any management decision derived in part from these studies. At Milltown wetlands:

- The preliminary survey of linear food-chain contamination showed evidence of metal bioaccumulation in small mammalian herbivores. Bioconcentration of metals was also occurring in emergent vegetation in some reaches of the deposition zones within Milltown wetlands, but biomagnification of metals in herbivores did not appear to be a problem for the endpoints considered. Field surveys at Milltown wetlands did not contradict these assessments, but the sparse comparative-toxicity data available, particularly for chronic endpoints, must be considered as a source of uncertainty.

- Vegetation tests, especially those used in evaluating water collected from the rhizosphere, suggested that no acute effects were associated with groundwater and surface water, but subtle growth-related effects were occasionally observed in samples collected from deposition zones at Milltown wetlands. These subtle indications were noted in both laboratory tests using emergent vegetation and in standard root-elongation tests. Again, field surveys found no sign of altered vegetation patterns and reduced cover was evident only in those areas that had previously been physically manipulated.

- Earthworm evaluations in both field and laboratory were consistently negative for acute toxicity, suggesting that soil macroinvertebrates may not be at great risk as long as the current soil conditions exist. (This is provided that earthworms are good sentinel species for assessing soil health.) Soil microbial communities, however, were not adequately described and should be evaluated when methods are available.

- Preliminary studies using amphibians suggested that subtle biological effects may be found at Milltown wetlands, but qualitative field surveys did not support any conclusions that those effects would be prominent nor adverse.

- Preliminary studies using bacterial tests yielded results consistent with the balance of biological-tests used at Milltown wetlands, but may not be representative of the soil community there.

- Plant-uptake studies suggest that garden crops bioconcentrate metals. Bioconcentration of metals in plants differs depending upon the plant species and anatomical feature considered (e.g., root versus leaf).

- Characterization and metal analysis of Milltown wetlands soils, sediments, and biota indicated that metals have accumulated in various environmental matrices, and that Milltown wetlands is spatially quite heterogeneous with respect to metal deposition. Within-sample unit variation was relatively less than across Milltown wetlands variation, and metal deposition was consistent within topographic settings. Soils within sample units were relatively homogeneous.

Oregon field site. While the present work was designed for data collection and survey, its role within an ecological risk assessment for Alkali Lake has become essential. The critical early phases (problem formulation, and pilot investigations for exposure and ecological effects assessment) of the ecological risk assessment process have been addressed, and existing data needs have been identified, which should allow more adequate characterizations of uncertainty during the risk assessment process. Baseline exposure and ecological effects assessments can now be developed and based upon site-specific data, and any future data needs may be clearly identified. For example, within the ecological effects assessment, field surveys and literature reviews have been considered, but by design little toxicity assessment has been completed. Future work could be developed to address this data gap, and additional comparative literature regarding contaminant effects could then be gathered for evaluating site-specific toxicity data. Whether future work regards these specific data needs, the baseline ecological assessment at Alkali Lake provides empirical information upon which decisions can be based.

Numerous technical recommendations can be identified as a result of these baseline data collections. While the studies at Alkali Lake were preliminary and not developed as a risk assessment, the information should be considered in developing management plans for Alkali Lake, including any future ecological risk assessment. On the basis of historical information and the completed field reconnaissance, the following may be relevant to future management decisions regarding Alkali Lake:

- With the baseline information gathered during these preliminary studies, efforts should be continued to evaluate vegetation pattern changes at Alkali Lake. The biological information subsequently generated in such a monitoring program could potentially benefit future evaluations of the effects of groundwater quality on vegetation. These should be completed using, for example, plant vigor tests modified to use representative species, e.g., Sacrobatus vermiculatus.

- Periodic soil sampling should be included in a monitoring program to evaluate soil contamination and the changing spatial patterns of the groundwater plume.

- Additional aquatic invertebrate sampling should be considered in conjunction with an evaluation of shorebird diet and foraging activities at Alkali Lake, particularly during the nesting season (e.g., spring and early summer field activity). Modified standard tests (ASTM 1992) using nestling shorebird exposures may be beneficial to evaluations of risks to this terrestrial vertebrate.

Future work must reflect management and policy related issues relevant to site managers, and field and laboratory efforts can directly address issues regarding risk characterization and uncertainty. Ecological risk assessments then could be developed more soundly and site management more adequately implemented.

ACKNOWLEDGEMENTS

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INCREASING THE SENSITIVITY OF FIELD HEADSPACE ANALYSIS FOR VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

The use of portable gas chromatographs for on onsite analysis of volatile organics using the headspace analytical technique has rapidly increased. The increased use of these methods is in response to the significant savings in both rapid turnaround time of results and savings of analytical costs as compared to conventional laboratory analysis. This and other field screening analytical methods have proven to be a valuble asset toward achievement of more rapid, cost effective strategies for performing site investigations.

This study evaluated the ability of several methods to increase the sensitivity of headspace analysis. The methods included the addition of salt, heating and agitation. A Photovac 10S50 field portable gas chromatograph equipped with a photoionization detector (PID) was used for the analysis of the samples. The target analytes were trichloroethylene (TCE), perchloroethylene (PCE), benzene, toluene, ethylbenzene, meta and ortho xylene. Three vials were prepared, one without salt, one with 5g Na_2SO_4 and one with 10g Na_2SO_4. The vials were spiked to yield a concentration of 50 ppb for each target analyte. Triplicate analysis was performed on each spiked sample. The vials were then placed in a hot water bath at 65^oC and analyzed, then shaken and analyzed. The percent increase in response was determined for each method and compound. Response increases of BTEX, TCE and PCE were greatest with the combination of adding salt and heat to the sample. Individually, the addition of heat to the sample produced the a greater response compared to the addition of salt alone, although both produced responses greater than 100% for all compounds, except for benzene, compared to the reference solution. This evaluation demonstrates several methods which can be used seperately or in conjunction to increase the sensitivity of headspace analysis under field conditions.

INTRODUCTION

Soil and ground water contamination by volatile organic compounds (VOC) is frequently encountered at industrial and

hazardous waste sites. The physical properties of VOCs allow for their rapid movement in the vadose zone to the groundwater. Once in the ground water, VOCs may rapidly impact potable wells causing immediate health concerns to receptors.

The concern for the rapid assessment of groundwater contamination has in turn created a need for rapid methods to assess the extent of a problem. The use of field screening analytical methods for the analysis of volatile organic compounds in groundwater offers a means for real-time decision making during groundwater contaminant studies.

Compound specific and quanitative field static headspace analytical techniques have been developed for gas chromatographs (GC) [1,2,3]. The static headspace method is based upon the partitoning of volatile organics between the aqueous and vapor phases when a sample is enclosed in sealed container. An aliquot of the headspace is then withdrawn and analyzed by the GC equipped with a photoionization detector (PID).

THEORY

The principle of all quantitative headspace analysis is based on the thermodynamic conditions of the phases. These conditions require that equilibrium be established between the liquid and gas phase. The concentration of a VOC in the headspace of a liquid under static conditions is based upon contaminant concentration in the liquid and its distribution coefficient or Henery's Law.

$$C^{I} = KC^{II}$$

Where:

C^{I} = Initial Concentration
K = Distribution Coefficient
C^{II} = Final Concentration

The distribution coefficient is a measure of the partitioning of a compound between the liquid and gas phases. The sensitivity of the static headspace method will vary between VOCs due to their extremely wide range of K values. Therefore, to increase the sensitivity of the static headspace technique, the value of the distribution coefficient must be decreased. This will increase the mass of VOCs driven into the headspace.

The techniques used to accomplish this under field conditions include the addition of salt or "salting out" which reduces the solubility of a compound and drives it into the headspace. The use of heat and agitation applied to a sample can also drive additional amounts of volatile

compounds into the gas phase, thus becoming availible for detection.

OBJECTIVE

The objective of this study was to evaluate the ability of various methods to increase the sensitivity of headspace analysis for selected compounds. The methods included the addition of sodium sulfate (Na_2SO_4), heating the sample to 65°C, and physical agitation.

The target analytes were common aromatics, benzene, toluene, ethylbenzene, meta-xylene, and ortho-xylene (BTEX). Also targeted were two common chlorinated aliphatic hydrocarbons, trichloroethylene (TCE) and perchloroethylene (PCE).

METHODOLOGY

Two groups of 40 ml. screw cap septum vials were prepared. Each group had one vial without salt (number 1), one with 5g of Na_2SO_4 (number 2) and the third with 10g of Na_2SO_4 (number 3). The solutions were prepared by filling each vial with laboratory grade ASTM Type II water with no headspace. The target analytes were added to each vial by piercing the septum with a syringe and injecting the compounds in sufficient quanity to yield a concentrationof 50 parts per billion (ppb) for each target analyte. The vials were shaken intermittantly for ten minutes to ensure the compounds were mixed thoroughly.

The headspace was created by withdrawing 10 ml of solution from the sealed vial with a 10 ml syringe. To allow air entry, a separate syringe needle with an attached charcaol tube to prevent the entry of any air contaminants, was placed through the septum and into the vial.

Each of the three vials in Group 1 were spiked with benzene, toluene, ethylbenzene, meta-xylene and ortho-xylene resulting in an approximate concentration of 50 ppb for each compound. Each of the vials in Group II were spiked with TCE and PCE resulting in a concentration of approximately 50 ppb. All vials were allowed to equilibrate at room temperature (20°C) for one hour.

A Photovac 10S50 field gas chromatograph equipped with a 10.6 ev photoionization detector (PID) and a CPSil 5 wide bore capillary column under isothermal conditions of 40°C was used to perform all analyses. All samples were manually injected with gas tight syringes. Syringes were purged between samples with ultra high purity air (Ultra Zero). A

one point calibration was performed using sample number 1 (without Na_2SO_4).

Each vial was analyzed in triplicate under ambient temperature (20°C) static headspace conditions. Each vial was then placed inverted in a hot water bath at 65°C for one hour for temperature equilibration. Each vial was again analyzed in triplicate, returning the vial to the hot water bath after each injection. Care was used to minimize agitation of the vial during handling. Sample Nos. 1 and 3 from each group were removed from the hot water bath, shaken for 60 seconds and immediately analyzed. The results for each sample were averaged and compared with Sample 1 of each group.

RESULTS

The results are included in Tables I and II which give the percent increases in response due to the addition of Na_2SO_4, heat, agitation and a combination of all as compared to sample number 1.

DISCUSSION

The results revealed the sensitivity for BTEX and selected chlorinated aliphatic hydrocarbons increased with the addition of heat, salt and agitation.

For TCE and PCE the addition of 10g of Na_2SO_4 resulted in a larger response compared to the vial containing 5g. Additional literature states mineralization over 20% would only result in slight increases in sensitivity, and would lead to excessive waste of the reagent.(1)

Heating the sample to 65°C resulted in sensitivity increases which were comparable to adding 10g of Na_2SO_4. Heated headspace for PCE gave a 14% greater response to the PID compared to the addition 10g Na_2SO_4.

When heat was applied to sample 3A, the increase in response was greater than the combined responses of heat and mineralization. This was most pronounced for TCE with a 488% increase in response.

Benzene and toluene were not as responsive to the mineralization as TCE and PCE. They were more responsive to the addition of heat, which gave on an average, a 1.5-2 fold increase in response compared to the 10g mineralization of the sample. The addition of heat and mineralization for the BTEX samples gave an increase in response greater than the sum of the seperate increased responses for both heat and mineralization. This result was similar to the response

TABLE I

PERCENT INCREASE IN RESPONSE TO BTEX

Sample #	2 Salt 5g	3 Salt 10g	1 HWB	2 Salt HWB	3 Salt HWB	1 HWB-SHK	3 Salt HWB-SHK
Benzene	70.4%	99%	138%	242%	345%	149%	534%
Toluene	103.9%	124%	223%	342%	391%	250%	570%
Ethyl-Benzene	112.3%	110%	287%	419%	444%	347%	699%
Meta-Xylene	127.1%	131%	312%	458%	483%	372%	758%
Ortho-Xylene	148.8%	198%	277%	634%	752%	413%	1255%

Salt - Sodium Sulfate.

HWB - Sample placed in hot water bath @ 65°C.

SHK - Sample shaken for one minute prior to analysis.

TABLE II

PERCENT INCREASE IN RESPONSE OF TCE AND PCE

Sample #	2A Salt 5g	3A Salt 10g	1A HWB	2A Salt HWB	3A Salt HWB	1A HWB-SHK	3A Salt HWB-SHK
TCE	125%	171%	161%	252%	488%	225%	947%
PCE	124%	137%	151%	228%	377%	273%	572%

Salt - Sodium Sulfate.

HWB - Sample placed in hot water bath @ 65°C.

SHK - Sample shaken for one minute prior to analysis.

of the chlorinated hydrocarbons under the same conditions. The greatest increases in response were with the later eluting and heavier compounds. Ortho-Xylene had the greatest increase in response (752%).

To further increase the response of the select compounds to the PID, the vials were shaken vigorously for one minute and an aliquot of the headspace immediately injected. This physical action moves additional VOAs out of solution into the headspace. Only one sample was injected, but responses over ambient temperature headspace for the BTEX compounds ranged from a 534% increase for benzene to a 1255% increase for ortho-xylene. Similar increases in responses were noted for TCE and PCE with 947% and 572% respectively.

Figures I and II show the comparison of chromatographs of the BTEX, TCE and PCE samples which were at ambient temperature, mineralized, heated, and agitated.

There was one problem encountered with the mineralization technique. When adding the water sample to the vial with Na_2SO_4, a bubble results ≈ 1-3 mls. This is due to air in the pore spaces of the Na_2SO_4. When 10 mls of water are removed to create the headspace varying volumes of headspace are created which can affect the comparability of results between samples. When the water sample is added to the vial slowly and the vial is gently agitated to saturate the Na_2SO_4, a loss of VOAs will result.

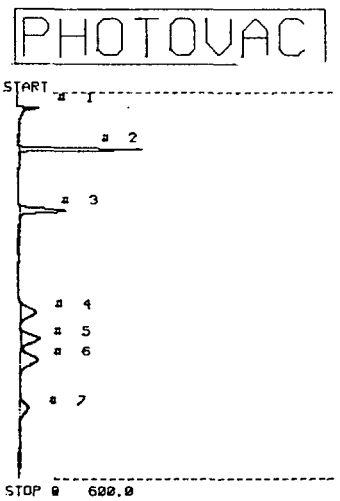
To eliminate the problem of varying headspace, all vials should be marked at a volume of 30 mls or graduated vials can be used. When the headspace is created, a volume of water is removed to the 30 ml mark. Therefore all vials will have an equal volume of headspace.

Caution should be taken when using heated headspace and shaking the vials with analysis by GC. The GC column should have a packing which is hydrophobic to eliminate moisture buildup in the column. Excessive moisture can clog the column and possibly damage the detector.

SUMMARY

This limited study has shown that increased analytical sensitivity can be obtained when employing any number of the techniques tested. The greater sensitivity to the PID can be used to detect lower concentrations of compounds in water with less sensitive instrument gains or less sensitive detectors such as an FID. This also reduces the problems of syringe contamination since at less sensitive settings, any

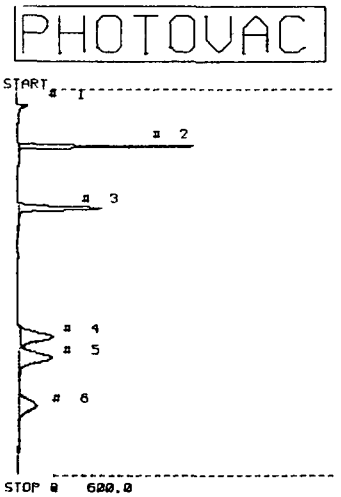
FIGURE I
CHROMATOGRAMS FOR BTEX



STOP @ 600.0
SAMPLE LIBRARY 1 DEC 30 1992 13: 1
ANALYSIS # 4 VOA TEST
INTERNAL TEMP 28 250 UL
GAIN 2 1-STD

COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	25.8	82.9 mVS
BENZENE	2	88.3	46.55 PPB
TOLUENE	3	186.1	45.46 PPB
UNKNOWN	4	347.9	311.8 mVS
ETHYLBENZENE	5	390.8	40.61 PPB
M-P XYLENE	6	423.6	39.14 PPB
O XYLENE	7	500.4	44.08 PPB

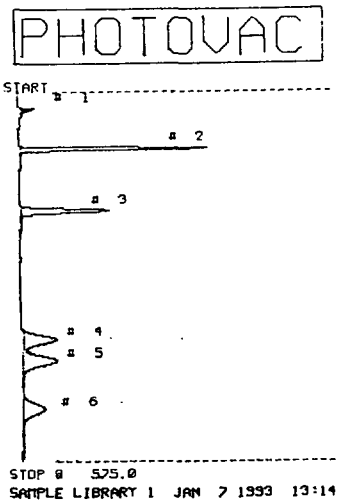
SAMPLE 1



STOP @ 600.0
SAMPLE LIBRARY 1 JAN 7 1993 12:40
ANALYSIS # 10 VOA TEST
INTERNAL TEMP 29 250 UL
GAIN 2 2-STD

COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	26.7	24.7 mVS
BENZENE	2	89.7	24.12 PPB
TOLUENE	3	186.9	83.12 PPB
ETHYLBENZENE	4	391.5	82.32 PPB
M-P XYLENE	5	424.4	80.06 PPB
O XYLENE	6	502.2	54.72 PPB

SAMPLE 2
5g Na_2SO_4

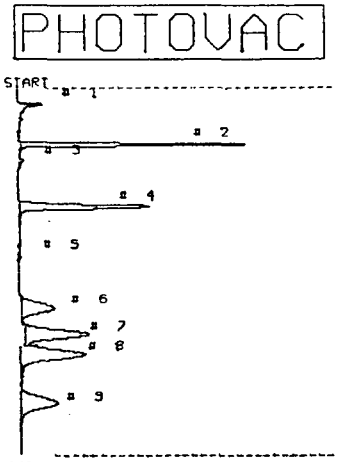


STOP @ 575.0
SAMPLE LIBRARY 1 JAN 7 1993 13:14
ANALYSIS # 13 VOA TEST
INTERNAL TEMP 29 250 UL
GAIN 2 3-STD

COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	26.0	48.9 mVS
BENZENE	2	88.9	82.52 PPB
TOLUENE	3	186.1	30.88 PPB
ETHYLBENZENE	4	391.5	83.32 PPB
M-P XYLENE	5	424.4	84.66 PPB
O XYLENE	6	501.3	120.1 PPB

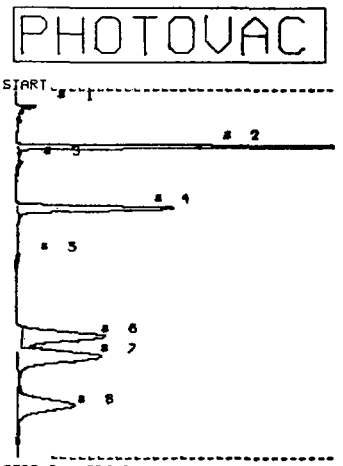
SAMPLE 3
10g Na_2SO_4

FIGURE I CONTED'
CHROMATOGRAMS FOR BTEX



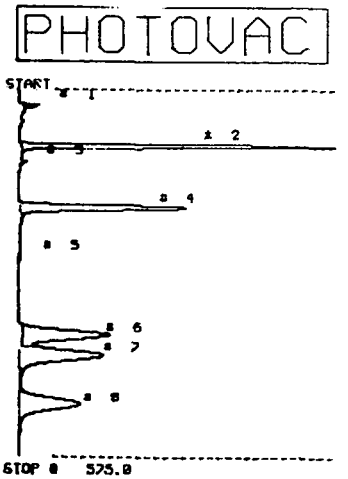
COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	26.8	79.7 mVS
BENZENE	2	89.9	110.2 PPB
UNKNOWN	3	114.7	31.2 mVS
TOLUENE	4	186.5	142.4 PPB
UNKNOWN	5	262.3	23.3 mVS
UNKNOWN	6	348.5	2.1 VS
ETHYLBENZENE	7	390.8	165.7 PPB
M-P XYLENE	8	423.6	161.2 PPB
O XYLENE	9	501.3	138.8 PPB

SAMPLE 1
HWB



COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	26.1	45.6 mVS
BENZENE	2	89.7	155.0 PPB
UNKNOWN	3	114.3	32.5 mVS
TOLUENE	4	185.7	131.5 PPB
UNKNOWN	5	262.3	31.5 mVS
ETHYLBENZENE	6	390.8	219.1 PPB
M-P XYLENE	7	423.6	217.2 PPB
O XYLENE	8	501.3	314.8 PPB

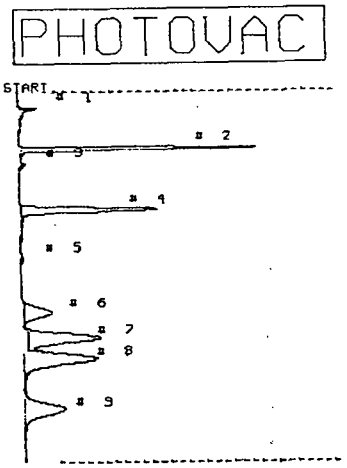
SAMPLE 2
5g Na_2SO_4, HWB



COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	25.8	46.8 mVS
BENZENE	2	89.1	202.7 PPB
UNKNOWN	3	114.1	50.0 mVS
TOLUENE	4	186.1	213.7 PPB
UNKNOWN	5	262.3	26.2 mVS
ETHYLBENZENE	6	390.8	223.8 PPB
M-P XYLENE	7	423.6	217.3 PPB
O XYLENE	8	501.3	341.1 PPB

SAMPLE 3
10g Na_2SO_4, HWB

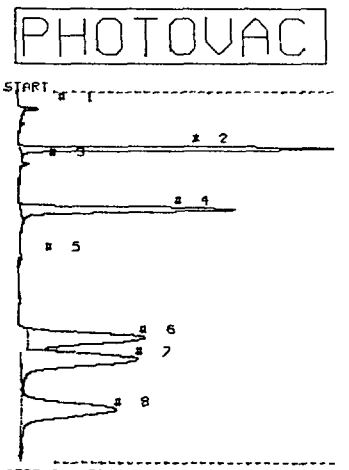
FIGURE I CONTED'
CHROMATOGRAMS FOR BTEX



STOP @ 575.0
SAMPLE LIBRARY 1 JAN 7 1993 16: 1
ANALYSIS # 26 VOA TEST
INTERNAL TEMP 29 250 UL
GAIN 2 1-STD HWB-SHAKE

COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	26.0	47.0 mVS
BENZENE	2	89.5	112.7 PPB
UNKNOWN	3	114.3	38.7 mVS
TOLUENE	4	186.1	152.1 PPB
UNKNOWN	5	262.3	41.5 mVS
UNKNOWN	6	343.1	1.8 VS
ETHYLBENZENE	7	391.5	189.1 PPB
M-P XYLENE	8	424.9	183.2 PPB
O XYLENE	9	501.3	217.6 PPB

SAMPLE 1
HWB-SHK

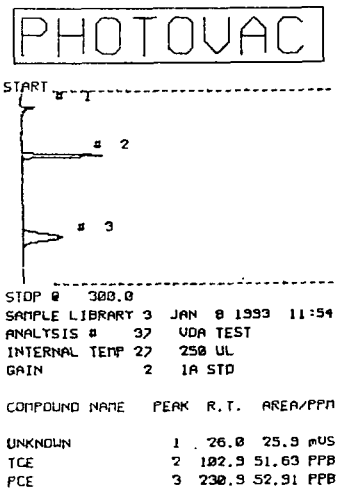


STOP @ 575.0
SAMPLE LIBRARY 1 JAN 7 1993 16:26
ANALYSIS # 28 VOA TEST
INTERNAL TEMP 29 250 UL
GAIN 2 3-STD HWB-SHAKE

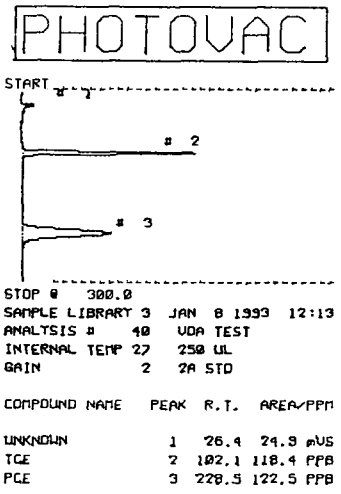
COMPOUND NAME	PEAK	R.T.	AREA/PPM
UNKNOWN	1	26.1	40.2 mVS
BENZENE	2	89.3	287.2 PPB
UNKNOWN	3	114.3	38.2 mVS
TOLUENE	4	187.3	231.5 PPB
UNKNOWN	5	262.8	64.8 mVS
ETHYLBENZENE	6	331.5	346.5 PPB
M-P XYLENE	7	424.4	333.0 PPB
O XYLENE	8	502.2	574.6 PPB

SAMPLE 3
10g Na_2SO_4, HWB-SHK

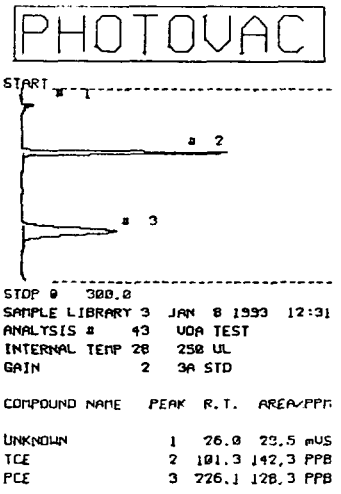
FIGURE II
CHROMATOGRAMS FOR TCE AND PCE



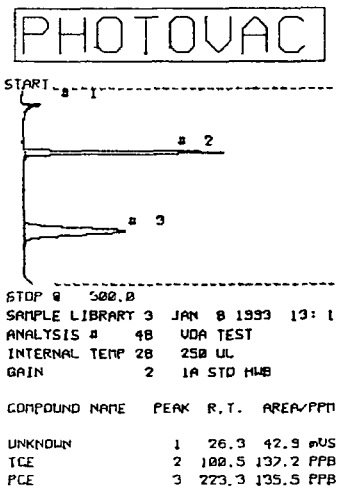
SAMPLE 1



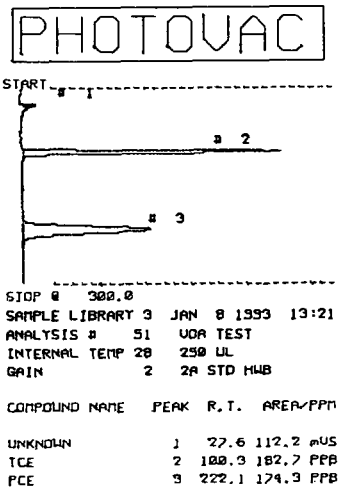
SAMPLE 2
5g Na_2SO_4



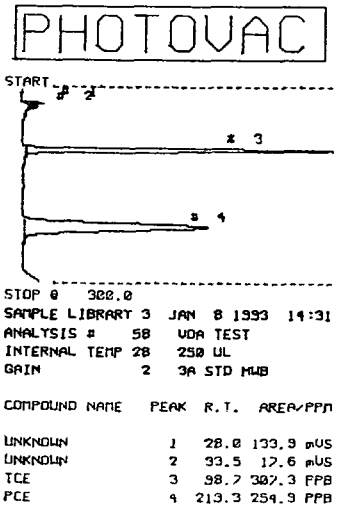
SAMPLE 3
10g Na_2SO_4



SAMPLE 1
HWB

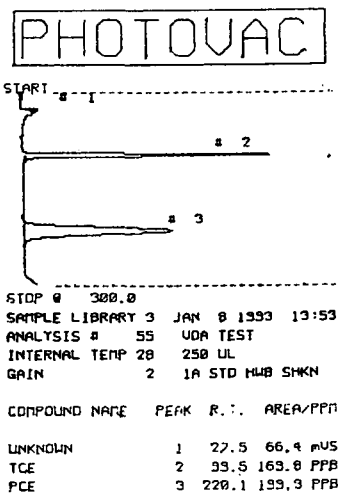


SAMPLE 2
5g Na_2SO_4, HWB

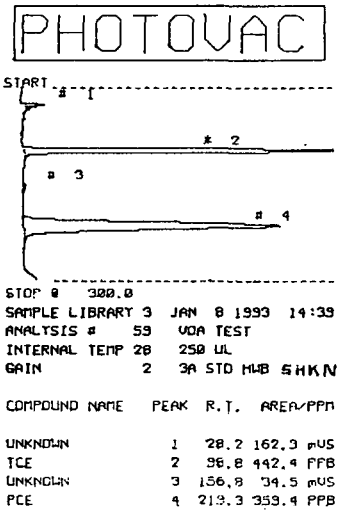


SAMPLE 3
10g Na_2SO_4, HWB

FIGURE II CONTED'
CHROMATOGRAMS FOR TCE AND PCE



SAMPLE 1
HWB-SHK



SAMPLE 3
10g Na_2SO_4, HWB-SHK

small amount of contamination under normal conditions is not detected. In situations where on site field analysis of water samples is implemented in the absence of line power to heat the samples, mineralization and shaking the vial can be utilized to increase the analytical sensitivity dramatically.

Further evaluation of these techniques is needed to assess their application to other compounds, detectors, headspace volume ratio, Na_2SO_4 concentrations and other types of mineral salts.

ACKNOWLEDGEMENTS

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ORGANICS

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REGULATORY ASPECTS OF RCRA ANALYSES

by Barry Lesnik, USEPA, Office of Solid Waste, Methods Section (OS-331), 401 M St., SW, Washington, DC 20460

What is RCRA?:

RCRA is the Resource Conservation and Recovery Act of 1976 which regulates the management of hazardous waste under Subtitle C. Administration of the program has been passed down to the states via authorization of State Programs in most States.

How is a waste classified as hazardous waste under RCRA Subtitle C?

A waste is classified as hazardous under RCRA Subtitle C if it exhibits any of the characteristics of ignitability, corrosivity, reactivity, or toxicity, or if it contains specific constituents which are listed as hazardous.

What is SW-846?

SW-846 is the compendium of analytical and test methods approved by EPA's Office of Solid Waste (OSW) for use in determining regulatory compliance under the Resource Conservation and Recovery Act (RCRA).

What are the drivers that determine which environmental analyses must be performed?

Specific regulations under RCRA Subtitle C are the determining factors as to which analyses need to be performed, and which specific target analytes need to be identified in order to be in compliance. Examples of these specific regulations include:

1) monitoring of leachates from hazardous waste landfills (Appendix IX),

2) determination of whether a waste is hazardous by characteristic,

3) compliance with boiler, incinerator, furnace (BIF) rules,

4) compliance with land disposal restrictions (LDRs),

5) permit compliance for surface impoundments, storage facilities, etc., and

6) corrective action.

Are SW-846 methods required to be used for all analyses performed under RCRA Subtitle C?

Except for the specific cases listed below, where use of SW-846 methods is mandatory, SW-846 functions as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, in responding to RCRA-related sampling and analysis requirements. The RCRA applications listed in 40 CFR Parts 260 through 270 where the use of SW-846 methods is mandatory are the following:

(1) § 260.22(d)(1)(i) - Submission of data in support of petitions to exclude a waste produced at a particular facility (i.e., delisting petitions);

(2) § 261.22(a)(1) and (2) - Evaluation of waste against the corrosivity characteristic;

(3) § 261.24(a) - Leaching procedure for evaluation of waste against the toxicity characteristic;

(4) §§ 264.190(a), 264.314(c), 265.190(a), and 265.314(d) - Evaluation of waste to determine if free liquid is a component of the waste;

(5) § 266.112(b)(1) - Certain analyses in support of exclusion from the definition of a hazardous waste of a residue which was derived from burning hazardous waste in boilers and industrial furnaces;

(6) § 268.32(i) - Evaluation of a waste to determine if it is a liquid for purposes of certain land disposal prohibitions;

(7) §§ 268.40(a), 268.41(a), and 268.43(a) - Leaching procedure for evaluation of waste to determine compliance with Land Disposal treatment standards;

(8) §§ 270.19(c)(1)(iii) and (iv), and 270.62(b)(2)(i)(C) and (D) - Analysis and approximate quantification of the hazardous constituents identified in the waste prior to conducting a trial burn in support of an application for a hazardous waste incineration permit; and

(9) §§ 270.22(a)(2)(ii)(B) and 270.66(c)(2)(i) and (ii) - Analysis conducted in support of a destruction and removal efficiency (DRE) trial burn waiver for boilers and industrial furnaces burning low risk wastes, and analysis and approximate quantitation conducted for a trial burn in support of an application for a permit to burn hazardous waste in a boiler and industrial furnace.

In Hazardous Waste Programs in RCRA-authorized States, the States can require the use of SW-846 methods. A number of States have regulations that require the use of SW-846 methods for hazardous waste analysis under their RCRA Programs. Some of these States require the use of Second Edition methods, while others require the use of Third Edition methods.

State policies on the use of draft methods vary from blanket approval of some methods to methods review on a case by case basis. In addition to the mandatory applications specified above, EPA Regions can request the use of specific Second Edition, Third Edition, or draft SW-846 methods for other regulatory applications.

What is the current version of SW-846 that must be used for mandatory applications?

The use of the SW-846 Second Edition, including Updates, is still mandatory for these applications. Also, the Final Rule replacing the Second Edition with the Third Edition of SW-846 (including Update 1) for these mandatory applications is passing through the final stages of the regulatory process. We expect to promulgate this Final Rule early in 1993.

What is an "EPA-approved" method?

This is a term that has been bantered about quite a bit recently, sometimes rather loosely, particularly with respect to some of the new analytical technologies. From the RCRA point of view, "EPA Approved" means that a method has been incorporated by reference in a Final Rule which has been published as a *Federal Register* Notice (FRN) either into SW-846 or directly into the RCRA regulations. In short "EPA Approved" methods are promulgated methods which can be used without special permission for RCRA applications where the use of SW-846 methods is mandatory. Therefore, until a method is promulgated by an FRN, it is not an approved method for these mandatory applications, no matter where it may be in the regulatory process.

EPA Regions may grant a general Regional approval to certain draft analytical methods for use within a Region for specific applications. In addition to this general Regional approval, Regions and States may grant facility-specific approval for the use of draft methods for permit-specific applications. Examples of facility-specific approval include the use of Method 8330 by some Regions for the analysis of explosives residues by High Performance Liquid Chromatography and Method 8290 for the analysis of dioxins by High Resolution GC/MS. Both Method 8330 and Method 8290 are currently draft methods which will be proposed in the Second Update.

How does a method become "EPA-Approved"?

This is a very brief overview of the EPA regulatory process, through which SW-846 regulatory packages must pass. SW-846 methods are not published in the Federal Register, but are incorporated by reference in the appropriate RCRA regulations. The process roughly follows the following steps and takes about 18 to 30 months to complete:

1) After methods are approved by the SW-846 Technical Workgroups,

technical comments are addressed, and a regulatory package is prepared. This regulatory package consists of a proposed rule, a preamble to the proposed rule, and the necessary transmittal documentation to pass it through the system.

2) After completion of the internal EPA review, the regulatory package is sent to the Office of Management and Budget (OMB) for its review and approval.

3) After OMB approval, the proposed rule is signed by the EPA Administrator, is published in the Federal Register, and becomes available for public comment. (The proposed methods are provided to SW-846 subscribers by the Government Printing Office for comment.)

4) After the public comments are addressed, the regulatory package goes through the same internal EPA and OMB reviews a second time, and the rule is promulgated through a second Federal Register notice.

Can "draft" methods be used for analyses performed under RCRA Subtitle C?

Yes, since most analyses performed for compliance with RCRA Subtitle C regulations fall outside of the scope of the mandatory applications of SW-846 methods, for which promulgated methods must be used. "EPA Approval" of methods is a factor only in the mandatory applications of SW-846 methods under RCRA, or in State Programs where use of SW-846 methods is mandated. For all other non-mandatory applications under RCRA, draft methods can, and, in many instances where they provide improved data, should be used.

Do SW-846 methods have to be performed exactly as written?

Monitoring requirements under RCRA Subtitle C specify only that the analyst must demonstrate that he can determine the analytes of concern in the matrix of concern at the regulatory level of concern. Since SW-846 methods are written as guidance for a wide variety of matrices, it is up to the individual analyst to optimize a particular method to his specific needs. Allowable modifications include adjustment of sample size or injection volumes, dilution or concentration of the sample, and modification or replacement of equipment. These method changes must be documented, as I stated previously the analyst must demonstrate that his method can meet the previously-stated analytical requirements.

However, methods are inflexible in some aspects, e.g. generation and use of an appropriate calibration curve, determination of recoveries and precision, and demonstration of applicable detection limits in the matrix of concern.

Philosophically, unlike other EPA Programs, RCRA specifies "what" needs to be determined, and leaves the "how" up to the analyst.

34 STEPWISE DEVELOPMENT PROCESS FOR REGULATORY ANALYTICAL METHODS

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ABSTRACT

It is unusual for an EPA Program Office to fund the development of new or untested technology for regulation analysis. In fact, most methods development projects are better described as the translation of a procedure practiced in a limited number of laboratories to a written SW-846 method that may be performed by many analysts. Although the same analytical techniques employed in commercial analyses may be employed during method development, there are significant differences in the approach to method development compared to commercial analysis. For example, there is no single approach to method development; scientists must make professional judgements during the conduct of a study. The quality assurance program is often a reflection of the analyst's commitment to measurement quality and familiarity with the analytical system rather than a set of defined acceptance criteria. This presentation describes a ten step process for method development and method validation conducted for the OSW: (1) Identification of need/definition of performance objectives, (2) Delineation of QC procedures, (3) Selection of analytical approach, (4) Determination of instrument sensitivity, (5) Method optimization, (6) Generation of performance data for a clean matrix, (7) Documentation of interferences, (8) Demonstration of matrix suitability, (9) Calculation of quantitation and detection limits, and (10) Workgroup review. These ten points will be illustrated using examples of method development efforts conducted for the OSW. Mechanisms that facilitate laboratories and manufacturers participation in the method development effort will also be discussed.

INTRODUCTION

The Methods Section of the Office of Solid Waste (OSW) has responsibility for developing and promulgating reliable analytical methods for the determination of chemicals on Appendix 8 or for waste characteristics (e.g., toxicity, flammability and corrosivity). These methods are designed for use in a variety of laboratories and have embedded quality control (QC) requirements that facilitate the intercomparison of data. Each method must be evaluated for suitability for the use in environmental or waste matrices. Central to the validation process is single laboratory testing, which establishes the quality of data that can be obtained using a method and its suitability for the soil matrix. Validation of potential SW-846 methods is an important element in OSW's quality assurance program. Following method validation, a SW-846 method and method validation report is reviewed by an OSW workgroup.

DEFINITION OF NEED

Each method development/evaluation project begins with a definition of need. This need is identified by the EPA Program Office responsible for the regulation driving the measurement. The statement of need generally includes the target analyte list, potential sample matrices, target detection levels, and QC requirements. At a minimum, method QC requirements must be compatible with SW-846 Chapter 1 as well as any other applicable general methods (e.g., Method 8000 - Chromatography). The definition of need is developed into the project data quality objectives and the target performance criteria.

ANALYTICAL APPROACH

The analytical approach for a method development or evaluation project is based on measurement sensitivity, stability/repeatability of the measurement, and bias. In addition, potential SW-846 procedures are evaluated on the basis of several qualitative criteria including the cost requirements for analytical hardware/equipment, any additional facilities requirements, ease of use/operator skill, cost per determination, and analyses per day.

In many cases, the analytical approach has been used for a similar application. Program Offices method studies are generally initiated after a technology has been demonstrated as useful for the analysis of environmental or waste matrices. Some of the sources for this information are provided below, along with the period of time that might be required to initiate a method evaluation study.

SOURCE	Available now	6-12 months	2-5 years
Instrument Vendors	X	X	X
EPA Regions and States	X		
DOE National Laboratories	X	X	X
ORD	X	X	X
USATHAMA/USDA	X	X	
Commercial Laboratories	X	X	
Chemical Literature		X	X

Program Offices often re-test methods obtained from other sources in order to establish that the sensitivity, precision, ruggedness or matrix suitability are appropriate for their regulatory needs.

INITIAL EVALUATION

Initial evaluation of a method generally starts with establishing that the technique is operating under statistical control. The detector linearity and dynamic range are then established for determinative methods using a calibration using at least five concentrations of standards. The analyst will determine whether there are interferences in a clean control matrix (i.e., no false positives) for sample preparation methods.

Critical measures of data performance will be established during single laboratory testing. These include the accuracy, precision, and limits of detection/quantitation that can be achieved in sample matrices of concern to the RCRA program. In addition, single laboratory testing will establish the probability of obtaining false positives and false negatives with the technique. Initial laboratory testing is generally conducted using soil and water spiked with known concentrations of target and interfering analytes.

OPTIMIZATION AND RUGGEDNESS TESTING

In many cases, additional method optimization may be conducted to provide the target sensitivity, accuracy, precision or matrix suitability required by the Program Office. This optimization is accomplished by systematic alteration of method conditions in order to achieve the performance targets.

Ruggedness testing may also be conducted on candidate methods if they perform erratically or when it is important to specify control limits for critical method parameters. AOAC-type ruggedness testing assumes that each method parameter varied in the test is independent. Limited factorial designs (e.g. Planket-Berman) are more appropriate when dependent method variables are tested. In either approach, previously identified method parameters are varied between two conditions and statistical evaluations of the results are used to interpret the performance changes.

PERFORMANCE TESTING

Method performance is first established using a spiked clean soil. Aliquots of one soil type prepared at three concentrations: one half the target detection limit, two times the target detection limit and 10 times the target detection limit. Method bias (accuracy) is determined at each concentration by calculating the mean recovery of the spiked (or characterized) analytes for the seven replicates. Method repeatability is established by running the method over several weeks.

$$bias = \frac{\bar{X}}{X} \times 100\%$$

$\bar{X}$ = Mean value for the seven replicate determinations

X = Spiked or characterized concentration

Method precision is determined by calculating the percent relative standard deviation of the spiked analyte recoveries for the seven replicates at each concentration.

$$precision = \frac{\sigma}{\bar{X}} \times 100\%$$

$\bar{X}$ = Mean value for the seven replicate determinations

σ = Standard deviation for the seven replicates

After demonstrating suitable performance for the analysis of a clean matrix, performance testing of more challenging matrices of interest to the Program Office is conducted. Most current SW-846 methods provide data on three different types of RCRA matrices. Those samples may be characterized reference materials or spiked matrices containing known amounts of target analytes. Analyses of these samples also provides information on the effects of matrix interference. However, it would be nearly impossible to generate data on all matrix/analyte interactions. As a result, Chapter 1 of SW-846 provides guidance on evaluating the suitability of methods for specific samples.

WORKGROUP REVIEW

Once methods are evaluated, they are submitted for approval by the Program Office. In the case of OSW, workgroups meet to discuss organic, inorganic, and miscellaneous methods as well as quality assurance issues. Workgroup members are provided methods in SW-846 format, which includes:

- Scope and Application including analytes and matrices for which the method is recommended
- a method summary (scope and principles)
- a list of required apparatus and reagents
- instructions for the preparation of standards
- sufficient detail and clarity in any sample preparation procedures
- detailed analytical procedure
- Calibration procedure

- Method interferences
- calculation procedures

The workgroup is also provided performance data, including:

- the accuracy and precision of recoveries
- detection and quantitation limits
- Example output
- Analytical QC data and control charts
- results of confirmatory analysis
- Results of ruggedness testing, if performed
- Discussion of selectivity and sensitivity of the method
- Discussion of limitations of the method

The workgroup reviews the method narrative and the performance review. They have the options of approving the method, rejecting the method or requesting additional information.

CONCLUSION

The process of method development and evaluation does not seem to be a growing activity in our industry. This is unfortunate given the analytical challenges that we face in producing scientifically credible data that is useful to decision makers. Chemists need to educate clients about what is the most appropriate type of analysis. Regulators need to show greater flexibility in allowing alternates to standard methods.

35 RECYCLING PROGRAM FOR LABORATORY ORGANIC SOLVENTS
Methylene Chloride and Freon-113

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ABSTRACT

Due to hazardous waste disposal costs and associated environmental concerns, programs for hazardous waste reduction and recycling of laboratory chemicals are of increasing importance. A large fraction of the hazardous wastes generated by environmental testing laboratories originate from the solvents used to extract organic hazardous constituents from aqueous, soil, and waste samples. These solvents include methylene chloride ($MeCl_2$), $MeCl_2$/acetone mixtures, diethyl-ether, hexane, and Freon-113. Glassware rinsing and chromatographic extract clean-up techniques such as gel permeation chromatography also produce significant quantities of waste solvents.

Minimization of solvent use is attained by selection/recommendation of the EPA method, methods development and modification, and instrument and glassware selections. Modified procedures must meet or exceed all Quality Assurance/Quality Control (QA/QC) parameters specified by the method. Continuous liquid-liquid extraction techniques for EPA method 8270 are currently developed to use less than 200 mL of $MeCl_2$ per sample. Similar solvent use reductions have been applied to pesticide/PCB and herbicide extractions. Solid phase extraction techniques such as those developed for the USEPA drinking water program use much less solvent and are recommended to clients when appropriate to the sample matrix and the desired analytical objective. A solvent recycling program can minimize solvent consumption by processing waste solvents for re-use within the laboratory. An on-site solvent recycling program using spinning band distillation to purify waste solvents is presented for $MeCl_2$ and Freon-113. Detailed work with $MeCl_2$ and preliminary results for Freon-113 are discussed.

Our solvent recycling program begins with the recovery, collection, and segregation of waste solvents. Recovered solvents are segregated according to the type of laboratory operation. Recovered $MeCl_2$ is divided into GPC waste, extractor waste, general waste, and recovered condensate from solvent concentrations. Each type of waste receives different handling and processing prior to purification by spinning band distillation.

Purification of $MeCl_2$ by spinning band distillation produces 3 or more fractions. Handling and quality testing of each collected fraction are determined by the original segregated waste source. Quality testing includes specific gravity, GC/FID, GC/MS, GC/ECD, and FT/IR. Recycled solvent is returned to suitable laboratory operations based on testing results. Recycled $MeCl_2$ is demonstrated to be suitable for re-use in sample preparation for semivolatile analysis by EPA Method 8270. Estimates of labor and material costs demonstrate the cost effectiveness of the recycling program.

INTRODUCTION

In EPA pollution prevention strategies, source reduction is the preferred method for reducing waste. However, for those wastes that cannot be reduced at the source, recycling is considered the next best alternative.

A large portion of the hazardous wastes generated by analytical laboratories orgiginates from use of organic solvents in laboratory operations. Methylene chloride, Freon-113, methyl alcohol, hexane, acetone, and xylene, constitute the bulk of the solvents used by environmental testing laboratories.

Laboratory procedures which generate organic solvent waste include: glassware cleaning and rinsing, sample extraction and preparation, and liquid chromatographic techniques used for extract clean-up and/or analysis. Collected condensate from evaporative extract concentration techniques are a source of additional waste solvent. Many laboratories vent solvent vapors from extract concentration procedures directly to the atmosphere. Recycling solvents encourages the condensation and recovery of these solvent emissions.

Land disposal of solvents was banned by the EPA in 1986. Laboratories typically handle their solvent wastes by off-site incineration. Halogenated solvent wastes are normally segregated from non-halogenated as they require more costly incineration at facilities specifically designed to handle these materials.

Laboratory solvent wastes are well suited for recycling programs using distillation technology. Solvent recycling can be performed either on-site or off-site. On-site recycling refers to the laboratory performing all aspects of the recycling program. Off-site recycling is recycling performed by a commercial solvent recycling facility. After off-site recycling, processed material is either returned to the original generator using a custom or toll processing, or is sold on the open market. In either on-site or off-site recycling programs, appropriate solvent collection and segregation is required in order to produce optimum recycled solvent quality.

Advantages to recycling on-site include: generally favorable economics; more control over waste management (feedback loops for appropriate solvent segregation); reduced transportation risks; and reduced reporting requirements (currently RCRA treatment permits are not required to recycle on-site). Analytical testing laboratories are well suited to an on-site recycling program. They can perform the quality testing necessary for their recycled solvents and can utilize the recycled material appropriately, based on the quality testing performance data. Analytical testing laboratories also should have the technical expertise to handle these hazardous wastes. Disadvantages to on-site recycling include the initial capital costs, safety hazards associated with handling solvent wastes, permitting requirements imposed by some states, and the additional labor, technical, and managerial concerns.

Advantages to off-site recycling are the reduced technical and managerial demands, and in limited cases-improved economics for small solvent volumes. Currently, economical off-site recycling of laboratory solvent waste is limited to certain geographic areas primarily due to hazardous waste transportation costs. Off-site recycling commonly recycles non-halogenated solvents (flammables) as a fuel source.

Energy Laboratories Inc (ELI)., of Billings, Montana is committed to reducing the generation of hazardous wastes and the consumption of solvents. This paper describes the ELI recycling program which is fully operational for methylene chloride, the solvent used in largest volumes. Preliminary results with Freon-113 recycling efforts are also discussed.

EXPERIMENTAL

Materials

Table 1 provides a list of materials and their uses in the recycling laboratory.

Methods

$MeCl_2$ Waste Processing

The handling of methylene chloride waste streams is illustrated in Figure 1. The $MeCl_2$ waste stream processing flow chart lists the procedures associated with recycling four categories of $MeCl_2$ waste. Throughout the solvent collection and recycling process, segregation of waste and distillate fractions is maintained.

Methylene chloride wastes are segregated according to the types of contaminants expected. Wastes with percent levels of other solvent contaminations are handled separately. Generally, higher boiling trace contaminants present few problems for purification by distillation. However, waste with high levels of higher boiling contaminants, such as phthalates, may require pre-distillation, or double-distillation in the high-purity distilling system. Solvent contaminated with high levels of low boiling compounds (other solvents), particularly those with similar boiling points, or which form azeotropes with $MeCl_2$, require specialized handling. Methyl alcohol and water are known to form azeotropes with $MeCl_2$.

Phase separation is performed by decanting or by transfer using separatory funnels. Bulk filtration (if required) uses sediment settling, decanting, and vacuum filtration through 10 inch diameter Whatman #4 filter paper. Pre-distillation is used to remove non-volatile soluble residues. Pre-distillation is performed with custom manufactured glassware which allows the teflon spinning band distilling column of the ABC Integrity 2000 system to be by-passed. Automation of pre-distillation is achieved by using the electronic control systems of the ABC Integrity 2000. Solvent drying is done by mixing calcium chloride pellets (5-10 g/L) with the pre-distilled waste solvent for 24 hours. In-line vacuum solvent filtration (see Table 1, Materials list) is used to separate the drying agent from the solvent. In-line filtration is favored since solvent vapor emmisions are controlled and recoverable.

Distillation is performed using the ABC Integrity 2000 spinning band distillation system. System operating parameters are per the manufacture's recommendations with modifications made relative to waste characteristics. The system is operated with manual switching between the collection of the forecut and the main fraction. Handling of forecut and still-bottom fractions is discussed later.

Collect fractions are preserved with cyclohexene to a level of 0.01% (v/v). The preservative prevents the accumulation of hydrochloric acid (HCl) in the methylene chloride. Cyclohexene or amylene are commonly used for this purpose. These compounds do not prevent the formation of acid in methylene chloride, but undergo an addition reaction with HCl across the double bond. Proper solvent storage minimizes decomposition.

GC/FID, GC/MS, and other screening procedures, are used to determine the collected fraction quality. Based on screening results, the material is segregated for re-distillation or appropriate use. Segregated material is composited with material of similar quality to generate larger lots of material. Composited material is further tested and distributed for appropriate use.

Freon-113 Waste Processing

A flowchart for recycling Freon-113 Waste Streams is shown in Figure 2. The procedures for handling Freon-113 are comparable to those for methylene chloride. Recycled Freon-113 quality is characterized according to intended use. Recycled IR grade Freon-113 (IRF113) has no significant absorbance at the C-H stretching wavelength 2950 (cm^{-1}) used to quantitate Total Petroleum Hydrocarbons by IR as per EPA Method 418.1. EPA method 413.2 for oil and grease by IR also has similar requirements. Trace levels of contaminants may be acceptable in IRF113 since quantitation by IR is performed by measuring the differences between the absorbance of the extracted sample against the reference solvent. Levels of acceptable purity have not yet been determined. Non-IR grade recycled Freon-113 (NIRF113) is contaminated with part per hundred or less (determined by GC/FID) of volatile solvents and exhibits a significant interfering IR absorbance.

Complete segregation of recyclable IRF113 from recyclable NIRF113 is critical. Certain compounds/solvents cannot be removed effectively from Freon-113 by spinning-band distillation. These compounds (yet to be identified) either azeotrope with, or have similar boiling points to Freon-113. These co-distilling compounds are considered contaminates when their concentration and/or interfering absorbance is significant. Co-distilling/interfering compounds may persist regardless of the number of re-distillations, and, if mixed with IRF113 would irreversibly contaminate the IRF113. Unleaded gasoline is known to contain non-removable compounds of this type.

NIRF113 is suitable for use in determining oil and grease by gravimetry since the contaminants are determined by the mass of extracted residues after evaporation. NIRF113 has insignificant residue after drying. Evaporated solvent condensate collected from procedures using NIRF113 is suitable for recycling only as NIRF113.

Distillate Fractions Handling

Handling of distillate fractions for $MeCl_2$ and Freon-113 is shown in Figure 3. Segregation of all materials is maintained by batch and fraction type. Pre-distillations are performed automatically using the modified ABC Integrity 2000 system. Distillations are performed using the ABC Integrity 2000 teflon spinning band distillation system. This distillation system has been tested by the manufacturer to have 50 theoretical plates or more with cyclohexane and methylcyclohexane.

High contaminant levels, regardless of boiling point, can effect the quality of any separation. Experience has shown that increasing the volume of the forecut and still-bottom fractions can improve the quality of the collected fraction. The number of collect fractions can be subdivided manually if desired.

The amount of forecut collected varies according to the waste type and system operating conditions. Azeotropes and lighter boiling materials are collected in the forecut. Water forms azeotropes with both $MeCl_2$ and Freon-113, and is always collected in the forecut. The solvent drying step prior to distillation reduces the amount of forecut needed to remove trace water from a Freon-113 or $MeCl_2$ solvent waste. Often, free water is observed as an immiscible layer in the initial portion of the forecut. Head temperature and observation of moisture condensate at the head of the distilling column are used to determine the presence or absence of water. Forecut is not complete until all moisture is removed. Collected forecuts should be dried and re-distilled with other similar materials. Due to possible percent levels of other solvents in a

re-distilled forecut, recycled forecut may be suitable only for glassware washing and other similar laboratory operations. Specialized handling techniques can be used to remove certain solvents prior to re-distillation.

Depending on the quality of starting material, still-bottoms (raffinate) from pre-distillations and distillations are either disposed of as hazardous waste or are retained and combined for further recycling with other similar still-bottom material. The amount of forecut collected when reprocessing them should be minimal.

QA/QC Procedures

Testing procedures are selected to characterize material suitability based on intended use of the recycled product. Recycled $MeCl_2$ and $MeCl_2$ waste solvents were prepared for GC/MS analysis using the solvent concentration procedure normally used for EPA method 3520/8270 analysis. J.T. Baker "Capillary Analyzed" $MeCl_2$ is used as the control solvent. Recycled solvents are concentrated from 200 mL to a 1 mL final volume in a Turbovap prior to analysis. Solvent concentrates are analyzed according to EPA method 8270 on a Hewlett Packard 5970 MSD. The selected list of 8270 analytes tested for represents most of the analytes from the CLP Semivolatile Target Compound List. A five point calibration ranging from 20 μg/ml to 150 μg/mL was used. Internal standards fortification levels were 40 μg/mL. The gas chromatograph was operated in the splitless injection mode with a 0.5 μL injection on a 30 meter 0.25 mm i.d., 25 μm film thickness, XTI-5 capillary column. The GC was temperature programmed: 40° C hold 4 minutes, 20° C/min. to 120° C., hold 1 minute, 10° C/min to 250° C hold 2 minutes, 10° C/min to 310° C hold 6 minutes.

Additional QA/QC testing for $MeCl_2$ such as density, acidity, solvent purity by GC/FID and GC/ECD (concentrated then hexane solvent exchanged) are performed, but not reported here. Freon-113 is tested for impurities by GC/FID, and also by Infrared (IR) according to EPA Method 418.1.

RESULTS AND DISCUSSION

Analytical data which demonstrate the effectiveness of recycling by distillation are shown in Figures 4 through 8. Chromatograms of solvent method blanks for these analyses are given in Figures 7 and 8. The material presented illustrates the results from recycling a highly contaminated $MeCl_2$ solvent waste. Figures 4, 5, 6, 7, and 8 are EPA method 8270 GC/MS reconstructed ion chromatograms (RIC) of the primary starting material, first distillation, second distillation, solvent method blank for Figures 4 and 5, and solvent method blank for Figure 6, respectively. Individual RICs are normalized to the largest peak present. Internal standards are at the same level in all RICs presented (40 μg/ml) and can be used to compare results between the RICs shown. Internal standards were added after concentration and thus concentration factors need to be accounted for. Target and non-target analyte GG/MS identifications and quantitations are discussed during the presentation.

Figure 4 is the RIC of the original starting material concentrated 20:1. The source of this material was general laboratory $MeCl_2$ waste. This waste required phase separation and bulk filtration to remove water and sediments. The resulting filtered product had a strong yellow tint and smelled of gasoline. The filtered material was pre-distilled to remove soluble non-volatile residues. The 1.5 L of still-bottom from the pre-distillation was disposed of as hazardous waste.

Figure 5 is the RIC of the collected fraction of the first distillation. The collected material was concentrated 200:1 for analysis by GC/MS. Total batch size was 19 L to give: 2 L of forecut; 15.5 L of collected fraction; and 1.5 L of still-bottom. No analytes on the EPA method 8270 list were detected above method reporting limits. However, the material was not considered suitable for use in EPA Method 8270 or other laboratory operations due a series of early eluting peaks observed in the RIC. The collected fraction was re-distilled and the forecut and still-bottom were recycled.

Figure 6 is the RIC of a second distillation which contained 15 L of the material shown in Figure 6, and 4 L of a similar material also requiring a second distillation. The distillate collected was concentrated 200:1 for GC/MS analysis. The distillation produced: 1.8 L of forecut; 13.5 L of collect; and 3.5 L of still-bottom. The forecut and still-bottom were recycled. The collected material is considered suitable for use in EPA Method 8270 and was also determined to be suitable for use in EPA method 8080 (data not shown).

Figures 7 and 8 are the solvent method blanks associated with the solvent concentration and analysis. Differences in GC/MS instrument sensitivity and the chromatographic peak shapes reflect analyses performed over two different time periods.

SUMMARY

Solvent recycling for analytical testing laboratories is environmentally responsible and economically viable. Recycling not only reduces disposal costs, but provides a reusable product at potentially less cost than the virgin solvent. Estimates of labor and material costs are given during the presentation.

The material presented here evaluates the potential for solvent recycling using purification by spinning band distillation. The purity of the recycled $MeCl_2$ solvent is evaluated relative to probable intended use. Quality assurance and quality control requirements for EPA method 8270, and other similar procedures, specify that target analyte cannot exist in the method blanks at concentrations above the reporting limits. Therefore, solvents used in sample preparations for EPA Method 8270 must be free of target analytes and interferences after equivalent solvent concentration techniques. American Chemical Society (ACS) specifications for solvent purity are also recommended guidelines for determining solvent quality. The quality of the recycled $MeCl_2$ product produced in the second distillation discussed here met these requirements. Some recycled materials not suited for use in sample extraction may be suitable for use in other laboratory operations such as glassware cleaning and rinsing.

Methylene chloride is particularly well suited for recycling by distillation since it is primarily used in analysis procedures for semivolatile compounds. Trace levels of other solvent impurities do not interfere in the analysis of semivolatile compounds. EPA Method 418.1 using Freon-113 extraction and analysis by IR is affected by trace levels of solvent impurities. Because trace levels of other solvents can interfere in IR analysis, recycling by distillation is more difficult and requires very careful waste solvent segregation.

ACKNOWLEDGEMENTS

The authors would like to thank the following people for their contributions: Gary Warren, Jack Hanewald, Jim Rasmussen, TJ Parker, Dan Dalbey, Bruce Williams, John Standish, and other chemists and staff of Energy Laboratories for their support and on-going cooperation in solvent collection, segregation, and testing; Jim Stunkel, Kevin Kelly, and Mark Orr of ABC laboratories for their technical assistance; Judy Gebhart of ICF-QATS for her editorial suggestions; and Roger Rourk Jr. and Paul Van Trieste of B/R Instruments for the pre-distilling glassware.

TABLE 1
SOLVENT RECYCLING LABORATORY – MATERIALS and EQUIPMENT LIST

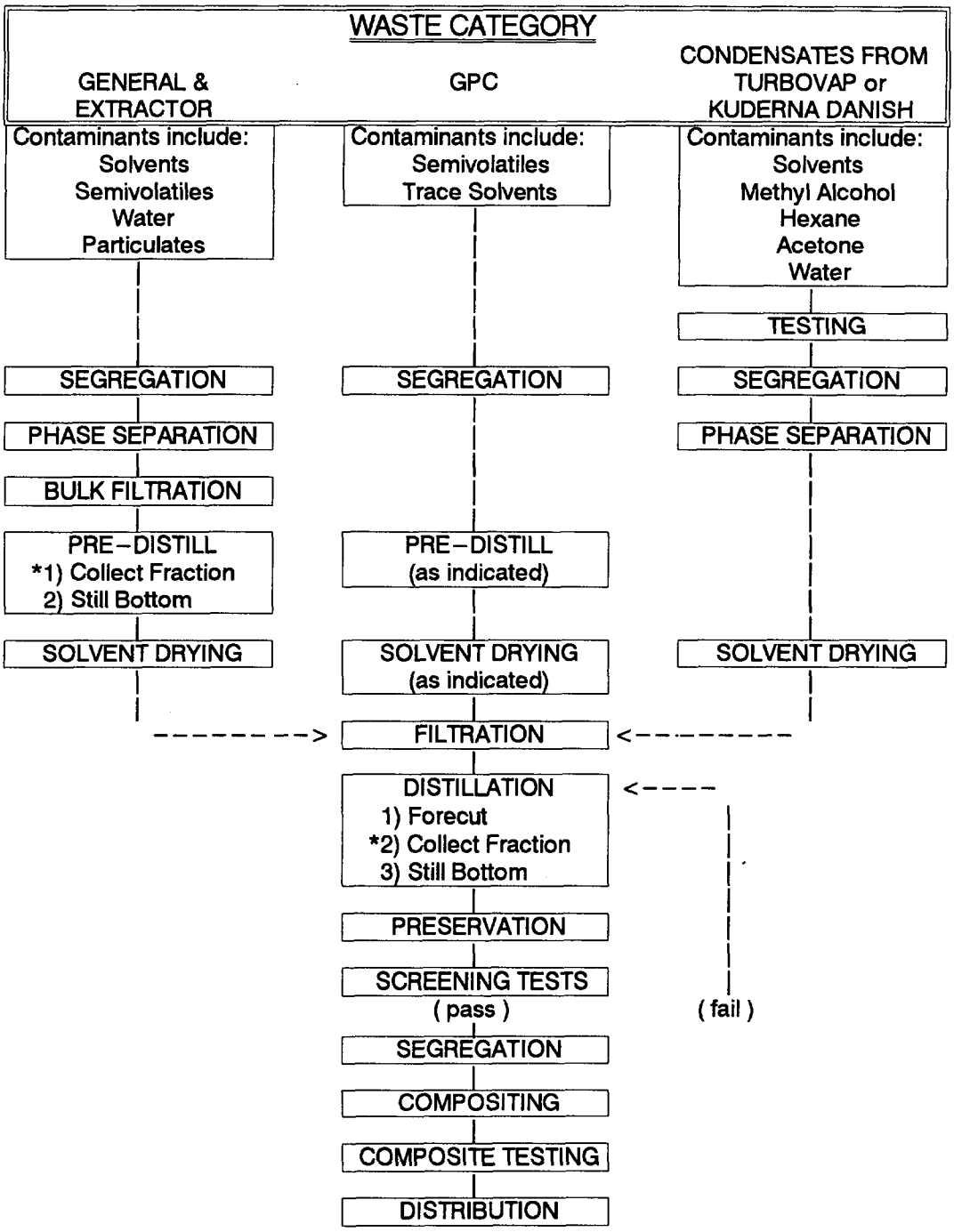
FACILITIES	FUNCTION
Solvent preparation area	Site for solvent handling
Distilling apparatus area	Site for distillations
Fume Hood or equivalent vapor control system	Solvent vapor removal
Bulk solvent storage area	Storage of solvents
Two, 110 volt 20 amp circuits	System power
Deep well sinks	Glassware washing

APPARATUS	FUNCTION
ABC Integrity 2000 automated spinning band distillation system – 19 Liter option	Distillation and Pre–distillation
Custom Glassware to fit ABC Integrity 2000	Pre–distillation
19 Liter pot flask (ABC)	Pre–distillation
2 Liter separatory funnels	Phase separation
5 inch powder funnels (glass)	Solvent transferring
Oilless solvent resistant vacuum pump (Cole Parmer teflon coated diaphragm pump)	Vacuum filtration and solvent transferring
Cryotrap	Vacuum filtration vapor recovery
Ice bath	Vacuum filtration vapor recovery
4 Liter vacuum flask	Bulk filtration
10 inch diameter buchner funnel	Bulk filtration
Whatman #4 filter paper, 24 cm	Bulk vacuum filtration
Alltech In–line filter degasser	In–line vacuum filtration and transferring
Whatman #41 filter paper, 4.7cm	In–line vacuum solvent filtration
Anhydrous calcium chloride pellets	Solvent drying
Cyclohexene	Methylene chloride solvent preservative
Hydrometers	Density determinations
Solvent storage containers (Clean empty 4 Liter amber glass solvent jugs) (Clean empty 100# Freon–113 Cans)	Solvent fraction storage
Sampling containers (40 ml VOA vials, 4 Liter amber glass jugs)	Sampling
Hazardous waste storage containers	Storage of un–recyclable solvent wastes
Analytical testing laboratory	Materials testing

MISCELLANEOUS APPARATUS	FUNCTION
Aluminum foil	Clean work surface, vapor control
Tools	Setup and maintenance
Teflon tape	Fittings and sealing solvent containers
Nitrogen gas supply (clean and dry)	Evacuating solvent vapors from containers
Drum cart	Drum handling
Cleaning brushes	Glassware cleaning
Glassware cleaning detergents	Glassware cleaning
1:1 Sulfuric acid	Glassware cleaning
Methyl alcohol	Glassware cleaning
Transfer pipets (5, 15 and 25 mL)	Sample collection
Safety equipment	Safety
Teflon tubing	Solvent transfer
Teflon squeeze bottle	Solvent handling
Rubber stoppers	Vacuum system connections

Figure 1

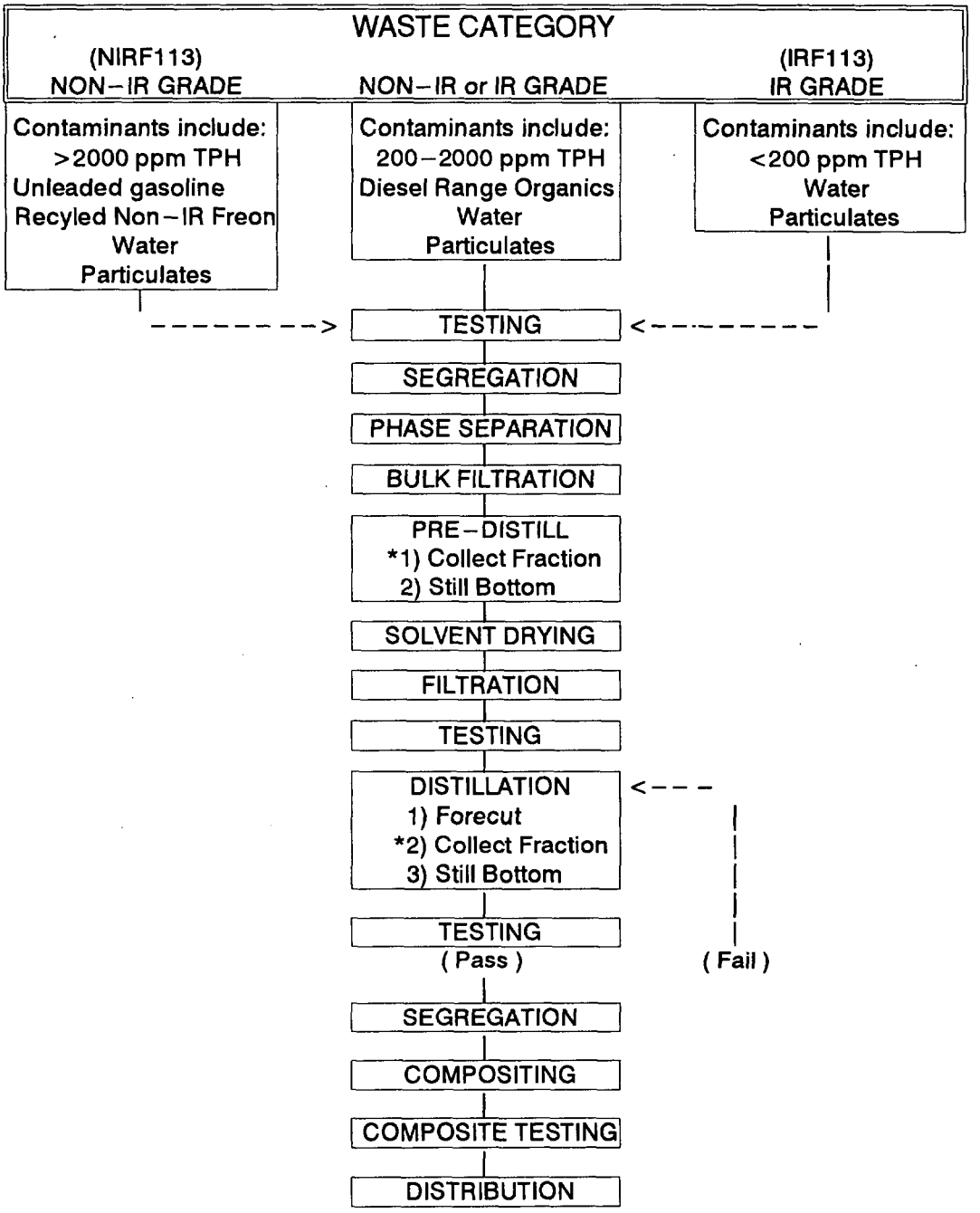
METHYLENE CHLORIDE WASTE STREAMS
Processing Flowchart



*Collect Fraction is processed towards final product. See Figure 3 "Distillations" for handling procedures of other fractions.

Figure 2

FREON-113 WASTE STREAMS
Processing Flowchart

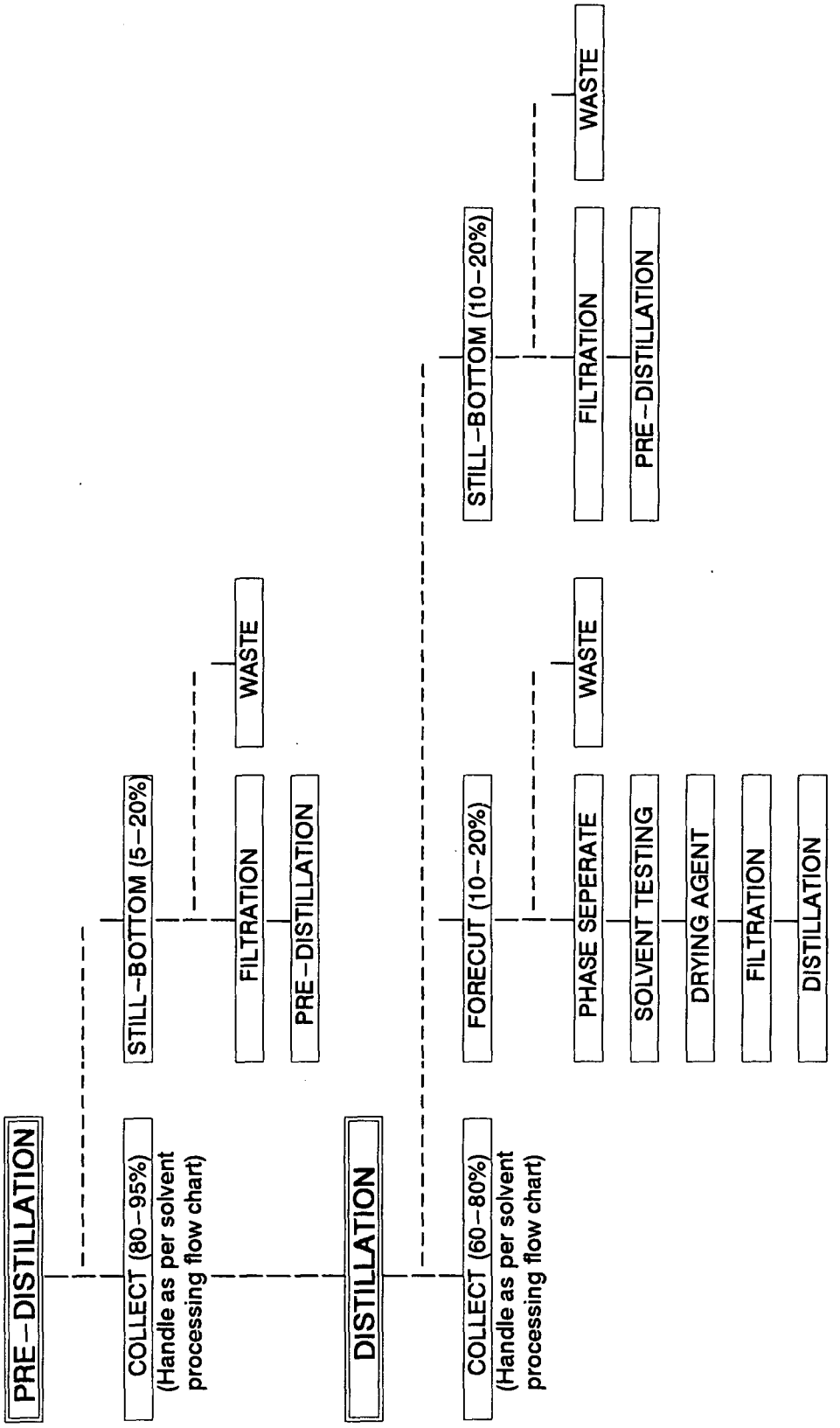


*Collect Fraction is processed towards final product. See Figure 3 "Distillations" for handling procedures of other fractions.

Figure 3

DISTILLATIONS

FRACTIONS HANDLING



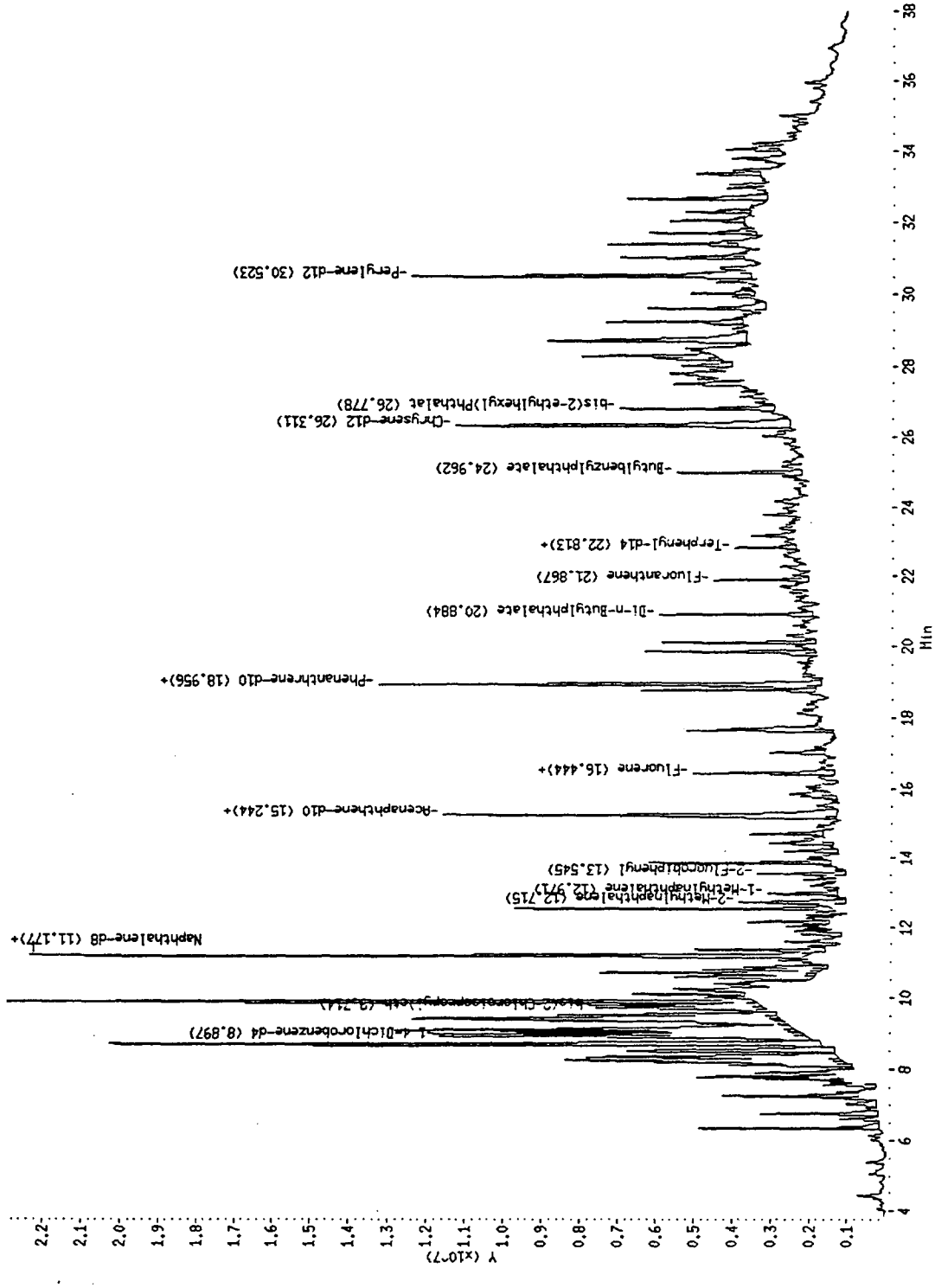


Figure 4. Reconstructed Total Ion Chromatogram of General Methylene Chloride Waste concentrated 20 : 1 and analyzed per EPA Method 8270. Internal Standards at 40ug/L

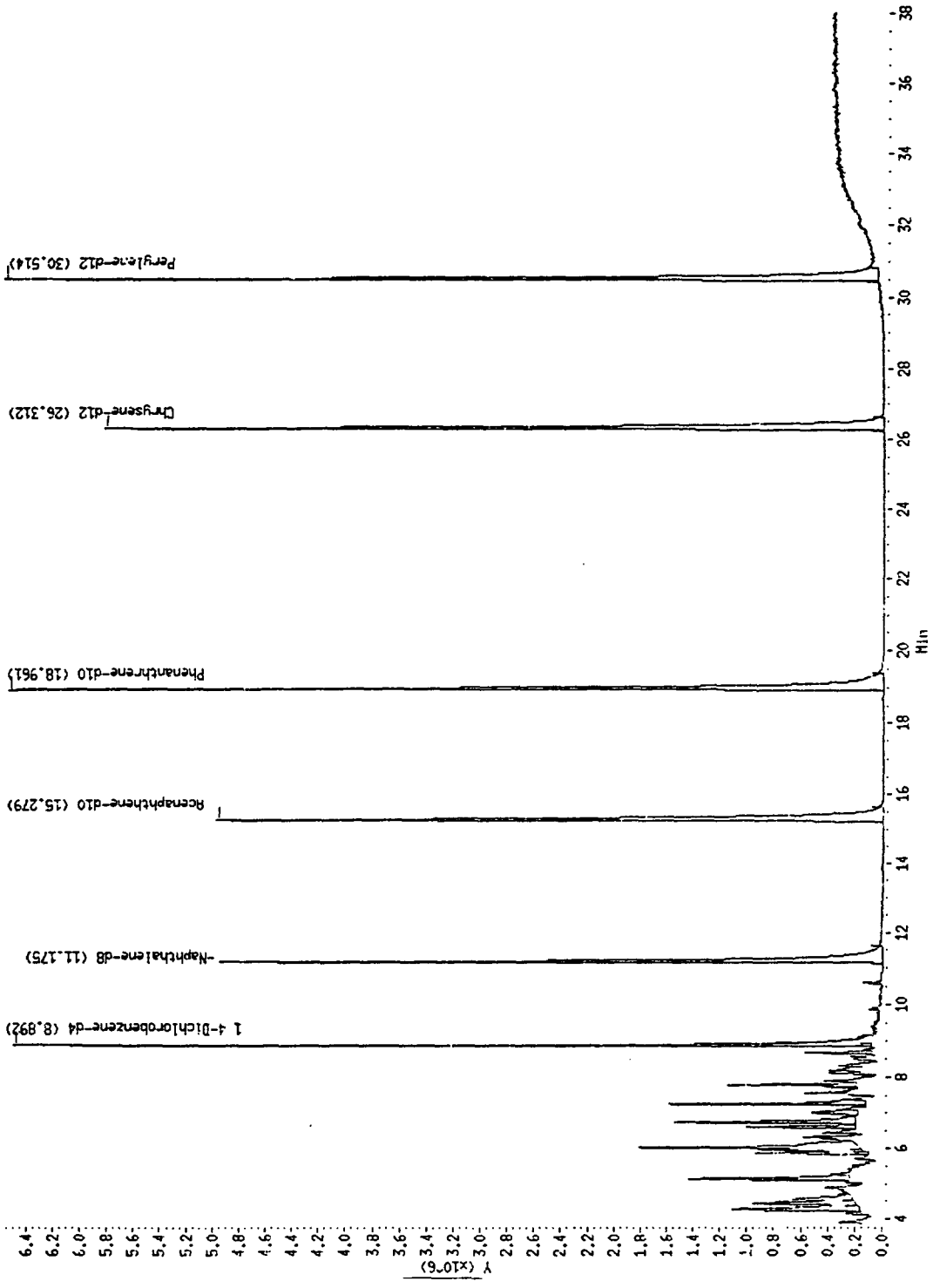


Figure 5. Reconstructed Total Ion Chromatogram from first distillation of General Methylene Chloride Waste concentrated 200:1 and analyzed per EPA Method 8270. Internal standards at 40ug/L

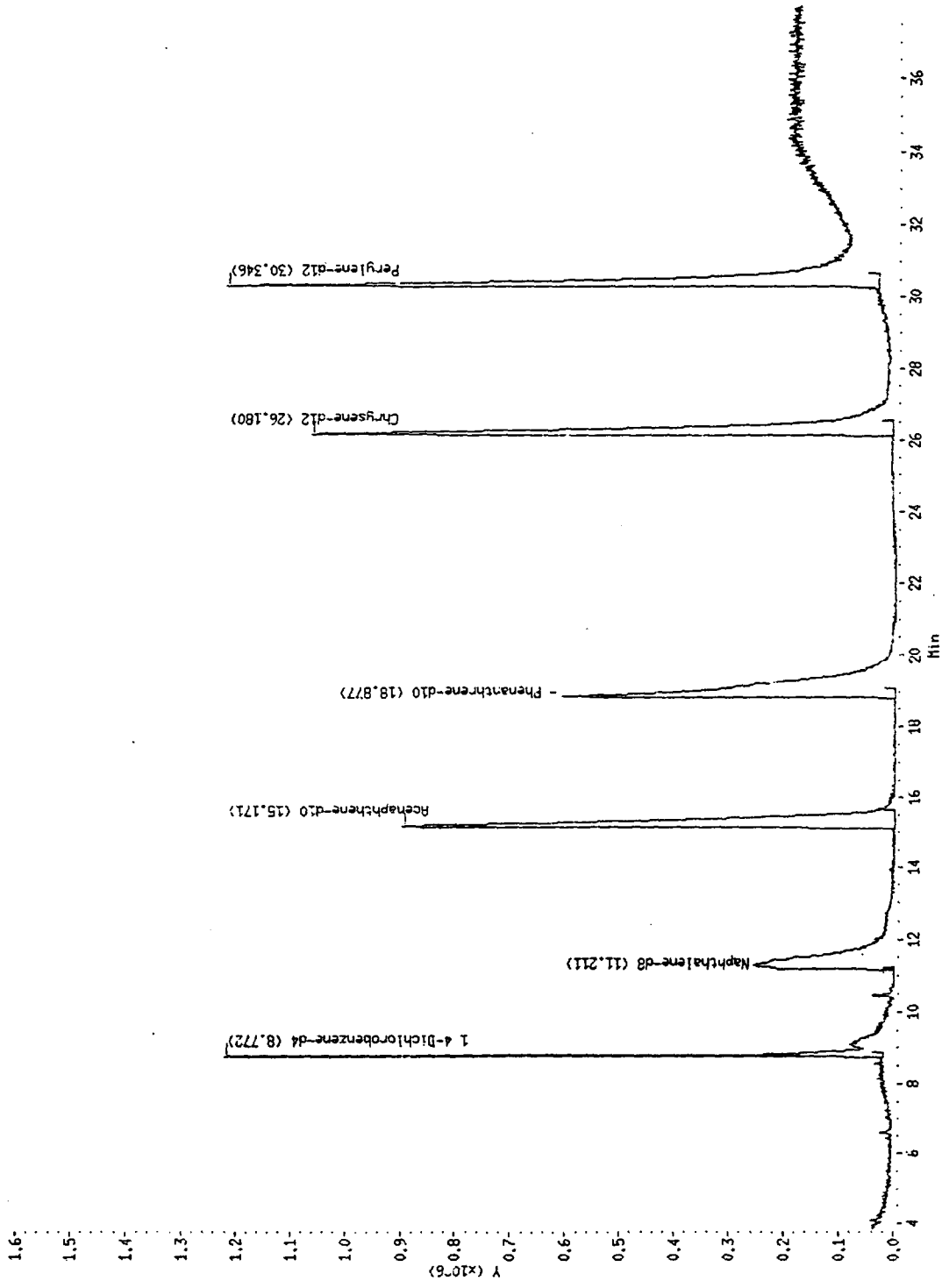


Figure 6. Reconstructed Total Ion Chromatograms from second distillation of General Methylene Chloride Waste concentrated 200:1 and analyzed per EPA Method 8270. Internal standards at 40ug/L

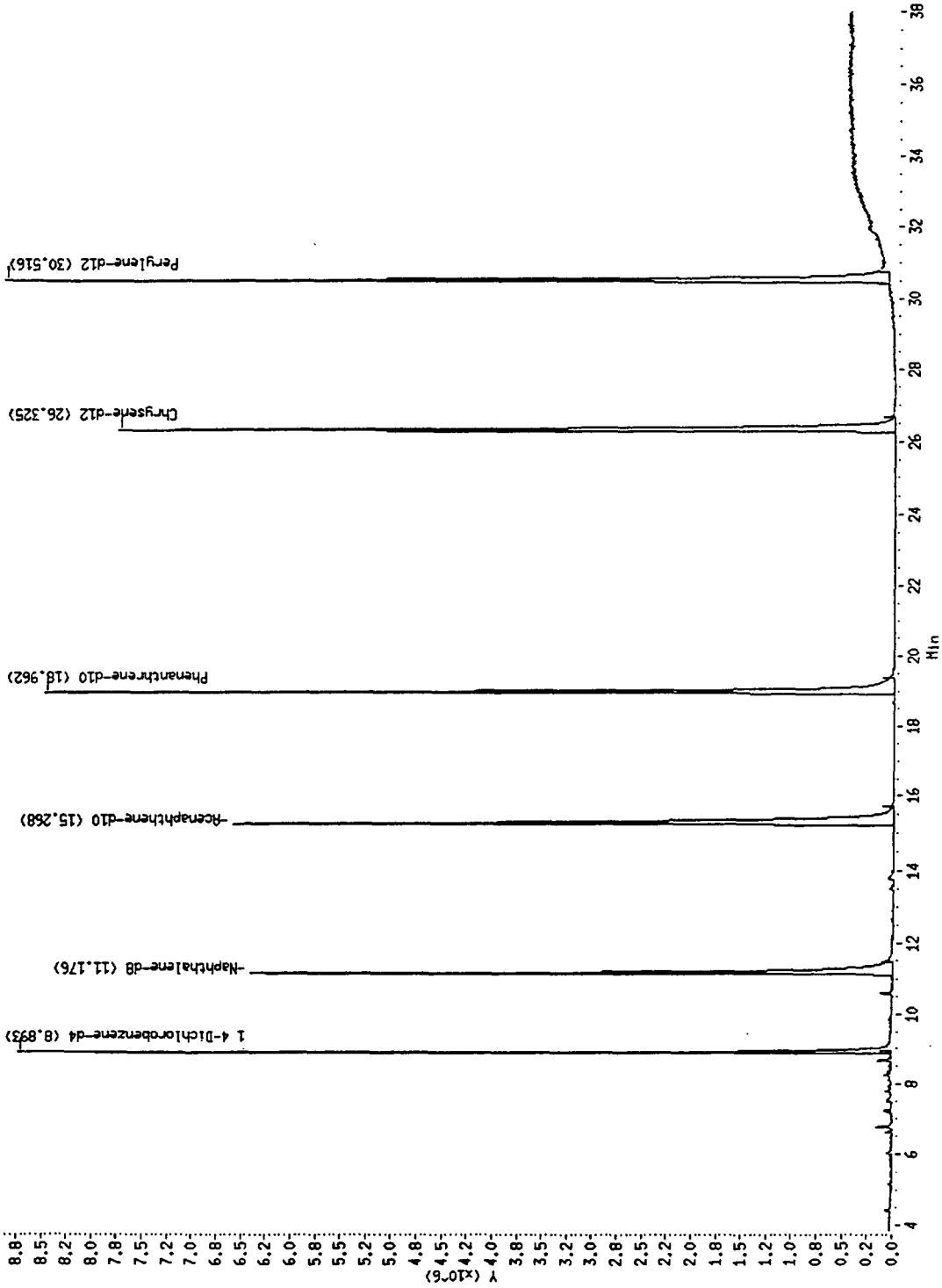


Figure 7. Reconstructed Total Ion Chromatograms of Solvent Method Blank for Figures 4 and 5. Solvent concentrated 200:1 and analyzed per EPA Method 8270. Internal standards at 40ug/L

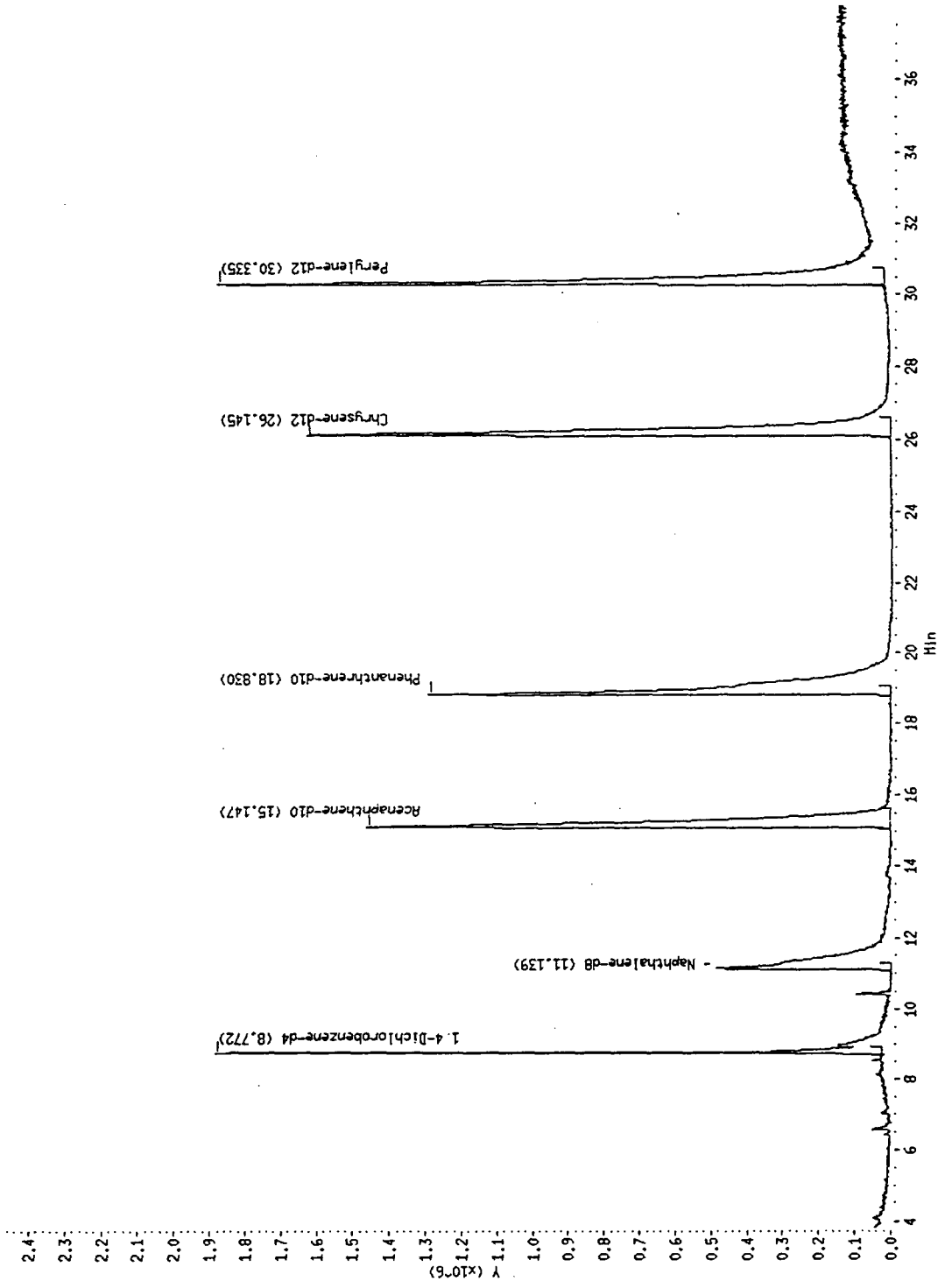


Figure 8. Reconstructed Total Ion Chromatograms of Solvent Method Blank for Figure 6. Solvent concentrated 200:1 and analyzed per EPA Method 8270. Internal standards at 40ug/L

36 The Technology and Performance of Several New Immunoassay Methods and the RISc 2000 Instrumentation System.

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EnSys Inc.

Data generation is often the rate-limiting element that influences the overall efficiency of the environmental clean-up process. New immunoassay methods are providing a faster and less expensive way to detect the pathogenic compounds that are present in the environment.

We have developed a number of immunoassay methods that expedite site mapping, remediation and monitoring activities by providing reliable results immediately and for less cost. The immunoassay methods for Pentachlorophenol, PCB's and Total Petroleum Hydrocarbon detection have been previously reviewed and have been accepted for use by the EPA.

Additional methods, and a RISc 2000 instrumentation system, have been developed and evaluated. These new methods will detect PAH's, explosives (i.e. TNT, RDx), and petroleum contamination in a variety of matrixes. The PAH and Petroleum Contamination tests use monoclonal antibody reagents in a chromogenic enzyme immunoassay format. The tests for explosives use the chromogenic chemistry of the recently accepted EPA method 8510. All of the tests permit the simultaneous testing of multiple samples at multiple detection levels and provide results within 30 minutes. The PAH, Explosives and Petroleum Test for Water all retain our conservative approach to environmental testing and have demonstrated a >95% confidence in their ability to detect contamination when used in accordance with the recommended protocols.

The EnSys RISc 2000 Instrumentation System has been developed to support the expanding library of immunoassay methods that are currently available or that will be introduced. The instrument rapidly analyzes the kinetics of the immunoassay's chromogenic reaction and uses this data in the calculation of results. The RISc 2000 instrument will read and record sample results at the rate of one every 10 seconds. System characteristics include faster results, additional quality control, and a printed report that summarizes the data obtained and the interpretation of results. This paper will review the applications, chemistry and performance characteristics of the methods and instrumentation developed.

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SCREENING OF TCLP EXTRACTS OF SOIL AND WASTEWATER FOR 2,4-D BY IMMUNOASSAY

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ABSTRACT

A commercially available enzyme immunoassay kit has been adapted to screen TCLP extracts of environmental samples for the regulatory action levels of the commonly used herbicide, 2,4-Dichlorophenoxyacetic Acid (2,4-D). The immunoassay was originally designed to quantitate very low concentrations of 2,4-D in water and includes calibrators at 1, 10 and 50 ppb. A simple one-step 1:1000 dilution of a TCLP extract brings the detection range of the assay in line with the 2,4-D toxicity characteristic established by the EPA at 10 ppm. The method which combines the standard TCLP extraction with dilution and subsequent analysis by a magnetic particle-based ELISA has been evaluated for sensitivity, matrix effects, accuracy and susceptibility to interferences. The results of the evaluation studies are described here.

INTRODUCTION

The Methods Section of the EPA Office of Solid Waste has stated a need for more rapid, less expensive field screening procedures that do not compromise the accuracy of pollutant evaluation. Availability of reliable, sensitive, inexpensive screening of large sample loads of potentially contaminated samples coupled with subsequent quantitative analysis of positives by established instrumental methods is an approach that addresses this need. The Methods Section of OSW has provided an outline of the type and quantity of work needed to demonstrate whether a proposed procedure is suitable for inclusion in SW-846 as a screening method. Using this outline as an experimental model, a demonstration of the performance characteristics of an immunoassay screening method for 2,4-dichlorophenoxyacetic acid (2,4-D) has been completed and is presented here.

Currently approved SW-846 methods for analysis of 2,4-D in soil or water samples require the performance of difficult solvent extractions and chemical derivatization reactions by highly trained chemists and the use of expensive analytical instruments (Methods #8150 and #8151). The use of the Toxicity Characteristic Leaching Procedure (TCLP/Method 1311) as the method of choice for preparing extracts of liquid and solid wastes for subsequent analysis of the original fourteen priority pollutants, including 2,4-D, heavily influenced the design of the study. All wastewaters and soils used in demonstrating the capability of the immunoassay method were subjected to the Method 1311 extraction procedure prior to analysis. The 2,4-D RaPID Assay® kit, a magnetic particle-based immunoassay for 2,4-D developed and manufactured by Ohmicron, has been commercially available since 1992 for the determination of part per billion levels of

the herbicide in water. This study shows that the immunoassay can be readily adapted for use as a screening method for analysis of TCLP extracts for the presence of 2,4-D at the regulatory level of 10 ppm.

MATERIALS AND METHODS

Equipment and reagents: 2,4-D RaPID Assay kits, 12 x 75 mm disposable plastic test tubes, 2,4-D TCLP Sample Diluent, precision pipets, magnetic separator, RPA-I photometer and vortex mixer are available from Ohmicron, Newtown, PA. 2,4-D powder for gravimetric preparation of spiking stock solutions was obtained from Reidel-de Haen (Hanover, Germany). All stock solutions were prepared in acetonitrile (pesticide grade). The accuracy of preparation of the stock solutions was assessed by comparison with an EPA certified standard solution (5000 µg/mL in acetonitrile) purchased from NSI Environmental Solutions, Research Triangle Park, NC.

Environmental Samples: Several water samples were studied for matrix effect. They included municipal tap water from Newtown, PA and surface water ("runoff") collected from a stream that flows through eastern Pennsylvania farmland. Wastewaters ("effluent") were collected from two separate drainage or discharge pipes in an agricultural community in south central New York State. Two soil types were evaluated: a Sassafras sandy loam (<5% organic matter) from New Jersey and a muck soil (46% organic matter) also from New Jersey.

Procedures: TCLP extractions were performed on soils and wastewaters as described in Method 1311. Spikes were made volumetrically into the final extract after filtration. The detailed TCLP extract screening procedure is published and available from Ohmicron as an "Application Procedure." All immunoassay results are converted to ppm 2,4-D in the waste extract for evaluation versus the regulatory level. Detailed directions on use of the immunoassay kit are found in the package insert.

Reference Method: Selected blank and spiked matrices were split and sent to a local reference lab for analysis by SW-846 Method #8150 for chlorinated herbicides.

RESULTS AND DISCUSSION

Establishing a cutoff concentration for the screening procedure. In order to use the quantitative results produced by the immunoassay in a qualitative way, a cutoff was established that could reliably discriminate the regulatory action level (10 ppm) from one-half that level (5 ppm). The TCLP extraction buffer (sodium acetate/acetic acid pH 4.9) was diluted with sample diluent and spiked with 2,4-D at 5, 7.5, 10 and 15 ppm. The spiking stock solutions were verified for accuracy before use by comparison with an EPA certified reference preparation. Results of this comparison are given in Table 1. Thirty replicates of each solution were then tested in three immunoassay batch runs. Figure 1 shows that use of a cutoff concentration of 7.5 ppm provides perfect discrimination

between 10 ppm and 5 ppm. This cutoff concentration falls near the mid-point on the calibration curve where precision is optimal. In fact, the distribution of results observed for a 7.5 ppm solution overlapped neither the 5 nor the 10 ppm distributions. In a similar manner the TCLP extract of a 2,4-D-free organic soil was spiked and tested by the immunoassay. In the case of the soil extract, ten replicates were tested at each level of interest in one assay run. A similar pattern of results distribution was observed when a TCLP extract of this muck type soil was used as the background matrix. Figure 2 demonstrates no overlap of the regulatory level with half its concentration. When the definitions of "positive" as greater than 7.5 ppm and "negative" as less than 7.5 ppm are applied to these data (Figure 3), the utility of the method as a screening procedure can be seen. A clear distinction is observed for the buffer and the soil extract matrices between 5 and 10 ppm.

Cross reactivity with chlorophenoxy compounds and other pesticides. The compounds listed in Table 2 were added to the immunoassay system until a response equal to 10 ppm 2,4-D was observed. When an effect equivalent to 10 ppm 2,4-D could not be found at a concentration of 5,000 ppm, cross-reactants were tested once at 10,000 ppm. Table 2 shows that most of the 2,4-D esters tested reacted with more potency in the assay than 2,4-D itself. However, these derivatized compounds are not ordinarily significant for environmental samples. Many commonly used pesticides that are structurally unrelated to 2,4-D showed no reactivity in the screening procedure up to 10,000 ppm. Structurally related compounds of regulatory interest, 2,4,5-T and 2,4,5-TP (Silvex), reacted much more weakly than 2,4-D. Greater than ten times more 2,4,5-T and approximately 135 times more Silvex would be required to produce a positive result with the screening method. In other words, a sample load of 130 ppm 2,4,5-T or 1375 ppm Silvex must be present to produce a result equivalent to a 10 ppm concentration of 2,4-D. Silvex was studied in greater detail because it is considered a priority pollutant and a regulatory action level for the TCLP Toxicity Characteristic has been published for this compound. Increasing amounts of Silvex were mixed with a 5 ppm 2,4-D solution in order to evaluate the amount of cross-reacting Silvex required to produce a response above the 7.5 ppm cutoff. Results shown in Table 3 indicate that between 100 and 200 ppm of Silvex would be required to elevate a marginal 2,4-D sample concentration (5 ppm spike) into the positive range. The regulatory action level for Silvex is 1 ppm. This concentration of Silvex by itself or in combination with negative or even borderline levels of 2,4-D in the immunoassay will not influence the baseline 2,4-D result whatsoever.

Matrix specific performance of the screening method. A variety of water and soil matrix types were studied to determine their interference, if any, with the immunoassay screening method. All matrices except the municipal water were first treated as solid or liquid waste according to the procedures given in Method 1311 (TCLP Procedure). Prior to spiking, each extract was diluted, tested in the immunoassay and determined to contain a non-detectable concentration of 2,4-D. Aliquots of the extract were then spiked volumetrically with 5, 10 and 15 ppm 2,4-D prior to 1:1000 dilution and subsequent immunoassay.

Municipal drinking water was not extracted or filtered but was spiked directly with 35, 70 and 140 ppb 2,4-D prior to 1:7 dilution and immunoassay. This dilution brought the drinking water concentrations into the same range of the calibration curve for analysis that was used for the waste extract testing. These lower spiking levels were chosen because the USEPA has proposed a MCLG of 2,4-D in drinking water of 70 ppb. Each of the 28 blank and spiked matrices were tested five times by the screening method.

Table 4 shows that the proposed screening method accurately discriminated negative and positive regulatory levels in all matrices tested. All results on matrices spiked at one-half the regulatory level (5 ppm) were less than 5.9 ppm 2,4-D showing no false positives (results >7.5 ppm). Results on matrices spiked at the 10 ppm regulatory level ranged from a low of 10.2 ppm to a high of 14.5 ppm with no false negatives (results <7.5 ppm). Samples spiked above the regulatory level at 15 ppm gave quantitative results from 15.5 to 19.1 ppm 2,4-D, again showing no negatives. The slight positive bias in quantitative results at the 10 and 15 ppm spike levels may be due to the fit of the calibration curve in this concentration range or may have been introduced in the spiking or dilution steps. The nature of the matrix appears to have no influence on the results. The results on the spiked drinking water demonstrates that the 2,4-D immunoassay can be applied in a similar manner (with a lesser dilution) to screening of drinking water matrices. Although the five replicates run here do not show statistical discrimination of the concentrations of regulatory interest demonstrated above, the drinking water results were calculated from the same portion of the 2,4-D calibration curve as for the waste extracts so the precision of the measurements should be identical to the buffer system shown in Figure 1. Undiluted drinking water from a variety of sources has been shown to produce no interference in the 2,4-D RaPID Assay (Lawruk, et al, 1993). Excellent discrimination of negative from positive results on drinking water samples in the 35 to 70 ppb range can therefore be expected.

Correlation with a quantitative SW-846 reference method. Selected samples from the spiking study were submitted for analysis by the SW-846 Method #8150 for chlorinated herbicides. The results of the analyses are given in Table 5. 100% method agreement was seen at 1/2 the regulatory level and at 1.5 times the regulatory level - an important goal for new screening methods as stated by EPA/OSW. The quantitative immunoassay results agreed with the spiked 2,4-D concentrations better than the GC results did. However, in cases where the spike level was frankly positive (15 ppm) or negative (5 ppm), the interpretations of the two methods were identical. The qualitative status agreement between the screening method and the reference method was more variable when the spiking concentration was at or near the cutoff of both methods (10 ppm). This was true in part because we are using different criteria to make the status judgment (7.5 ppm cutoff for the immunoassay vs. 10 ppm cutoff for the reference method). In addition, the GC method is expected to show a normal distribution of results around 10 ppm in repeated analyses. If the GC result is used as the criteria for correct assessment of the sample status, then only three results (#7, 19 and 23) show opposite status interpretations. In all

three cases, the immunoassay would give a positive when GC was negative (<10 ppm). This indicates that there may be a greater tendency toward false positive interpretation than false negative interpretation when the screening method is evaluated in this way. The correlation of the quantitative results of the two methods on eleven spiked samples in the 5 to 15 ppm range shown in Figure 4 confirms this observation. Regression analysis of this limited data set predicts a 10 ppm GC concentration would be read at about 13 ppm by immunoassay. The apparent higher concentration predicted by immunoassay could result from the fit of the calibration curve in the 10 to 20 ppb range giving results that are slightly higher than expected or lower results by the reference method could be due to some loss of analyte during sample extraction, concentration and or derivatization steps. A larger sample correlation study across a broader concentration range would provide a better characterization of the correlation of these two methods, but quantitative comparison of methods was not an important objective of this study. In another study done with 56 water samples in the 10 to 500 part per billion range collected from various locations across the United States, the 2,4-D RaPID Assay was shown to correlate very well ($r = 0.970$) with a GC/MS method (Lawruk et al, 1993).

SUMMARY

A magnetic particle based immunoassay for 2,4-D has been successfully adapted for use as a screening method with TCLP extracts of some commonly encountered forms of liquid and solid waste. The method is inexpensive compared to GC methods, is easy to perform and can provide results on as many as 50 samples in less than an hour. The quantitative accuracy of the immunoassay results in the ppm range has been demonstrated by comparison of selected spiked samples with the currently accepted SW-846 method. A screening cutoff concentration has been established that discriminates between the 10 ppm regulatory level and half that level with no false negatives or false positives based on spiking studies. Cross-reactivity with environmentally relevant compounds has been shown to be insignificant and masking agents are of little consequence because of the thousand fold dilution made prior to the immunoassay. This test should now be applied to field testing situations where it is expected to be a valuable tool for producing rapid results for site mapping of contaminated soils, for effluent monitoring in agricultural applications and in remediation activities.

REFERENCES

Lawruk, T.S., Hottenstein, C.S., Fleeker, J.R., Hall, J.C., Herzog, D.P., Rubio, F.M., Quantitation of 2,4-D and Related Chlorophenoxy Herbicides by a Magnetic Particle-Based ELISA, 1993, (manuscript submitted for publication).

Table 1. Calibration of spiking solution with EPA reference standard. Two hundred fifty milligrams of 2,4-D (free acid) was dissolved in acetonitrile in a 25 mL volumetric flask. Aliquots from 0.5 mL to 3.5 mL were diluted in one liter volumetric flasks to prepare solutions containing 5, 10, 15 and 35 ppm of 2,4-D. A 2,4-D EPA reference standard (NSI Environmental Solutions, Research Triangle Park, NC) with a certified concentration of 5000 µg/mL (in acetonitrile) was diluted volumetrically in a similar manner in order to produce solutions at the same concentrations. 100µL aliquots of each solution were then diluted in 100 mL of TCLP Diluent prior to immunoassay.

	concentration of 2,4-D (ppm)		
source of 2,4-D	predicted	measured	% difference
spiking solution	5	5.05	101
	10	11.33	113
	15	17.40	116
	35	37.30	106
reference standard	5	5.05	101
	10	10.70	107
	15	17.14	114
	35	38.91	111

TABLE 2. Cross-reactivity of chlorophenoxy compounds and structurally unrelated pesticides in the 2,4-D RaPID Assay. The compounds shown below were prepared in the TCLP Sample Diluent and added to the immunoassay in increasing amounts until a result equal to that seen in a sample containing 10 ppm 2,4-D was seen.

Compound	Concentration that causes a 10 ppm 2,4-D result
2,4-D	10 ppm
2,4-D propylene glycol ester	0.52 ppm
2,4-D ethyl ester	0.54 ppm
2,4-D isopropyl ester	0.96 ppm
2,4-D methyl ester	1.09 ppm
2,4-D sec-butyl ester	1.40 ppm
2,4-D butyl ester	1.60 ppm
2,4-D butoxyethyl ester	2.00 ppm
2,4,5-T methyl ester	12.0 ppm
2,4-D isooctyl ester	20.0 ppm
2,4-D butoxy-propylene ester	20.6 ppm
2,4-DB	95 ppm
MCPA	110 ppm
2,4,5-T	130 ppm
Silvex methyl ester	665 ppm
4-chlorophenoxyacetic acid	815 ppm
MCPB	980 ppm
Silvex (2,4,5-TP)	1375 ppm
Dichlorophenol	2380 ppm
Dichlorprop	5000 ppm
Triclopyr	>10,000 ppm
MCPP	>10,000 ppm
Mecoprop	>10,000 ppm
Pentachlorophenol	>10,000 ppm
Picloram	>10,000 ppm
Alachlor	>10,000 ppm
Aldicarb	>10,000 ppm
Aldicarb sulfate	>10,000 ppm
Aldicarb sulfoxide	>10,000 ppm
Atrazine	>10,000 ppm
Benomyl	>10,000 ppm
Butylate	>10,000 ppm
Captan	>10,000 ppm
Captofol	>10,000 ppm
Carbaryl	>10,000 ppm
Carbofuran	>10,000 ppm
Dicamba	>10,000 ppm
1,3-Dichloropropene	>10,000 ppm
Dinoseb	>10,000 ppm
Metolachlor	>10,000 ppm
Metribuzin	>10,000 ppm
Simazine	>10,000 ppm
Terbufos	>10,000 ppm
Thiabendazol	>10,000 ppm

Table 3. Effect of silvex on 2,4-D results near the positive/negative cutoff point. Solutions of silvex alone and silvex/2,4-D mixtures were prepared in TCLP buffer to demonstrate the potential effect of a structurally similar, environmentally significant cross-reactant on the immunoassay results. Silvex alone produced non-detectable 2,4-D results in concentrations as high as 100 ppm. When increasing amounts of silvex were mixed with a 5 ppm 2,4-D solution no change in the status of the result was seen until 200 ppm of silvex was present in the mixture.

Silvex concentration (ppm)	2,4-D concentration (ppm)	2,4-D RaPID Assay result (ppm)	Interpretation
0	0	nd	negative
0.5	0	nd	negative
1.0	0	nd	negative
2.0	0	nd	negative
100	0	nd	negative
200	0	0.8	negative
0	5.0	4.46	negative
0.5	5.0	4.99	negative
1.0	5.0	4.48	negative
2.0	5.0	5.03	negative
100	5.0	7.09	negative
200	5.0	9.17	positive

nd = non-detectable

Table 4. 2,4-D spiking results on TCLP extracts of environmental waste matrices.

2,4-D was spiked into buffer, water or a TCLP extract of the matrices shown after the final filtration step. Each matrix was diluted 1:1000 and tested by immunoassay five times. Each result was then compared with the 7.5 ppm cutoff to determine if its status was positive or negative.

			2,4-D concentration by Immunoassay Determination #							
I.D. #	Matrix/Spike	conc. units	1	2	3	4	5	mean	% POS	% NEG
1	TCLP buffer	ppm	nd	nd	nd	nd	nd	-	0	100
2	TCLP buffer + 15 ppm	ppm	15.5	16.9	16.3	16.6	17.9	16.6	100	0
3	TCLP buffer + 10 ppm	ppm	10.6	12.0	10.2	10.9	10.4	10.8	100	0
4	TCLP buffer + 5 ppm	ppm	5.0	4.7	5.0	4.9	4.3	4.8	0	100
5	Sandy soil extract	ppm	nd	nd	nd	nd	nd	-	0	100
6	Sandy extract + 15 ppm	ppm	16.0	15.8	17.5	16.5	16.0	16.4	100	0
7	Sandy extract + 10 ppm	ppm	11.1	12.4	11.8	10.8	12.7	11.8	100	0
8	Sandy extract + 5 ppm	ppm	5.8	5.9	6.4	4.9	5.5	5.7	0	100
9	Organic soil extract	ppm	nd	nd	nd	nd	nd	-	0	100
10	Organic extract +15 ppm	ppm	16.1	17.4	16.3	16.5	17.5	16.8	100	0
11	Organic extract + 10 ppm	ppm	11.2	11.2	11.5	10.4	11.0	11.1	100	0
12	Organic extract + 5 ppm	ppm	5.2	5.1	5.0	4.5	5.1	5.0	0	100
13	Effluent #1	ppm	nd	nd	nd	nd	nd		0	100
14	Effluent #1 + 15 ppm	ppm	19.1	18.2	18.9	17.9	18.8	18.6	100	0
15	Effluent #1 + 10 ppm	ppm	11.7	12.6	14.5	11.1	13	12.6	100	0
16	Effluent #1 + 5 ppm	ppm	5.1	5.7	5.1	4.8	5.6	5.3	0	100
17	Effluent #2	ppm	nd	nd	nd	nd	nd	-	0	100
18	Effluent #2 +15 ppm	ppm	16.3	18.1	17.0	17.9	15.8	17.0	100	0
19	Effluent #2 + 10 ppm	ppm	12.1	12.5	10.4	10.2	12.6	11.6	100	0
20	Effluent #2 + 5 ppm	ppm	5.1	5.8	4.5	5.0	4.9	5.1	0	100
21	Runoff	ppm	nd	nd	nd	nd	nd	-	0	100
22	Runoff + 15 ppm	ppm	16.7	19.0	18.8	17.5	19.3	18.2	100	0
23	Runoff + 10 ppm	ppm	11.5	11.2	11.1	11.8	11.4	11.4	100	0
24	Runoff + 5 ppm	ppm	5.1	5.4	5.7	5.2	5.8	5.4	0	100
25	Municipal water	ppb	nd	nd	nd	nd	nd	-	N/A	N/A
26	Municipal water + 140 ppb	ppb	162	168	155	156	165	161	N/A	N/A
27	Municipal water +70 ppb	ppb	75	71	75	63	78	72	N/A	N/A
28	Municipal water + 35 ppb	ppb	38	42	37	40	33	38	N/A	N/A

N/A = not applicable to wastewater regulatory limit

Table 5. Comparison of screening results with quantitative 2,4-D results obtained with SW-846 Method #8150.
Selected samples described in Table 4 were split and sent to a local reference lab for analysis. The mean of five immunoassay results and the status of that mean with reference to the 7.5 ppm cutoff is shown. Quantitative GC results by method #8150 are given. Some samples were submitted in duplicate. The status of the GC result is reported as positive if greater than or equal to the 10 ppm regulatory limit, negative if less than 10 ppm. Agreement of the screening result with the GC result is assessed .

I.D. #	Matrix/Spike	conc. units	immunoassay mean	immunoassay status	2,4-D result by Method #8150	GC status	Agreement of screen and GC?
1	TCLP buffer	ppm	nd	negative	nd	negative	yes
2	TCLP buffer + 15 ppm	ppm	16.6	positive	13.0	positive	yes
3	TCLP buffer + 10 ppm	ppm	10.8	positive	11.0	positive	yes
4	TCLP buffer + 5 ppm	ppm	4.8	negative	5.6	negative	yes
5	Sandy soil extract	ppm	nd	negative	nd	negative	yes
6	Sandy extract + 15 ppm	ppm	16.4	positive	*	*	*
7	Sandy extract + 10 ppm	ppm	11.8	positive	5.9, 5.2	neg, neg	no
8	Sandy extract + 5 ppm	ppm	5.7	negative	*	*	*
9	Organic soil extract	ppm	nd	negative	nd	negative	yes
10	Organic extract +15 ppm	ppm	16.8	positive	*	*	*
11	Organic extract + 10 ppm	ppm	11.1	positive	10.0, 9.5	pos, neg	equivocal
12	Organic extract + 5 ppm	ppm	5.0	negative	*	*	*
13	Effluent #1	ppm	nd	negative	*	*	*
14	Effluent #1 + 15 ppm	ppm	18.6	positive	*	*	*
15	Effluent #1 + 10 ppm	ppm	12.6	positive	11.0, 7.8	pos, neg	equivocal
16	Effluent #1 + 5 ppm	ppm	5.3	negative	3.6	negative	yes
17	Effluent #2	ppm	nd	negative	*	*	*
18	Effluent #2 +15 ppm	ppm	17.0	positive	11.0	positive	yes
19	Effluent #2 + 10 ppm	ppm	11.6	positive	8.8, 9.5	neg, neg	no
20	Effluent #2 + 5 ppm	ppm	5.1	negative	*	*	*
21	Runoff	ppm	nd	negative	nd	negative	yes
22	Runoff + 15 ppm	ppm	18.2	positive	*	*	*
23	Runoff + 10 ppm	ppm	11.4	positive	9.7, 8.6	neg, neg	no
24	Runoff + 5 ppm	ppm	5.4	negative	5.5	neg	yes
25	Municipal water	ppb	nd	N/A	nd	N/A	N/A
26	Municipal water + 140 ppb	ppb	161	N/A	*	N/A	N/A
27	Municipal water +70 ppb	ppb	72	N/A	58, 59	N/A	N/A
28	Municipal water + 35 ppb	ppb	38	N/A	*	N/A	N/A

nd = non-detectable
N/A = not applicable to wastewater regulatory limit
* = no analysis with method # 8150

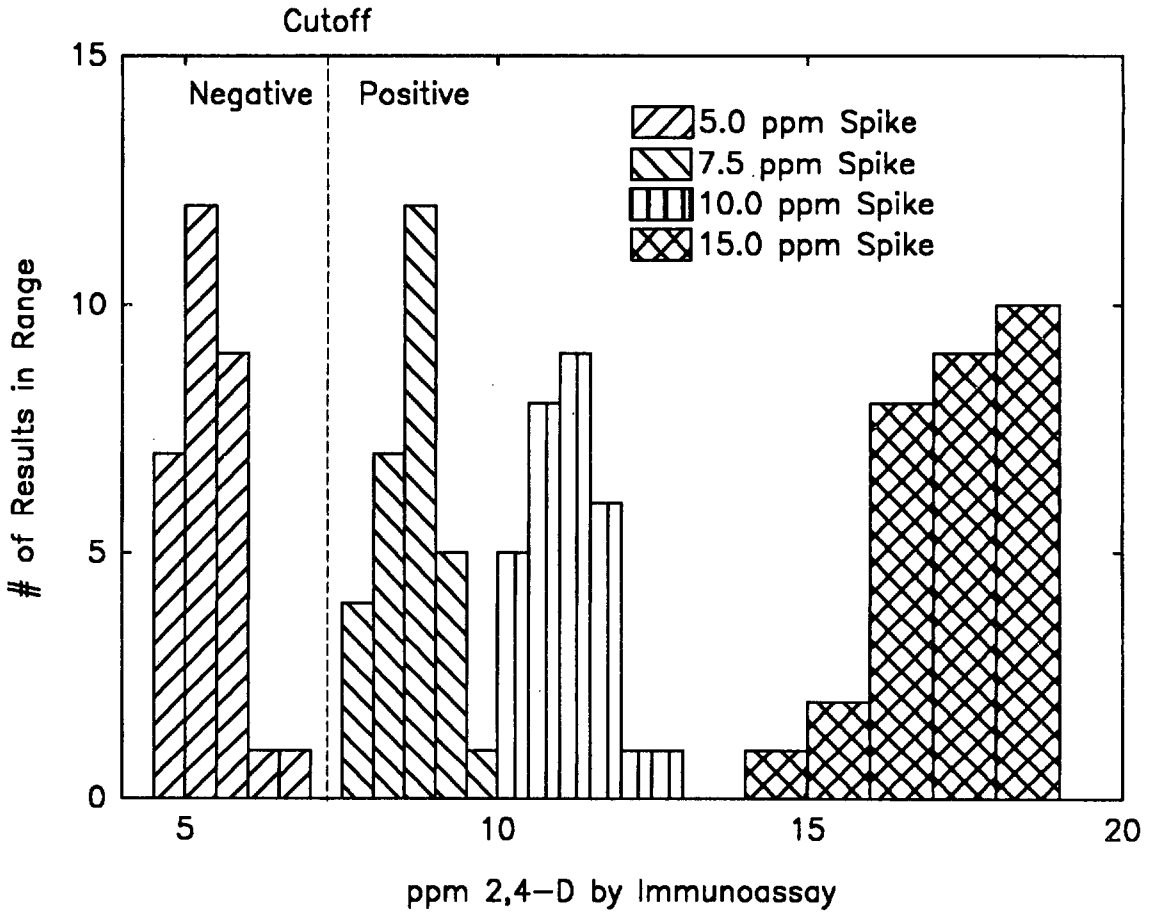

Figure 1. Demonstration of the sensitivity of the selected cutoff for 2,4-D in the TCLP buffer matrix. 2,4-D was spiked into TCLP extraction buffer at concentrations of 5, 7.5, 10 and 15 ppm. Each spiked solution was then diluted 1:1000 in Ohmicron 2,4-D TCLP Sample Diluent. Thirty immunoassay determinations were then made on each diluted solution. The frequency of occurence of the results is plotted against the range of 2,4-D concentrations measured.

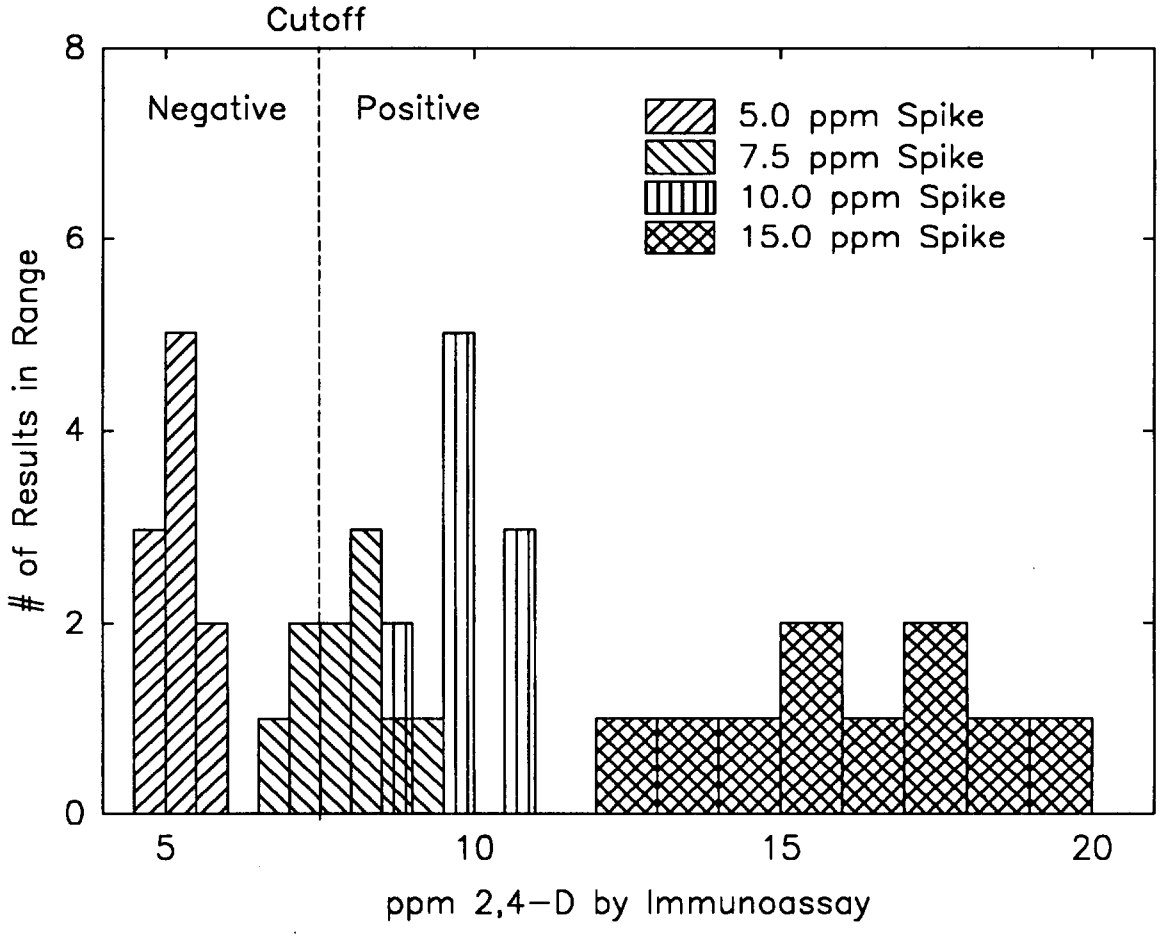

Figure 2. Demonstration of the sensitivity of the selected cutoff for 2,4-D in the TCLP extract of an organic soil. 2,4-D was spiked into the TCLP extract of an organic soil at concentrations of 5, 7.5, 10 and 15 ppm. Each spiked solution was then diluted 1:1000 in Ohmicron 2,4-D TCLP Sample Diluent. Ten immunoassay determinations were made on each diluted solution. The frequency of occurence of the results is plotted against the range of 2,4-D concentrations measured.

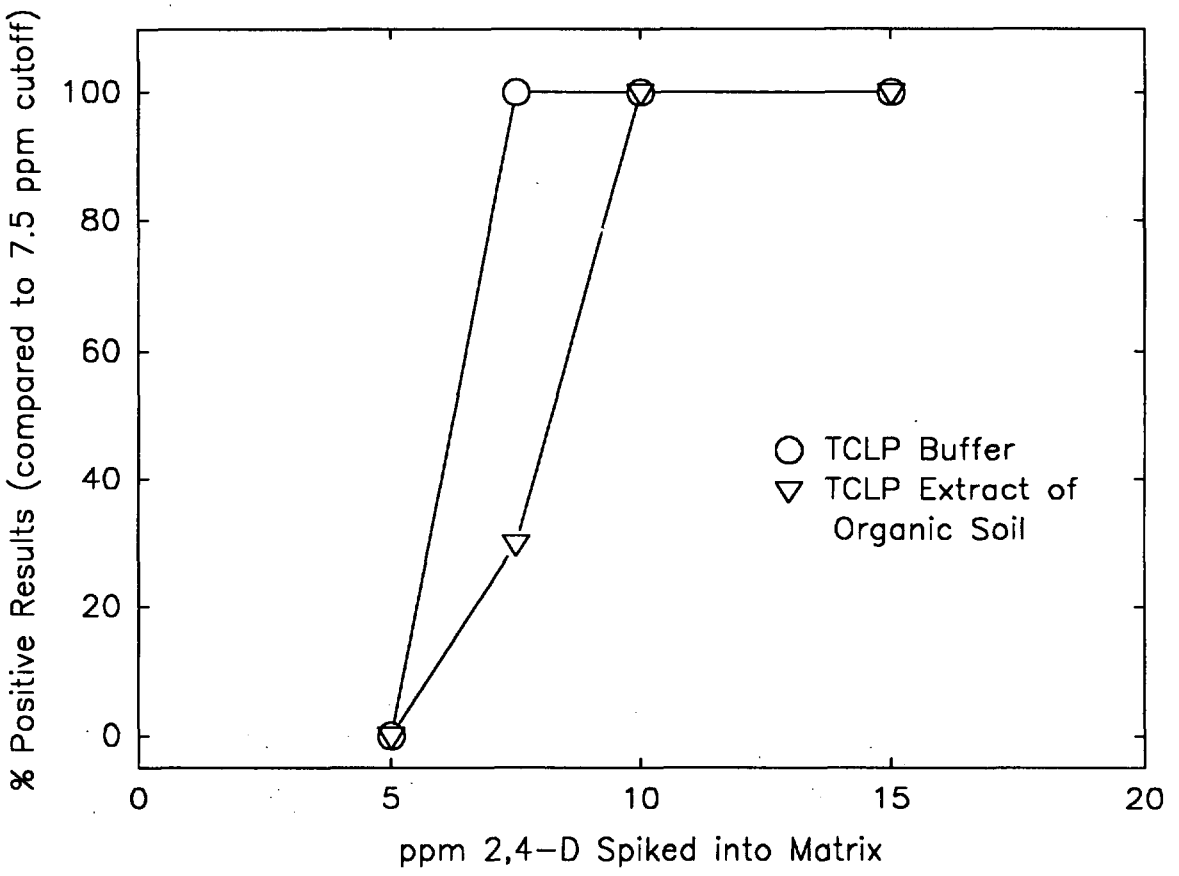

Figure 3. Break point of the 2,4-D screening test in buffer and soil extract. Spiked buffer or soil extracts described in Figs. 1 and 2 were graded for positivity or negativity based on the 7.5 ppm cutoff. In both matrices the 10 ppm regulatory level is distinguishable from 5 ppm (one-half the regulatory level) 100 % of the time.

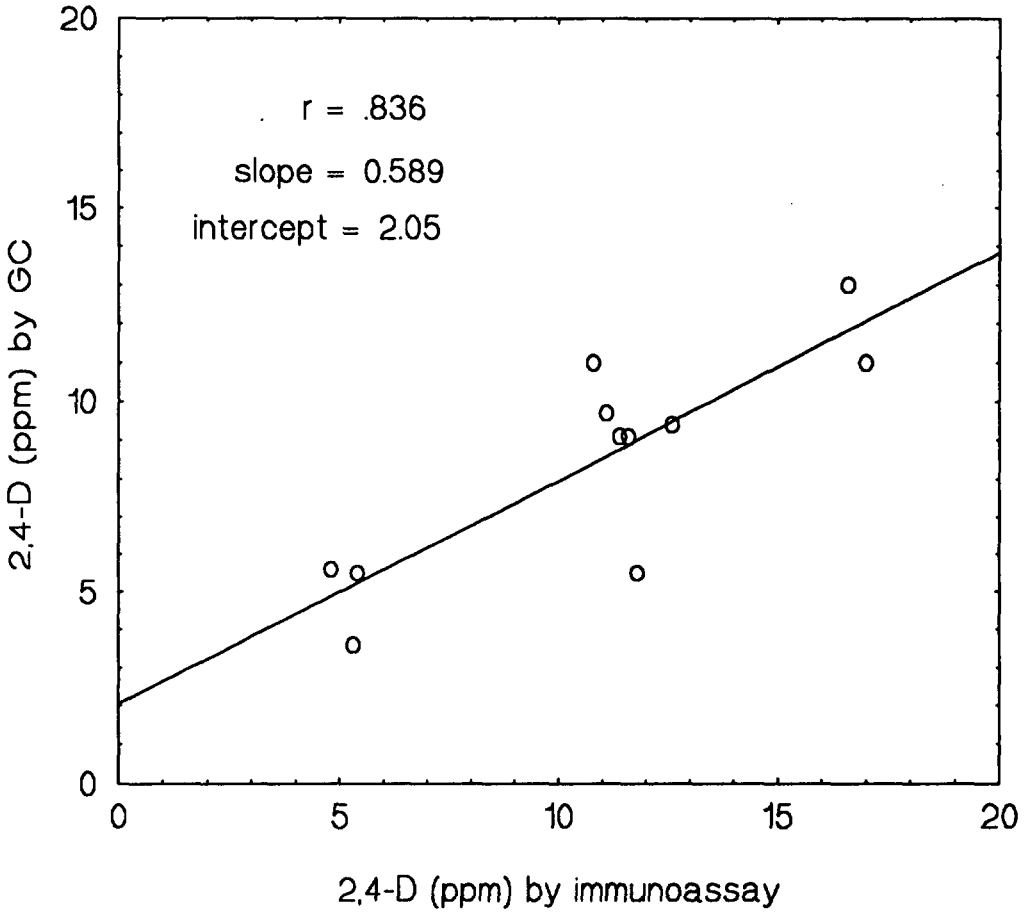

Figure 4. Quantitative correlation of 2,4-D immunoassay with method #8150. TCLP extracts of various matrices that were spiked at 5, 10 or 15 ppm 2,4-D were split and submitted for quantitative analysis by method #8150 for chlorinated herbicides (GC detection.) The GC result (average of duplicates in some cases) was plotted against the corresponding immunoassay result (average of five replicates). The correlation coefficient, slope and intercept was calculated by regression analysis for results on these eleven samples.

PETRO RIS® WATER - A RAPID, ON-SITE IMMUNOASSAY FOR DETECTING PETROLEUM PRODUCTS IN GROUND WATER.

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ABSTRACT

There is a recognized need for innovative and cost-effective field methods for identifying and assessing contamination of ground water with petroleum products. A rapid, on-site enzyme immunoassay was developed for the detection of low levels of gasoline, diesel fuel and other petroleum components in contaminated ground water samples. The test sensitivity for gasoline is 165 ppb, for diesel is 245 ppb and for m-xylene is 100 ppb. The test can also be used to measure other petroleum fuels such as fuel oil and jet fuel. The immunoassay was developed as a complete kit to be used on-site. The test is rapid, taking less than 30 minutes to complete the immunoassay.

Validation studies established that the test is specific for refined petroleum hydrocarbon (PHC) constituents. Ground water samples which were PHC-free by GC analysis tested negative in the immunoassay. Minimal matrix interferences were observed from ground water obtained from different regions of the United States. The evaluation of field samples demonstrated good correlation between the results obtained by the immunoassay and by standard analytical methods for petroleum hydrocarbons. The test serves as an accurate field based alternative to traditional lab methods for screening contaminated waste sites.

INTRODUCTION

The contamination of ground water by petroleum hydrocarbons frequently occurs during the processing and storage of refined petroleum products. A rapid procedure for evaluating contaminated sites has been developed using competitive immunoassay methodology. Immunoassay technology has been successfully applied to environmental testing (1-6). To make it easier and less expensive to test for petroleum fuels in water, we have developed and validated an on-site immunoassay for the detection of gasoline at 165 ppb and diesel at 245 ppb. In many states, regulations concerning water contamination focus on the BTEX components. This test was designed to specifically detect the significant components in gasoline and diesel contaminated samples. The balanced response to both aliphatic and aromatic compounds gives the Petro RIS® Water Test wide applicability to testing petroleum fuels at low detection levels.

This test has an advantage over traditional analytical methods because it is an inexpensive means of evaluating samples on site. For this reason, some of the variability which is

observed in PHC analysis, due to problems with sampling and handling of volatile analytes, is reduced.

EXPERIMENTAL METHODS

This paper presents data that was obtained using the Petro RISc® Water Immunoassay kit (EnSys, Inc., cat no. 70410) and the procedure outlined in the kit instructions. The kit contains all the components necessary to process the water sample and conduct the assay in the field.

The test consists of 3 principal steps. The first step is to prepare the ground water sample for use in the immunoassay. The sample is collected in a VOA vial containing buffer salts which are dissolved in the sample by mixing. The sample is briefly stored in ice to allow the sample to cool and the sediment to settle. The second step is to perform the immunoassay. The sample is transferred to a tube containing an enzyme conjugate pellet (in a stable lyophilized form). The reconstituted conjugate and sample mixture is poured into an antibody-coated tube. After incubating for 10 minutes to allow the competitive assay to proceed, the tube is washed and the color producing substrates are added. The final step is the interpretation of results which compares the color intensity of the sample to the kit standard which is run in parallel with the sample. A lighter color for the sample indicates that the sample is contaminated.

RESULTS AND DISCUSSION

The Petro RISc® Water Test was validated by evaluating several performance criteria including the immunoassay sensitivity, specificity, and precision. The test was also examined for correlation to a reference method using field samples and gasoline spikes. The kit storage stability was evaluated at both ambient and elevated temperatures. All of these performance characteristics are important to assure that the test is accurate and field compatible.

The Petro RISc® Water Test was configured to give less than 5% false negative results for samples containing concentrations of petroleum fuels at or above the detection level. This was accomplished by setting the m-xylene standard at 55 ppb. At this concentration, 95% of samples containing 100 ppb m-xylene, 165 ppb gasoline or 245 ppb diesel will be detected as positive. Other compounds were tested in the assay to determine a cross-reactivity profile. The concentrations of PHC needed to give a positive result in the assay are listed in Table 1. The test recognizes several petroleum hydrocarbon constituents with the greatest sensitivity to short chain aliphatic and small aromatic compounds.

The assay specificity was examined using two approaches. First, PHC-free water samples were evaluated and found to be negative in the immunoassay compared to the standard. Second, the matrix interference was examined in the assay using PHC-free water samples

from different geographical locations across the United States. When the signals of the PHC-free samples were compared to the signal from a PHC-free laboratory (deionized > 18MΩ with an organic removing filter) water control, the mean signal ratio (B_{SAMPLE} OD/ B_{LAB} OD) was 0.96 ± 0.07. The absence of matrix effect would yield a ratio of 1. This data demonstrates that there was minimal matrix interference in the immunoassay.

The precision of the test was evaluated by measuring intra-assay repeatability and inter-assay reproducibility. Replicate determination of assay signals for samples containing 100 ppb m-xylene spikes were obtained. The intra-assay percent coefficient of variation was < 8% which was equivalent to 12 ppb m-xylene. The inter-assay percent coefficient of variation was <12% which was equivalent to 19 ppb m-xylene.

The storage stability of the test kit was evaluated by testing the assay performance in real-time and temperature-accelerated (storage at 37°C) studies for 3 months (Figure 1). The regression analysis of assay signal decay and sensitivity ($B_{STANDARD}/B_{0\ PPM\ CONTROL}$) currently suggests that long-term stability will be attained for at least 6 months when the kits are stored at room temperature (about 22°C).

Field trials were used to establish a correlation between the Petro RISc® Water Test and the reference USEPA method 5030/modified 8015. In these studies, there was an overall correlation of 84% with individual site correlation ranging from 71% to 100%, Table 2. No false negative results were observed which is consistent with the test configuration.

CONCLUSION

This paper has presented an alternative method for quick field screening of petroleum hydrocarbon contamination of ground water samples. We have validated a competitive enzyme immunoassay for the detection of gasoline and diesel at low concentrations in water. The rapid screening of multiple samples is a significant advantage to traditional analytical methods.

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(6) Goh, K. S., Hernandez, J., Powell, S. J., Garretson, C., Troiano, J., Ray, M., & Greene, D.D. (1991) *Bull. Environ. Contam. Toxicol.* **46**, 30-36

Table 1. Petro RIS® Water Test Sensitivity

Compound or Substance	Conc. Needed to Give a Positive Result (ppb)
Petroleum Fuel Products	
Gasoline	165
Diesel fuel, #2	245
Jet A fuel	280
Jet fuel, JP-4	185
Kerosene	215
Fuel oil, #2	210
Formulated Petro Products	
Mineral spirits	490
Aromatic Compounds	
Toluene	740
Ethylbenzene	65
o-Xylene	100
m-Xylene	**100**
p-Xylene	590
Styrene	65
Naphthalene	8
Acenapththene	10

Methanol was spiked individually with the listed compound. Standard curves were performed with each compound and compared to the m-xylene standard. The concentration of cross-reactant necessary to give a positive result was calculated from the relative ED_{50}s (estimated dose at 50% binding) of the compounds and m-xylene.

Table 2. Correlation of Petro RIS® Water Test Field Trial Results with EPA GC-FID Method (5030/modified 8015) Laboratory Results

Trial No.	Correlation of Immunoassay Results with GC-FID Results	False Pos. Results (FP/Total)
1	93%•	1/14
2	100%•	0/10
3	71%•	4/14
4	75%•	3/11
Total	84%	7/49

Four field trials were conducted with the Petro RIS® Water Test at former service stations. Contaminated groundwater samples were collected in duplicate. One set of samples was analyzed on-site and the other set was sent to the laboratory for analysis by GC-FID. Gasoline field spikes were made in blank water at the time of collection.

• The laboratory underestimated the gasoline field spikes by > 25%.

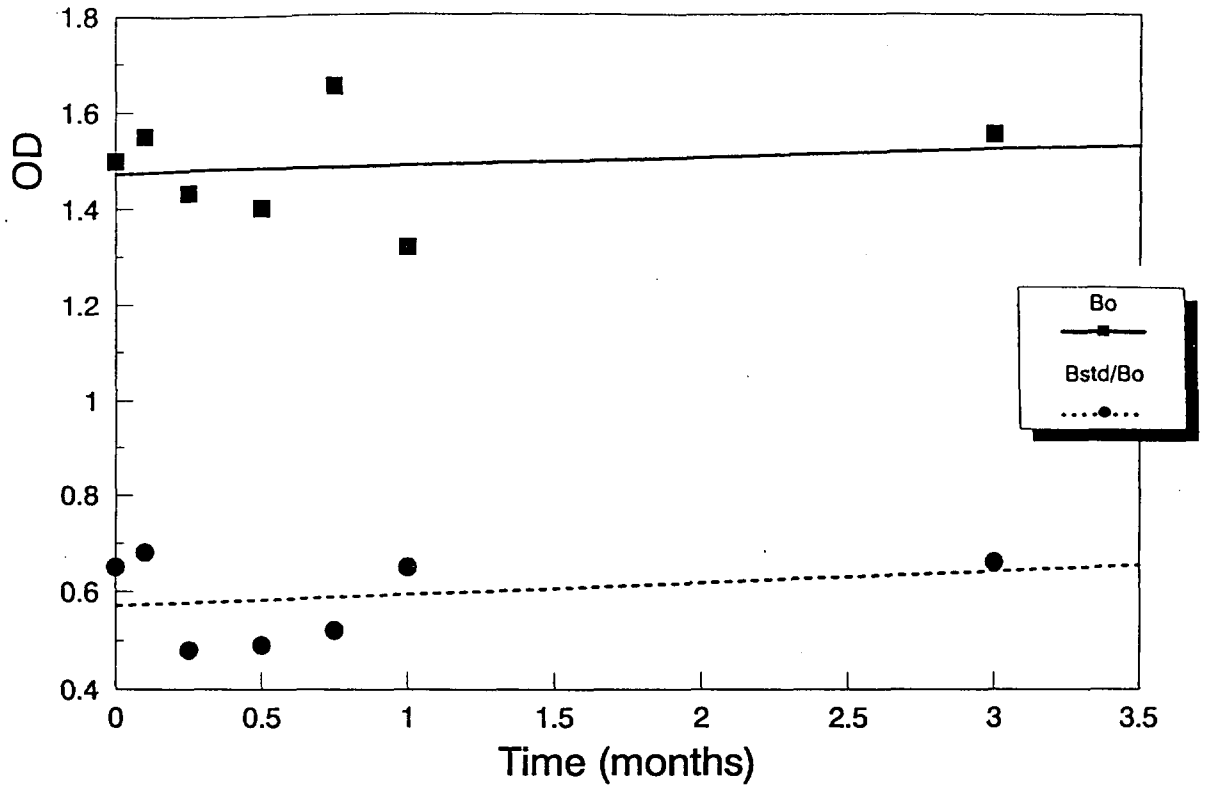

Figure 1. Storage stability of the Petro RISc® Water Test
The test kit was stored at 37°C. At each of the indicated time points the kits were allowed to cool to ambient temperature and were used for analysis. Bo is the absorbance at 450 nm from an unspiked methanol sample. Bstd is the absorbance obtained with the kit standard, and the Bstd/Bo is the ratio of the two absorbance values. A change in the ratio would indicate a change in the test sensitivity.

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APPENDIX IX EXTRACTIONS BY ACCELERATED ONE STEP™ EXTRACTOR / CONCENTRATOR

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ABSTRACT

The Accelerated One Step™ system shortens extraction time from 18 to 5.5 hours. The solvent requirement is reduced from 500 to 100 mL. This new liquid-liquid extraction system was validated by spiking all Appendix IX organochlorine pesticide and semivolatile (BNA) analytes into 3 aqueous matrices at 2 concentration levels. Ground water, TCLP buffer #1 and waste water were spiked near the expected method detection limits and at levels 20 to 50 times higher. Organochlorine pesticide and BNA accuracy and precision are within the limits published in SW-846. The average recovery for all Appendix IX pesticides and BNAs is 77% with 13%RSD.

The Accelerated One Step™ system reduces solvent requirements by eliminating the solvent pool at the bottom of the extraction chamber, reducing the volume of the boiling flask and minimizing solvent vapor losses. The extraction is accelerated by shortening the analyte transfer time from extraction chamber to boiling flask and maintaining a high solvent boiling rate. The membrane resists plugging by most common environmental samples. Only very oily samples have impeded proper solvent cycling.

The Corning Accelerated One Step™ extractor/concentrator system is equivalent to conventional continuous liquid-liquid extraction while using $^1/_5$ the solvent and $^1/_3$ the extraction time. The accuracy, as measured by percent recovery, is equivalent to conventional continuous liquid-liquid extraction. Precision, as measured by %RSD, is better with the Accelerated One Step™ system. The extracts contain fewer interfering polar compounds, this improves analysis (particularly for TCLP). The new system also reduces labor requirements and increases lab extraction capacity. The Accelerated One Step™ system will contribute to more timely and cost effective environmental analyses while reducing laboratory use, exposure and disposal of hazardous solvents.

INTRODUCTION

Solvent reduction has become one of the battle cries of the Environmental Protection Agency for the 1990's. The EPA has received considerable environmental and political pressure to reduce the amount of pollution generated by analytical methods which are required to demonstrate compliance with EPA regulations. The largest volume of analytical waste is from the organic solvents required by current organic extraction methodologies. Both SW-846 methods, 3510 (separatory funnel) and 3520 (continuous liquid-liquid), are used for aqueous samples and require large amounts (300-500 mL) of organic solvents such as methylene chloride. In addition, continuous liquid-liquid extraction times are typically 18 hours, plus setup and cleaning time.

Two technologies in particular are being touted by the EPA as the "solution" to the organic solvent waste disposal problem. Solid Phase Extraction (SPE) and Supercritical Fluid Extraction (SFE) offer much promise to reduce solvent use and shorten extraction time. The largest impediment to full-scale environmental application of SPE and SFE is the lack of

methodologies rugged enough to handle the great diversity of environmental matrices and target analytes. Solid phase extraction has been successful for selected analytes in clean water matrices such as drinking water. However, some chemical and mechanical problems remain. Extraction of very water soluble analytes (such as phenol) from 1L samples has usually yielded recoveries less than 20%. Particulates from waste water samples are prone to plug both SPE cartridges and disks. Prefilters and larger disks have reduced the plugging problem but many environmental samples are still too problematic to be handled routinely by SPE. Current SPE technology cannot replace conventional liquid-liquid extraction for all analytes and matrices. However, this does not mean that solvent reduction efforts must be postponed.

The Accelerated One-Step™ extractor/concentrator system is an excellent interim solvent reduction solution that is available now. The solvent volume reduction from 500 mL to 100 mL (or less) is very attractive. In addition, reducing the extraction time from 18 hr to 5.5 hr is also beneficial. The extraction chemistry of the new One-Step™ system is the same as conventional liquid-liquid extraction. Thus, the data are equivalent.

This new extractor was evaluated in several areas to test its viability for routine organic extractions. **Analyte**, can the target compounds covered by the Appendix IX list be quantitatively extracted? **Matrix**, can all usual water matrixes be extracted without mechanical problems from emulsions or particulate plugging? **Accuracy & precision**, are method bias and reproducibility equal to or better than conventional liquid-liquid extraction? **Ruggedness**, is the method and glassware durable enough to tolerate misuse and still produce acceptable results? Is the extract "dry" enough that drying with sodium sulfate is no longer needed?

In short, the goal was to develop an apparatus which would extract as well as conventional continuous liquid-liquid extraction for all common environmental water matrixes yet be safer, faster and more cost effective.

EQUIPMENT AND SUPPLIES

Hardware

Accelerated One-Step extractor / concentrator systems (see Figure 1)
Neslab refrigerated circulator, CFT-75
Tecator heated circulators, 1046

Reagents

Methylene chloride, hexane, methanol, acetone, sulfuric acid, sodium hydroxide

RESULTS & DISCUSSION

Glassware

The accelerated One-Step™ apparatus differs from conventional continuous liquid-liquid extraction (and the current One-Step™ extractor) in four key areas. 1) The solvent pool at the bottom of the conventional extraction chamber has been eliminated. The solvent is returned from the bottom of the extraction chamber to the distillation flask (or K-D) via gravity feed rather than siphon action. A hydrophobic membrane is placed across the bottom of the extraction chamber. Organic solvent is dripped through the sample in the conventional manner. However, the solvent passes through the membrane at the bottom and runs back to the distillation flask. No pool of solvent is required at the bottom of the extraction vessel for siphon purposes. Thus, less solvent is required. The extraction time is also shorter since it is not necessary to transfer analytes from the solvent pool to the distillation flask via the solvent pool dilution process of a conventional continuous liquid-liquid extractor. Figure 1 shows the flow of solvent. 2) The hydrophobic membrane effectively excludes water from the solvent thus eliminating the need for a sodium sulfate drying step. 3) The solvent volume in the boiling flask has also been reduced from 300 mL to 100 mL. 4) Evaporative solvent losses are reduced by the shortened extraction time and well-sealed joints. Employee and environmental exposure to solvent vapor are reduced. Also, initial solvent volume can be reduced, which saves on solvent cost.

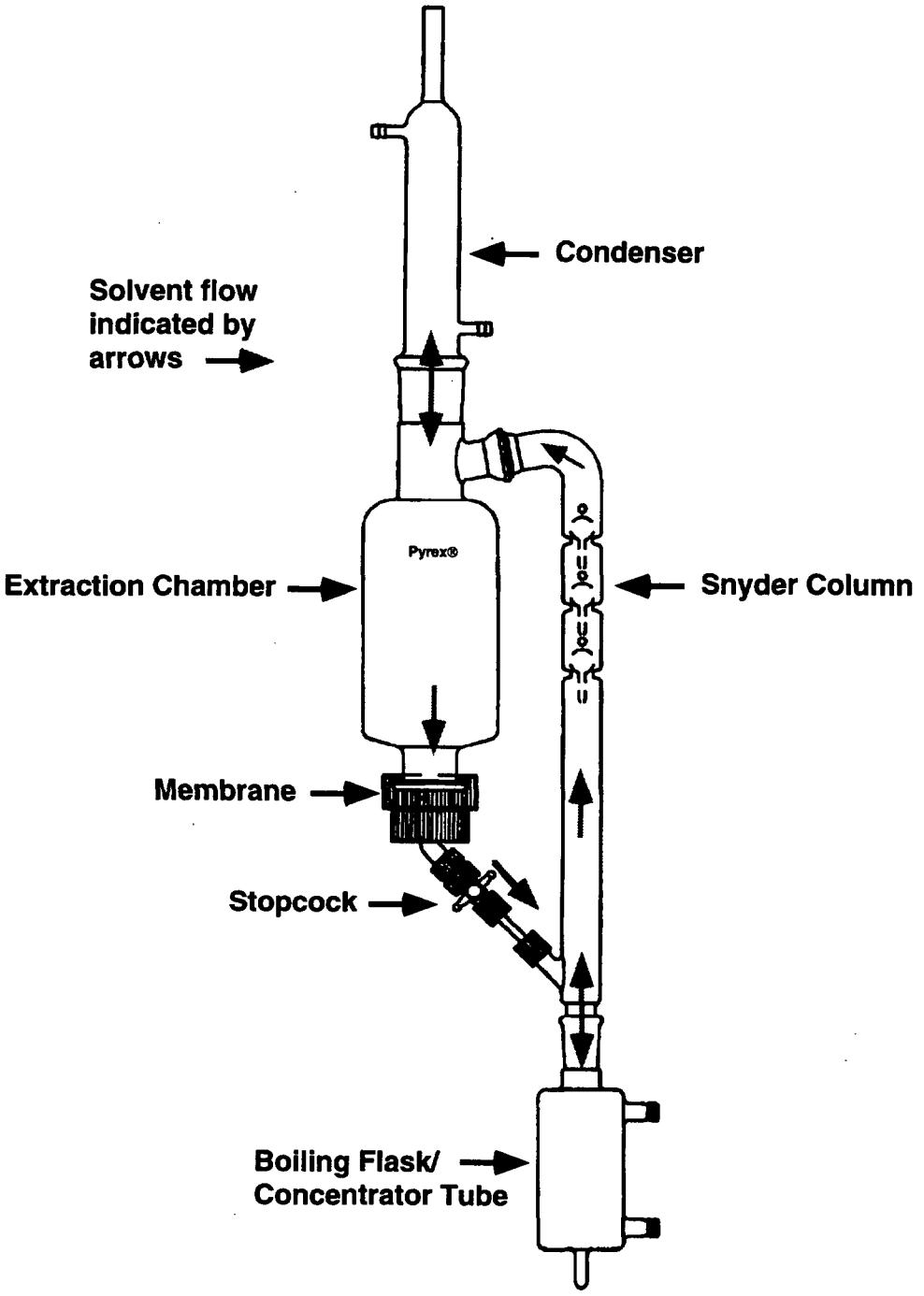

Figure 1. The Accelerated One Step™ Extractor/Concentrator System.

Extraction Method

Most extraction parameters are the same as described in SW-846 Method 3520. The slight differences were glassware assembly and use, solvent volume, extraction time and acid / base extraction order. The disposable hydrophobic membrane was sealed in place above the stopcock. The stopcock was closed and 100 mL of methylene chloride was added to the extraction chamber. The water sample was poured into the extraction chamber. Surrogate and matrix spiking were performed normally, as well as pH adjustment. Once the boiling flask was hot, the stopcock was opened allowing the solvent to run through the membrane into the boiling flask. Solvent cycled through the extraction system. The solvent boiled off at a rate of 15 mL/min. The stopcock was closed to concentrate the extract after the extraction was complete in 5.5 hours. The acid fraction of the semivolatile BNAs was extracted first, followed by the base fraction. Acid and neutral analytes remained in the boiling flask during the basic extraction. Nitrogen blow-down was performed in the combination boiling flask-concentrator tube. The pesticide fraction extract was exchanged to hexane after the extraction was complete. The hydrophobic membrane excludes water during the extraction so sodium sulfate drying was not required.

METHOD VALIDATION

Three aqueous matrices were spiked at two concentration levels with Appendix IX Organochlorine pesticide and BNA analytes. Analyte percent recovery (accuracy, bias) and percent relative standard deviation of recovery (precision) were calculated using the results of the appropriate analysis techniques. Each high level matrix spike was extracted in triplicate, while there were 7 to 8 replicates of the low level spike. Method Detection Limits (MDL) and Reliable Quantitation Limits (RQL) were calculated from the low level data. MDL = standard deviation $\times$ 3.143 (for seven replicates). RQL = MDL $\times$ 4.

Ground water, TCLP buffer #1 and waste water were spiked with the analytes in Tables 1 and 2. These tables contain most of the semivolatile analytes from Appendix IX. The low and high concentration spike levels are also shown. SW-846 analysis methods 8270 and 8080/8081 were used as appropriate. Also, several samples with "native" analytes were extracted. The results were compared with data from the current liquid-liquid extraction method.

Test Matrices

Three aqueous matrices were studied; ground water, TCLP buffer #1 and industrial waste water. The ground water was taken from a residential drinking water well, which had high concentrations of calcium, magnesium and iron. TCLP buffer #1 is a sodium acetate - acetic acid buffer solution used by the Toxicity Characteristic Leaching Procedure to simulate landfill leaching. Its pH is 4.93 $\pm$ 0.05. Industrial waste waters have very diverse matrices. Therefore no single waste water can be selected which completely represents all of the possibilities. Nevertheless, a paint stripper effluent waste water sample was selected that represents many common waste waters.

Matrix Spike Study

The three matrices were spiked with the compounds listed in Tables 1 and 2 just prior to extraction. The BNA extractions were acidified first to extract the acid-neutral fraction. Next, the sample was basified and the basic analytes extracted (note: the acid-neutral analytes remained in the boiling flask). After the basic extraction was completed, the extract was concentrated to 1 mL by closing the stopcock to perform the macro concentration followed by N_2 blowdown. Pesticide extraction was at a neutral pH as described by the current liquid-liquid extraction methods. The high level matrix spikes were extracted first followed by the low levels to test for analyte carryover. No carryover from one extraction to the next was observed.

Mechanical Performance

The membrane's resistance to plugging was tested with very fine inorganic solids, dissolved solids, dissolved organics and settleable organic *muck*. The membrane did not plug or restrict proper solvent cycling under any of these conditions. The plugging effect of inorganic solids was tested by adding 50 g of Kaolin to 1 L of tap water. Dissolved solids effects were tested with TCLP buffer #1. Dissolved organics were examined with a pond water sample. The settleable organic *muck* sample was prepared by taking 50 g of *muck* from the bottom of a pond at a local hog farm.

Two types of contaminants have reduced membrane performance. High concentrations of surfactants and very oily samples may generate enough emulsion to *consume* the entire 100 mL of solvent.

VALIDATION STUDY RESULTS

The Accelerated One Step™ extractor/concentrator system showed equivalent accuracy and better precision than conventional liquid-liquid extraction for semivolatile BNAs and organochlorine pesticides. The average recovery for all compounds and spike levels was 85% for pesticides and 69% for BNAs. The average %RSD was 10 and 16 for pesticides and BNAs, respectively. Calculated MDLs were consistent with published EPA data. Since the chemistry of the extraction has not changed, extraction efficiency should not change either. In short, those compounds that extract well with current methodology are "well behaved" with the new system. Those analytes that were "problem compounds" are still "problem compounds". Precision is improved because sample extract handling is reduced. Space restrictions limit presentation of all validation results. The full validation study results are available upon request.

Organochlorine Pesticides

Accuracy and precision were excellent for all ground water and full strength TCLP buffer extractions. The high level waste water extractions were also good. As expected, the low level waste water extractions were not as good as the others because of the high levels of non-target compounds present in the sample. Pesticide recovery and %RSD data for each Appendix IX compound are listed in Table 3. No data are available for endosulfan II because it coelutes with other target analytes on both the RTX-5 and RTX-1701 GC columns used in this study. Non-target compounds in the waste water prevented the analysis of several analytes at the low spike level.

Figure 2 shows a frequency plot of recovery for the high level spikes and the data published in method 8080B. The number of compounds with a particular recovery for each matrix is shown. For example, 13 pesticides from the EPA data had recoveries between 80 and 90%. The shape of the distribution plots show that overall analyte recovery is the same between the EPA data using conventional liquid-liquid extraction and the new One Step system. The recovery frequency plot in Figure 3 clearly shows that low level analyte recovery for ground water and TCLP buffer compares well with the high level spikes. Recovery from low level waste water spikes decreased and was more varied. The third replicate of the high level TCLP buffer spike was invalidated because of a lab error. Thus, the recovery and %RSD for this data subset are based on 2 replicates.

Figures 4 and 5 show the corresponding frequency distributions for %RSD. The EPA data show typical %RSDs between 10-20%. Most %RSDs for the Accelerated One Step™ system were less than 10%.

Table 4 compares overall average recovery and %RSD from this study with the method proficiency data published in 8080B. All average recoveries were well within the range specified in 8080B and compared well with the published EPA recoveries. All average %RSDs

were lower than both the published EPA %RSD limit and the single analyst %RSD. This is very encouraging since several extractionists participated in this study.

Pesticide MDL and RQL data are summarized in Tables 5 and 6 and Figure 6. All MDLs from ground water and TCLP buffer are lower than the published reagent water MDLs from 8081 except for α-chlordane and methoxychlor. The difference for α-chlordane is not significant. The higher MDL for methoxychlor is probably attributable to the higher spike level for this compound in the commercially prepared mixtures. As expected, waste water MDLs are elevated because of non-target compounds. This serves as a reminder that MDLs are matrix dependent.

Semivolatile - BNAs

Accuracy and precision were excellent for the high level ground water and full strength TCLP buffer extractions. The high level waste water extractions were also good. As expected, accuracy and precision decreased in the low level extractions because of the lower spiking level. BNA recovery and %RSD data for each Appendix IX compound are listed in Table 7.

Figure 7 shows a frequency plot of recovery for the high level spikes and the data published in method 8270. The number of compounds with a particular recovery for each matrix is shown. For example, 16 BNAs from the EPA data had recoveries between 80 and 90%. The shape of the distributions show that overall analyte recovery is the same between the EPA data using conventional liquid-liquid extraction and the Accelerated One Step™ system. The recovery frequency plot in Figure 8 shows that analyte recovery for low level spikes decreased and was more varied though quite acceptable.

Figures 9 and 10 show the corresponding frequency distributions for %RSD. The EPA data show typical %RSDs between 10-30%. Most %RSDs for the new One Step system were less than 10% for the high level spikes. Low level spike %RSDs were about 20%.

Table 8 compares overall average recovery and %RSD from this study with the single analyst method proficiency data published in 8270. Over 95% of the average recoveries were within the single analyst range specified in 8270 and compared well with the published EPA recoveries. This is very good since multiple extractionists and GC/MS analysts performed this study. The average recovery for 2 compounds did not fall within the EPA single analyst limits. The average high level recovery for 4,6-dinitro-2-methylphenol was 74%, which is within the EPA guidelines. The low pyrene recovery may be related to an analysis limitation in 8270. The internal standard for pyrene does not consistently mimic pyrene's chromatographic performance. The average pyrene recovery of 59% is within the overall performance range of 52-115%. All average %RSDs (except 4 analytes) were lower than both the published EPA %RSD limit and the single analyst %RSD. The 4 analytes which exceeded the single analyst %RSD window did pass the %RSD limit criteria. Those compounds were: 2-chloronaphthalene, 4,6-dinitro-2-methylphenol, 2,4-dinitrophenol, and pentachlorophenol. This indicates the Accelerated One Step™ system has very good precision since several extractionists participated in this study.

BNA MDL and RQL data are summarized in Table 9 and Figure 11. All MDLs are consistent with previous internal MDL studies. No EPA MDL data was available for comparison. As expected, ground water MDLs were the best, demonstrating once again that MDLs are matrix dependent.

Extract Cleanup

This new extraction system is chemically equivalent to conventional continuous liquid-liquid extraction with 2 exceptions. First, extract drying with sodium sulfate is not necessary for pesticides/PCBs or BNAs because the membrane effectively excludes water from the methylene chloride extract. Second, full strength TCLP buffers can be extracted without transferring large

quantities of acetic acid to the extract that interferes with GC and GC/MS analysis. Thus, the RQLs are at least one order of magnitude lower than current Toxicity Characteristic regulatory limits. The membrane does not exclude interferences such as diethylene glycol from the extract.

CONCLUSION

Extraction with the Corning Accelerated One Step™ extractor/concentrator system is equivalent to conventional continuous liquid-liquid extraction while using $^1/_5$ the solvent and $^1/_3$ the extraction time. The accuracy, as measured by percent recovery, is equivalent to conventional continuous liquid-liquid extraction. Precision, as measured by %RSD, is better with the Accelerated One Step™ system. The extracts contain fewer interfering polar compounds, this improves analysis (particularly for TCLP). The membrane resists plugging for all common environmental samples. The new system also reduces labor requirements and increases lab extraction capacity. The Accelerated One Step™ system will contribute to more timely and cost effective environmental analyses while reducing laboratory use, exposure and disposal of hazardous solvents.

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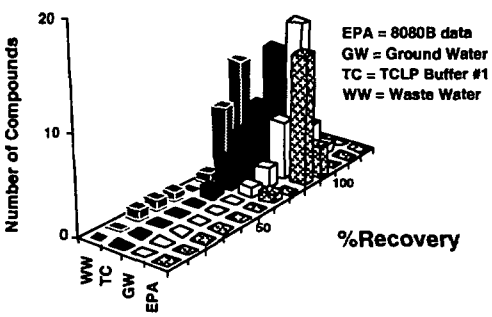

Figure 2. High Level Pesticide Recovery.

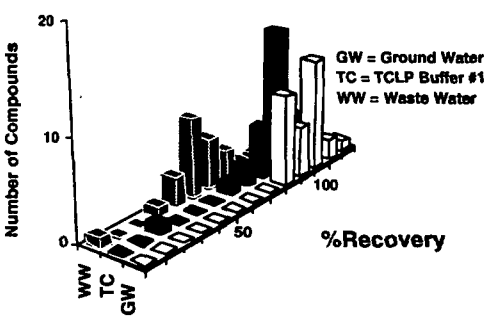

Figure 3. Low Level Pesticide Recovery.

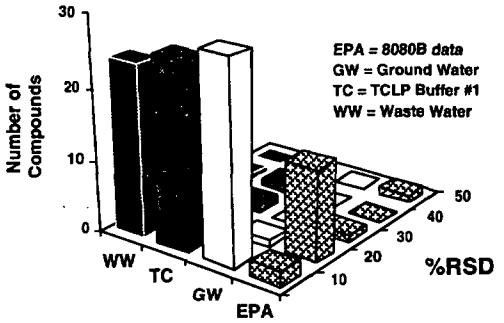

Figure 4. High Level Pesticide %RSD.

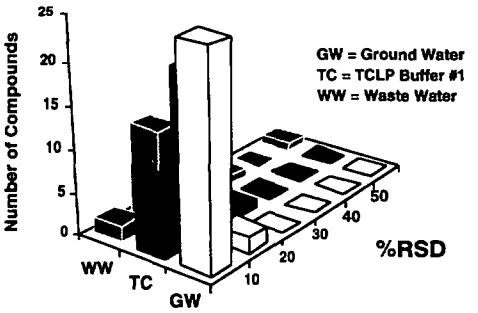

Figure 5. Low Level Pesticide %RSD.

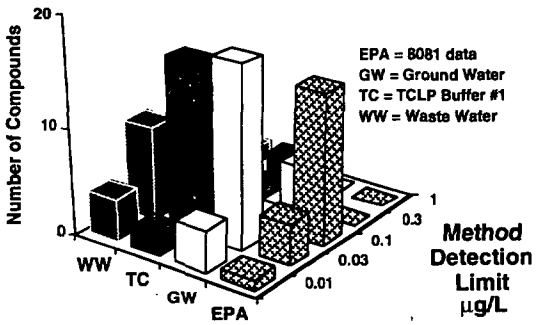

Figure 6. Pesticide Method Detection Limits.

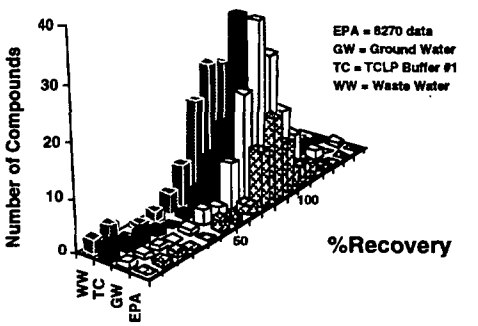

Figure 7. High Level BNA Recovery.

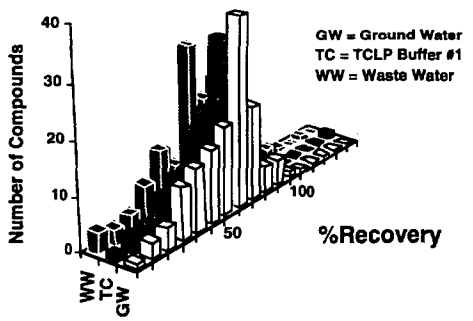

Figure 8. Low Level BNA Recovery.

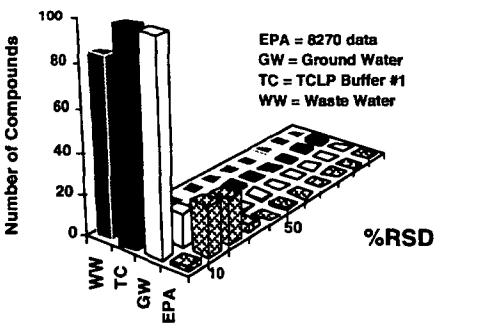

Figure 9. High Level BNA %RSD.

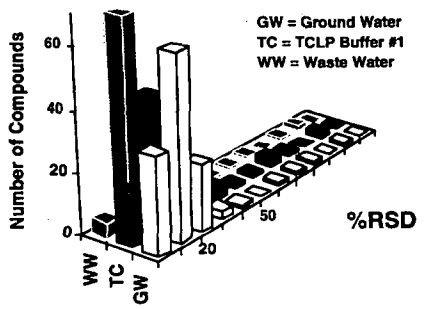

Figure 10. Low Level BNA %RSD.

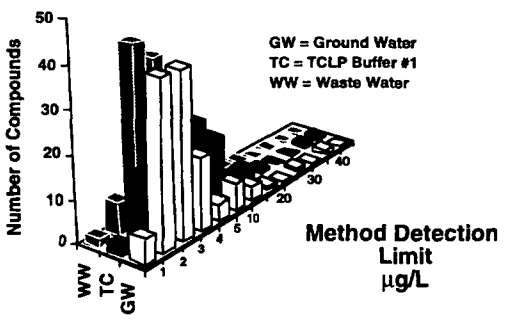

Figure 11. BNA Method Detection Limits.

Table 1. Organochlorine Pesticides and Spike Concentrations

Compound	Low (µg/L)	High (µg/L)
Aldrin	0.05	2.5
α-BHC	0.05	2.5
β-BHC	0.05	2.5
δ-BHC	0.05	2.5
γ-BHC	0.05	2.5
α-Chlordane	0.05	2.5
γ-Chlordane	0.05	2.5
p-Chlorobenzilate	0.10	5.0
4,4'-DDD	0.10	5.0
4,4'-DDE	0.10	5.0
4,4'-DDT	0.10	5.0
Diallate (I & II)	1.0	50.
Dieldrin	0.10	5.0
Endosulfan I	0.05	2.5
Endosulfan II	0.10	5.0
Endosulfan sulfate	0.10	5.0
Endrin	0.10	5.0
Endrin aldehyde	0.10	5.0
Endrin Ketone	0.10	5.0
Heptachlor	0.05	2.5
Heptachlor epoxide	0.05	2.5
Isodrin	0.05	2.5
Kepone	0.5	25.
Methoxychlor	0.5	25.
Methyl parathion	0.05	2.5
Parathion	0.10	5.0
Surrogates		
Decachlorobiphenyl	0.20	10
Dibutylchlorendate		5.0
Tetrachloro-m-xylene	0.10	5.0

Table 2. Semivolatile Compounds (BNAs) and Spike Concentrations (µg/L)

Compound	Low	High*
Acenaphthene	10	500
Acenaphthylene	10	500
Acetophenone	10	500
2-Acetylaminofluorene	20	1000
4-Aminobiphenyl	10	500
Aniline	10	500
Anthracene	10	500
Aramite	20	ns
Benzo[a]anthracene	10	500
Benzo[b]fluoranthene	10	500
Benzo[k]fluoranthene	10	500
Benzo[g,h,i]perylene	10	500
Benzo[a]pyrene	10	500
Benzyl alcohol	10	500
Bis(2-chloroethoxy)methane	10	500
Bis(2-chloroethyl)ether	10	500
Bis(2-chloroisopropyl)ether	10	500
Bis(2-ethylhexyl)phthalate	10	500
4-Bromophenyl phenyl ether	10	500
Butyl benzyl phthalate	10	500
Carbazole	10	500
4-Chloroaniline	10	500
p-Chlorobenzilate	10	500
4-Chloro-3-methylphenol	10	500
2-Chloronaphthalene	10	500
2-Chlorophenol	10	500
4-Chlorophenyl phenyl ether	10	500
Chrysene	10	500
Diallate	10	500
Dibenz[a,h]anthracene	10	500
Dibenzofuran	10	500
Di-n-butyl phthalate	10	500
1,2-Dichlorobenzene	10	500
1,3-Dichlorobenzene	10	500
1,4-Dichlorobenzene	10	500
3,3'-Dichlorobenzidine	10	500
2,4-Dichlorophenol	10	500
2,6-Dichlorophenol	10	500
Diethyl phthalate	10	500
Dimethoate	20	1000
p-(Dimethylamino)azobenzene	10	500
7,12-Dimethylbenz[a]anthracene	10	500
3,3'-Dimethylbenzidine *(accidentally left out of spike)*		
α, α-Dimethyl-phenethylamine	50	2500
2,4-Dimethylphenol	10	500
Dimethyl phthalate	10	500
1,3-Dinitrobenzene	20	1000
4,6-Dinitro-2-methylphenol	10	500
2,4-Dinitrophenol	10	500
2,4-Dinitrotoluene	10	500
2,6-Dinitrotoluene	10	500
Di-n-octyl phthalate	10	500
Dinoseb	10	500
Diphenylamine *(coelution problem, not spiked)*		
Disulfoton	10	500
Ethyl Methacrylate	20	1000
Ethyl methanesulfonate	10	500
Famphur	10	500
Fluoranthene	10	500
Fluorene	10	500
Hexachlorobenzene	10	500
Hexachlorobutadiene	10	500
Hexachlorocyclopentadiene	10	500
Hexachloroethane	10	500

Compound	Low	High*
Hexachlorophene	50	2500
Hexachloropropene	10	500
Indeno(1,2,3-cd)pyrene	10	500
Isophorone	10	500
Isosafrole	10	500
Methapyrilene	10	500
3-Methylcholanthrene	10	500
Methyl methanesulfonate	10	500
2-Methylnaphthalene	10	500
2-Methylphenol	10	500
3-Methylphenol *(coelution problem, not spiked)*		
4-Methylphenol	10	500
Naphthalene	10	500
1,4-Naphthoquinone	10	500
1-Naphthylamine	10	500
2-Naphthylamine	10	500
2-Nitroaniline	10	500
3-Nitroaniline	10	500
4-Nitroaniline	10	500
Nitrobenzene	10	500
2-Nitrophenol	10	500
4-Nitrophenol	10	500
4-Nitroquinoline 1-oxide	44	2200
N-Nitrosodi-n-butylamine	10	500
N-Nitrosodiethylamine	10	500
N-Nitrosodimethylamine	10	500
N-Nitrosodiphenylamine	10	500
N-Nitrosodi-n-propylamine	10	500
N-Nitrosomethylethylamine	10	500
N-Nitrosomorpholine	10	500
N-Nitrosopiperidine	10	500
N-Nitrosopyrrolidine	10	500
5-Nitro-o-toluidine	20	1000
Pentachlorobenzene	10	500
Pentachloroethane	50	2500
Pentachloronitrobenzene	10	500
Pentachlorophenol	10	500
Phenacetin	20	1000
Phenanthrene	10	500
Phenol	10	500
p-Phenylene diamine	50	2500
Phorate	10	500
2-Picoline	10	500
Pronamide	10	500
Pyrene	10	500
Pyridine	10	500
Safrole	10	500
1,2,4,5-Tetrachlorobenzene	10	500
2,3,4,6-Tetrachlorophenol	10	500
Tetraethyl dithiopyrophosphate	10	500
o-Toluidine	20	1000
1,2,4-Trichlorobenzene	10	500
2,4,5-Trichlorophenol	10	500
2,4,6-Trichlorophenol	10	500
O,O,O-Triethyl phosphorothioate	10	500
1,3,5-Trinitrobenzene	44	2200
Surrogates		
Nitrobenzene-d_5	50	500
2-Fluorobiphenyl	50	500
p-Terphenyl-d_{14}	50	500
Phenol-d_5	100	1000
2-Fluorophenol	100	1000
2,4,6-Tribromophenol	100	1000

ns - not spiked

* High level spike concentration for ground water is 40% of the listed value and the high level spike concentration for waste water is 50% of the listed value.

Table 3. Pesticide Accuracy and Precision

Compound	Ground Water				TCLP Buffer				Waste Water			
	High		Low		High		Low		High		Low	
	%R	%RSD	%R	%RSD	%R	%RSD	%R	%RSD	%R	%RSD	%R	%RSD
Aldrin	97	5	92	9	90	5	93	10	78	8	110	22
α-BHC	86	7	85	6	87	11	92	12	79	7	interference	
β-BHC	91	6	95	7	82	5	88	11	81	7	65	7
δ-BHC	90	8	89	8	89	6	94	8	69	9	64	22
γ-BHC	82	7	83	6	78	6	80	12	76	8	51	10
α-Chlordane	99	5	105	7	91	3	99	5	83	9	74	22
γ-Chlordane	98	5	102	8	90	6	93	7	86	9	45	14
Chlorobenzilate	94	6	101	10	80	3	105	12	106	7	interference	
4,4'-DDD	89	6	91	7	79	4	88	4	88	9	81	23
4,4'-DDE	92	5	92	7	83	5	83	11	79	9	53	14
4,4'-DDT	97	6	101	9	89	4	94	15	102	10	94	30
Diallate I	70	5	84	7	62	5	84	12	79	6	70	21
Diallate II	74	5	84	6	59	7	69	17	88	6	44	51
Dieldrin	98	5	100	7	92	7	92	10	89	8	55	11
Endosulfan I	97	5	102	7	93	4	93	9	89	9	74	12
Endosulfan Sulfate	91	4	95	9	91	4	92	11	79	9	41	28
Endrin	97	5	100	7	91	4	96	9	89	10	59	14
Endrin Aldehyde	91	6	106	7	69	34	91	12	42	3	36	28
Average of all pesticides	93	6	97	8	85	7	90	11	81	10	60	20

Table 4. Average Pesticide Accuracy and Precision vs EPA Data

Compound	Accelerated One-Step™ Extractor/Concentrator		8080B			
	Average %R	Average %RSD	%R	%R Range	%RSD Limit	%RSD Single Analyst
Aldrin	93	10	81	42-122	21	16
α-BHC	86	9	84	37-134	24	13
β-BHC	84	7	81	17-147	32	22
δ-BHC	83	10	81	19-140	36	18
γ-BHC	75	8	82	32-127	23	12
α-Chlordane	92	9	82	45-119	20	13
γ-Chlordane	86	8	82	45-119	20	13
Chlorobenzilate	97	8				
4,4'-DDD	86	9	84	31-141	28	20
4,4'-DDE	80	9	85	30-145	28	13
4,4'-DDT	96	12	93	25-160	36	17
Diallate I	75	9				
Diallate II	70	15				
Dieldrin	88	8	90	36-146	38	12
Endosulfan I	91	8	97	45-153	25	10
Endosulfan Sulfate	82	11	89	26-144	27	13
Endrin	89	8	89	30-147	37	20
Endrin Aldehyde	73	15				
Average of all pesticides	85	10	85		29	16

Table 5. Pesticide Method Detection Limits

Compound	Ground Water Low Level		TCLP Buffer Low Level		Waste Water Low Level	
	MDL	RQL	MDL	RQL	MDL	RQL
Aldrin	0.012	0.049	0.014	0.057	0.036	0.143
α-BHC	0.008	0.031	0.016	0.066	interference	
β-BHC	0.010	0.039	0.014	0.057	0.007	0.027
δ-BHC	0.011	0.044	0.012	0.046	0.022	0.088
γ-BHC	0.008	0.032	0.014	0.057	0.008	0.032
α-Chlordane	0.012	0.047	0.007	0.029	0.026	0.106
γ-Chlordane	0.013	0.052	0.010	0.039	0.010	0.040
Chlorobenzilate	0.032	0.127	0.038	0.152	interference	
4,4'-DDD	0.018	0.074	0.010	0.041	0.056	0.225
4,4'-DDE	0.020	0.079	0.027	0.107	0.022	0.089
4,4'-DDT	0.026	0.105	0.044	0.174	0.084	0.337
Diallate I	0.169	0.678	0.301	1.206	0.435	1.739
Diallate II	0.159	0.637	0.343	1.373	0.676	2.703
Dieldrin	0.020	0.080	0.028	0.112	0.018	0.071
Endosulfan I	0.010	0.042	0.013	0.050	0.015	0.060
Endosulfan Sulfate	0.025	0.098	0.030	0.120	0.036	0.142
Endrin	0.021	0.085	0.027	0.110	0.027	0.110
Endrin Aldehyde	0.024	0.094	0.032	0.130	0.027	0.109
Average of all pesticides	0.038	0.152	0.053	0.213	0.083	0.332

Table 6. Average Pesticide Method Detection Limits vs. EPA Data

Compound	Accelerated One-Step™ Extractor/Concentrator		8081
	Average MDL	Average RQL	MDL
Aldrin	0.021	0.083	0.034
a-BHC	0.012	0.048	0.035
b-BHC	0.010	0.041	0.023
g-BHC	0.010	0.040	0.025
d-BHC	0.015	0.059	0.024
a-Chlordane	0.015	0.061	0.008
g-Chlordane	0.011	0.044	0.037
Chlorobenzilate	0.035	0.140	
4,4'-DDD	0.028	0.113	0.050
4,4'-DDE	0.023	0.091	0.058
4,4'-DDT	0.051	0.205	0.081
Diallate I	0.302	1.207	
Diallate II	0.393	1.571	
Dieldrin	0.022	0.088	0.044
Endosulfan I	0.013	0.051	0.030
Endosulfan Sulfate	0.030	0.120	0.035
Endrin	0.025	0.101	0.039
Endrin Aldehyde	0.028	0.111	0.050
Average of all pesticides	0.055	0.221	0.043

Table 7. BNA Accuracy and Precision

Compound	Ground Water				TCLP Buffer				Waste Water			
	High		Low		High		Low		High		Low	
	%R	%RSD	%R	%RSD	%R	%RSD	%R	%RSD	%R	%RSD	%R	%RSD
Acenaphthene	88	9	70	7	91	4	74	11	69	6	54	15
Acenaphthylene	87	8	60	6	89	5	66	8	72	5	52	15
Acetophenone	97	6	67	9	81	5	67	17	83	4	86	13
2-Acetylaminofluorene	95	11	36	12	115	3	30	39	102	10	71	14
4-Aminobiphenyl	75	15	41	30	140	10	57	28	114	16	29	21
Aniline	69	7	72	11	92	8	75	20	125	12	89	13
Anthracene	87	7	57	6	76	4	61	7	60	5	41	21
Aramite 1	not spiked		92	19	not spiked		101	17	not spiked		77	22
Aramite 2	not spiked		70	26	not spiked		87	21	not spiked		74	18
Benzo[a]anthracene	88	7	57	9	80	4	62	11	71	5	37	30
Benzo[b]fluoranthene	108	5	45	14	86	7	56	13	66	7	37	30
Benzo[k]fluoranthene	97	7	60	8	79	5	66	26	81	4	37	31
Benzo[g,h,i]perylene	81	5	35	13	77	2	48	20	71	3	21	37
Benzo[a]pyrene	86	7	33	8	87	5	40	19	74	8	34	29
Benzyl alcohol	83	8	58	13	100	1	59	21	97	12	68	12
Bis(2-chloroethoxy)methane	108	9	91	7	113	4	94	17	112	4	93	13
Bis(2-chloroethyl)ether	78	7	72	9	80	5	68	25	91	7	68	17
Bis(2-chloroisopropyl)ether	69	8	86	15	118	5	85	18	131	6	57	15
Bis(2-ethylhexyl)phthalate	89	7	23	17	94	1	156	49	76	17	111	22
4-Bromophenyl phenyl ether	104	10	77	14	87	4	82	6	63	4	44	16
Butyl benzyl phthalate	91	5	42	20	92	5	47	16	68	14	42	22
Carbazole	35	8	25	10	43	5	28	9	39	6	35	18
4-Chloroaniline	49	9	62	9	87	8	71	19	92	7	55	21
p-Chlorobenzilate	84	4	40	19	71	3	46	20	56	11	39	19
4-Chloro-3-methylphenol	77	7	55	7	110	5	55	8	113	4	59	15
2-Chloronaphthalene	88	10	97	6	131	5	100	13	108	10	88	14
2-Chlorophenol	70	7	45	8	70	7	45	31	81	7	52	22
4-Chlorophenyl phenyl ether	102	8	90	10	104	4	93	10	78	9	56	15
Chrysene	93	9	71	10	83	4	69	16	73	1	39	30
Diallate 1	113	12	72	16	83	4	80	14	64	7	58	17
Diallate 2	114	8	61	9	78	4	66	10	58	10	53	12
Dibenz[a,h]anthracene	83	7	29	16	80	4	40	22	70	5	19	45
Dibenzofuran	97	8	78	6	96	4	82	7	77	11	64	12
Di-n-butyl phthalate	100	7	60	21	97	4	81	16	70	12	87	20
1,2-Dichlorobenzene	69	4	56	13	65	9	55	24	68	2	51	19
1,3-Dichlorobenzene	67	4	55	13	60	8	50	27	64	4	50	20
1,4-Dichlorobenzene	69	4	60	9	65	7	56	28	70	3	52	19
3,3'-Dichlorobenzidine	109	19	25	33	117	2	23	43	94	9	32	7
2,4-Dichlorophenol	74	11	45	12	83	5	47	18	86	8	54	13
2,6-Dichlorophenol	101	10	49	20	93	0.4	55	21	96	9	77	15
Diethyl phthalate	100	6	72	13	106	7	84	12	87	10	92	11
Average of all BNAs	86	9	55	17	84	8	59	25	76	10	56	23

Table 8. Average BNA Accuracy and Precision vs EPA Data

Compound	Accelerated One-Step™ Extractor/Concentrator		8270 Rev 2 1990			
	Average %R	Average %RSD	%R	%R Range	%RSD Limit	%RSD Single Analyst
Acenaphthene	74	9	96	60-132	28	15
Acenaphthylene	71	8	89	54-126	40	24
Acetophenone	80	9				
2-Acetylaminofluorene	75	15				
4-Aminobiphenyl	76	20				
Aniline	87	12				
Anthracene	64	8	80	43-118	32	21
Aramite 1	90	19				
Aramite 2	77	22				
Benzo[a]anthracene	66	11	88	42-133	28	15
Benzo[b]fluoranthene	66	13	93	42-140	39	22
Benzo[k]fluoranthene	70	14	87	25-145	32	19
Benzo[g,h,i]perylene	55	13	98	D-195	59	29
Benzo[a]pyrene	59	13	90	32-148	39	22
Benzyl alcohol	77	11				
Bis(2-chloroethoxy)methane	102	9	112	49-165	35	16
Bis(2-chloroethyl)ether	76	12	86	43-126	55	35
Bis(2-chloroisopropyl)ether	91	11	103	63-139	46	24
Bis(2-ethylhexyl)phthalate	91	19	84	29-137	41	26
4-Bromophenyl phenyl ether	76	9	91	65-114	23	13
Butyl benzyl phthalate	63	14	66	D-140	23	18
Carbazole	34	9				
4-Chloroaniline	69	12				
p-Chlorobenzilate	56	13				
4-Chloro-3-methylphenol	78	8	84	41-128	37	23
2-Chloronaphthalene	102	10	89	65-114	13	7
2-Chlorophenol	60	14	78	36-120	29	18
4-Chlorophenyl phenyl ether	87	9	91	38-145	33	20
Chrysene	71	12	93	44-140	48	28
Diallate 1	78	12				
Diallate 2	72	9				
Dibenz[a,h]anthracene	53	17	88	D-200	70	30
Dibenzofuran	82	8				
Di-n-butyl phthalate	82	13	59	8-111	17	13
1,2-Dichlorobenzene	61	12	80	49-112	31	20
1,3-Dichlorobenzene	58	13	86	17-154	42	25
1,4-Dichlorobenzene	62	12	73	37-106	32	24
3,3'-Dichlorobenzidine	67	19	123	8-213	71	28
2,4-Dichlorophenol	65	11	87	53-122	26	15
2,6-Dichlorophenol	78	13				
Diethyl phthalate	90	10	43	D-100	27	28
Average of all BNAs	69	16	83		36	21

Table 9. BNA Method Detection Limits

Compound	Ground Water Low Level		TCLP Buffer Low Level		Waste Water Low Level		Overall Average	
	MDL	RQL	MDL	RQL	MDL	RQL	MDL	RQL
Acenaphthene	1.5	6.1	2.5	9.9	2.5	9.9	2.2	8.6
Acenaphthylene	1.1	4.5	1.6	6.2	2.3	9.2	1.7	6.6
Acetophenone	1.8	7.3	3.4	13.5	3.3	13.1	2.8	11.3
2-Acetylaminofluorene	2.6	10.5	7.0	28.0	6.0	23.9	5.2	20.8
4-Aminobiphenyl	3.6	14.5	4.8	19.2	1.8	7.2	3.4	13.6
Aniline	2.3	9.3	4.5	17.9	3.3	13.3	3.4	13.5
Anthracene	0.9	3.8	1.2	4.8	2.6	10.2	1.6	6.3
Aramite 1	10.4	41.4	10.1	40.6	10.0	40.0	10.2	40.7
Aramite 2	11.1	44.4	10.8	43.1	7.8	31.3	9.9	39.6
Benzo[a]anthracene	1.5	6.1	2.1	8.4	3.3	13.3	2.3	9.3
Benzo[b]fluoranthene	1.9	7.5	2.2	8.7	3.3	13.1	2.4	9.8
Benzo[k]fluoranthene	1.4	5.4	5.2	20.9	3.5	13.8	3.3	13.4
Benzo[g,h,i]perylene	1.4	5.7	2.9	11.7	2.3	9.3	2.2	8.9
Benzo[a]pyrene	0.8	3.1	2.2	8.9	3.0	11.9	2.0	8.0
Benzyl alcohol	2.3	9.1	3.7	14.7	2.4	9.4	2.8	11.1
Bis(2-chloroethoxy)methane	2.0	7.9	4.9	19.4	3.7	14.7	3.5	14.0
Bis(2-chloroethyl)ether	2.0	8.0	5.0	20.1	3.5	14.2	3.5	14.1
Bis(2-chloroisopropyl)ether	3.9	15.7	4.5	18.2	2.6	10.4	3.7	14.8
Bis(2-ethylhexyl)phthalate	1.1	4.5	22.9	91.8	7.4	29.6	10.5	42.0
4-Bromophenyl phenyl ether	3.3	13.1	1.4	5.8	2.1	8.3	2.3	9.1
Butyl benzyl phthalate	2.5	9.9	2.2	8.7	2.8	11.2	2.5	10.0
Carbazole	0.8	3.0	0.8	3.0	1.9	7.7	1.1	4.6
4-Chloroaniline	1.6	6.4	4.1	16.5	3.5	14.0	3.1	12.3
p-Chlorobenzilate	2.3	9.1	2.8	11.1	2.3	9.1	2.4	9.8
4-Chloro-3-methylphenol	1.1	4.5	1.4	5.6	2.6	10.5	1.7	6.9
2-Chloronaphthalene	1.7	6.9	3.8	15.1	3.8	15.3	3.1	12.4
2-Chlorophenol	1.0	4.1	4.1	16.6	3.4	13.6	2.9	11.4
4-Chlorophenyl phenyl ether	2.8	11.0	2.9	11.7	2.6	10.5	2.8	11.1
Chrysene	2.2	8.7	3.2	12.9	3.5	14.0	3.0	11.9
Diallate 1	3.4	13.7	3.2	13.0	2.9	11.6	3.2	12.8
Diallate 2	1.6	6.3	1.9	7.7	1.9	7.4	1.8	7.2
Dibenz[a,h]anthracene	1.4	5.6	2.7	10.8	2.5	10.0	2.2	8.8
Dibenzofuran	1.3	5.2	1.8	7.1	2.3	9.4	1.8	7.2
Di-n-butyl phthalate	3.8	15.1	3.8	15.0	5.3	21.3	4.3	17.2
1,2-Dichlorobenzene	2.2	9.0	3.9	15.8	2.8	11.4	3.0	12.0
1,3-Dichlorobenzene	2.2	8.9	4.0	16.0	3.1	12.2	3.1	12.4
1,4-Dichlorobenzene	1.6	6.5	4.6	18.5	2.9	11.7	3.1	12.2
3,3'-Dichlorobenzidine	2.4	9.7	3.0	11.8	0.7	2.6	2.0	8.1
2,4-Dichlorophenol	1.6	6.5	2.5	10.1	2.1	8.5	2.1	8.4
2,6-Dichlorophenol	3.0	11.8	3.5	14.1	3.6	14.3	3.3	13.4
Diethyl phthalate	2.8	11.0	3.0	12.1	2.9	11.7	2.9	11.6
Average of all BNAs	3.3	13.2	5.3	21.3	4.1	16.3	4.5	18.0

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MICROSCALE SOLVENT EXTRACTION METHODS FOR TARRY SOILS FROM FORMER MANUFACTURED GAS PLANT (MGP) SITES

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ABSTRACT

This paper discusses two microscale solvent extraction (MSE) methods developed for the Electric Power Research Institute (EPRI) for use at former Manufactured Gas Plant (MGP) sites: one method is for the determination of monocyclic aromatic hydrocarbons (MAHs), particularly benzene, and the other method is for the determination of polycyclic aromatic hydrocarbons (PAHs).

The MAH MSE method was developed for a soil sampling and analysis project in which it was important to be able to quickly and accurately determine the concentration of benzene in soil samples in the field, and to use the soil concentrations to predict TCLP benzene results. This method consists of a solvent extraction using methylene chloride (DCM) that is carried out quickly over dry ice using refrigerator-chilled glassware and tools. The extraction is followed by analysis using gas chromatography with flame ionization detection (GC/FID).

The PAH MSE method was developed as a rapid method for use in the field to help aid in the placement of borings or monitoring wells and for screening contaminant levels during remedial activities. This method is a modification of EPA Methods 3550 and 8100. It consists of solvent extraction with DCM/acetone (1:1) followed by analysis using GC/FID.

Both methods were compared with standard EPA laboratory methods in different studies. The results of these comparison studies show that the MSE methods can provide accurate, rapid, and cost-effective results that are comparable to those of standard laboratory methods. Although the methods were developed primarily for field use at former MGP sites, they can be used at most sites where soils are contaminated with MAHs or PAHs, and can be used either in a field or standard laboratory setting.

INTRODUCTION

In recent years there has been an increasing interest in potential environmental or human health problems resulting from contaminants remaining at former manufactured gas plant (MGP) sites (Moore, 1989). As a result of this concern, the Electric Power Research Institute (EPRI) initiated a program to study several aspects of former MGP site contamination problems. One portion of the research sponsored by EPRI has been the development of analytical chemistry methods for the determination of the major constituents in tarry materials derived from MGP processes.

In a recent study (META, 1993), tarry residues from eight former MGP sites across the country were collected and analyzed. Although the tarry residues from former MGP processes are known to be complex mixtures of hundreds of compounds (EEI, 1984), concentrations as high as 328,000 mg/kg (or 32.8% of the total mass of the sample) of 19 polycyclic aromatic hydrocarbons (PAHs) and 25,200 mg/kg (or 2.52% of the mass of the sample) of 7 monocyclic aromatic hydrocarbons (MAHs) were observed among the eight samples tested. These high concentrations clearly show the likely abundance of MAHs and PAHs in MGP-related tars and tar-contaminated soils.

As a result of the significance of the MAH and PAH content in residues from former MGP sites, META Environmental, Inc. (META) developed, under EPRI sponsorship, two methods for analysis of tarry MGP residues and soils. One method is for the determination of MAHs and the other method is for the determination of PAHs in MGP tars and soils. Both methods use microscale solvent extraction (MSE) methods followed by analysis using gas chromatography with flame ionization detection (GC/FID), and both methods are designed for easy adaptability for field use to provide accurate, rapid, and cost-sensitive analysis of samples during site investigations or remedial activities.

MICROSCALE SOLVENT EXTRACTION (MSE) METHODS

Both of the MSE methods presented here were developed for EPRI for use at former MGP sites, although the circumstances were different. The PAH MSE method was developed first, for use in rapidly characterizing subsurface soils during site characterization or remedial activities at MGP sites. Initially, the PAH results were used to help define the horizontal and vertical extent of contamination in subsurface soils, as well as to determine the most accurate placement of groundwater monitoring wells. The PAH MSE method has gone through several revisions in the years since it was first developed, and has been successfully used at approximately a dozen MGP sites across the country.

The MAH MSE method was developed more recently, primarily for the accurate determination of benzene in the field. Because benzene is a known constituent of MGP tarry residues and is included among the Toxicity Characteristics Leaching Procedure (TCLP) constituents, high concentrations of benzene in soils or residues will cause them to be classified as characteristically hazardous when the TCLP benzene concentration is

greater than 0.5 mg/L. If a relationship between the total benzene level and the TCLP benzene level in MGP samples can be established, then monitoring for total benzene levels in the field can be used to determine the probability that a given sample will fail the TCLP test for benzene. Being able to predict TCLP failure rapidly in the field can save considerable time and money during a variety of site activities.

Currently, there are several field methods for determining the concentration of benzene in soil samples, including purge and trap, portable photoionization detector (PID), and heated headspace methods. However, purge and trap analysis in the field is problematic, and in addition there has been growing concern that standard purge and trap techniques may significantly underestimate levels of volatile constituents, such as benzene, in soils and other solid matrices (Sawhney, 1988 and Steinberg, 1987). Field portable PIDs are not really appropriate because they monitor total volatile compounds and are not selective for the compound benzene. Heated headspace has been shown to be significantly less effective for soils that are high in organic content, such as soils containing MGP residues (Volce, 1993). Thus, there was a need to develop an alternate method for analysis of benzene in soils at former MGP sites.

As well as providing rapid turnaround of results either in a field or in-house laboratory setting, the MSE methods are cost-effective, with savings usually in the range of 20 to 50% of standard laboratory analysis fees. In addition, the MSE methods are more environmentally sound because of the reduced volumes of solvent used and solid and solvent waste produced. Furthermore, the smaller sample size necessary for the analysis significantly increases the options for available sampling techniques.

MAH MSE Method

In the MAH MSE method, all samples, solvents, glassware, and equipment are kept chilled to minimize the amount of volatilization that occurs during the sample preparation procedure. The MAH MSE method consists of the following steps:

1. approximately 2 grams of sample are placed in a 15 ml glass centrifuge tube that is in a holder over dry ice;
2. approximately 2 grams of anhydrous sodium sulfate are added;
3. surrogate standard and 5 ml of methylene chloride (DCM) are added and the tube is tightly capped;
4. the sample is shaken vigorously for at least 2 minutes, then centrifuged for 5 minutes; and
5. the extract is filtered through glass wool and sodium sulfate.

The extract is analyzed by gas chromatography using flame ionization detection (GC/FID), and positive results are quantified using the external standard method of calculation. Extraction efficiency is monitored by the recovery of the surrogate standard

compounds fluorobenzene (FB) and difluorotoluene (DFT). The detection limit for this method is 0.250 mg/kg (ppm).

PAH MSE Method

The PAH MSE method is a modification of EPA Methods 3550 and 8100 and consists of the following steps:

1. approximately 2 grams of sample are placed into a 20 ml glass scintillation vial along with 2 to 4 grams of anhydrous sodium sulfate;
2. surrogate standard and 10 ml of DCM/acetone (1:1) are added;
3. the sample is disrupted using an ultrasonic microtip probe for 2 minutes;
4. the extract is filtered through glass wool and sodium sulfate into a Kuderna-Danish (K-D) concentrator tube;
5. the soil sample is extracted twice more by shaking briefly with 2 X 5 ml of DCM/acetone; and
6. the extracts are combined and the volume reduced to 0.5 ml by K-D.

The final extract is analyzed by GC/FID and positive results are quantified using the internal standard method of calculation. Extraction efficiency is monitored by the recovery of the surrogate standard compound 2-fluorobiphenyl (2-FBP). The detection limit for this method is 0.025 mg/kg.

RESULTS AND DISCUSSION

The results of several studies comparing the MSE methods to standard methods are presented and discussed in the following paragraphs. It should be noted that graphical representations of the data are sometimes presented in units of μg/kg (ppb) rather than the standard units of mg/kg (ppm) used throughout this report. The use of μg/kg units in some figures is for convenience and visual simplicity only, and does not affect the discussion of the results.

MAH MSE Method

The MAH MSE method was compared to standard EPA methods in two studies. In one small study with 4 MGP soil samples, ranging in total MAH concentration from non-detect to 1,500 mg/kg, the MAH MSE method showed significantly higher concentrations for all MAHs than EPA Method 8020 (when concentrations were greater than the MAH MSE detection limit of 0.250 mg/kg). The results of this small study are presented in Table 1. As shown in this table, most of the Method 8020 results are 60 to 70% of the values obtained using the MAH MSE method.

In a second, larger study, 92 MGP soils were collected from ten different sites around the country. The samples were extracted and analyzed by META's laboratory using the MAH MSE method, and by a second laboratory using Methods 5030 and 8240 for the purge and trap extraction of volatile organic compounds followed by GC/MS analysis.

MAH MSE results for benzene ranged from non-detect (0.250 mg/kg) to 2,500 mg/kg while the Method 8240 benzene levels ranged from non-detect (0.005 mg/kg) to 1,100 mg/kg. The results are shown in Figure 1, which is a graphical representation of the base ten log of the MAH MSE benzene results (in μg/kg) plotted versus the base ten log of the Method 8240 benzene results (in μg/kg). Figure 1 also includes a 1:1 ratio line, and any points located to the left of this line indicate results where the benzene value obtained by the MAH MSE method was greater than the result obtained by Method 8240. As can be seen in this figure, the majority (88%) of the MAH MSE benzene results were greater than the Method 8240 benzene results. The correlation coefficient of the best fit line is 0.912, indicating that the results are comparable, and visual inspection of the graph indicates that the relationship is probably linear except for concentrations near or below the MAH MSE detection limit. As can also be seen in this figure, the greatest variability in the data occurs at the left hand side of the graph, when the MAH MSE benzene results are in the range of 1.0 mg/kg (ppm). This is not surprising since those measurements are made near the MAH MSE method detection limit of 0.250 mg/kg, and greater variability near the detection limit is common.

The ratio of the MAH MSE benzene results to the Method 8240 results has an average value of 34.7, indicating that measurements made using the MAH MSE method are an average of 35 times greater than measurements made using Method 8240. However, the standard deviation of the ratios is 103, indicating a large range of ratios, with a few very high ratios skewing the mean upwards. The median ratio is 3.4, and is a better indication of the actual difference observed between the methods.

Soil samples extracted by Method 5030 may be prepared in one of two ways, and the large differences between the analytical results can be accounted for regardless of the sample preparation technique. Low level soil samples are extracted by weighing 5 grams of soil into a tube, adding 5 ml of water, and bubbling an inert gas through. Studies performed by Steinberg (1987) and Sawhney (1988) indicate that low level purge and trap analysis only removes volatile compounds that are located in the soil pore spaces, and does not remove compounds that have diffused into the internal micropores of the soil. Since the MAH MSE method is a solvent extraction technique, it should be able to penetrate the soil particles and liberate the substances trapped inside, resulting in higher observed volatile compounds levels. In Method 5030, high level samples are first extracted by shaking 4 grams of soil with 10 ml of methanol, then spiking 5 ml of water with an aliquot of the methanol and bubbling inert gas through. Some of the soils analyzed for this project contained visible quantities of tarry residues, and would have been prepared using the high level technique. MGP tar residues are not very soluble in methanol, so the interaction between the volatile compounds and the extraction solvent is significantly reduced, resulting in impaired extraction efficiency. It has also been shown that methanol extraction of soils yields highly variable results and poor analytical precision (Volce, 1993). In contrast, the MAH MSE method utilizes DCM as an extraction solvent, which is capable of solubilizing a much greater proportion of the tar

matrix constituents than methanol, again resulting in an increase in the observed levels of volatile compounds.

The MAH MSE method for solvent extraction of soils for volatile components may be problematic in that the sample preparation procedure must be carried out quickly and carefully, preferably in a cool environment using chilled tools. However, the results of this study clearly indicate that it is a feasible alternative, and yields data that are a better representation of the true concentrations of volatile compounds in soil.

PAH MSE Results

The PAH MSE method was compared to standard EPA methods in two different studies. The first study was conducted as an interlaboratory study, with splits of 73 MGP soil samples extracted at META's laboratory by the PAH MSE method with analysis by GC/FID, and at a second laboratory by the EPA Method 3550 for the sonication extraction of soils with analysis by GC/MS (Method 8270). The total PAH results for these soils ranged from non-detect to 100,000 mg/kg by Method 8270, and from non-detect to 110,000 mg/kg by the PAH MSE method. Figure 2 is a graphical comparison of the total PAH results, with the base ten log of the PAH MSE total PAH results plotted versus the base ten log of the Method 8270 total PAH results. As can be seen in this figure, the PAH MSE data compared very well with the Method 8270 data. The relationship is nearly 1:1 (slope of best fit line = 1.01), indicating that the magnitude of the individual results from the two methods are very similar. Also, the correlation coefficient of the data is 0.996, again indicating that the results are very comparable, and that the relationship is linear.

One of the major concerns regarding the use of microscale modifications of standard methods has been the issue of sample size and the representativeness of samples (Kratochvil and Taylor, 1981). It has been speculated that the decrease in sample size (from 30 grams to 2 grams) may mean that a representative subsample would be difficult to collect given the observed heterogeneity of soil samples. If this were truly a problem, then the results of this study would have shown outlying points where non-representative subsamples were analyzed. A wide range of soil types (from clay to coarse sand and gravel) and concentration ranges (from visibly clean to visibly tarry) were examined during this study, so any problems with non-homogeneous sample matrices should have been readily apparent. The excellent correlation of the data points shown in Figure 2 indicates that such outliers were not present, so representative subsampling was not a problem in this study.

The second study was also conducted as an interlaboratory study, with splits of 49 MGP soil samples extracted at META's laboratory by the PAH MSE method with analysis by GC/FID, and at a second laboratory by the EPA Method 3540 for the Soxhlet extraction of soils followed by GC/MS analysis (Method 8270). The total PAH results ranged from non-detect to 1,310 mg/kg by Method 8270, and from non-detect to 3,130 mg/kg by the

PAH MSE method. Figure 3 shows a graphical comparison of the total PAH results, which is similar in format to Figure 2. The results of this study were somewhat different than those of the first study. Figure 3 includes a 1:1 ratio line, and any points located to the left of this line indicate results where the total PAH value obtained using the PAH MSE method was greater than the result obtained using Method 8270. As shown in this figure, the majority (85%) of the results are to the left of the 1:1 line, indicating that the PAH MSE method yielded consistently higher total PAH results than Method 8270. However, the correlation coefficient of the best fit line is 0.990 indicating that the results are still comparable, and the relationship appears linear, as it did in the first study.

There are two main differences between the first and second studies which could account for the different results. First, a different laboratory was used for the Method 8270 analyses in each study, whereas the same laboratory performed the PAH MSE method for both studies. Second, in the first study the samples were extracted by Method 3550 for the sonication extraction of soils and in the second study the samples were extracted by Method 3540 for the Soxhlet extraction of soils. Since the PAH MSE method is a modification of Method 3550, it is very similar to that method. The excellent correlation between the results in the first study may be a reflection of the similarity of the sample preparation procedures employed by the two laboratories. In the same way, the consistent under-recovery of analytes in the second study may be a reflection on the dissimilarity of the sample preparation procedures, or it may simply be a result of some kind of operational error by the second laboratory.

Operational factors that could result in a systematic bias in the sample results (i.e., consistent over- or under-recovery of analytes) include holding times (if exceeded), storage conditions (if the refrigerator is too warm), extraction efficiency (as monitored through the use of surrogate standards), and calibration of the analytical system (if old or degraded standard solutions are used). Operational factors that could result in non-systematic bias (i.e., only some sample results are affected) include sample matrix and heterogeneity (reflected in matrix spike recovery and duplicate RPD results), holding times (if only some samples exceed them), extraction efficiency (if only some surrogate recoveries are outside criteria), and improper handling of samples (left at room temperature, extract volume reduced too much). There was not enough information available for the second study to allow full evaluation of the source of error, although the fact that the PAH MSE and Method 8270 results correlate well certainly indicates a systematic source of bias rather than a non-systematic source.

In an attempt to learn more about the differences between the PAH MSE data and the Method 8270 data in the second study, the PAH results were summed according to the number of rings in each compound, then graphed in a fashion similar to the total PAH results. The graphs for the three to six ring compounds were very similar to the total PAH graph (Figure 3), and are not presented here. However, the graph for the two ring compounds was interesting, and is presented as Figure 4. Figure 4 illustrates that the

difference between the results for the two ring compounds was even greater than the difference between the total PAH results. Over 91% of the values obtained by using the PAH MSE method were greater than those obtained by using Method 8270. Furthermore, the average ratio of the MSE to 8270 results was 5.5, indicating that the MSE results were an average of five times greater than the 8270 results. (Whereas the average ratio for total PAHs was only 2.3). The two ring compounds are the most volatile of the PAH compounds, and as such are the most likely to be lost during the sample preparation procedure. The Soxhlet extraction procedure involves continuous heated solvent extraction of the soils for 16 to 24 hours. Soxhlet extraction is generally believed to be a more thorough extraction technique for soils than sonication because of the length of time involved. However, if not closely controlled it can lead to lower recoveries of the more volatile components. Volatile components may also be lost during the concentration procedure if the extract volume is reduced too much. It is probable that some combination of these factors resulted in the lower PAH results, particularly the two ring compound results, for the samples analyzed by Method 8270.

It should be noted that the PAH MSE analysis of the samples for the second comparison study was complicated by the presence of large quantities of interfering compounds. The peaks for those compounds sometimes coeluted with the target PAH peaks, making quantitation difficult. At sites containing interfering compounds, it is possible to introduce a cleanup or fractionation step to the PAH MSE method that would reduce or remove the analytical interference. Another possibility would be to analyze the PAH MSE extracts by GC/MS (if available) rather than GC/FID, which would also serve to remove the analytical interference.

QUALITY CONTROL

Standard Quality Control (QC) measures were employed for the MSE methods in all of the studies described in this paper. Parameters including surrogate standard recovery, internal standard performance, matrix spike recovery, and duplicate sample performance were investigated to evaluate the overall efficiency, precision, and accuracy of the methods. In addition, instrument detection limits and linearity were monitored through the analysis of initial and continuing calibration standards. Holding times were established to preserve sample integrity and representativeness. As many aspects of the standard EPA CLP Methods QA/QC program were emulated as was feasible for each MSE method. Some of the QC summary results of the MSE and standard methods are discussed here.

MSE Methods

Table 2 provides a summary of the QC data for the MSE methods. In this table, average recovery values for matrix spike samples, and average RPD values for duplicate samples refer to the average calculated for all compounds in all samples. The range given is for the maximum and minimum calculated values, considering all individual compound results in all samples.

As can be seen in Table 2, all EPA CLP criteria were met overall, although some individual measurements did exceed the stated criteria. Some fluctuation in QC results is normal and expected, even under the best operating conditions. The results in Table 2 depict a method that is in control, and performing satisfactorily.

Standard Methods

Table 3 provides a summary of the QC data for the standard methods. QC results for MAH MSE comparison study number 1 were not available for review, and are not included in Table 3. Table 3 includes QC results only for the matrix spike compounds that were directly comparable to the results of the MSE methods (i.e., MAHs and PAHs). Similarly, recoveries were evaluated only for the surrogate standards associated with the MAH and PAH compounds of interest.

As can be seen in Table 3, all EPA CLP criteria were met overall, although some individual measurements did exceed the stated criteria. The results in Table 3 indicate that the laboratory analytical system was in control during the analysis of the samples for these studies.

SUMMARY

Two microscale solvent extraction (MSE) methods for the analysis of MAHs and PAHs were introduced. Use of the methods is particularly suited to the analysis of soils containing MGP-related residues, in support of investigatory or remedial activities. Also, the methods are easily adaptable to a field laboratory setting, and are capable of providing rapid turnaround of analytical results.

The MSE methods were compared to their EPA GC/MS counterparts, and the comparisons were favorable. The MSE methods were shown to correlate well with results obtained using standard methods. Furthermore, it was demonstrated that QC results from the MSE methods were acceptable under the EPA criteria, and that acceptable precision and accuracy were possible.

It was suggested that use of the MSE methods would greatly benefit site investigation and remedial activities at former MGP sites, both in terms of reductions in costs and generated wastes and the efficiency and accuracy of the sampling/remedial program. Although the MSE methods have not been tested at other sites, it is speculated that their use is applicable at any site containing similar types of organic contamination, provided that significant analytical interferences are not present or are minimized appropriately.

Table 1

MAH MSE Comparison Study No. 1
(in mg/kg)

Compound	Sample 1		Sample 2		Sample 3		Sample 4	
	MSE	8020	MSE	8020	MSE	8020	MSE	8020
Benzene	ND[1]	ND[2]	ND	ND	1.0	0.32	62	42
Toluene	ND	ND	ND	0.002	ND	0.19	330	220
Ethylbenzene	ND	ND	ND	ND	0.94	0.57	110	77
Total Xylenes	ND	ND	ND	0.003	2.8	1.7	1,000	630
Total MAHs	**ND**	**ND**	**ND**	**0.005**	**4.7**	**2.8**	**1,500**	**970**

1 The detection limit for the MAH MSE Method is 0.250 mg/kg.

2 The detection limit for Method 8020 is 0.0013 mg/kg.

Figure 1

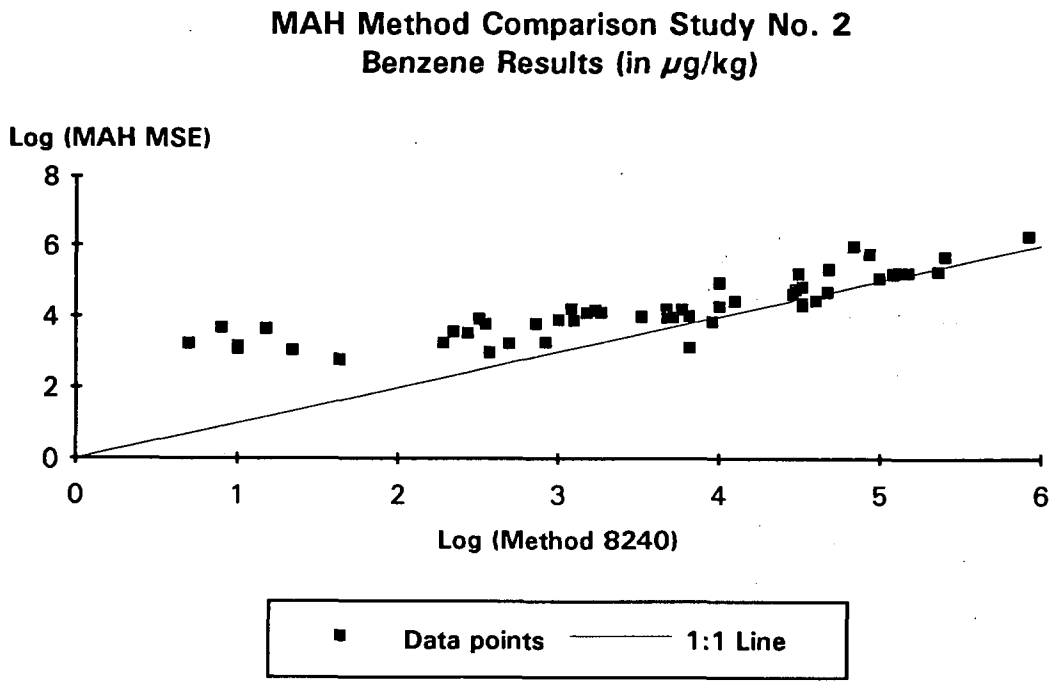

Figure 2

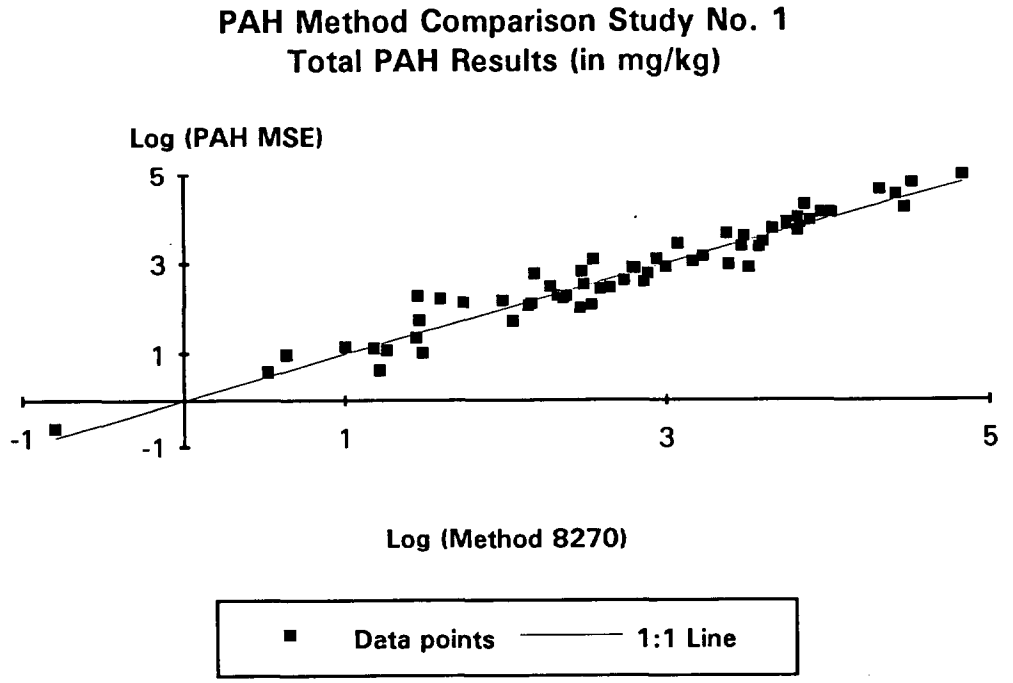

Figure 3

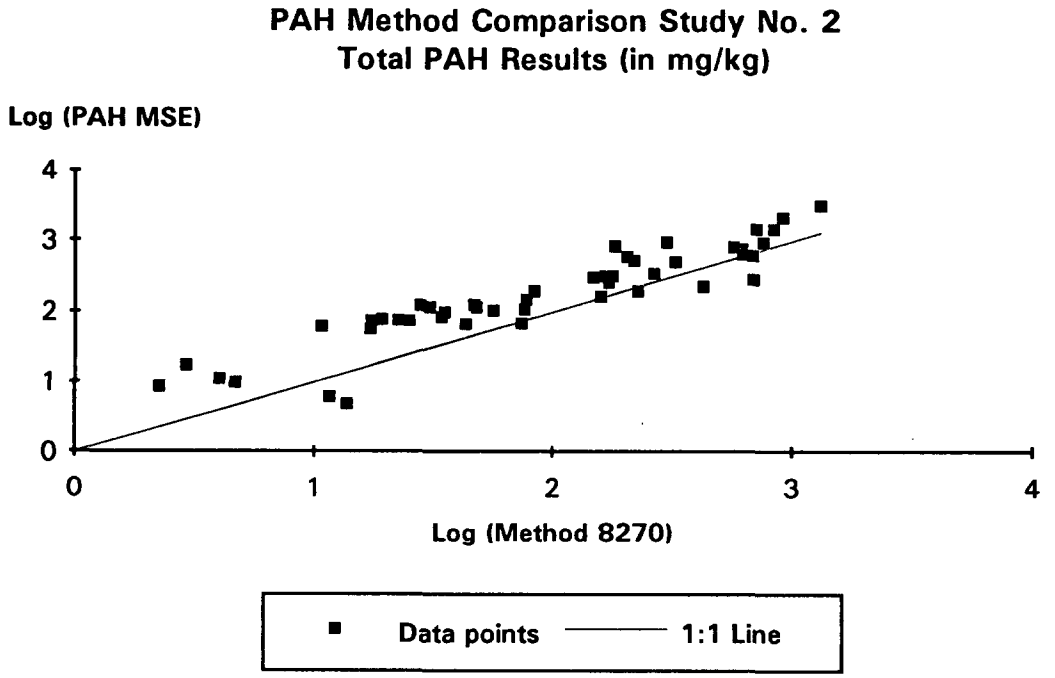

Figure 4

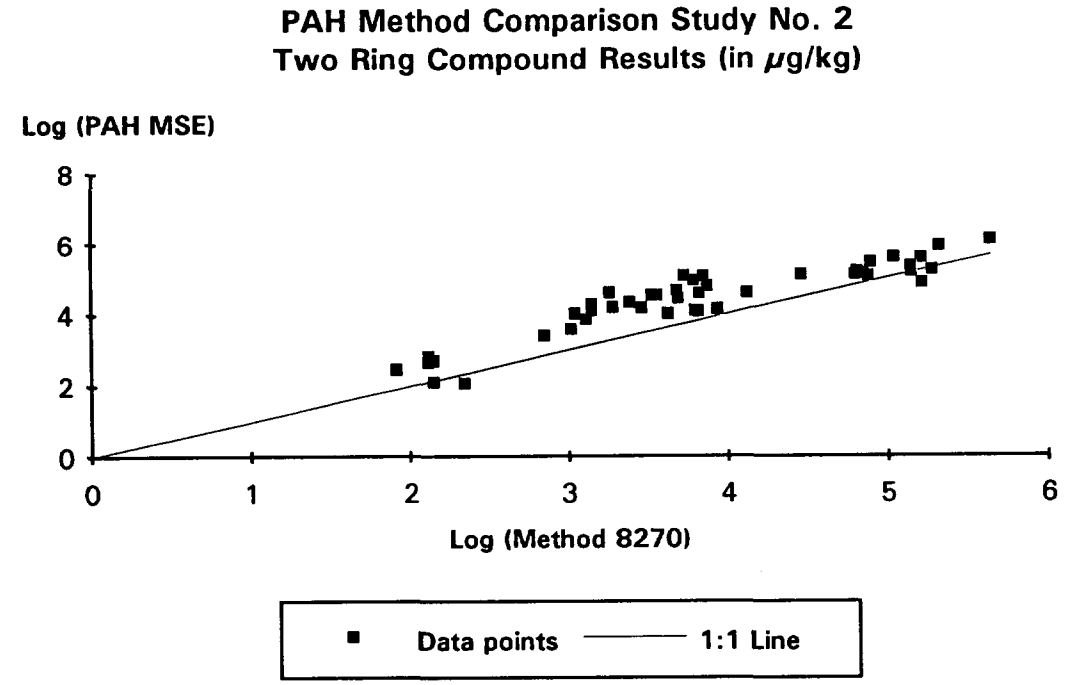

Table 2

Summary of MSE Methods QC Results

Audit		EPA CLP Criteria[4]	MAH MSE		PAH MSE	
			Study No. 1	Study No. 2	Study No. 1	Study No. 2
Matrix Spike %Recovery	Average	M: 66 - 139 P: 35 - 137	84%	82%	79%	85%
	Range		83 - 85	41 - 105	37 - 120	45 - 118
Duplicate Sample RPD[1]	Average	50%	9%	37%	38%	34%
	Range		6 - 11	0 - 120	0.4 - 180	0 - 90
Surrogate Standard 1[2] %Recovery	Average	M: 59 - 113 P: 43 - 116	107%	85%	91%	95%
	Range		93 - 131	38 - 119	52 - 123	56 - 141
Surrogate Standard 2[3] %Recovery	Average	59 - 113	101%	82%	NU	NU
	Range		90 - 119	41 - 127	NU	NU

1 Relative Percent Difference.

2 Surrogate standard 1 is fluorobenzene for MAH MSE, and 2-fluorobiphenyl for PAH MSE.

3 Surrogate standard 2 is difluorotoluene for MAH MSE, and is Not Used (NU) for PAH MSE.

4 EPA CLP criteria are taken from SOW OLM01, and are approximated using the most stringent criteria for compounds that are chemically similar to those analyzed for by the MSE methods. M and P refer to criteria for the MAH and PAH MSE methods, respectively.

Table 3

Summary of Standard Methods QC Results

Audit		EPA CLP Criteria[5]	Method 8240	Method 8270	
			Study No. 2	Study No. 1	Study No. 2
Matrix Spike Compound 1[1]	Ave %Rec	V: 66 - 142 S: 31 - 137	96%	91%	94%
	Range		45 - 125	42 - 141	34 - 186
	Ave RPD	V: 21 S: 19	5%	13%	24%
	Range		2 - 14	1 - 85	0.8 - 83
Matrix Spike Compound 2[2]	Ave %Rec	V: 59 - 139 S: 35 - 142	97%	145%	125%
	Range		46 - 134	0 - 440	52 - 228
	Ave RPD	V: 21 S: 36	7%	32%	34%
	Range		0 - 18	1 - 100	1.7 - 77
Duplicate Sample RPD	Average	50%	32%	12%	10%
	Range		0 - 100	0 - 67	0 - 52
Surrogate Standard Compound 1[3]	Ave %Rec	V: 84 - 138 S: 30 - 115	105%	92%	NA
	Range		81 - 141	42 - 139	NA
Surrogate Standard Compound 2[4]	Ave %Rec	V: 59 - 113 S: 18 - 137	90%	119%	NA
	Range		62 - 112	38 - 220	NA

1 Matrix spike compound 1 is benzene for Method 8240, and acenaphthene for Method 8270.

2 Matrix spike compound 2 is toluene for Method 8240, and pyrene for Method 8270.

3 Surrogate standard 1 is toluene-d8 for Method 8240, and 2-fluorobiphenyl for Method 8270.

4 Surrogate standard 2 is bromofluorobenzene for Method 8240, and p-terphenyl-d14 for Method 8270.

5 EPA CLP criteria are taken from SOW OLM01. V and S refer to criteria for Methods 8240 and 8270, respectively.

NA Information not available.

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DEVELOPMENT OF AN ENVIRONMENTAL METHOD FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOILS BY STATIC HEADSPACE GC/MS

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There are several methods available for analyzing volatile organic compounds in soils. The purge and trap technique is widely applied to the analysis of these compounds in soils. An analytical method is being developed using static headspace as an alternative approach to purge and trap.

Static headspace is a discontinuous gas extraction where the analytes partition between the sample and the headspace. Various soil types were analyzed using a GC/Saturn II Mass Spectrometer and conditions were optimized for separation, precision, detection limits and linearity. Standards were prepared by diffusing analytes through the soil (i.e. under zero headspace conditions) in order to simulate plume contaminated soils in the field. This was compared to the traditional technique of spiking the surface of the soil.

This method also studies the effects of pre-mixing of soils and the addition of organic modifiers to increase the gas phase concentration within the headspace in order to increase overall method sensitivity. Internal standards were added to a matrix modifying solution for quantitation.

INTRODUCTION

The most problematic concern of soils analysis is how to deal with the varying characteristics of the soil matrix. EPA methodologies which focus on the analysis of Volatile Organic Compounds (VOC's) in water have been developed around the Purge and Trap technique (1). Variables such as moisture content, density, % organic matter, amount of sand and silt, mineral content, and ionic interactions do not pose a major concern in water analysis as they do with soils.

Soil characteristics need to be identified because each region of the country will have a particular type of soil profile. These characteristics depend upon the native geology, vegetation, the presence of the agriculture, and the qualities of the local climate. Soil types may be grouped on the basis of their characteristics into two groups: Pedocals and Pedalfers. Pedocals are distinguished by the accumulation of carbonates, calcium, or magnesium in all or part of the soil. Pedalfers are distinguished by the absence of carbonates and usually by an accumulation of iron and aluminum compounds (2). Once the soils have been assigned to either of these two groups, they are further sub-typed into hundreds of classes based upon ten distinct characteristics describing the soil and its horizon (i.e. color, texture, structure, chemical composition including % organic matter, % clay, % sand, type, and geology, etc.).

All of these characteristics indicate that soils exhibit highly variable matrices. The reduction of variability in density, mineral content, and ionic interactions are some of the problems addressed in this paper.

Two types of soils were analyzed in this study: topsoil, and sand. These soil types represented extremes in % organic matter, mineral content, moisture, and densities. Each soil type has a different density ranging from 0.5 gm/mL (topsoil) to 3.00 gm/mL (sand). These densities cause the volume distribution within the headspace vial to vary. A way to reduce this variability within the vial is to add a Matrix Modifying Solution (MMS). The MMS is made up of a 100% saturated aqueous salt solution that is pH buffered below 2.

Utilizing a 100% aqueous salt solution eliminates the variability in mineral content and helps to offset the sodication process. The sodication process is a natural occurrence in areas of the country where precipitation is less than 20 inches annually. As the water evaporates in the atmosphere, the salts are left behind in the soil. The process of increasing the sodium saturation of the soils exchange process is called sodication. The hydrolysis of the Na^+ ions or Na_2C0_3 compounds can cause a strong alkaline reaction changing the pH of the soil also (3). With the addition of salt saturated MMS each sample has the same Na^+ concentration prior to analysis. The MMS also increases the ionic strength of the sample which leads to increased sensitivity in the headspace analysis.

Addition of acidified MMS to soil samples aids in the maintenance of constant pH

conditions prior to analysis (resistance to strong alkaline reactions such as those occurring in the sodication process). A low pH also helps to prevent dehydrohalogenation of compounds and serves as a preservative against microbial activity in the sample which could ultimately lead to degradation of analytes.

EXPERIMENTAL

The two types of soils analyzed in this study consisted of topsoil (very high organic content) and sand (very low organic content). Each of these soil types has a different density ranging from 0.5 gm/mL (topsoil) to 3.00 gm/mL (sand). These densities cause the volume distribution within the headspace vial to vary. An average 2g sample of each soil type used in this study occupied 4.0 mL (topsoil) and 0.67 mL (sand) volume within the vial. The resulting phase ratios (V_g/V_m) produced by a 2g sample of each soil type within a 22 mL vial was 4.5 (topsoil) and 31.8 (sand). This large difference in phase ratio produces significant differences in headspace measurements (4).

To reduce this volume and phase ratio variability, 10 mL of matrix modifying solution (MMS) was added to each 2g sample for a final volume of 14 mL (topsoil) and 10.67 mL (sand). The resulting phase ratio differences were significantly reduced (0.57 for topsoil and 1.06 for sand). The MMS is made up in 500 mL of reagent grade water. The solution is then pH buffered below 2 with Phosphoric Acid (H_3PO_4) and saturated to 100% with 170g Sodium Chloride (NaCl).

The analytes chosen for this study were the 502 A/B standards purchased from AccuStandard. A key factor in developing this method was finding an appropriate internal standard/surrogate mixture so that the analytes could be tracked throughout the entire chromatogram. The molecular weights, boiling points, and relative reaction chemistries (polarities) were studied for each of the 502 A/B analytes. The Method 8260 mix was selected because it contained four internal standards and three surrogates with similar properties of the 502 A/B analytes. Each internal standard was responsible for tracking approximately 13 compounds in each section of the chromatogram (see Table 1 for listing).

Internal Standards	RT	Surrogates	RT
Pentafluorobenzene	17:50	Dibromofluoromethane	16:30
1,4-Difluorobenzene	19:53	Toluene-d8	24:19
Chlorobenzene-d5	27:08	4-Bromofluorobenzene	29:16
1,4-Dichlorobenzene-d4	31:37		

Table 1. The relative retention times for the Method 8260 internal standards and surrogates. Each internal standard is responsible for tracking approximately 13 analytes.

Once the analyte list has been established, the next step in the development process is to select the proper detector and column for the analysis. Due to the volatility of the analytes, the detector should be very sensitive and the column should possess relatively high retention characteristics to give good chromatographic separation. The following GC conditions and 7000 Headspace Autosampler parameters used in this analysis are listed below.

Tekmar 7000 Headspace Autosampler

Platen temperature:	85°C
Sample equilibration time:	10 min. (FET mode)
	50 min. (samples)
Loop Size:	250 uL (EFT)
Vial size:	22 mL
Pressurize time:	0.20 min.
Pressure equilibration time:	0.08 min.
Loop fill time:	0.10 min.
Loop equilibration time:	0.08 min.
Mix:	10.00 min.
Mix power:	8
Injection time:	1.00 min.
Line temperature:	85°C
Loop temperature:	85°C
Transfer line:	0.32 mm fused silica
Transfer line back pressure:	15 psig
Vial pressurization setting:	15 psig
Vial needle flow rate:	40 mL/min.

Varian 3400 Gas Chromatograph/Saturn II Ion Trap Detector

Injector temperature:	200°C
Manifold temperature:	265°C
Transfer line temperature:	220°C
Oven temperature program:	
Initial temperature:	10°C hold 7 min.
Ramp 1 temperature:	4°C/min. to 100°C
Ramp 2 temperature:	10°C/min. to 200°C
Final temperature:	200°C hold 4 min.
Electron multiplier:	1400 mV
Target value:	17,000
Scan range:	48-260 amu

J&W DB-VRX (J&W Scientific, Folsum, California)
60 M x 0.32 mm ID x 1.8 udf
Carrier gas: Helium @ 1.0 mL/min.
Phase ratio: B=44 (High K= High retention)

The transfer line from the 7000 Headspace Autosampler was connected to the analytical column via a zero dead volume union.

RESULTS and DISCUSSION

I. Gas Sampling and Injection (FET)

Full Evaporation Technique (FET) is a process by which an aliquot of methanolic standard containing the volatile analytes of interest (usually 1-20 uL) is taken and placed into a headspace vial. The vial is then sealed and the analytes are fully vaporized. This technique is used to establish relative retention times and chromatographic separation. Figure 1 is an example of chromatographic separation from an FET injection. All compounds exhibit good chromatographic separation and response. The reproducibility study showed that 95% of the analytes fell below 5% RSD.

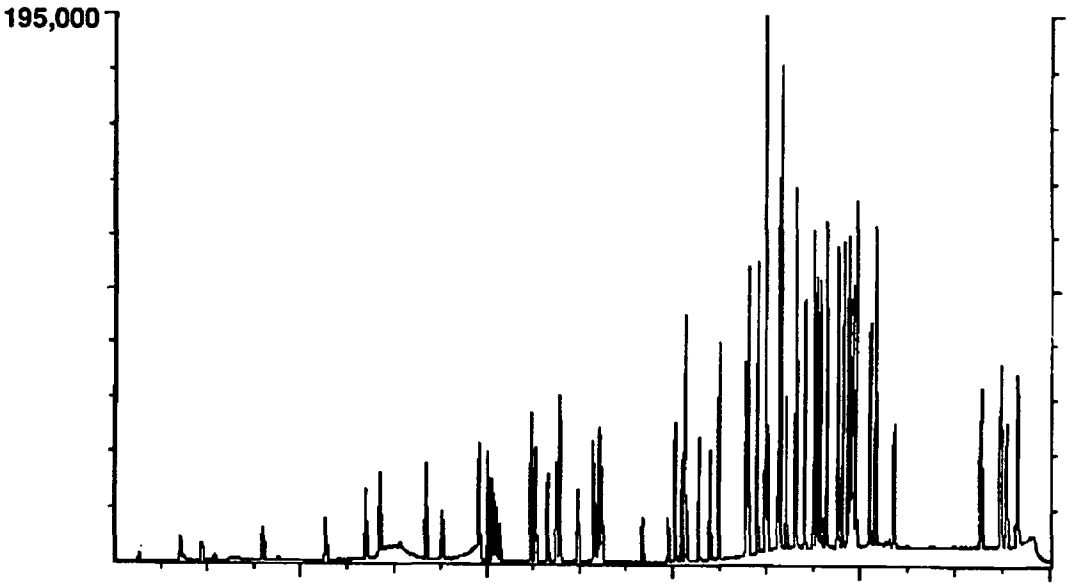

Figure 1: Chromatographic Separation from an FET injection

II. Static Partitioning/Mass Distribution- 2 Phase Equilibration

Once the retention times and chromatography were established, the reproducibility of a two phase gas/liquid headspace system was evaluated. For this experiment, 10 mL of the MMS containing an analyte concentration of 100 ppb and 50 ppb internal standards/ surrogates was added to a headspace vial. The analytes in solution were equilibrated at 85°C for 50 minutes. This standard represents a baseline for 100% recovery and serves as a comparison for soils analysis. It is a reference point to establish how much compound is being absorbed when a soil matrix is analyzed. The chromatogram in Figure 2 shows good response and chromatographic resolution. Four analytes and two surrogates were selected from each section of the chromatogram for reproducibility studies. Table 2 shows the %RSD's for 10 mL MMS based upon six replicate runs.

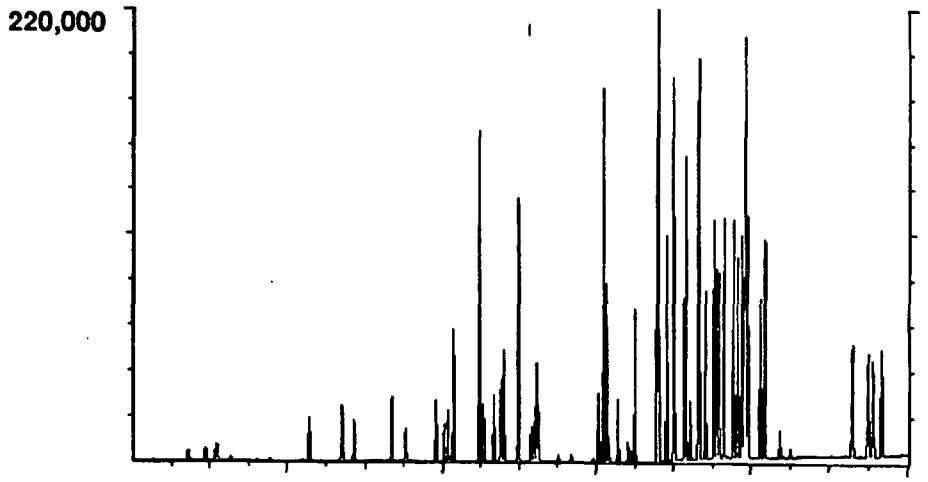

Figure 2: 10 mL MMS Spiked with 100 ppb 502 A/B Standard (IStd = 50 ppb)

	RSD
Trichloroflouromethane	2.4%
1,2,2-Trichloroethane	6.1
o-Xylene	2.8
1,2-Dichlorobenzene	2.0
Dibromoflouromethane (surr)	3.0
Toleuene - d_8 (surr)	0.5

Table 2. Reproducibility of a two phase gas/liquid headspace system (10 mL MMS)

III. Static Partitioning/Mass Distribution- 3 Phase Equilibration

A. Spiked sand vs. Diffused sand

The next experiment looked at the addition of 2 g of soil to the headspace vials for analysis. The addition of soil creates a three phase equilibrium system (solid, liquid, gas). The analytes must migrate from the soil into the MMS, and then partition between the MMS and the headspace. The first sample chosen for analysis was 2 g of sand. This represented the best case scenario because it has low adsorptivity and very low organic content. These characteristics indicate that sandy soils exhibit low matrix interferences.

Figure 3 illustrates an example of a 2 g spiked sand sample versus a 2 g diffused sand sample. Spiked sand represents a technique where the analyst spikes the analytes, internal standards, and surrogates directly into the sand. The 10 mL of MMS is then added to the sand and the vial capped. In a diffused sand sample, the analytes, internal standards, and surrogates are added directly to the MMS. The MMS (10 mL) is added to the 2 g soil sample and mixed on a rotator for one hour. The purpose of the diffused technique is to simulate real world plume contaminated samples.

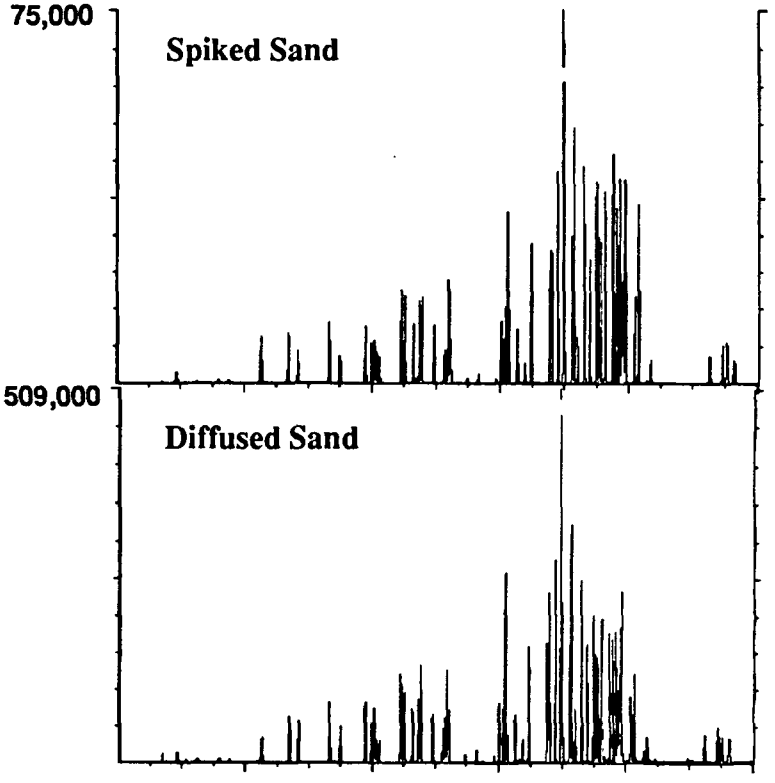

Figure 3: Spiked Sand technique VS. Diffused Sand technique

Table 3 shows the area counts and %RSD's comparing the two types of samples. The same four analytes and surrogates selected in the above study were used as reference points again. The area counts of the diffused sand sample are between six to twenty-two times greater than the spiked sand. This is because the analytes in the spiked sand have not been evenly diffused throughout the sample. The reproducibility over the average of six replicate runs indicated that 87% of the analytes had RSD's less than 10% for both samples.

	Spiked Area	Sand RSD	Diffused Area	Sand RSD
Tricholoroflouromethane	15715	11.5	147974	2.5
1,1,2-Trichloroethane	7324	8.2	160146	2.0
o-Xylene	37728	3.6	236264	2.5
1,2-Dichlorobenzene	10905	5.0	82523	8.5
Dibromoflouromethane (surr)	5352	4.8	45694	5.1
Toluene-d_8	17048	2.1	385076	2.2

Table 3. Area counts and % RSD's comparing spiked VS. diffused technique (sand)

B. Spiked topsoil vs. Diffused topsoil

The next sample consisted of 2 g of topsoil. This represented the worst case scenario because it has high adsorptivity and very high organic content. These characteristics indicate that topsoils exhibit a high degree of matrix interferences.

Figure 4 illustrates and example of a 2 g spiked topsoil versus a 2 g diffused topsoil. The technique for spiking and diffusing the analytes into the soil was the same as that used in the above sand study. When the analytes are spiked directly into the soil, the high organic content of topsoil results in localized adsorption. The localized spike has a limited surface area for analyte exchange and migration from the soil into the MMS. In a field sample, where contaminants have "plumed" through the soil, the surface area for analyte migration is much greater in comparison to a spiked sample.

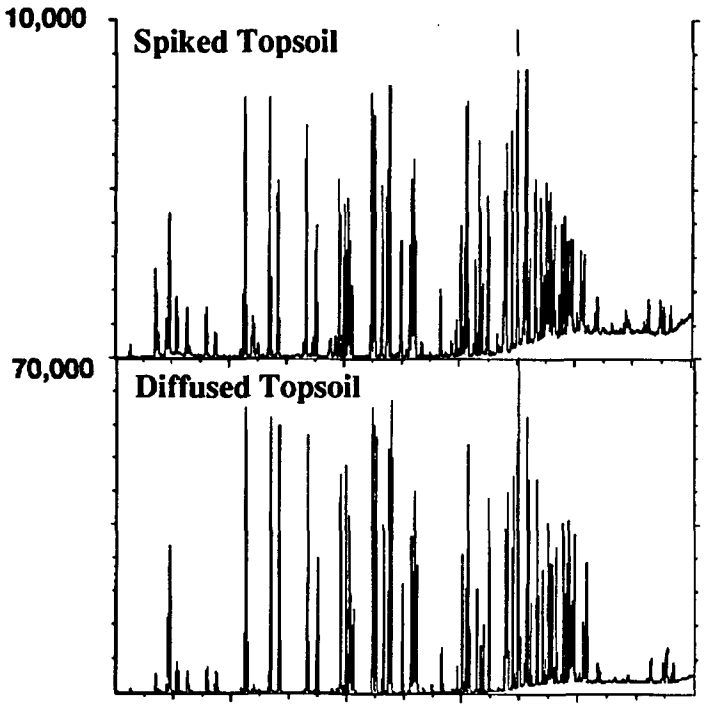

Figure 4: Spiked Topsoil technique VS. Diffused Topsoil technique

Table 4 shows the area counts and %RSD's for the comparison of the two types of samples. The same four analytes and surrogates selected in the above study were used as reference points again. The area counts of the diffused topsoil sample are once again greater than that of the spiked topsoil. The reproducibility over the average of six replicate runs indicated that 99% of the analytes in the diffused topsoil had RSD's less than 20%. Only 68% of the analytes in the spiked topsoil had RSD's less than 20%.

	Spiked Topsoil		Diffused Topsoil	
	Area	RSD	Area	RSD
Tricholoroflouromethane	22704	14.6	145993	7.5
1,1,2-Trichloroethane	1896	9.3	15998	5.0
o-Xylene	4796	35.1	33956	16.2
1,2-Dichlorobenzene	1112	16.9	8058	3.4
Dibromoflouromethane (surr)	2355	3.6	15765	7.9
Toluene-d_8	4025	3.1	23333	4.8

Table 4. Area counts and % RSD's comparing spiked VS. diffused technique (topsoil)

IV. Effects of Increasing Organic Content

Soil samples that contain a very high organic content tend to very adsorptive. The analytes tend to adhere to organic sites in the soil which reduces the release of contaminants. The addition of the MMS helps to reduce some of this variability because the analytes are able to migrate more rapidly from the soil to a liquid solvent (MMS).

Figure 5 is the resultant chromatogram illustrating a diffused sand sample to a diffused topsoil sample.

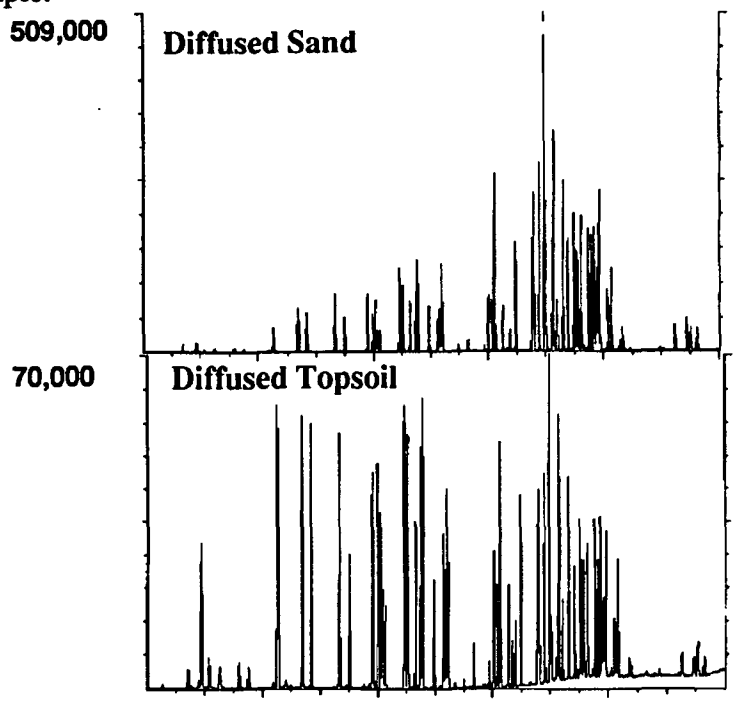

Figure 5: Effects of increasing organic content.

Table 5 shows the difference in peak area counts when comparing soils that have varying amounts of organic content. In both soil samples, Trichlorofluoromethane (gas) exhibits

	Topsoil Area	Sand Area
Tricholoroflouromethane	145993	147974
1,1,2-Trichloroethane	15998	160146
o-Xylene	33956	236264
1,2-Dichlorobenzene	8058	82523
Dibromoflouromethane (surr)	15765	45694
Toluene-d_8	23333	385076

Table 5. Area counts illustrating the effect of increasing organic content

very similar area counts. This is because Trichlorofluoromethane is a relatively volatile compound with a high diffusion coefficient. The other five compounds in table 5 show between a seven to sixteen fold decrease in area counts with the topsoil sample. The topsoil tends to hold onto the analytes, especially those heavier compounds found in the middle and very end of the chromatogram.

V. Diffused Topsoil- 14 Day Time Study

Many EPA laboratories today have a period of up to 14 days before the sample has to be run. The purpose of this next study was to examine the relative degradation of analytes over a period of 14 days. Three replicates of samples for each day were prepared using 2g of topsoil and 10 mL of MMS. The MMS was spiked with an analyte concentration of 100 ppb (internal standards and surrogates were at 50 ppb) and the samples were all mixed for one hour to simulate the diffusion technique. Each day, for 14 days, three replicates were pulled from a 4°C refrigerator and run by headspace.

Figure 6 is a graph of the area counts from early eluting compounds vs time (Pentafluorobenzene as the internal standard). Four additional compounds were selected from the front end. The graph shows that over a period of 14 days, there is some degradation of the analytes. The important point to notice is that the internal standard degraded at the same rate as all the other analytes. This indicated that the internal standard was properly tracking the analytes of interest. As long as the internal standard falls at the same rate as the analytes, quantitive results may be expected over the time period tested.

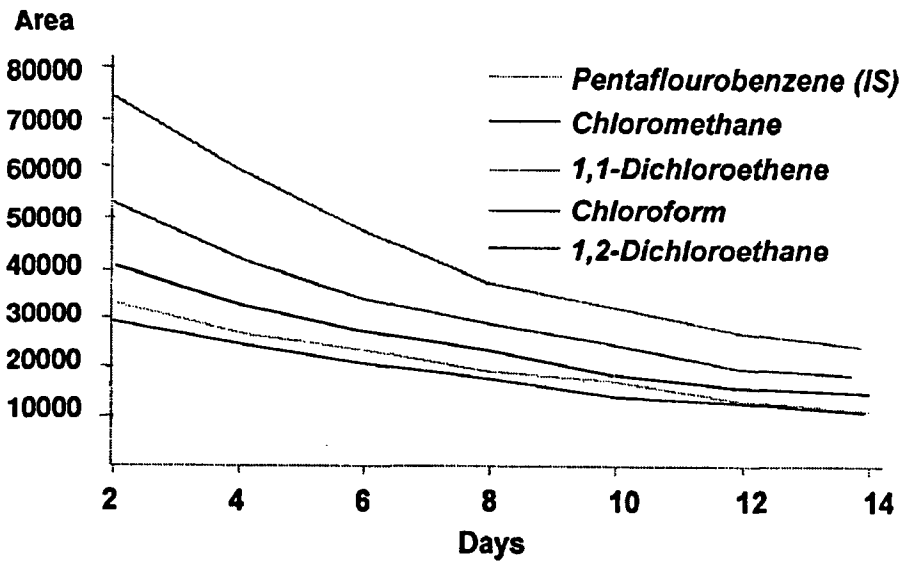

Figure 6: Area Counts of early eluting compounds VS. time

Figure 7 is a graph of the area counts of late eluting compounds vs time (1,4-Dichlorobenzene-d4 as the internal standard). Once again, all analytes are properly being tracked and degrading at the same rate as the internal standard.

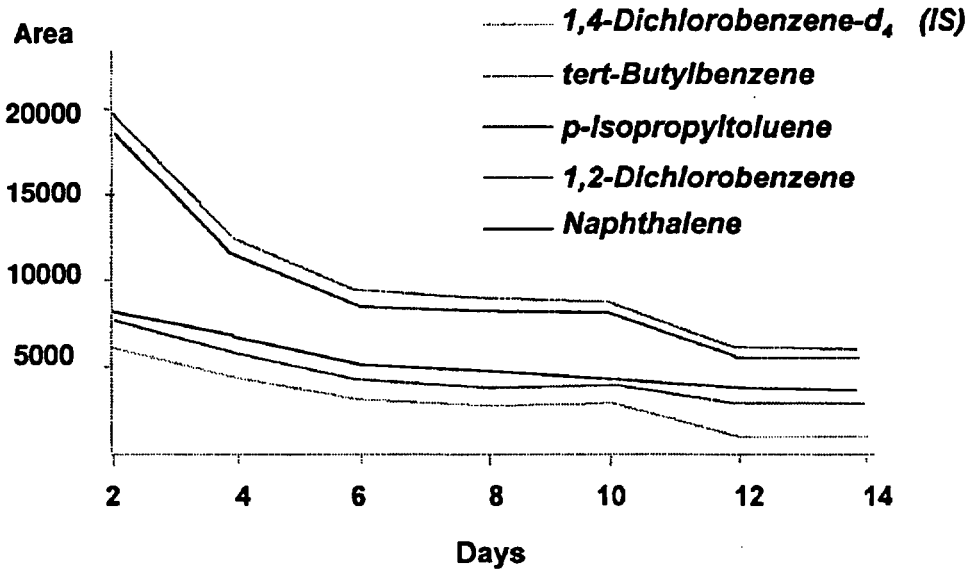

Figure 7: Area counts of late eluting compounds VS. time

VI. Carryover

A common problem associated with soil analysis today is carryover from very highly contaminated samples. Samples in the high ppm range can shut down an instrument and halt sample processing due to high level contamination and carryover. The major advantage of headspace analysis over purge and trap is that there is no carryover or contamination problems associated with this technique. The relative carryover percentage is less than 0.2% for all analytes run after a 10 ppm sample. The Saturn Mass Spectrometer and the column also showed no major effects of contamination.

CONCLUSION

The soils analysis method by static headspace is very clean, sensitive, and reproducible. It also eliminates many variables found in current soil methodologies. Future work will focus on practical field sampling techniques. One example of this is to use disposable syringes that will deliver a volume of soil to a screw top headspace vial. The MMS with the internal standards and surrogates will automatically be added to the sample in the field and the vial sealed. This mode of field sampling is simple, less prone to error, and eliminates losses associated with sample transfer prior to analysis.

Another focus will be on the addition of a non-volatile organic modifier to the MMS in order to increase the sensitivity of compounds analyzed from highly organic matrices. Final detection limits and dynamic ranges will then follow.

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42 *IN-SITU* DERIVATIZATION OF SOIL AND SEDIMENT SAMPLES IN A SUPERCRITICAL FLUID EXTRACTION CELL; THE EXTRACTION OF PHENOLS AND CHLORINATED PHENOLS

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ABSTRACT

This manuscript will describe a series of experiments which allow the simultaneous derivatization of analytes in solid and semi-solid samples containing phenolic compounds including the more intractable chlorinated species. The derivatizing reagents acetic anhydride and triethyl amine were added by admixing the separate reagents to the extraction cell before the cell was placed in the SFE apparatus.

Further experiments with respect to the reaction and extraction efficiency for methylphenols and nitrophenols as well as the chlorophenols and permutations of mixed moieties is in progress, collectively in the Little Falls and National Water Research Institute, Environment Canada labs. Preliminary results suggest that dinitrophenols do not react under the conditions described previously, although mononitrophenols appear to react as phenol and chlorinated phenols do. This work is continuing and will be described in a later publication.

INTRODUCTION

The supercritical fluid extraction (SFE) of phenols and chlorinated phenols from soils and sludges is an analyte/matrix pair receiving significant attention with respect to getting an acceptable, robust SFE method developed and ultimately formalized as a registered EPA method. The group of H.B. Lee (1) has published a method which employs in situ derivatization and post-SFE clean-up of the extract to remove the unreacted derivatizing agent.

Experimental

SFE Conditions:

Hewlett-Packard Models 7680T and 7680A were used without modification.

SFE Method The following conditions are grouped according to function.

Modifiers/reagents added to the thimble; 100 uL acetic anhydride, 100 uL triethyl amine (sample size is usually 1 gram).

1. Extraction -- pressure, 5250 psi; extraction chamber temperature, 80 C; density, 0.80 g/mL; extraction fluid composition, CO2; static equilibration time, 5 minutes; dynamic extraction time, 10 minutes; extraction fluid flow rate, 2.0 mL/min; resultant thimble-volumes-swept, 2.

2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 15 C; nozzle (variable restrictor) temperature, 45 C.

3. Reconstitution (of collected extracts) -- rinse solvent, 50/50 (v/v) isooctane; collected fraction volume, 1.2 mL; trap temperature, 40 C; nozzle (variable restrictor) temperature, 45 C; rinse solvent flow rate, 1.0 mL/min; fraction destination, vial #n.

GC Conditions:
Carrier gas = hydrogen,15 psi head pressure ,splitless injection, injection volume = 1.0 uL; column = HP 5 fused silica capillary 0.200 mm x 25 meters; column temperature program , initial temperature = 70 ^{o}C, initial program rate = 30 ^{o}C/min (to 120^{o}C) 2nd program rate = 2^{o}C/min, final temperature = 200 ^{o}C.

Results and Discussion

This is a study (FIGURE 1) which was started by the lab in Canada, and is being continued towards some interesting possibilities. It was stated earlier that phenols and substituted phenols are reasonably polar compounds, and are particularly difficult to extract out of solid matrices. Another problem that causes them to be more intractable, or more difficult to extract and analyze, is that they often occur in solid wastes in ratios of high-low concentrations. This is seen in a chromatogram in a later diagram (FIGURE 5). The phenols are usually distributed in a broad range of phenolic constituents--chloro, nitro, methyl and every mix that might be possible.

There are at least three possibilities to the extraction of phenolic compounds. From solid waste, one approach would be to use carbon dioxide by itself. Carbon dioxide is a relatively non-polar solvent, and for these relatively polar analyses, does not yield particularly good results in real samples. Another approach might be to add a liquid to the CO2 stream--a modifier or additive. The approach which was done by Bill Lee and his co-workers was actually to do an in-situ derivatization in the extraction vessel and then extract the derivatized materials. We also will take a brief look at supercritical fluid chromatography to suggust a third interesting approach for the extraction.

FIGURE 1. Outline of SFE extraction Study

Phenols and substituted phenols are polar

- phenols occur in high/low concentration ratios
- broad range of substituents
  * chloro
  * methyl
  * nitro
  * all permutations of above substituents mixed

3 Possible avenues of structuring the SFE method

- CO_2 only
- in-situ derivatization with CO_2 only
- CO_2 + modifier + additive (as in packed column SFC)

Hard look at Canadian method and any limitations

Automation

- PrepStation to automate manual cleanup steps
- SFE- GC Bridge to speed throughput and minimize operator error

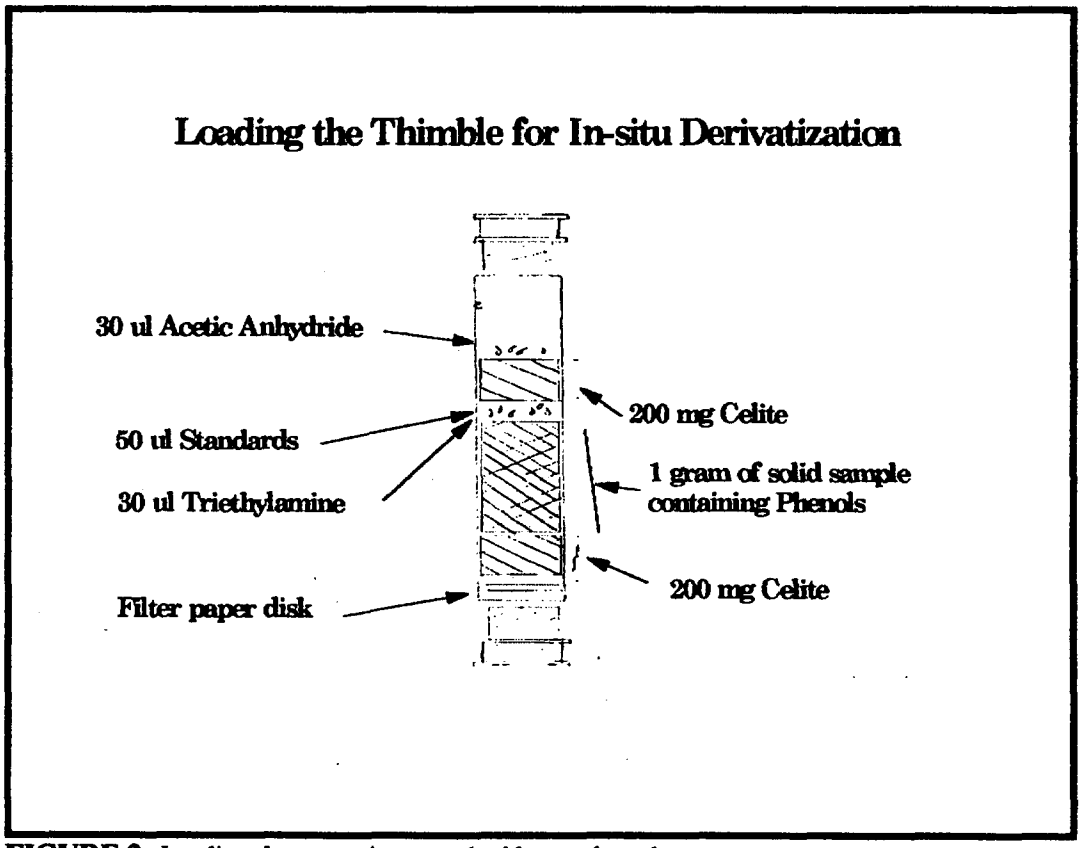


FIGURE 2. Loading the extraction vessel with sample and reagents

There are fewer manual steps as you automate, therefore, less hands-on time per method, and time is very costly in environmental laboratories. Improved accuracy, precision and the overall method become less dependent upon the skill level and the particular approach of a given technician or operator. Derivatization coupled with analysis allows just-in-time delivery of each sample for analysis when the analytical device is finished with the last sample and is ready for the next one. Automated optimization of reaction conditions will allow some interesting possibilities for unattended execution of designed experiments. Samples in report out in a very timely manner, and unattended, you can set a set of eight samples into the extractor and come back in the morning and find your results unattended.

Figure 2 illustrates the basic approach that's used in the *in-situ* derivatization. This is a schematic drawing of the extraction vessel . The sample, reagents and other materials are placed in the extraction vessel starting from the bottom. The end-piece is attached to the metal thimble first, then a filter paper disk is placed on the face of the end-piece frit. Then, 200 mg, of an inert material such as celite is placed on top of the filter paper disk, followed by a 1 gram sample of solid waste or sludge. A liquid aliquot (30 uL) of triethyl amine (TEA) is added to the sample via a micro syringe. This serves to raise the effective pH to an optimum level for the reaction that will occur between the phenols and the acetic anhydride. Another layer consisting of 200 mg of celite is then placed on top of the sample. Another lquid aliquot (30 uL) of acetic anhydride is metered onto the celite with a micro syringe. This acetic anhydride is the derivatizing reagent to form acetyl derivatives of the various phenols. Finally, another disk of filter paper is placed on top of this. The exit end-piece (fritted cap) is placed on the metal extraction vessel and the entire sample vessel is placed in the carousel of the SFE.

The reconstitution solution resulting from the SFE step is removed from the extractor and a clean-up procedure is carried out. This procedure is done manually (separate from the SFE equipment). Work is underway to incorporate this into automatic PrepStation SPE manipulations to facilitate automating clean up these steps. The reconstituted extract solution (derivatized phenol acetates dissolved in hexane) is mixed with 3 ml of a one percent solution of potassium carbonate and is agitated for one minute. That potassium carbonate neutralizes the excess TEA reagent, which was added to obtain an effective optimum pH for the derivatization reaction in the supercritical CO2. The extract solution is then passed through a small bed of magnesium sulfate (this can be packed into a Pasteur pipet) to remove excess water. That resulting filtrate is then passed through another short bed of 5% deactivated silica.The analytes are eluted in a 10 ml solution. consisting of a 1:1mixture of petroleum ether/methylene chloride. This solution is evaporated and re-exchanged to 5 ml of isooctane. A 1uL aliquot is injected into the gas chromatograph. The SFE method used a temperature of 80 degrees at a constant density of 0.8 g/ml. with a 5 minute static period for the derivatization and soaking of the sample. This was followed by a 10 minute period of dynamic extraction at a volume flow rate (measured as liquid carbon dioxide at 4 degrees centigrade) of 2 ml per minute.

Results from Lee (1) and co-workers with a commercially available reference soil 130-100 , comparing steam distillation to supercritical fluid extraction *in-situ* derivatization are seen in Figure 3.

FIGURE 3. Recovery and Precision from Reference Soil 130-100 (Ref. 1)

	Steam Distillation Recovery mg/kgm	SFE Recovery mg/kgm	Steam Distillation Precision mg/kgm	SFE Precision mg/kgm
2,3,5 Tri Cl	0.40	0.36	0.01	0.01
2,3,4,5 Tetra Cl	14.4	13.9	0.40	0.30
2,3,4,6 Tetra Cl	20.6	20.2	0.40	0.30
2,3,4,5 Tetra Cl	1.9	1.8	0.10	0.10
Pentachlorophenol	1,499.0	1,483.0	67.0	93.0

The recoveries for the supercritical fluid extraction correspond very well with the steam distillation for all of the compounds. Steam distillation requires many additional manual manipulations--most are quite

operator- dependent. In comparison, the SFE equipment used in this study is operated in the same manner by all operators, because all steps are computer controlled and recalled from a stored method.

This table (Figure 3.) shows the results of a representative phenol containing sample. This particular sample is from a site in Canada adjacent to stored railroad ties (treated with creosote to promote long lifetime of the wood). It is normally expected that there will be a large concentration of many chlorinated phenols. In addition, as mentioned above, there was a very small concentration of trichloro phenol and a very high concentration of the pentachlorophenol.

In Figure 4, we see the chromatogram which yielded the information presented in the table (Figure 3.).The first peak annotated is 2-3-5 trichlorophenol, the next three annotated (small peaks) are tetrachlor phenols and the large off-scale peak at the end of the chromatogram is pentachlorophenol. As noted above, the small peak, the trichloro phenol, was found at a concentration of 0.4 mg/kgm and the largest peak, pentachlorophenol was found at 1483 mg/kgm. This illustrates the large range of phenolic compounds to be expected, greater than three orders of magnitude range.

FIGURE 4. GC/ECD Chromatogram of Reference Soil Containing Chlorinated Phenols

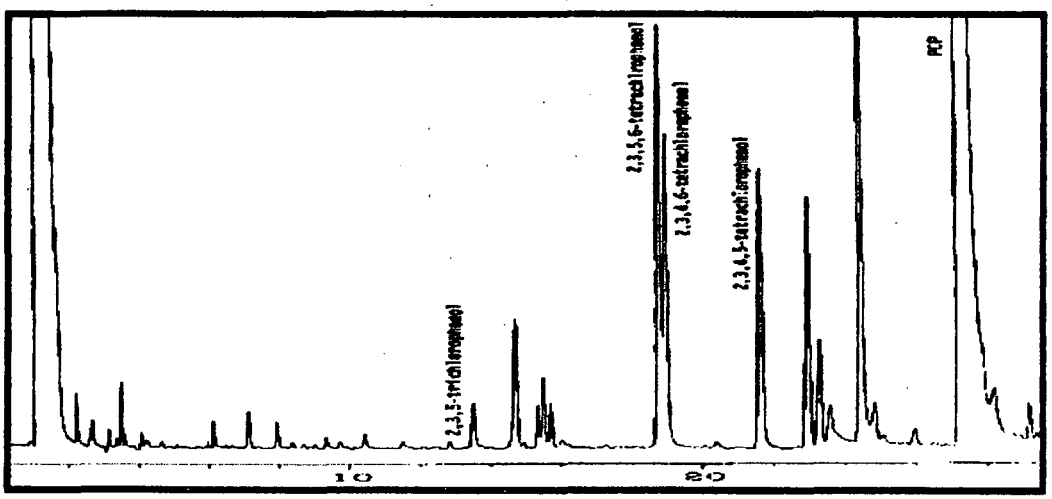


FIGURE 5. Recovery from Spiked Sample - 6 replicates (Ref. 1)

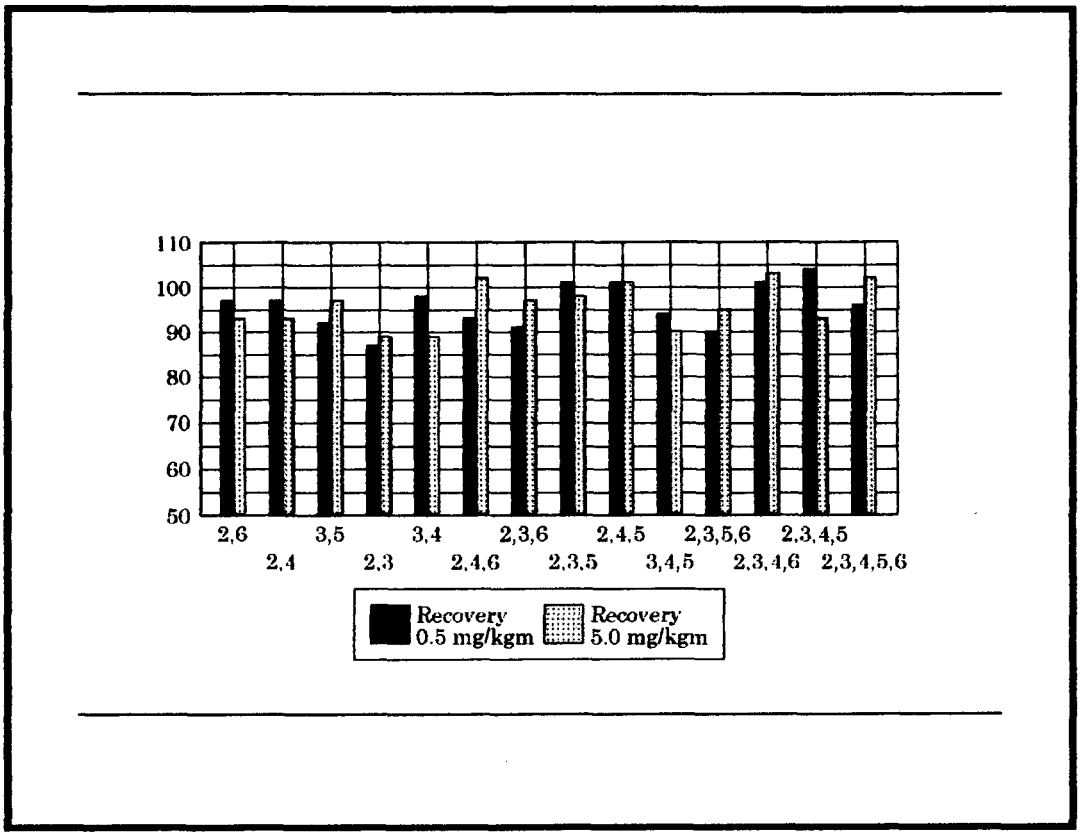
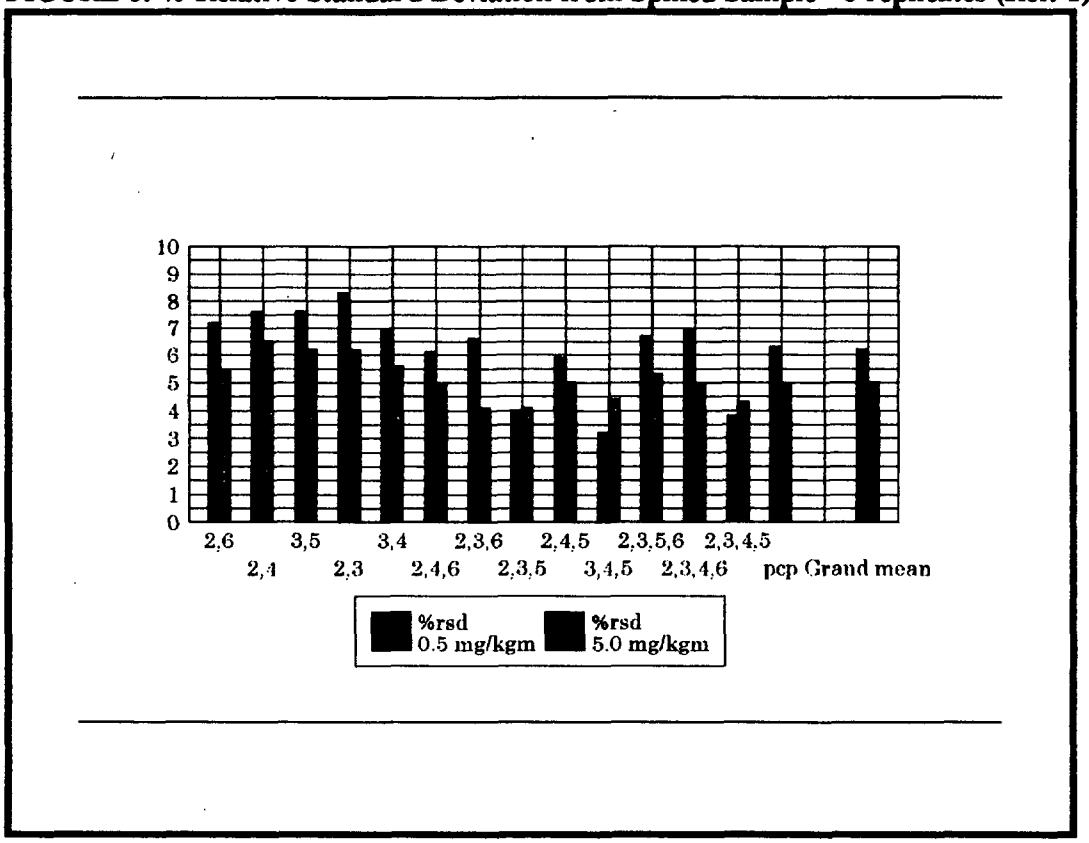


Figure 5 shows the recovery of a number of the substituted chlorophenols ranging from the di-substituted up to the penta chlorinated substituents. The solid (darkest) bar graphs represent recovey of spiked levels of 0.5 mg/kgm (parts per million on a weight-per-weight basis). The lighter patterned bar graphs represent recoveries for the same compounds at 10 times higher concentration, approximately 5 mg per kg level. It is relevant to note the significance of the recovery across this variety of chlorinated phenols at the two different levels. As expected, there is a slightly lower recovery at the sub- part per million level compared to the 5 part per million level, however, the average recovery for six replicates is greater than 87 % in the worst case and greater than 104 % in the best case, with an overall grand mean recovery greater than 95 %.

FIGURE 6. % Relative Standard Deviation from Spiked Sample - 6 replicates (Ref. 1)

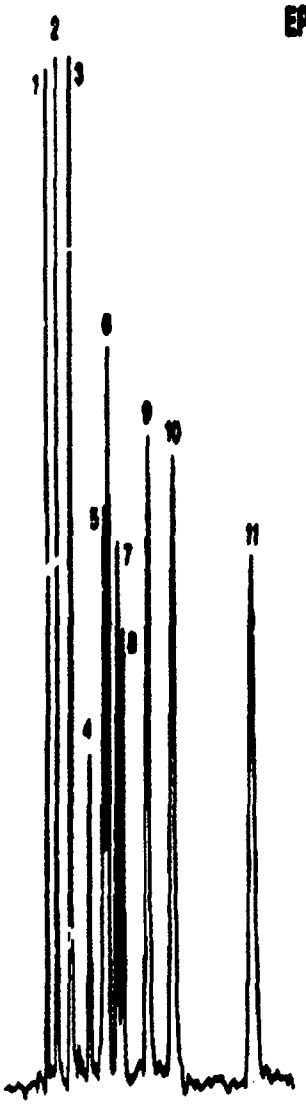


In Figure 6 we see that in addition to good recovery, the SFE in-situ derivatiztion/extraction yields very acceptable precision. The solid (darkest) bar graphs show that precision for the compounds at the 0.5 (parts per million) mg/kg level ranges from 3% rsd to 8 % rsd. The (lighter) patterned bar graphs show the precision at 5 mg/kgm (ppm). As one would normally expect, in trace analysis, the precision improves significantly as the detected concentrations are 10 times greater. That is, the grand mean % rsd for the 14 compounds at the 0.5 ppm level is 6.5 % while at the 5.0 ppm level it improves to 5.0%.

Because the derivatization method as described here does not derivatize dinitro phenols, we are examining another possiblity for the broader set of phenols. We are following some experiments that our colleagues at HP are doing with packed column SFC. When analyzing mixtures with packed column SFC, the conditions in many respects are analogous to supercritical fluid extraction. If one can find experimental data on packed column SFC, this may suggust good conditions for SFE with solid matrices. Jerry Deye and Terry Berger of our laboratories at Hewlett-Packard in Wilmington, DE have an SFC chromatogram performed the separation of many of the same phenols described in this study, as well as dinitro phenols Figure 7).

Figure 7

SFC of un-derivatized Phenols (no SFE)



Peaks:

	RT min	
1	0.64	2-Nitrophenol
2	0.77	4,6-Dinitro-o-cresol
3	0.88	2,4-Dinitrophenol
4	1.23	2-Chlorophenol
5	1.43	2,4-Dimethylphenol
6	1.48	2,4,5-Trichlorophenol
7	1.61	2,4-Dichlorophenol
8	1.68	Phenol
9	2.03	4-Chloro-3-methylphenol
10	2.38	Pentachlorophenol
11	3.46	4-Nitrophenol

Conditions:

Column dimensions:	diol-silica (Hewlett-Packard), 20 ...m x 4.6 mm I.d., 5 µm particle;
Mobile phase:	...ocratic, 4 mL/min CO_2, 210 µL/hr in 0.05% trichloroacetic acid in methanol
Pressure:	outlet pressure fixed at 2000 psi
Column temperature:	37°C
Sample introduction:	0.5 µL, on-column, CH_3OH
Detector:	UV, 210/430 nm, signal/reference

The total elution time for the eleven phenols, is only three and a half minutes. That is a fast , high resolution separation of the eleven phenol compounds. These include 2-nitro, the 4-6 dinitromethylphenol and phenol itself. This is a packed SFC DIOL-bonded silica column. The mobile phase was supercritical CO2 with a mixture of trichloro acetic acid (0.05 %) in methanol . The methanol/trichloro acetic acid mixture was then introduced as a 5% volume of the carbon dioxide. This represents an additive in methanol, then added to CO2--it is actually a ternary mixture. The pressure was very low, 2000 psi, at 37 degrees centigrade. The phenols are not derivatized. We are taking a look at this simultaneously with the derivatization steps and the automation.

Summary

We are evaluating simplification of running the proposed method routinely by automating the post-SFE fraction clean-up using automated (HP PrepStation) instrumentation.

We have further looked at the reaction and extraction efficiency for methyl phenols and nitro phenols as well as the chlorophenols described in the original study. We find the in-situ method very good for the chlorinated phenols. For dinitrophenols, we are considering un-derivatized extraction with co-solvents and additives to enhance the extraction and recovery. One or more of these approaches will be offered to the USEPA SW846 committee in the form of "deliverables" (3) for consideration as methods for extracting phenols and substituted phenols. This normally would result in a round robin study to test the ultimate robustness in a wide variety of laboratories.

Acknowledgment

The authors would like to thank all of the people who are helping with these SFE phenol studies and especially Barry Lesnik, Robert Hong-You, Tom Peart, Pat Castelli, Joel Cheng, William Pipkin and many others who helped in their own way

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3. Personal communication from Barry Lesnik, Office of Solid Waste, US Environmental Protection Agency, 401 M Street, SW, Washington, DC 20460 USA.

43 SUPERCRITICAL FLUID EXTRACTION (SFE) of PCBs

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ABSTRACT

Supercritical fluid extraction parameters will be optimized using fractional factorial experimental designs. Matrix modification with water will also be investigated. Preliminary results with Aroclor 1248 indicate more rigorous extraction conditions than those specified in Method 3560 may be necessary.

INTRODUCTION

Extraction of hydrocarbons from soil samples was one of the first applications of analytical SFE with carbon dioxide. Similarly hydrocarbon extractions were the first SFE method from the EPA Office of Solid Waste. The commercial instrumentation has improved significantly in the past two years. The environmental lab can choose between several SFE instruments specifically geared for the high through-put lab. The next step is to extend the current SFE methodology to other environmental analytes. Non-polar compounds such as PAHs and PCBs should be extractable under conditions similar to hydrocarbons. SFE of TPHs will dramatically reduce the volume of Freon-113® used by the lab. Extending this technology to other analyte fractions will reduce the use of methylene chloride. This will reduce both environmental and employee exposure to this suspected carcinogen.

Work by Langenfeld, Hawthorne, Miller and Pawliszyn (1) shows good PAH and PCB recovery using high temperature (200°C) extractions. Preliminary work at Enseco-Wadsworth/ALERT indicates that the parameters of the TPH method may not be sufficient to achieve good PCB recovery. Two approaches are possible, 1) use co-solvents (modifiers) or 2) use higher temperature, pressure and flow. Modifiers have both advantages and disadvantages. We will focus on the second option. If acceptable PCB recovery can be obtained without modifiers for off-line extraction then the eventual switch-over to on-line extraction will be simpler.

INSTRUMENTATION, EQUIPMENT AND SUPPLIES

Supercritical Fluid Extractor
- Suprex, PrepMaster, AccuTrap
  - Restrictor, prototype variable restrictor (manual)
- Suprex, AP44
- 5 mL extraction vessel

Gas Chromatograph
- Hewlett Packard 5890
- Electron Capture Detector
- Column RTX-5, 30 m, 0.32 mm ID, 0.5 μ DF

Solvents
- Hexane, EM Science
- CO_2, SFC grade with 1500 PSIA Helium headspace with dip tube, Scott Specialty

DISCUSSION

There are several supercritical fluid extraction parameters to optimize. They are extraction time (static & dynamic), CO_2 pressure, CO_2 flow rate, extraction temperature, analyte trap, modifier type, and amount. Solid matrices such as loam, ash and various clays (kaolin, Fuller's earth, montmorillonite) will be examined. Fractional factorial experiment designs will be used to investigate and optimize this large number of variables.

Water affects organic extractions in several interesting ways. Too much water is detrimental and reduces analyte recovery. However, too little water can also reduce analyte recovery. Extracting TPHs from dry clays with Freon-113® was facilitated by adding water to the sample (2). A similar effect was noted for supercritical fluid extraction of TPHs in draft Method 3560 (3). However, too much water was a detriment. Very wet clay samples must be partially dried before good TPH recovery can be achieved (4,5). These water effects are inconsistent if one views water in the role of a CO_2 solubility modifier. Water as a polar solvent should only decrease the extraction efficiency of non-polar analytes such as hydrocarbons. However, Hawthorne has noted at several conferences (6, 7, 8) that co-solvents should also be viewed as matrix modifiers. McNally observed physical changes in soil matrices when water was added (9). These physical changes may explain in part how water affects the extraction process. This raises the possibility of using water as an SFE modifier even for non-polar analytes. If effective, water would be the least expensive and safest modifier.

Preliminary work with PCBs indicates that the SFE conditions specified in draft Method 3560, December 1992 may not be sufficient for good PCB recovery. Aroclor 1248 recovery from Kaolin was 51% using these parameters. The final goal is an extraction method that yields acceptable PCB recovery in a short time frame under production laboratory conditions.

SUMMARY

Fractional factorial experimental designs will be used to optimize the key variables affecting PCB recovery from various solid matrices. The use of water as matrix modifier will be investigated.

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44 Determination of Organic Compounds in Ground Water by Liquid-Solid Extraction Followed by Supercritical Fluid Elution and Capillary Column Gas Chromatography/Ion-Trap Mass Spectrometry

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Methylene chloride ($MeCl_2$) has been widely used in RCRA/CERCLA monitoring as an extraction solvent for extraction of organic contaminants in ground water and solid waste samples. The testing protocol using methylene chloride liquid-liquid extraction is wasteful in time for preparation of analytical samples and also costly in disposing the waste solvent. Environmental Monitoring Systems Laboratory-Cincinnati (EMSL-Cincinnati) of USEPA has initiated a research project to develop alternative extraction methods to replace methylene chloride. One alternative method for extraction of organic pollutants from water is a liquid-solid extraction (LSE). This method uses solid sorbents (i.e. C_{18}) to trap analytes and uses solvents to elute the adsorbed analytes. The LSE method offers low solvent consumption (i.e. 15-60 mL of $MeCl_2$ compared to >400 mL of $MeCl_2$ in the liquid-liquid extraction) and less waste. The EMSL-Cincinnati is also investigating a novel technique, analytical scale supercritical fluid extraction (SFE), to replace the methylene chloride solvent elution. The SFE uses a fluid (i.e. CO_2) that is non-toxic, non-combustible, chemically inert, and easy to discard. For the LSE method, water samples are first passed through 47-mm diameter Empore™ C_{18} disks. Then, different amounts of $MeCl_2$ are used to elute the adsorbed analytes from the disks. An amount of 15 mL $MeCl_2$ is used for clean samples without particulates, while at least 60 mL of $MeCl_2$ are required for dirty samples containing particulates. These $MeCl_2$ extracts need further concentration before injecting into a capillary column gas chromatograph for trace analysis. The use of SFE as an alternative elution technique to the solvent elution of LSE is more attractive. After filtering the analytes from the water by using the C_{18} disk, the adsorbed analytes are eluted with supercritical CO_2 (about 30 mL) and collected in a small amount of solvent (1-2 mL). The SFE method combines the elution and the concentration procedures into one step. In comparison with the solvent elution of LSE, the SFE reduces the solvent consumption by 90% and generates much less waste. Detailed discussions of the recovery efficiencies, relative standard deviation (RSD) and detection limits as well as the effects of various solvent modifiers on the SFE extraction will be presented at symposium. The disk liquid-solid extraction (LSE) coupled with the supercritical fluid elution (SFE) provides clear advantages in terms of extraction time, solvent used, and solvent disposal especially for samples containing particulates like ground water sample.

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COMPARISON OF SOLID PHASE EXTRACTION WITH SALTING-OUT SOLVENT EXTRACTION FOR PRECONCENTRATION OF NITROAROMATIC AND NITRAMINE EXPLOSIVES FROM WATER

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ABSTRACT

Residues of high explosives are one of the most significant pollution problems at DOD facilities. Recently, the EPA has lowered the concentration at which these compounds are thought to be harmful to human health. Because TNT, RDX, and HMX, as well as several manufacturing impurities and environmental transformation products, are quite mobile in the soil and have caused groundwater pollution, there is an increasing demand for low-level analysis of these compounds in groundwater from installation boundary wells.

RDX and HMX are very polar, and normal liquid-liquid extraction/preconcentration techniques result in poor recovery. Two innovative preconcentration techniques have been reported that appear to offer improved recovery and adequate preconcentration: solid-phase extraction (SPE), and salting-out solvent extraction (SOE). This paper compares cartridge-SPE, membrane-SPE, and SOE using a series of reagent-grade water samples fortified with low concentrations of 11 nitroaromatics and nitramines and a set of groundwater samples from an explosives-contaminated DOD facility.

Results indicated that the three methods were comparable with respect to low-level detection capability, which ranged from 0.05 to 0.30 µg/L. Percent recoveries were generally greater than 80% except for HMX and RDX by membrane-SPE, which were consistently lower. Interferences were found in extracts from about half of the groundwater samples preconcentrated using the two SPE procedures but were not found in any of the extracts from the SOE. These interferences were traced to matrix interaction of the groundwater with the polymeric resins.

INTRODUCTION

Batch liquid-liquid extraction (LLE) has often been used to extract organic analytes from water prior to analysis. The success of this approach depends upon favorable solvent/water partition coefficients (K_p) for the analytes of interest. Since many organic pollutants are relatively non-polar, batch extraction with an immiscible organic solvent has been successful.

TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), along with several of their manufacturing impurities and environmental degradation products, have been observed in groundwater at a number of Army installations [1–5]. Health advisories have been issued by the EPA for many of these compounds (Table 1), with drinking water criteria at sub-part-per-billion concentrations. For this reason, the Army has developed analytical methods to determine these compounds at trace levels in water. To detect these compounds at the sub-ppb level, the first step has been preconcentration of the analytes using an extraction process.

Classical LLE of these analytes has been reported, but poor extraction efficiency has been found for RDX and HMX. Octanol/ water partition coefficients (K_{ow}) for HMX and RDX are 1.15 and 7.24 [6], respectively, indicating the compounds are quite polar and will be difficult to extract from water using nonpolar solvents.

For this reason, several alternative procedures were developed. The most successful of these have been the use of solid-phase extraction (SPE) [13, 14] and salting-out liquid-liquid extraction (SOE) [15–17].

The objective of the work described here was to obtain a direct comparison of the cartridge SPE [13] and membrane SPE methods [14] with the SOE method [17]. Aqueous test solutions of nitroaromatics and nitramines prepared in groundwater without the use of organic solvents allowed a realistic comparison at concentrations of analytes below the proposed drinking water criteria (Table 1). In addition, all three procedures were tested with a set of groundwater samples from a military toxic waste site known to be contaminated with explosives.

Table 1. Proposed drinking water criteria for nitroaromatics and nitramines.

Compound	*Proposed drinking water limit (µg/L)*	*Reference*
HMX	400*	[7]
RDX	2.0*	[8]
TNT	2.0*	[9]
2,4-DNT	50**	[10]
	0.1	[11]
2,6-DNT	40**	[10]
	0.007	[11]
1,3-DNB	1.0*	[12]

* EPA Lifetime Health Advisory Number
** EPA number for increased cancer risk of 1.0×10^{-6}.

EXPERIMENTAL

Salting-out solvent extraction/nonevaporative preconcentration procedure

This method was based on the salting-out solvent extraction procedure [17] in combination with the nonevaporative preconcentration technique [18] reported elsewhere. A 251.3-g portion of reagent-grade sodium chloride was added to a 1-L volumetric flask along with a 770-mL sample of water. A stir bar was added, and the contents were stirred at maximum speed (rpm) until the salt was completely dissolved. A 164-mL aliquot of ACN was added and stirred for 15 minutes. The stirrer was turned off and the phases allowed to separate. The ACN phase (about 8 mL) was removed, and 10 mL of fresh ACN were added. The flask was again stirred for 15 minutes, followed by phase separation. The ACN was removed and combined with the initial extract. The combined extract was placed in a 100-mL volumetric flask and 84 mL of salt water (325 g NaCl per 1000 mL of water) was added, and the contents were stirred for 15 minutes. After allowing the phases to separate, the ACN phase was carefully removed and placed in a 10-mL graduated cylinder. An additional 1.0-mL aliquot of ACN was then added to the volumetric flask and the contents were stirred. Again the phases were allowed to separate, and the resulting ACN phase was added to the 10-mL graduated cylinder. The resulting extract, about 5–6 mL, was than diluted 1:1 with reagent-grade water prior to analysis [19].

Cartridge solid-phase extraction

Porapak R (80/100 mesh) was obtained from Supelco and precleaned by Soxhlet extraction using ACN [19]. After precleaning, the material was air-dried briefly and then oven-dried at 105°C for 2 hr.

Empty 3-mL extraction cartridges were packed with 0.5 g of the precleaned Porapak R. The cartridges were placed on a Visiprep Solid-Phase Extraction Manifold (Supelco) and conditioned by eluting with 30 mL of ACN followed by 50 mL of reagent-grade water. A 500-mL aliquot of each water sample was pulled through a cartridge at about 10 mL/min.

The cartridges were eluted by passing a 5-mL aliquot of ACN through the cartridge at about 2 mL/min, and the eluate was collected in a 10-mL graduated cylinder. The resulting extract, about 5 mL, was diluted 1:1 with reagent-grade water prior to analysis [19].

Membrane solid-phase extraction

The 47-mm Empore styrene-divinyl benzene disks were precleaned by soaking them in 50 mL of ACN [19]. Each membrane was soaked for four 24-hour periods with fresh ACN. Each disk was rinsed with ACN, then centered on a 47-mm vacuum filter apparatus and leached with a 20-mL portion of ACN and a 50-mL aliquot of reagent-grade water. Just before the last of this water was pulled through the membrane, the vacuum was stopped and the reservoir was filled with sample. The vacuum was then turned on again and a 500-mL aliquot of a water sample was pulled through the membrane. This took from 5 to 7 minutes, with resulting flow rates ranging from 70 to 100 mL/min. Air was then drawn through the membrane for 1 minute to remove excess water. A 5-mL aliquot of ACN was then used to extract the analytes from the disk, and the extract was diluted 1:1 with reagent-grade water prior to analysis [19].

RP-HPLC analysis

All analyses were conducted using reversed-phase HPLC as described elsewhere [19, 20].

Preparation of standards and samples

Since we felt it was important that test samples be completely free of organic solvents, we prepared all test samples in a totally aqueous matrix. This was done by preparing individual aqueous analyte stock solutions by placing a few hundred milligrams of Standard Analytical Reference Material (SARM) of each specific analyte in individual 4-L brown glass bottles, filling the bottles with reagent-grade water, adding a stir bar, and stirring for two days at room temperature.

Each solution was filtered through a 0.45-mm nylon-66 membrane (Supelco) into a clean brown glass bottle. Aliquots of each solution were then analyzed against standards prepared in acetonitrile to estimate the concentration of analyte in each aqueous stock solution.

RESULTS AND DISCUSSION

Certified reporting limit test

Spiked test solutions were used to conduct a four-day Certified Reporting Limit Test (CRL) as described elsewhere [19]. This test allows a comparison of low-concentration detection capability, percent recovery, interferences, and overall precision. A discussion of the CRL and how results compare with the EPA Method Detection Limit are presented elsewhere [21]. Chromatograms for samples containing target analytes at about 0.2 µg/L and preconcentrated by the three procedures are presented in Figure 1.

The CRLs obtained are shown in Table 2. Overall, the CRLs for a given analyte are quite similar for all three preconcentration techniques. None of the procedures is consistently superior to the others in low-concentration detection capability. CRL values range from a low of 0.032 µg/L for DNB using cartridge SPE to a high of 0.83 µg/L for tetryl using membrane-SPE. All values for HMX, RDX, TNT, 2,4-DNT, and 1,3-DNB are below the proposed drinking water limit for these compounds. While 2,6-DNT was not tested, it is very unlikely that a CRL as low as the proposed value of 0.007 µg/L would be obtained. The only CRL value that appears to be out of line is the 0.83 µg/L value of tetryl using membrane-SPE. Inspection of the data indicates this high CRL is due to low recovery on one of the four days.

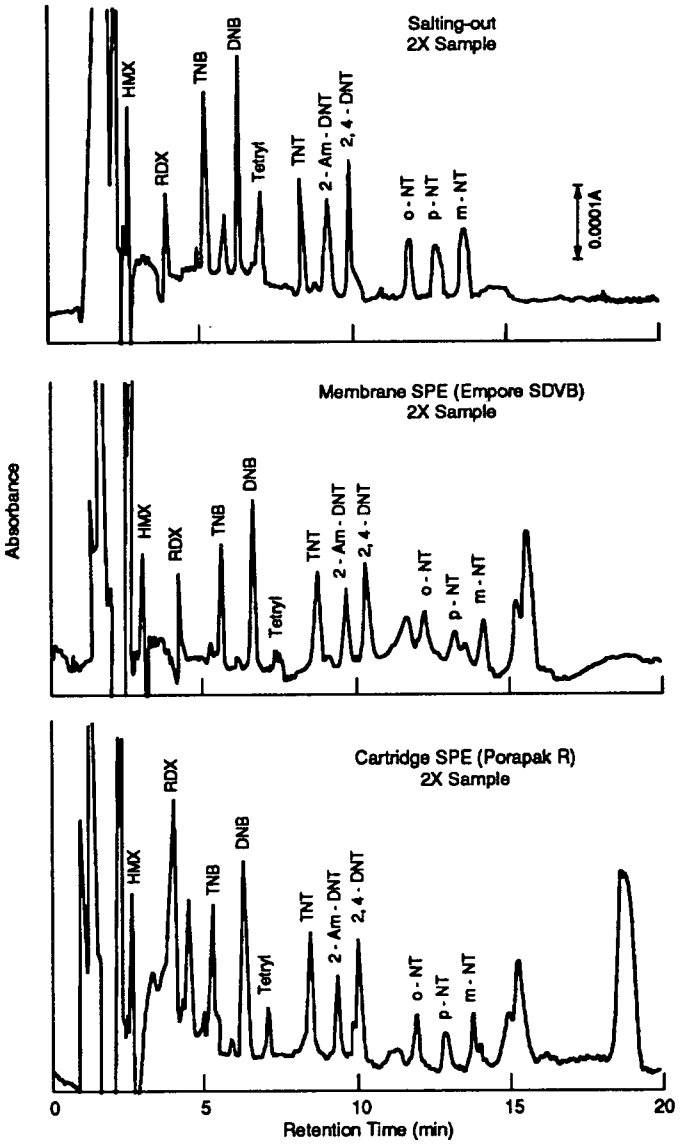

Figure 1. LC-18 chromatograms for 2X sample preconcentrated by salting-out, cartridge-SPE, and membrane-SPE methods at CRREL.

The regression line obtained from the plot of found vs. spiked concentrations was also examined for curvature using lack-of-fit testing. Linear relationships described the data at the 95% confidence level. The slopes of these linear regression lines are measures of the overall percent recoveries of these analytes using each preconcentration method. Recoveries (Table 3), in general, are quite good (near a theoretical value of 100%). Measured recoveries for the salting-out procedure range from 93–119%. Likewise, recoveries for cartridge-SPE and membrane-SPE range from 83–133% and 81–116%, respectively.

Table 2. Certified reporting limits for various preconcentration techniques.

	CRL (µg/L)		
Analyte	Salting-out	Cartridge-SPE	Membrane-SPE
HMX	0.19	0.21	0.33
RDX	0.13	0.27	0.12
TNB	0.052	0.042	0.051
DNB	0.081	0.032	0.036
Tetryl	0.20	0.24	0.83
TNT	0.086	0.068	0.13
2-Am-DNT	0.10	0.046	0.055
2,4-DNT	0.083	0.085	0.044
o-NT	0.13	0.10	0.20
p-NT	0.22	0.12	0.23*
m-NT	0.21	0.13	0.37

* One outlier removed for this analyte/method combination.

Table 3. Overall percent recovery and relative standard deviation (RSD) from Certified Reporting Limit Test.

	% recovery* (% RSD)		
Analyte	Salting-out	Cartridge-SPE	Membrane-SPE
HMX	106 (10.5)	107 (9.6)	81 (14.0)
RDX	106 (8.7)	116 (22.0)	116 (11.1)
TNB	119 (7.6)	133 (8.7)	116 (10.3)
DNB	102 (6.6)	115 (2.6)	103 (6.5)
Tetryl	93 (16.4)	83 (32.8)	83 (46.4)
TNT	105 (7.6)	111 (7.5)	97 (10.5)
2-Am-DNT	102 (9.1)	113 (4.1)	103 (8.9)
2,4-DNT	101 (5.8)	109 (6.8)	94 (6.6)
o-NT	102 (9.1)	107 (8.1)	92 (15.6)
p-NT	96 (18.1)	104** (6.6)	89† (18.0)
m-NT	97 (12.4)	100 (7.3)	86 (17.2)

* Slope of regression line of spiked concentration vs. found concentration ×100.

** Lack-of-fit test indicates data not adequately described by linear relationship at the 95% confidence level.

† One outlier removed for this analyte/method combination.

Comparison using groundwater samples

A further test was conducted using 58 groundwater samples from the Rockeye site at the Naval Surface Warfare Center. All of the samples were analyzed by the direct method and after preconcentration as well using the three procedures (SOE, cartridge-SPE, and membrane-SPE). Table 4 summarizes the results for samples where the concentrations of at least one nitroaromatic or nitramine analyte was high enough to be obtained using the direct method. Since the concentrations obtained by the direct analysis are subject to fewer sources of error than those obtained using preconcentration, we are treating these values as "true" values for purposes of comparison. We can then compare the results from the various preconcentration techniques relative to these "true" values.

Examination of Table 4 indicates that all three preconcentration procedures did a fairly good job of recovering these analytes (generally greater than 80%). The membrane-SPE method, however, recovered less of HMX and RDX than the other two procedures. Recovery of HMX, RDX, and TNT by the cartridge-SPE and salting-out methods was greater than 80% in all cases, with a slightly better recovery for the cartridge-SPE method for HMX and RDX.

For about half of the samples, the chromatogram for the salting-out method is blank with respect to target analytes and interferences, but the chromatograms for both the two solid-phase methods, at the same attenuation, show large peaks at a number of retention times across the entire chromatogram (Figure 2). Second-column confirmation indicated that none of these peaks resulted from the presence of nitroaromatic or nitramine explosives. Their presence, how

ever, interfered with the ability to detect nitroaromatic and nitramine analytes at concentrations well above the CRLs. These large interference peaks were not found when these groundwater samples were analyzed without preconcentration and hence appear to be introduced by the solid phases themselves. Since the Porapak R and the SDVB membranes were cleaned separately and all the Porapak R cartridges were packed from material cleaned in the same batch, we do not believe these peaks were a result of poorly cleaned material. Rather it appears that some component of these samples interacted with the solid phases to either degrade the polymer or release contaminants from within the polymer by either swelling or collapsing the polymer matrix.

Table 4. Comparison of results for direct analysis of groundwater samples from the Rockeye site at the Naval Surface Warfare Center, Crane, Ind., with the three preconcentration methods.

		Concentration (μg/L)				
Sample	*Method**	*HMX*	*RDX*	*TNB*	*TNT*	*4A*
20649	Direct	151	135		33	9.6
	SPE-M	98	121		32	11.2
	SPE-C	156	147		34	12.2
	SOE	161	138		38	13.7
20650	Direct	119	82		9.0	
	SPE-M	60	64		7.6	
	SPE-C	107	85		9.2	
	SOE	98	66		10.3	
20662	Direct	26	160		42	
	SPE-M	19	176		51	
	SPE-C	17	138		34	
	SOE	22	154		46	
20663	Direct	281	94		21	65
	SPE-M	153	89		22	75
	SPE-C	214	109		26	78
	SOE	232	90		26	78
20667	Direct	318	618	19.2	284	166
	SPE-M	199	488	19.5	317	216
	SPE-C	356	666	19.6	328	239
	SOE	319	558	18.6	320	217

* Membrane-SPE (SPE-M), cartridge-SPE (SPE-C), and salting-out (SOE).

CONCLUSIONS AND RECOMMENDATIONS

SOE and cartridge- and membrane-SPE were compared with respect to their ability to preconcentrate nitroaromatic and nitramine explosives from water prior to RP-HPLC analysis. Both fortified reagent-grade water and contaminated groundwater samples were used in this assessment.

Low detection capability and overall precision were comparable among the three procedures. Recoveries of HMX and RDX are better using cartridge-SPE and SOE than membrane-SPE. Recovery of the nitroaromatics was acceptable for all three procedures.

At present the major problems associated with the use of the SPE procedures are the inadequacy of the current cleaning procedures. While use of the Soxhlet procedure on a batch basis for the Porapak R material appears to be adequate, cleaning must be accomplished on-site just before use or the contamination reappears. The cleaning procedure we used for the membranes is cumbersome and wastes solvent.

Problems with interferences were encountered using both the cartridge-SPE and membrane-SPE procedures for a number of actual groundwater samples. These interferences appeared to be iden

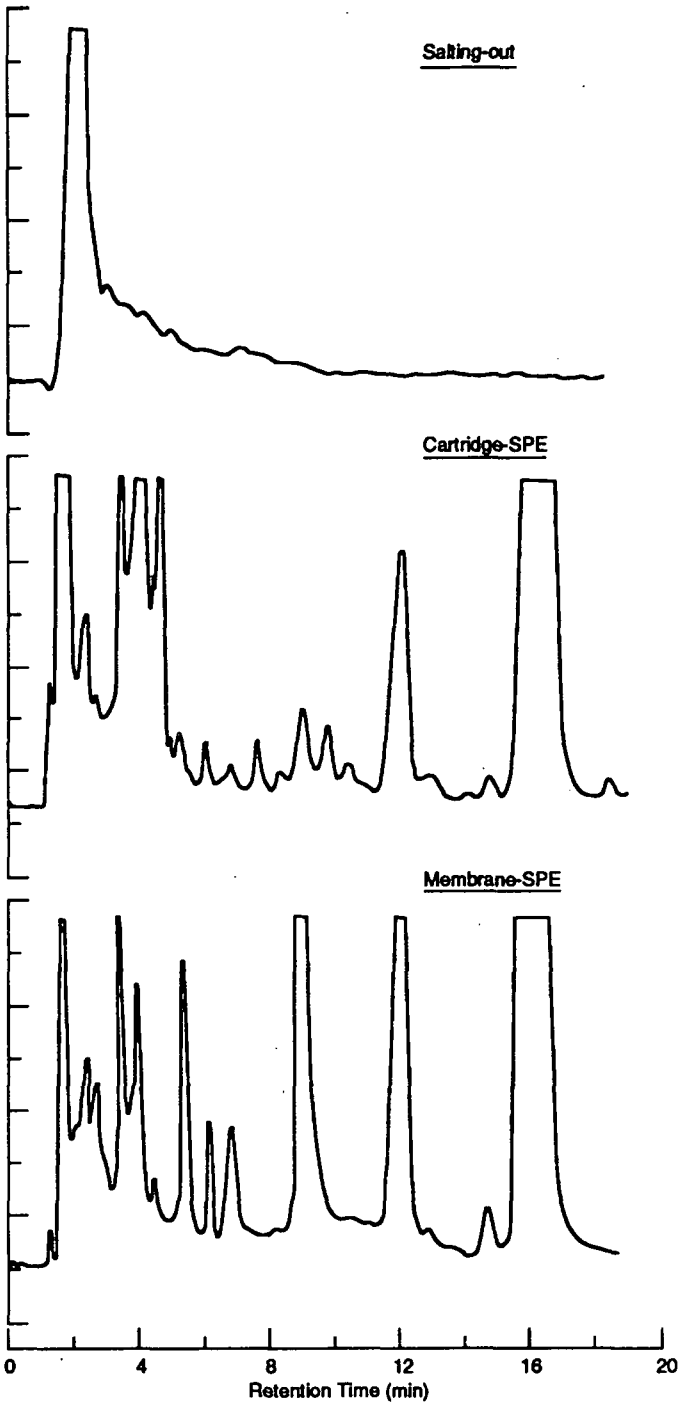

Figure 2. LC-18 chromatograms for sample 20641 from Rockeye site, Naval Surface Warfare Center, preconcentrated by salting-out, cartridge-SPE, and membrane-SPE methods at WES.

tical to the compounds released from the solid phases during cleaning, but were apparently released from the SPE phases due to a matrix interaction with a number of groundwater samples. The nature of this interaction is still unclear. These compounds would interfere with determination of nitroaromatic and nitramine explosives even at reasonably high concentrations.

The elimination of the need to use evaporative preconcentration with the salting-out procedure is a major improvement. We believe the new procedure will be more precise and less subject to error in routine use than the initial method, which utilized a Kudena–Danish evaporator.

In summary, the SOE, cartridge-SPE, and membrane-SPE preconcentration techniques are all capable of providing adequate analyte preconcentration of nitroaromatics and nitramines prior to RP-HPLC determination. Of the three, the SOE method appears to be least prone to interferences. The membrane-SPE method requires the least sample-processing time, but its recovery of HMX is the poorest of the three methods. The cartridge-SPE method requires the least solvent per sample, but its routine use with the currently available processing manifold appears prone to problems with cross contamination [19].

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46 DINOSEB ANALYSIS IN THE FIELD AND THE LABORATORY

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ABSTRACT

Dinoseb, 6-sec-butyl-2,4-dinitro phenol, is a herbicide and a plant desiccant. The multiple functional groups of Dinoseb provide both opportunities and challenges to the analytical chemist. Dinoseb is generally measured using Method 8150/8151; unfortunately, the method is time consuming and requires the use of diazomethane (an explosive and a carcinogen). In addition, several Dinoseb-specific difficulties are not fully explained in Method 8150 (which was developed as a multianalyte method for phenoxyacid herbicides). As a result, engineers and field staff have had the experience of seeing the characteristic yellow color of Dinoseb on site while the laboratory receiving samples reports non-detects. The performance of alternate, more specific, techniques for analyzing for Dinoseb are described, including a colorimetric field screening procedure. This screening procedure produces a distinctive yellow color on Florisil™ and has been used to measure Dinoseb concentrations of 5 ppm in soil. Techniques for improving laboratory analysis of Dinoseb such as HPLC are also discussed. Optimized sample preparation procedures for Dinoseb are presented including derivatizing samples using diazomethane and alternate extraction techniques allowed under Method 8150. Finally, the conversion of Dinoseb to reduced (amino substituted) analogs will be discussed. Dinoseb analyses offer a chemist a tremendous opportunity to design a site-specific analytical program. This presentation will provide guidance and performance data to those interested in designing the most appropriate and cost-effective Dinoseb monitoring program.

INTRODUCTION

Dinoseb, 2-(1-methylpropyl)-4,6-dinitrophenol is a plant desiccant and defoliant. Prior to its ban by EPA, dinoseb was used on a variety of crops including potatoes and cotton. Dinoseb residues are often visible at a site because of its intense yellow color and its propensity to crystalize out of soil. Standard analytical practice is to send samples to a laboratory for herbicide (Method 8150) or GC/MS analysis (e.g., Method 8270). This can greatly increase the time to make a remediation decision and does not necessarily improve the data available to the site manager.

This paper describes alternate, more rapid analytical techniques for dinoseb. These include a field screening procedure, a smaller volume

laboratory extraction procedure, direct GC (non-derivatized) analysis and an HPLC procedure for Dinoseb. In addition, some guidance is offered in extracting and derivatizing samples when Method 8150/8151 are employed. The results were generated by Agricultural and Priority Pollutant Laboratory of Fresno, CA and Science Applications International Corporation in a number of studies for commercial and government clients. Support for comparison of the swirling methanol extraction with Soxhlet extraction (Method 3540) was provided by the Methods Section of the US EPA Office of Solid Waste (OSW) and the Risk Reduction Engineering Laboratory (RREL). The OSW study involved generation of performance data for 27 substituted phenols from spiked soils using both extraction techniques and is reported in a poster presentation at this symposium. The RREL study determined the recovery of spiked dinoseb and a surrogate (bromoxynil) from soil and compared in situ contamination of Dinoseb using both extraction techniques.

DINOSEB SCREENING PROCEDURE

Dinoseb has a bright yellow color that can be used to screen for the compound. Dinoseb is extracted from soil using methylene chloride in a scintillation vial. The sample is agitated and the solids are allowed to settle and the methylene chloride is transferred to a second scintillation containing a small amount of Florisil. The Florisil adsorbs the dinoseb and presence of dinoseb is indicated by yellow color.

PREPARATION OF DINOSEB AS A PHENOL

Dinoseb data was developed during a performance study of several SW-846 methods including Method 8041 (phenols). Although a total of 27 phenols were evaluated, data presented in this report is limited to mixture #1 which contains dinoseb.

Each of the phenols were spiked into a clean, sandy loam soil from San Diego. Each 5 g aliquot was spiked separately, then extracted using a Soxhlet apparatus (Method 3540) or the aqueous methanol leaching procedure. Methylene chloride was used as the solvent in Method 3540; acidic aqueous methanol (1:1 methanol/pH 2 water) was used to leach the phenols from soil on a orbital shaker (150 rpm). Following extraction, methylene chloride extracts (Method 3540) were exchanged to methanol so that all sample extracts could be treated in the same fashion. Sodium chloride, distilled water and hydrochloric acid was added to each extract so that it was primarily aqueous. Phenols were extracted using 3 X 3 mL portions of methylene chloride. The methylene chloride was concentrated under nitrogen and analyzed by GC/FID.

A subsequent study for RREL evaluated the use of HPLC for the analysis of dinoseb. Reversed phase HPLC is an attractive complement to the methanol

leach procedure because no solvent exchange is required prior to analysis. Five replicates of sample spiked at 1, 5 and 25 μg/mL were extracted using pH 2 methanol to demonstrate recovery using the methanol procedure. The suitability of spiking dinoseb into soil on the same day of analyses was supported by comparison of recoveries 1 and 2 days after spiking. The recovery of dinoseb was virtually the same when spiked samples were extracted and analyzed 1 and 2 days after fortification.

The RREL study also included a comparison of Soxhlet extraction and the methanol leaching procedure using a single sample contaminated with dinoseb. Five 10.0 g aliquots of the sample were placed in an Erylenmyer flask. The surrogate bromoxynil was spiked into each sample and thoroughly mixed. A volume of 10 mL pH 2 methanol was added to the flask to extract the phenols. Flasks containing the five replicate samples and the lab blank were placed on a shaker table and swirled for 25 minutes at 150 RPM. The 10 mL methanol was pipetted off and an additional volume of 5 mL pH 2 methanol was added to the sample. The shaker table extraction was repeated. The two portions of methanol were combined for HPLC analysis. Five additional aliquots of the sample were extracted by the Soxhlet procedure (Method 3540) using methylene chloride. The methylene chloride was exchanged to methanol prior to analysis.

PREPARATION OF DINOSEB USING METHOD 8150

Dinoseb is an analyte for Method 8150/8151 (phenoxyacid herbicides). In some cases, the acid/base partitions specified in the method may be required to achieve adequate cleanup or to meet project DQOs. However, analysts are cautioned that dinoseb may be lost when a 30 g sample is used because of the increased sample handling and solvent transfers required. Loss of dinoseb can be minimized by reducing the sample size, the number of solvent transfers, and completing the preparation as quickly as is prudent (i.e., there is no convenient place to stop Method 8150/8151 is used for dinoseb). Acid washing of all glassware will also improve recovery of dinoseb.

GC ANALYSIS

After acquisition of the target chemicals for the OSW study, gas chromatographic (GC) conditions were evaluated in order to achieve separations of the target analytes and to establish nominal low level calibration concentrations. GC analyses were performed on both underivatized phenols and phenols derivatized using diazomethane. Data for the underivatized phenols only are reported here as this report is focused on rapid techniques for the analysis of dinoseb. The GC conditions recommended for the direct analysis of substituted phenols, including Dinoseb, are:

GC CONDITIONS

Column:	DB-5 30m x 0.53 mm id
Initial Temperature:	80°C
Program:	Hold 1.5 minute
	6°C/min to 230
	10°C/min to 275
Final Hold:	4.5 min
Run time:	35 min
Detector:	FID, 300°C
Carrier gas:	Nitrogen, 6 mL/min
Hydrogen:	30mL/min
Total nitrogen:	30 mL/min (carrier and makeup)
Injector:	1/4 inch Packed w/ megabore liner, at 200°C

Initial five-point GC/FID calibration established the linear portion of instrument response for each of the phenols including Dinoseb. The concentrations of the calibration solutions, retention times (R_t) and relative standard deviations of the individual response factors (RSD) for the mixture containing Dinoseb are provided in Table 1. The later-eluting analytes in mixture 1 generally had higher RSDs (18-21%) and more narrow calibration ranges (10-20 fold) than the other phenols. The problems in using GC to measure underivatized dinitro-, trichloro-, tetrachlor-, and pentachlorophenols are evident in the IQL (Table 2) and recovery values (Table 6 and 7).

Examination of the GC chromatograms of underivatized phenols reveals broad and non-Gaussian peaks. The use of a temperature programmed injector (Varian SPI) did narrow peaks somewhat, methylation is the only reliable technique for producing narrow phenol peaks on GC. Therefore, if there is significant co-extracted interferences or lower detection limits are required for the GC analysis of dinoseb, sample extracts should be derivatized. Diazomethane should be used for derivatization, boron triflouride - methanol does not perform reliably with dinoseb.

TABLE 1 - GC/FID Calibration of Phenols - Mix 1

Analyte	Calibration solutions μg/mL	R_t, min	%RSD
Phenol	5,25,50,100,200	6.37	2.5
2-Cresol	5,25,50,100,200	8.17	3.4
3-Cresol	5,25,50,100,200	8.65	4.9
2,4-Dimethylphenol	5,25,50,100,200	9.63	3.1
2,6-Dimethylphenol	5,25,50,100,200	10.54	5.8
2,3-Dimethylphenol	5,25,50,100,200	11.32	6.1
3-Chlorophenol	5,25,50,100,200	11.68	12.3
4-Chloro-3-methylphenol	5,25,50,100,200	14.07	14.8
2,3,5-Trichlorophenol	5,25,50,100,200	15.47	18.2
2,4,5-Trichlorophenol	5,25,50,100,200	16.05	18.3
2,5-Dinitrophenol	10,40,50,100,200	18.37	15.3
2,4-Dinitrophenol	40,50,100,200,400	19.29	20.8*
2,3,5,6-Tetrachlorophenol	5,20,25,40,50	20.42	17.6
4,6-dinitro-o-cresol	10,40,50,100,200	21.72	14.9
Dinoseb	5,20,25,50,200	25.71	15.6

* may require non-linear calibration

TABLE 2 - Phenol GC/FID IQL - Mix 1

Analyte	R_t, min	conc, µg/mL	std dev (s)	IQL 10s µg/mL
Phenol	6.37	10	0.35	3.5
2-Cresol	8.17	10	0.36	3.6
3-Cresol	8.65	10	0.47	4.7
2,4-Dimethylphenol	9.63	10	0.36	3.6
2,6-Dimethylphenol	10.54	10	0.46	4.6
2,3-Dimethylphenol	11.32	10	0.47	4.7
3-Chlorophenol	11.68	10	0.69	6.9
4-Chloro-3-methylphenol	14.07	10	0.82	8.2
2,3,5-Trichlorophenol	15.47	10	0.96	9.6
2,4,5-Trichlorophenol	16.05	10	1.03	10.3
2,5-Dinitrophenol	18.37	20	3.63	36.3
2,4-Dinitrophenol	19.29	20	2.82	28.2
2,3,5,6-Tetrachlorophenol	20.42	10	1.96	19.6
4,6-dinitro-o-cresol	21.72	20	3.18	31.8
Dinoseb	25.71	10	1.56	15.6

HPLC ANALYSIS

HPLC/UV is employed for the analysis of dinoseb. It is an attractive technique for rapid laboratory analysis because of the low detection level for dinoseb, the compatibility with the methanol leach procedure and the relatively poor chromatographic performance of underivatized dinoseb using GC/FID. A study was conducted for RREL to evaluate the practicality of HPLC for the analysis of bioremediation samples. Dinoseb was analyzed using a Hewlett-Packard model 1090A series II Liquid Chromatograph equipped with a diode array UV/VIS detector and a computerized data system. Dinoseb concentrations in water, soil, sediment and treated soil were determined by HPLC/UV with a PSP-Spherisorb ODS2 column (5 μm, 250 x 4 mm i.d.). Dinoseb and a surrogate (bromoxynil) were detected by the diode array UV/VIS detector at 254 nm.

A gradient solvent program was employed: 30% methanol and 70% 0.1% acetic acid buffer for 2 minutes, and then the methanol was increased to 100% over the next 6 minutes and held at that level for 2 minutes. The methanol was then decreased to 30% over 4 minutes and held for 6 minutes. The solvent flow rate was 0.5 mL/minute and the column temperature was at 40°C. The pH of the mobile phase was critical as the chromatographic behavior of Dinoseb and bromoxynil are very dependent on the ionization of these phenols; this is particularly true for the surrogate bromoxynil. Total run time was 20 minutes.

Tables 3 and 4 provide six-point initial calibration data for dinoseb and the surrogate bromoxynil. The tables provide the concentration of the calibration solutions, the retention times of the target analytes, peak area counts from the data system, response factors, and the percent RSD of the response factors.

TABLE 3 - Calibration of Dinoseb

Conc. µg/mL	RT	Area Count	RF
0.50	14.47	20.0	0.02500
1.0	14.48	39.2	0.02551
5.0	14.47	186	0.02688
10.0	14.48	374	0.02674
50.0	14.52	1862	0.02685
100.0	14.55	3663	0.02730
200.0	14.55	7199	0.02778
		Mean =	0.02658
		Std =	0.00098
		%RSD =	3.7

TABLE 4 - HPLC Calibration of Bromoxynil

Conc. µg/mL	RT	Area Count	RF
0.50	12.95	21.8	0.02294
1.0	12.96	44.3	0.02257
5.0	12.96	221	0.02262
10.0	12.96	447	0.02237
50.0	12.97	2215	0.02257
100.0	12.98	4394	0.02276
200.0	12.98	8653	0.02311
		Mean =	0.02271
		Std =	0.00025
		%RSD =	1.1

FIELD SCREENING RESULTS

The dinoseb screening procedure provides a rapid means of monitoring dinoseb in soil. It can provide a detection level of 5 ppm and can be used to establish the presence or absence of *in situ* dinoseb in the field. The technique has been demonstrated to perform reliably at several sites and has reduced the equipment costs associated with soil removal. A normal practice for the removal of dinoseb at a contaminated site is to "chase the color". That is, to remove soil until all of the yellow color is gone. Unfortunately, this technique is quite subjective and is subject to problems when dinoseb is bound within soil particles. A site may appear to be clean at the end of the day but show color the next day. The dinoseb screening procedure reduces the potential for mis-interpretation of soil color by providing a reliable test for dinoseb extracted from soil.

PHENOL STUDY

Dinoseb can be leached from soil using a variety of solvents including methanol, methylene chloride and ether. Studies to date indicate that leaching is as effective as the standard extraction procedures (Methods 3540 and 3550). However, the leaching procedure may need to be tailored to specific soil types. Studies at SAIC have demonstrated that acidic methanol provides the best recoveries from Idaho soil; while studies at APPL demonstrate that an aqueous sodium sulfate/ether leach provides better recoveries from California soil. Additional studies will required to establish the ruggedness of leaching procedures for dinoseb and other substituted phenols in additional sample matrices.

GC/FID analysis of underivatized phenols demonstrate that there is a positive bias for the recoveries of the higher molecular weight species. This was particularly evident for the samples extracted using Soxhlet (Method 3540) which are reported in Table 5 (i.e., a recovery of 200% was reported for dinoseb). Perhaps the co-extracted interferences in soil contributed to the quantitation difficulties observed using GC/FID analysis.

The difficulties of analyzing underivatized phenols was also observed with the alternate extraction procedures. The recoveries from the methanol leaching procedure in Table 6 also reveal a consistent high bias for dinoseb and other phenols. However, the recoveries of using the leaching procedure are generally closer to 100% than those obtained with Soxhlet extraction. This observation could support the supposition that a co-extracted material is interfering with the GC analysis of phenols. In any case, there appears to be the potential for significant difficulties when dinoseb and other phenols are analyzed by GC/FID without derivatization.

TABLE 5 - Recovery of Underivatized Phenols by GC and Method 3540

Analyte	Spiking conc µg/g	Recovery (%)	% RSD	n
Phenol	20	93	16.9	5
2-Cresol	20	95	13.6	5
3-Cresol	20	98	10.3	5
2,4-Dimethylphenol	20	93	11.5	5
2,6-Dimethylphenol	20	101	8.1	5
2,3-Dimethylphenol	20	106	7.1	5
3-Chlorophenol	20	116	6.7	5
4-Chloro-3-methylphenol	20	128	3.8	5
2,3,5-Trichlorophenol	20	136	4.1	5
2,4,5-Trichlorophenol	20	139	3.0	5
2,5-Dinitrophenol	40	177	5.1	5
2,4-Dinitrophenol	40	157	7.3	5
2,3,5,6-Tetrachlorophenol	20	236	3.5	5
4,6-dinitro-o-cresol	40	201	3.8	5
Dinoseb	20	210	4.9	5

TABLE 6 - Recovery of Phenols by Leaching and GC

Analyte	Spiking conc µg/g	Recovery (%)	% RSD	n
Phenol	20	94	2.6	5
2-Cresol	20	97	2.8	5
3-Cresol	20	99	2.8	5
2,4-Dimethylphenol	20	89	3.8	5
2,6-Dimethylphenol	20	82	4.0	5
2,3-Dimethylphenol	20	101	2.6	5
3-Chlorophenol	20	111	2.7	5
4-Chloro-3-methylphenol	20	119	2.4	5
2,3,5-Trichlorophenol	20	127	2.8	5
2,4,5-Trichlorophenol	20	134	2.9	5
2,5-Dinitrophenol	40	123	6.6	5
2,4-Dinitrophenol	40	131	6.8	5
2,3,5,6-Tetrachlorophenol	20	204	3.3	5
4,6-dinitro-o-cresol	40	166	4.3	5
Dinoseb	20	169	4.2	5

HPLC STUDY

HPLC was evaluated as an alternate procedure for the rapid analysis of underivatized dinoseb. Use of HPLC analysis allows the analysis of the methanol leachate without derivatization or solvent exchange. The strong UV absorption of dinoseb provides an opportunity for a low detection level. An initial evaluation of the methanol leaching procedure combined with HPLC analysis was conducted by measuring the recovery of dinoseb and proposed surrogate, bromoxynil, from spiked samples. The performance of the method seems reliable based on the results provided in Table 7.

The methanol leach/HPLC technique was tested against Method 3540/HPLC by extracting aliquots of the same contaminated samples using methanol leaching (Table 8) and Soxhlet extraction (Table 9). The results obtained for dinoseb using either extraction procedure are very similar; higher recoveries for bromoxynil were obtained using Soxhlet extraction. Additional work may be required to provide a more suitable surrogate.

Table 7. 1 µg/g dinoseb spiked soil extracted with pH2 methanol

1 µg/g spiked soil				5 ppm Bromoxynil			
RT	Area	Conc.	% Rec.	RT	Area	Conc.	%Rec.
14.26	37	1.1	108	11.51	151	5.5	110
14.24	38	1.1	111	11.49	140	5.1	102
14.24	36	1.1	106	11.48	152	5.5	110
14.22	31	0.9	91	11.45	151	5.5	110
14.22	32	0.9	94	11.47	147	5.3	107
Mean =		1.0	102	Mean =		5.4	108
Std =		0.091	9.1	Std =		0.18	3.6
%RSD =		8.9	8.9	%RSD =		3.4	3.4

TABLE 8 Methanol Leach/HPLC - Five Replicates of a Contaminated Sample

sample #21-Dinoseb conc. µg/mL				5 ppm Bromoxynil recovery			
RT	Area	Extract Conc.	Sample Conc.	RT	Area	Conc.	%Rec.
14.44	1333	30.3	45.4	13.03	116	2.3	46.9
14.46	1758	39.9	59.9	13.02	194	3.9	78.5
14.47	1607	36.5	54.7	13.02	198	4.0	80.1
14.44	1722	39.1	58.7	13.02	148	3.0	59.9
14.44	1795	40.8	61.1	13.01	146	3.0	59.0
Mean =		37.3	56.0	Mean =		3.2	64.9
Std =		4.2	6.4	Std =		0.7	14.1
%RSD =		11.4	11.4	%RSD =		21.8	21.8

TABLE 9 - Method 3540/HPLC - Five Replicates of a Contaminated Sample

sample #21-Dinoseb conc. μg/mL				5 ppm Bromoxynil recovery			
RT	Area	Extract Conc.	Sample Conc.	RT	Area	Conc.	%Rec.
14.50	1468	33.3	50.0	12.95	277	5.6	112
14.49	1912	43.4	65.1	12.95	266	5.4	108
14.50	1887	42.9	64.3	12.95	267	5.4	108
14.49	1530	34.7	52.1	12.94	239	4.8	96.7
14.49	1580	35.9	53.8	12.95	256	5.2	104
Mean =		38.0	57.1	Mean =		5.3	106
Std =		4.7	7.1	Std =		0.5	5.8
%RSD =		12.4	12.4	%RSD =		5.5	5.5

CONCLUSIONS

In our experience the screening procedure described for Dinoseb can provide reliable evidence that Dinoseb is present at a site. The performance data presented here that a methanol leach can provide adequate extraction of dinoseb from some soils particularly when combined with HPLC analysis. The lower IQL and larger linear range of HPLC vs. GC/FID indicate that HPLC may be a more appropriate technique than underivatized phenol analysis for providing rapid laboratory measurements. Project managers should consider the use of screening or simplified laboratory procedures (HPLC) for the analysis of Dinoseb when Project DQOs do not require the use of Methods 8150/8151 or 8270..

47 QUANTITATION OF POLYCHLORINATED BIPHENYLS USING 19 SPECIFIC CONGENERS

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ABSTRACT

Polychlorinated biphenyls (PCBs) are ubiquitous and persistent pollutants that have been banned for over 20 years. Despite our long history in measuring PCBs in the environment, the interpretation of analytical results for PCBs are often a problem during monitoring activities. A major analytical difficulty results from the fact that most PCB methods specify the use Aroclor standards as the basis of quantitative analysis. Aroclors are complex mixtures of chlorinated biphenyls (*e.g.*, analysis of an Aroclor 1260 standard using capillary GC/ECD should produce more than 50 peaks). While most of the PCBs found in the environment were originally discharged as Aroclors, the PCBs found in sediments today have been altered by environmental weathering processes. As a result, they may not produce the same pattern of peaks as the original Aroclor contaminant. In order to improve the reliability of PCB analyses, a mixture of 19 specific PCB congeners is proposed as an alternative calibration standard. These individual congeners can be resolved on an SE-30 type capillary column (*e.g.*, DB-5), are available through commercial vendors, and represent the major peaks of the individual Aroclors. Spiked soil and reference materials have been analyzed using quantitation based on Aroclor and congener calibration. Analysts have demonstrated that mercury and sulfuric acid clean up do not effect the recovery of these congeners or Aroclors.

INTRODUCTION

PCB's were produced in the United States under the trade name Aroclor by Monsanto until they were banned in 1972. Aroclors are mixtures of many individual chlorinated biphenyls (congeners) which were sold as products on the basis of their weight percentage of chlorine. For example, each molecule in Aroclor 1254 contains 12 carbons and an average chlorine content (w/w) of the mixture was 54%. The exception to this system was Aroclor 1016, which is similar to Aroclor 1242 except that 1016 contains only 0.4% pentachloro congeners while 1242 contains 4.2%. The lack of higher chlorinated congeners allows Aroclors 1016 to be combined with Aroclor 1260 in a single calibration standard. All other Aroclors must be analzed as individual standards.

PCBs are generally analyzed using gas chromatography with electron capture detection (GC/ECD) (e.g., SW-846 Methods 8080/8081 or Method 608). These

methods specify that analyte identification and quantitation be accomplished by comparing the peak pattern observed in a sample with the peak patterns from commercial Aroclor mixtures. This approach of patten matching is appropriate when the pattern in the sample is similar to an Aroclor standard and when the analyst is experienced in PCB measurements. However, the practice of pattern matching can be difficult when a sample contains a heavily weathered or an incompletely treated Aroclor. Use of Aroclor pattern matching is also a questionable practice when the sample contains more than one Aroclor or PCBs created as an industrial side product (e.g., chlorination of a still keeper).

Capillary GC analysis increases the complexity of PCB quantitation based on pattern matching while it provides opportunities to improve PCB measurement based on congener analysis. The complexity has increased because 40-100 peaks may be observed for an individual Aroclor using capillary GC (Figure 1) in contrast to the seven to ten peaks observed using packed column. Laboratories often utilize poorly documented quantitation procedures for capillary data that are highly dependent on the training of the analyst. Differences in quantitation practices probably contribute to the interlaboratory variability observed for PCB analyses (i.e., 36% of the 1991 WP PCB values were incorrect[2]). At the same time, capillary GC provides a tool to resolve individual PCB congeners which can be exploited to improve analyses[3,4]. This can be a significant effort, chlorination of biphenyl ($C_{12}H_{10}$) produces 209 PCB congeners. The IUPAC has adopted a numbering system for the PCB congeners which is used in this paper.

While Method 8081B provides some guidance on the use of congeners for quantitation of PCBs in Method 8081, no sample performance data are provided. In addition, the recommended mixture of congeners needs to be refined by adding higher chlorinated species. Calculation of concentrations using a mixture of 12 congeners provides results very similar to Aroclor-based quantitation for Aroclors 1016, 1232, 1242, and 1248. Unfortunately, calculation of concentrations using the congeners produces values that are only 45-60% of the values obtained using Aroclors 1254 and 1260.[5] Use of a longer list of congeners suggested by Draper of California's Hazardous Materials Laboratory (HML) provides better correlation (76-85%) for Aroclors 1254 and 1260.[6] However, HML's list inclues forty congeners.

This study was designed to provide the Office of Solid Waste with performance data for a congener-specific analysis of PCBs in solid matrices. One of the considerations in designing this study is the requirement for a five-point calibration of all target analytes. It is also hoped that these data will assist the Methods Section in establishing whether congener-specific analysis of PCBs has application for the RCRA program.

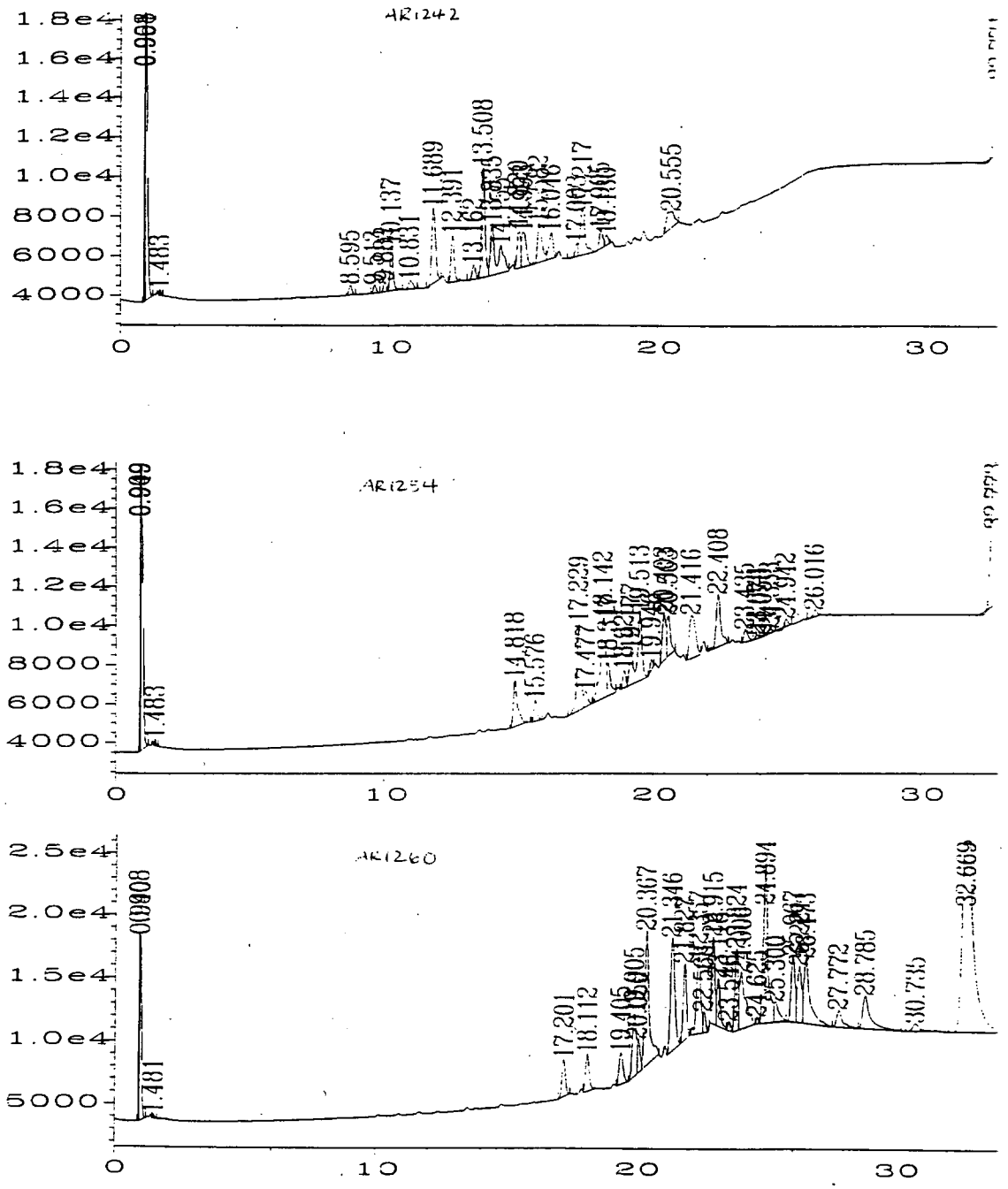

Figure 1. Chromatograms of Aroclors 1242, 1254 and 1260

EXPERIMENTAL PROCEDURES

SELECTION OF CONGENERS - During the first stage of this study, candidate quantitation congeners were selected and chromatographic separations of the compounds were established. Each congener solution was analyzed individually to establish the retention time. The retention times of the congeners were compared with the retention times of the major peaks of Aroclors 1242, 1254 and 1260. These results were compared with Draper's findings[6]. A group of 19 congeners were selected which represented the major peaks in Aroclors. Table 1 lists the congeners and a chromatogram of the standards is provided in Figure 2.

Comparison of the response factors generated in this study with the relative response factors reported by Mullen[4] shows considerable differences between the two data sets. The response factors generated in this study were based on standards in hexane purchased from Ultra Scientific. Mullen's relative response factors were obtained using standards from S. Safe of Texas A&M. Because of the difficulties in preparing pure congeners, it is recommended that additional analysis of standards be completed to establish response factors for the selected congeners. It is also recommended that relative response factors be included in any specific-congener method as a quality control measure.

CHROMATOGRAPHIC CONDITIONS - Some analysts recommend 60 m columns with very slow temperature ramps (e.g., 1°C/min, Mike Mullen) in order to separate almost all the PCB congeners. This approach requires run times from 90 to 120 minutes, results in short column lifetimes and allows only 6-7 analyses in a 12 hour shift. As the object of this study was to develop a practical and routine analytical procedure, use of a 30 m DB-5 column seemed more appropriate for this procedure. The carrier gas was nitrogen to demonstrate that these separations could be achieved in commercial laboratories.

GC Conditions

Initial temperature	150°C, hold 0.5 min
Temperature ramp	5°C/min
Final temperature	275°C, hold 9.5 min
Run time	35 min
Carrier	6 mL/min, nitrogen
Makeup	54 mL/min, nitrogen
Injector	packed, 200°C
Detector	electron capture, 300°C
Column	30m X 0.53mm id, DB-5

TABLE 1 - CONGENER MIX

Congener	IUPAC#	R_t
2-Chloro	1	6.52
2,3-Dichloro	5	10.07
2,2',5-Trichloro	18	11.62
2,4',5-Trichloro	31	13.43
2,2',5,5'-Tetrachloro	52	14.75
2,2',3',5'-Tetrachloro	44	15.51
2,3',4,4'-Tetrachloro	66	17.20
2,2',4,5,5'-Pentachloro	101	18.08
2,2',3,4,5'-Pentachloro	87	19.11
2,3,3',4',6-Pentachloro	110	19.45
2,2',3,5,5',6-Hexachloro	151	19.87
2,2',4,4',5,5'-Hexachloro	153	21.30
2,2',3,4,4',5'-Hexachloro	138	21.79
2,2',3,4,5,5'-Hexachloro	141	22.34
2,2',3,4',5,5',6-Heptachloro	187	22.89
2,2',3,4,4',5',6-Heptachloro	183	23.09
2,2',3,4,4',5,5'-Heptachloro	180	24.87
2,2',3,3',4,4',5-Heptachloro	170	25.93
2,2',3,3',4,4',5,5',6-Nonachloro	206	30.70
Decachlorobiphenyl (surrogate)	209	32.63

Column flow rate - 6 mL/min

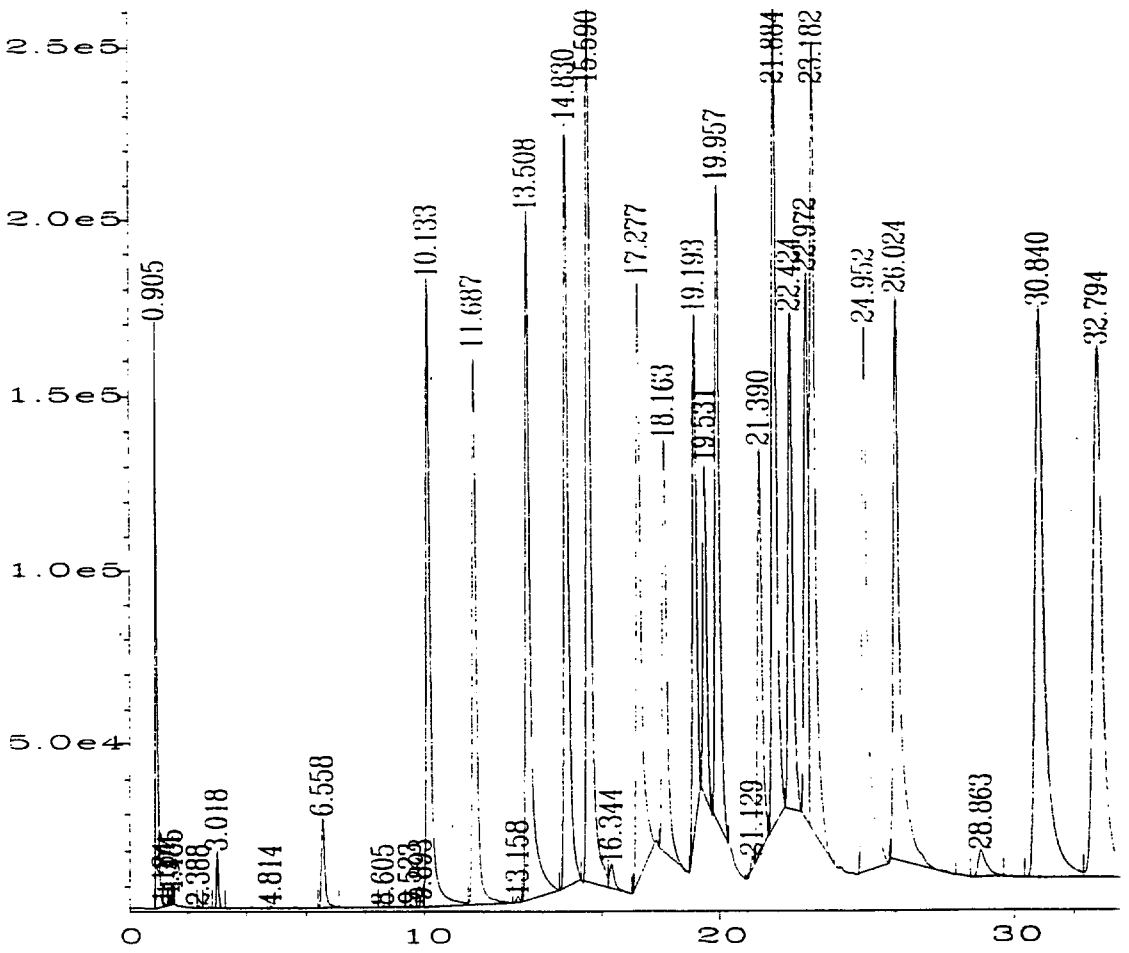

FIGURE 2 - Chromatogram of Specific Congeners

Five-point calibrations were performed using the congener mixture according to the criteria specified in Method 8000 of SW-846. The calibration mixtures and the RSDs are reported in Table 2.

TABLE 2 - INITIAL CALIBRATION DATA

IUPAC#	R_t	Calibration solutions ng/mL	% RSD
1	6.52	25, 100, 250, 500, 1000	14.1
5	10.07	25, 100, 500, 1000, 5000	4.6
18	11.62	25, 100, 500, 1000, 2500	10.5
31	13.43	25, 100, 500, 1000, 5000	3.1
52	14.75	25, 100, 500, 1000, 2500	9.1
44	15.51	25, 100, 500, 1000, 5000	4.2
66	17.20	25, 100, 500, 1000, 5000	6.1
101	18.08	12.5, 50, 250, 500, 2500	6.4
87	19.11	12.5, 50, 250, 500, 2500	9.4
110	19.45	12.5, 50, 250, 500, 2500	7.0
151	19.87	12.5, 50, 250, 500, 2500	4.8
153	21.30	12.5, 50, 250, 500, 1250	9.2
138	21.79	25, 125, 250, 500, 1250	13.4
141	22.34	12.5, 50, 125, 250, 500	7.8
187	22.89	25, 50, 250, 500, 2500	5.9
183	23.09	25, 50, 250, 500, 2500	5.3
180	24.87	25, 125, 250, 500, 2500	19.6
170	25.93	25, 125, 250, 500, 2500	23.0*
206	30.70	5, 25, 250, 500, 2500	5.6
209 (surrogate)	32.63	5, 25, 250, 500, 2500	7.3

*reduce calibration range
Column flow rate - 6 mL/min

Sulfuric acid and sulfur cleanups were evaluated to ensure that they did not result in the loss of Aroclors or congeners. Although these techniques are in common use in environmental laboratories, there is

little documentation that they can not destroy any PCBs[7]. A mixture of congeners, Aroclor 1242, Aroclor 1254, and Aroclor 1260 were each subjected to both cleanup procedures. Peak areas of the individual congeners were compared before and after cleanup to determine congener recoveries. The sum of the areas of six or seven peaks from each of the Aroclor standards were compared before and after cleanup to determine Aroclor recoveries. The results for the cleanup of Aroclor 1254 are presented in Table 3 as illustration of the fact that neither cleanup destroys PCBs.

TABLE 3 - Cleanup of Aroclor 1254

R_t	Isomer #	Area of std	Area after cleanup	% Recovery
14.26	52	22824	25170	
15.01	44	9401	10149	
16.65	66	41318	42677	
18.92	110	35594	36032	
20.82	153	33339	33964	
21.82	138	34882	34839	
total		192790	197521	103

Column flow - 7 mL/min

RESULTS

Performance testing of congener quantitation was conducted using two EPA freeze dried soil samples provided by the RT Corporation and two spiked soils. PCBs were quantitated using the specific-congeners and Aroclor standards. The EPA Soil Group 1 sample was contaminated with a reported concentration of 44.1 mg/Kg of Aroclor 1242. The EPA Soil Group 2 sample was contaminated with a reported concentration of 2.08 mg/Kg of Aroclor 1254. San Diego soil sample spiked with Aroclors 1254 and 1260 were spiked at the 500 ppb level. A aliquot of 5 grams of each sample was mixed with anhydrous sodium sulfate and extracted using a Soxhlet apparatus (Method 3540) with methylene chloride as a solvent. A duplicate determination of the spiked Aroclor 1254 was also prepared and analyzed. The extracts were exchanged to hexane prior to analysis, no cleanup was employed. Three of the soils were also extracted using a Dionex Model 703 supercritical fluid extractor with carbon dioxide at 100°C, 300 atm for 10 minutes static and 45 minutes dynamic. The restrictor was maintained at 150°C and the receiving vial at 4°C. The vial was filled with 15 ml of hexane and decachlorobiphenyl as an internal standard. The recovery of

internal standard was used to correct for the loss of solvent that occurred during the extraction. Each extract was analyzed using a 30 m DB-5 column using the conditions described above. Tables 4 and 5 present the recoveries from the EPA soils determined using Soxhlet extraction based on congener and Aroclor quantitation as well as supercritical fluid extraction (SFE) using Aroclor quantitation. Table 6 provides the amount of individual congeners determined in duplicate soils spiked with Aroclor 1254 as well as recoveries for Soxhlet and SFE. Table 7 provides recovery data for soil spiked with Aroclor 1260.

In all cases, the concentrations based Aroclor standards were larger than those obtained using congener analysis. The recoveries based on congeners were lowest for the EPA soils in part because interference prevented measurement of congener #66. It is worth noting that while the congener values are also lower in the spiked samples, they are closer to the nominal values than were obtained using Aroclor quantitation

TABLE 4 - Group 1 Soil (44.1 ppm Aroclor 1242)

Recovery category	Recoveries		
	Quantities based on congeners using Soxhlet	Quantities based on Aroclors using Soxhlet	SFE (by Aroclor)
TOTAL (ppb)	22744 ppb	49800 ppb	
TOTAL (%)	51.6%	113%	79.9%

column flow rate 6mL/min
SFE recovery = apparent recovery/(surrogate recovery*100)

TABLE 5 - Group 2 Soil (2.08 ppm Aroclor 1254)

IUPAC#	Recoveries		
	Quantities based on congeners using Soxhlet	Quantities based on Aroclors using Soxhlet	SFE (by Aroclor)
TOTAL (ppb)	1363	2202	
TOTAL (%)	65.5%	106%	73.2%

column flow rate 6mL/min
SFE recovery = apparent recovery/(surrogate recovery*100)

TABLE 6 - Duplicate Spiked Soil (500 ppb Aroclor 1254)

IUPAC#	R_t	Recoveries		
		Concentration of congeners by Soxhlet	Aroclor conc	SFE by (Aroclor)
52	14.83	36.5, 40.0	x	x
44	15.59	10.5, 11.2	x	x
66	17.24	82.6, 88.2	x	x
101	18.15	66.3, 71.4	x	x
87				
110	19.53	107.5, 109.8		
151	19.96	3.7, 4.6		
153	21.45	59.4, 59.4	x	x
138	21.88	3.6, 3.9		
141	22.41	54.0, 59.4	x	x
187				
183				
180	24.96	3.7, 4.4		
170	25.04	3.2, 3.9		
206				
209	32.63	102, 101		218
TOTAL (ppb)		431	661	
TOTAL (%)		86.2%	132%	83%

column flow rate 6mL/min
SFE recovery = apparent recovery/(surrogate recovery*100)

TABLE 7 - Spiked Soil (500 ppb Aroclor 1260)

IUPAC#	R_t	Recoveries	
		Concentration of congeners by Soxhlet	Aroclor conc
66	17.25	15.7	x
101	18.17	11.7	
87		-	
110	19.44	82.8	
151	19.96	33.2	
153	21.41	70.4	x
138	21.88	18.9	x
141	22.41	40.8	x
187	22.97	34.1	x
183	23.17	9.4	x
180	24.95	85.9	
170	26.03	18.8	
206	30.85	2.4	
209	32.63	99%	
TOTAL (ppb)		424.1	687
TOTAL (%)		84.8%	137%

column flow rate 6mL/min

CONCLUSIONS

The approach of using a mixture of 19 specific congeners appears to be a viable approach to measuring PCBs in the environment. Recoveries of soils spiked with Aroclors 1254 and 1260 determined using the specific congener mixture were between 80 and 90%. Aroclors in environmental samples were recovered at 51-66% of the certified values.

While this approach is promising, it is not yet ready to be distributed as formal method. At least one of the selected congeners (#153) coelutes with another Aroclor congener. In addition, the correct response factors for the congeners relative to the surrogate decachlorobiphenyl needs to be established. Finally the list of congeners

should be further evaluated in terms of common matrix interferences. For example, isomer # 66 was buried beneath a chlorinated pesticide peak, possibly DDE or DDT, in the EPA soil samples. Despite these shortcommings, congener specific analysis could be applied to more environmental and waste studies.

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DIRECT DETERMINATION OF TCLP PHENOLS AND HERBICIDES BY HPLC

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A method for determining TCLP acidic semivolatile compounds (cresols, chlorophenols, and herbicides) is being developed to permit radioactive mixed wastes and their leachates to be analyzed with a minimum of operator exposure to sample radioactivity and very little laboratory waste generation versus current GC-ECD methods. The HPLC method features direct injection of a 25 μL aliquot of aqueous waste or leachate (with filtration and acidification, if needed) onto a 150 mm X 4.1 mm ID (5 μm particles) PRP-1 polystyrene column. The mobile phase is a gradient of 0.1 M acetic acid in 10/90 (v/v) acetonitrile/water and acetonitrile. Quantitation is by the method of external standards at wavelengths of 235 and 280 nm using a diode array UV detector. Compound confirmation is by UV spectrum or retention time on an ODS column. The detection limits meet TCLP Regulatory Limits, and run times are 16 min per sample, including mobile phase reequilibration. Matrix spike recoveries at or below the Regulatory Limits in TCLP Fluid No. 2 ranged from 88.6 to 128.2 %, but were much lower in alkaline, high-nitrate wastes simulating nuclear wastes. Surrogate standard recoveries determined over the course of 12 months for 2,4,5-T spiked into 61 TCLP leachates at 5.0 to 7.5 mg/L averaged 96.7 $\pm$ 14.8%. A better confirmation column phase and mass spectrometric confirmation will be added in the future.

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49 Approaching the Sensitivity of an Electron Capture Detector (ECD) for the Analysis of Pesticides by using GC/MS

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ABSTRACT

Pesticides are analyzed routinely by GC/ECD with dual column confirmation. The ECD has excellent sensitivity and can be used to determine some pesticides at levels in the low femtogram range. Unfortunately, it is easily contaminated and lacks the linearity of other detectors. Also the chromatography must be optimized, to eliminate any co-eluting analytes.

We decided to approach the analysis of pesticides using a selected ion monitoring (SIM) based GC/MS method. The MS tolerates dirty samples much more readily than the ECD and is easier to clean. SIM has the benefit of giving up to 4 orders of magnitude linearity, much better than an ECD. It also accommodates co-eluting analytes by allowing for their separation based on mass. This speeds up method development time.

The USEPA Method 608[1] pesticides were used for these experiments. (PCBs, toxaphene and chlordane were excluded.) Initially a standard at the 100 pg level was analyzed by electron impact (EI) GC/MS in the scan mode (60-430 a.m.u.). One or two significant ions were chosen for each pesticide from the mass spectrum. Because pesticides have unique EI fragmentation patterns, the specific ions chosen were indicative of the pesticide. The SIM method was developed using those ions. The pesticides were separated into elution groups to get the best results. Four groups of ions were used. Standards were injected over a 30 fold concentration range to best mimic the range required by the Contract Laboratory Program 3/90 Statement of Work[2]. All pesticides were linear over this range. The hexachlorocyclohexanes standards (BHCs) were analyzed from 0.1 pg to 1000 pg. Standards were then spiked with reference gas oil and analyzed in both SIM and scan mode. Solutions were spiked at both the 0.1 and 1.0% levels.

INTRODUCTION

Historically the ECD has been used for the identification and quantitation of chlorinated, electrophilic pesticides. As mass spectrometers improve in sensitivity other approaches to the analysis of pesticides need to be tried. Mass spectrometry affords the analyst the ability to obtain a third dimension of information to confirm the presence or absence of a certain pesticide. The following work explores the use of selected ion monitoring (SIM) for the analysis of chlorinated pesticides.

EXPERIMENTAL

The GC/MS system was composed of an HP 5890 Series II GC with Electronic Pressure Control (EPC). EPC allows the user to control the pressure or flow of GC carrier gas accurately. The autosampler was an HP 7673B ALS. The mass spectrometer was the HP 5972A. The GC was installed with an HP-5MS column (30 m, 0.25 mm ID, 0.25 µm film). A single tapered, deactivated glass liner with glass wool (HP P/N 5062-3587) was installed in the injection port.

GC:

Injection port	250° C
Initial oven temperature	85° C, 1.5 minute hold 30° C /min to 190° C 3.6° C/min to 240° C
Purge on	1.5 minutes
EPC program	15 psi for 1.5 minutes, then constant flow
Transfer Line	280° C
Injection size	2 stops (1 µl, 5 µl syringe)

MS:

SIM (4 groups)

Group 1 start time 6.7 minutes
Group 1: m/z= 180.9, 108.95

Group 2 start time 8.7 minutes
Group 2: m/z= 100, 66, 240.8, 196.9

Group 3 start time 12.7 minutes
Group 3: m/z= 246, 79.05, 81, 67, 194.9

Group 4 start time 15 minutes
Group 4: m/z= 234.9, 271.8

max sensitivity autotune
EM = tune + 700 V

SCAN

60-430 amu
A/D =2^2
Threshold = 0
max sensitivity autotune
EM = tune + 700 V

Group 1 included the four hexachlorocyclohexane pesticides (BHCs). Group 2 included Heptachlor, Aldrin, Heptachlor Epoxide and Endosulfan I. Group 3 included 4,4'-DDE, Dieldrin, Endrin, Endosulfan II, 4,4' DDD and Endrin Aldehyde. Group 4 included Endosulfan Sulfate and 4,4'-DDT.

Some standards were prepared from a 100 ppb pesticide solution (HP Pesticide Evaluation Sample P/N 5062-3589). Solutions for the standard curves were made with a stock solution diluted from a Method 8080 standard (HP P/N 8500-6011) . All

solutions were prepared in iso-octane. ASTM Reference Gas Oil #1 (HP P/N 5060-9086) was spiked into standards for the "dirty matrix" experiments.

RESULTS

Scan Mode:

All pesticides were analyzed, as standards, down to 10 pg injected. The data collected in scan mode gave quality library searches at 25-50 pg depending on the pesticide. The standard curves were linear from 25-1000 pg for all of the pesticides. Certain pesticides gave three orders of magnitude linearity. The sensitivity level was dependent on the pesticide. Some of the compounds fragmented easily. Figure 1 shows the mass spectrum of Endosulfan I versus DDE. DDE can be seen at much lower concentrations than Endosulfan I. This is because the ion current for Endosulfan I is spread over many masses and not concentrated into one or two masses.

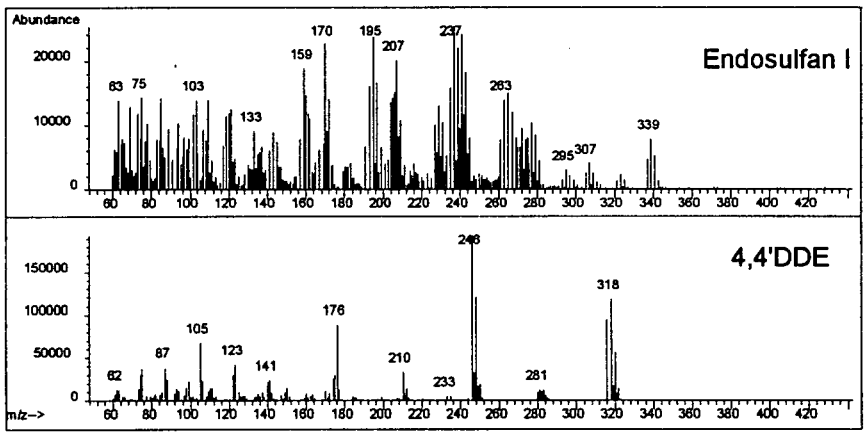

Figure 1. A comparison of the spectra for two pesticides to show the amount of fragmentation. Notice the difference in maximum abundance counts. The largest ion for Endosulfan is about 50X smaller than m/z= 246 for DDE.

The most prominent ion (the base peak) in the spectrum also affects the ultimate detection limit. The base peak is generally used as the quantitation ion. Figure 2 shows the spectrum of DDE versus Dieldrin. The base peak in DDE is m/z= 246 were the base peak for Dieldrin is m/z= 79. The higher the mass of the ion, the less likely that there will be co-eluting background at the same mass. In Figure 3 a chromatogram of a standard at 100 pg is displayed.

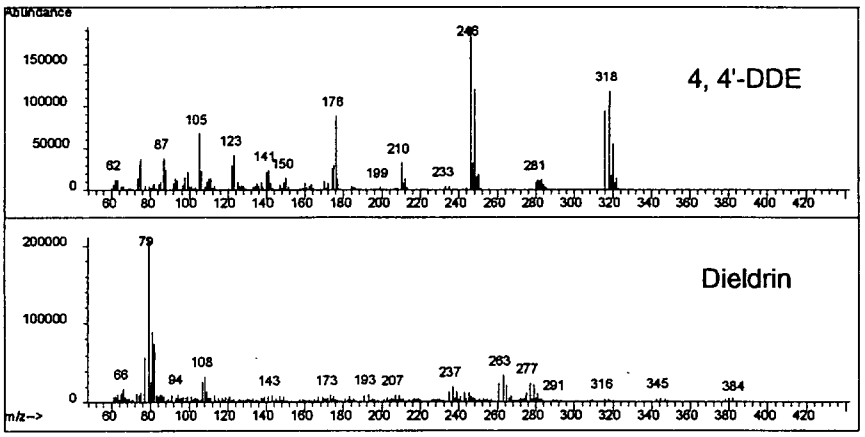

Figure 2. Spectra for two pesticides where the base peak differ in mass. The higher the mass of the base peak, the less background interference. Signal-to-noise improves at higher masses. Notice the abundance counts for the base peak are similar.

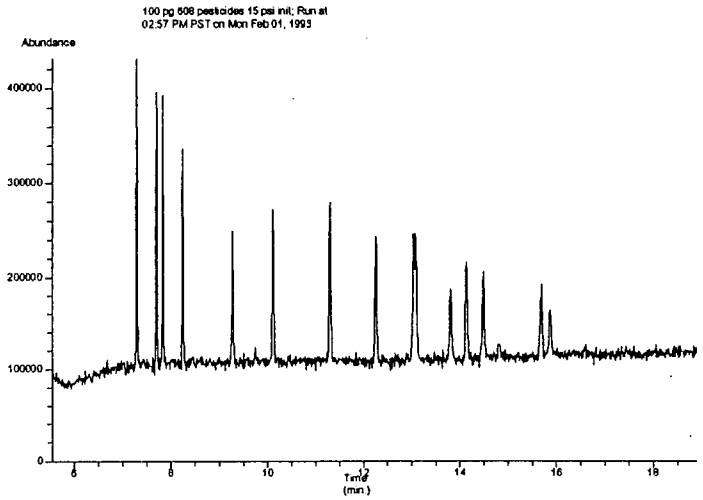

Figure 3. The total ion chromatogram of a 100 pg pesticide standard analyzed in the scan mode.

One benefit of mass spectrometry is the ability to separate co-eluting peaks without extensive chromatographic method development. Figure 4 shows an example of this. Dieldrin and DDE are co-eluting but still easily quantifiable.

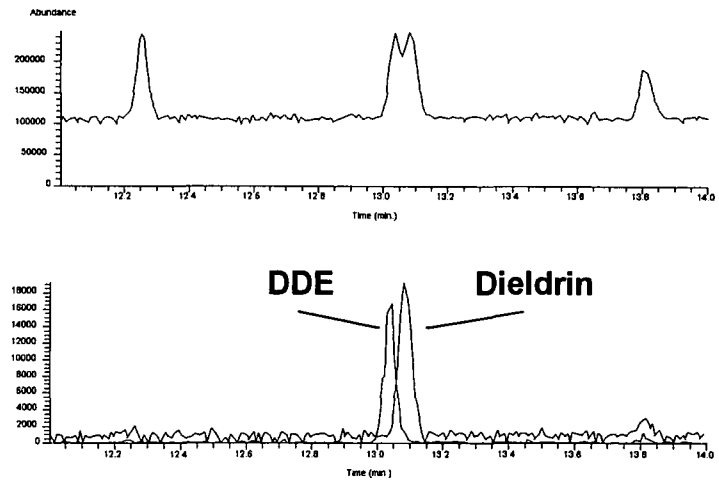

Figure 4. Separation of co-eluting DDE and Dieldrin by mass.

Standards were then spiked with reference gas oil #1 (RGO #1). A standard 100 pg solution was spiked at the 0.1 % (1 µl to 1000 µl) and 1% levels (10 µl to 1000 µl). DDE and DDD gave high quality library searchable results at the 0.1% spiked level.

SIM

SIM experiments were run to get the lowest detection limits. SIM also gives better quantitation reproducibility over scan. Since SIM allows for a higher rate of data acquisition, more points are collected across a GC peak and the GC peak is better defined and integrated. For dirty samples, SIM will reduce background noise, increasing the sensitivity.

Standards were prepared and run from 5 pg to 1000 pg for all pesticides. The hexachlorocyclohexane pesticides were analyzed down to 100 fg. Figure 5 shows the calibration curve for Lindane. The RGO spiked standards were also analyzed in SIM. Figure 6 gives a SIM/scan comparison for DDE in the presence of the RGO matrix.

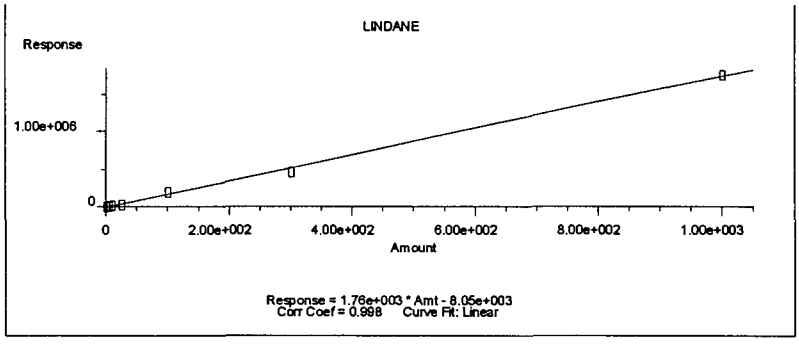

Figure 5. The calibration curve for Lindane from 100 fg to 1000 pg injected splitless.

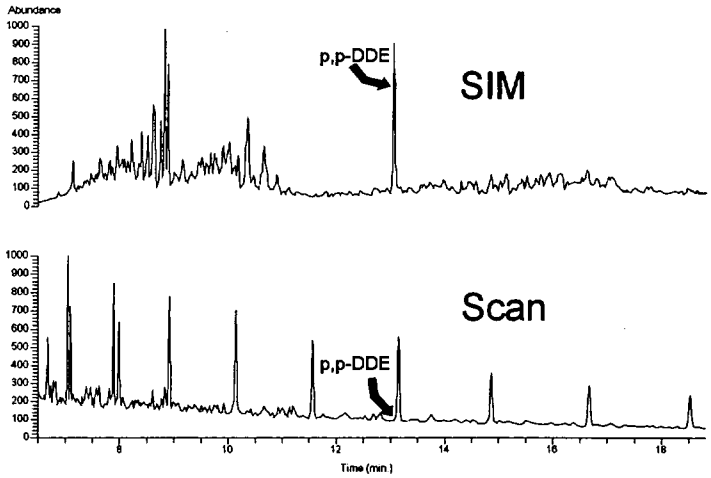

Figure 6. A comparison between SIM and scan for the 0.1% spike standards. The concentration for DDE is 100 pg.

SUMMARY

Results look favorable for substituting a mass spectrometer for an ECD. Detection limits of MS approach those of an ECD and give a much less ambiguous confirmation for the pesticides. By using one or two unique ions per pesticide for confirmation, false positives and negatives are much easier to eliminate.

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[1]USEPA Method 608, Document Number EPA-600/4-82-057, July 1982

[2]USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Document Number OLM01.8, August 1991

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DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN SOIL AT 1 µg/kg USING GC/MS

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Abstract: A GC/MS method has been developed which is capable of determining PAHs below 1 µg/kg in soil samples. It uses a 100 g initial sample, soxhlet extraction using toluene, extensive sample cleanup including alumina column fractionation, and a 300 µL final extract volume. Measurements are made using selected ion monitoring techniques on a quadrupole GC/MS.

INTRODUCTION

Because several polynuclear aromatic hydrocarbons (PAHs) are potent carcinogens, it is appropriate to determine them at relatively low concentrations in environmental samples. At present there are two accepted ways to measure PAHs in soils, Method 8270 and Method 8310. Method 8270 is a reasonably robust GC/MS method with indicated PAH detection limits of 660 µg/kg. Method 8310 is an HPLC-fluorescence method with indicated detection limits ranging from 9 to 1550 µg/kg depending on the analyte. Because of its generally lower detection limits, Method 8310 is frequently identified as the method of choice for field studies. Unfortunately, Method 8310 is often unable to provide these lower detection limit values due to interference from non-target materials present in field samples. This is especially true in situations where alkyl-PAHs are present.

The advent of more sensitive GC/MS instrumentation has made it possible to detect PAHs at considerably lower levels than those identified in Method 8270. When this more sensitive instrumentation is combined with extensive sample cleanup, it is possible to generate PAH detection limits which are less than 1 µg/kg.

METHOD SUMMARY

A 100 g aliquot of soil sample is fortified with the labeled analogs (Cambridge Isotopes) of the target PAH analytes. Moisture is removed from the sample by boiling the sample in toluene using a Barrett moisture trap attached to a boiling flask. The dehydrated sample and toluene are then transferred to a soxhlet apparatus to generate the sample extract. The extract is subjected to alumina column fractionation (SW-846 Method 3611, Appendix B). Sulfur is removed using the tetrabutylammonium sulfite procedure if it is present in substantial quantities.

The final extract is spiked with an internal standard and analyzed by GC/MS (VG MD800) in the SIR data acquisition mode. Two mass descriptor groups are used which

incorporated the quantitation mass for each analyte. The dwell time on each mass is 60 msec and the cycle time is 1 sec. The instrument is calibrated with solutions containing 0.01, 0.1, 1, 10 and 100 ng/μL of each PAH plus 2 ng/μL of each labeled (deuterated) analog of each PAH. No labeled analog was available for indeno(1,2,3-cd)pyrene.

EXPERIMENTAL

Several experiments were undertaken during the course of the study summarized here. They included a method detection limit (MDL) study, an analysis of the NIST SRM 1941, plus determinations on a variety of field samples many of which were contaminated with coal tar derived materials. The MDL study was undertaken using Ottawa Sand as the substrate. Seven aliquots were spiked to 2.0 μg/kg with each PAH plus the labeled analogs and then prepared and analyzed as described above.

In another experiment a 1 gram aliquot of the NIST SRM 1941 (river sediment) was taken and processed as if it were a 10 gram sample. Calculated concentrations were multiplied by a factor of ten to account for the different sample size.

A wide variety of field samples were prepared and analyzed using the above procedure. These samples were associated with waste sites involving petroleum and coal tar related materials contamination.

RESULTS AND DISCUSSION

The GC/MS instrument was readily calibrated for the lower molecular weight PAH compounds from 0.01 to 10 ng/μL. For the higher molecular weight PAH compounds calibration was from 0.1 to 100 ng/μL. The reason for this was peak shape. The lower molecular weight PAHs resulted in very narrow peaks, so detector saturation was encountered with the 100 ng/μL injections. The higher molecular weight PAHs did not yield such narrow peaks and consequently did not saturate the detector, but for the same reason they did not produce reliable peak areas for the 0.01 ng/μL injections. SICP traces for the low point standards for chrysene and benzo(a)anthracene are shown in Figure 1 and a typical calibration curve for benzo(a)pyrene is shown in Figure 2. After these experiments were performed, an improved transfer line was fitted to the GC/MS. It greatly improved peak shape for the higher molecular weight PAHs, but no calibration curves have been generated since it's installation.

The MDL study proceeded without incident and produced the results shown in Table 1. All of the MDL values were less than 1 μg/kg. Percent recovery and analytical precision values were also calculated from the MDL study data. These are also shown in Table 1.

Analysis of NIST SRM 1941 resulted in generally excellent agreement with the NIST provided values (Table 2). There may be a slightly positive bias in the measurements but it is not consistent. Also, the acenaphthylene value was quite different from the NIST value. The rest, however, were reasonably close.

Initial experiments were performed without benefit of sulfur removal but several field samples as well as SRM 1941 contained substantial quantities of sulfur. With some of the field samples there was so much sulfur that little else was evident on initial inspection of the total ion current trace. While the sulfur did not seem to create measurement problems through ionization supression, the removal step was added to assure that it would not become a problem. Figure 3 shows a full scan chromatogram for a high sulfur sample. The broad peak centered at scan 1124 is for S_8. The baseline "hump" starting at about scan 750 and continuing through 2500 is caused by the alkyl-PAHs which interfer severely with Method 8310 measurements.

Finally, it is important to note that problems were encountered occasionally with deuterium exchange on some of the labeled PAHs. This should not be surprising because exchange is almost certainly the mechanism used to generate the labeled analogs. Due to the potential for exchange, a secondary set of quantitative references was identified for those compounds having analogs which exhibit exchange. Because this is only an occasional problem and it is one that can be monitored and solved through the use of the secondary references, it is not considered a serious problem. Further, Cambridge Isotopes was contacted with regard to this problem and they have now initiated a program to develop ^{13}C-labeled PAHs which will be used in future experiments.

SUMMARY

By slightly increasing sample size, using extensive sample cleanup, slightly decreasing final volume and making use of today's more sensitive GC/MS equipment, it is possible to determine PAHs in soils at less than 1 µg/kg. Care must be taken to monitor for label exchange if deuterated analogs are used for quantitation.

Figure 1 - SICP TRACES FOR 0.01 ng/µL STANDARD

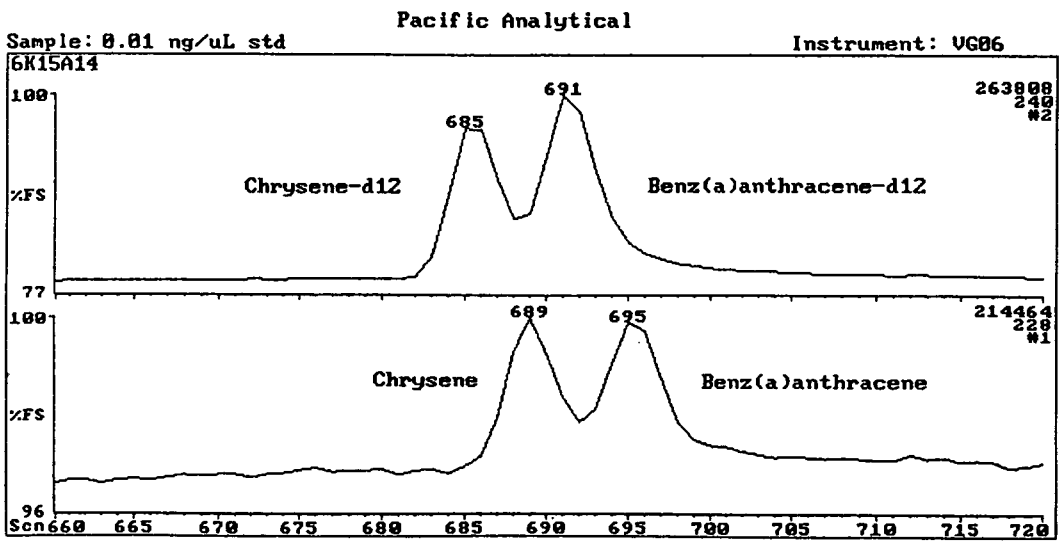

Figure 2 - BENZO(A)PYRENE CALIBRATION CURVE

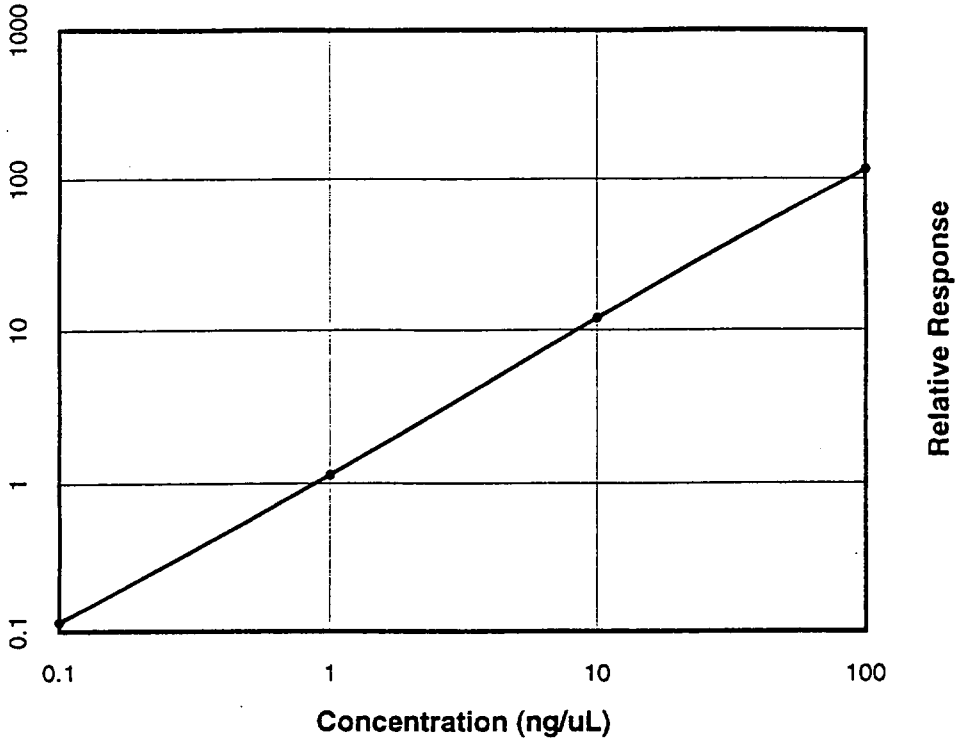

Figure 3 - SOIL SAMPLE EXTRACT PRIOR TO SULFUR REMOVAL

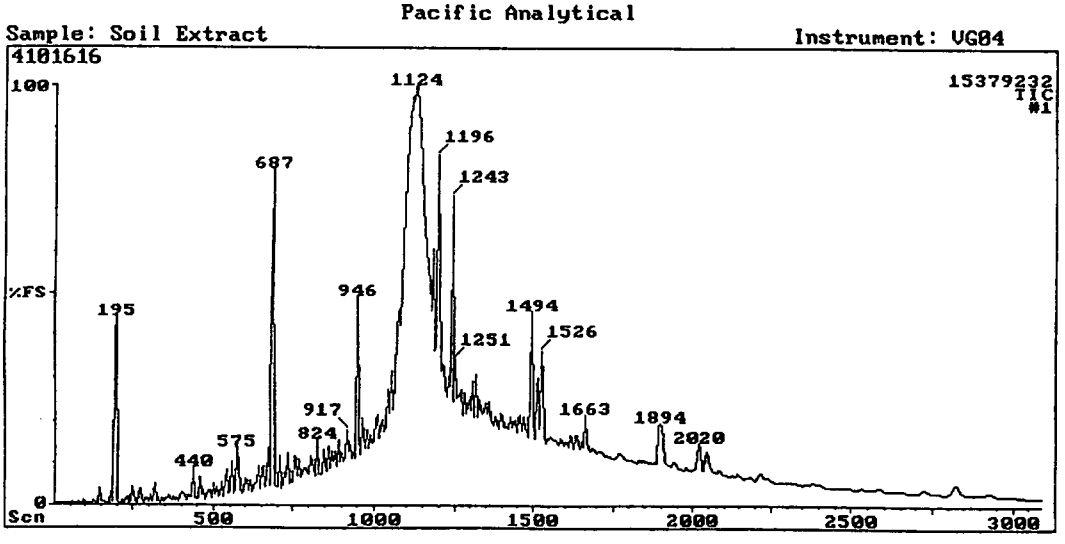

Table 1 - PRECISION, RECOVERY AND MDL RESULTS

Analyte	Recovery (%)	Precision (%sd)	MDL (µg/kg)
Acenaphthene	99	4.4	0.27
Acenaphthylene	93	12.7	0.74
Anthracene	101	3.5	0.22
Benz(a)anthracene	92	7.2	0.42
Benz(a)pyrene	124	10.1	0.79
Benz(b)fluoranthene	102	6.0	0.39
Benz(k)fluoranthene	102	6.1	0.39
Benz(ghi)perylene	95	13.9	0.83
Chrysene	91	4.8	0.27
Dibenz(a,h)anthracene	112	10.3	0.73
Fluoranthene	101	4.7	0.30
Fluorene	100	13.0	0.82
Indeno(1,2,3-cd)pyrene	84	18.0	0.95
Naphthalene	111	5.1	0.36
Phenanthrene	107	4.6	0.31
Pyrene	112	11.5	0.81

Table 2 - COMPARISON WITH NIST SRM 1941 RESULTS

Compound	PA µg/kg	NIST µg/kg	% Diff.
Acenaphthene	50	52	-4
Acenaphthylene	220	115	63
Anthracene	310	228	30
Benz(a)anthracene	560	599	-7
Benz(a)pyrene	610	754	-21
Benz(b)fluoranthene	1100	864	24
Benz(k)fluoranthene	1100	857	25
Benz(ghi)perylene	623	566	10
Chrysene	860	702	20
Fluoranthene	2000	1401	35
Fluorene	110	104	6
Indeno(1,2,3-cd)pyrene	570	559	2
Naphthalene	1360	1322	3
Phenanthrene	640	603	6
Pyrene	1600	1238	26

51 APPLICATION OF LEE RETENTION INDICES TO THE CONFIRMATION OF TENTATIVELY IDENTIFIED COMPOUNDS FROM GC/MS ANALYSIS OF ENVIRONMENTAL SAMPLES

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ABSTRACT

In the EPA methods for the analysis of semivolatile organics by GC/MS, samples are generally analyzed for the target compound list (TCL) components by an automated data system and for non-TCL components by a library search. The non-TCL components identified and reported as tentatively identified compounds (TIC) are rarely confirmed. The retention indices (RI) of TICs may provide a means of confirmation. The purpose of this study was to investigate the applicability of Lee retention indices to the confirmation of TICs for several classes of compounds. The classes of compounds studied are PAHs, heterocyclic PAHs, n-alkanes, straight chain primary alcohols, and fatty acid methyl esters. The RIs of these classes of compounds have been reported by Rostad et al. and were used for comparison with our data. In addition, the RIs for Appendix IX compounds, free fatty acids, and explosives and their related compounds were also determined by us in this study. The results show that high reproducibilities between our RIs and the published data and between our data determined by different GC conditions (normal and slow ramps) were observed for PAHs and heterocyclic PAHs. However, poor reproducibility was observed for other classes of compounds studied. It should be noted that high reproducibilities of RIs determined under different GC conditions can only be achieved if compounds of interest and RI standards are eluted during the temperature ramping period. The high reproducibility for PAHs can be explained by the fact that the four Lee RI standards are all PAHs, the change in their chromatographic retention behavior under different GC conditions should be similar with other PAHs of interest. Though the reproducibility of RIs for non-PAH compounds is not good for inter- and intra-laboratory comparisons, they provide the elution order and position for isomers and homologs which are very useful for compound identification or confirmation purpose.

INTRODUCTION

In the EPA methods for the analysis of semivolatile organics by GC/MS, samples are generally analyzed for the target compound list (TCL) components by an automated data system and for non-TCL components by a forward library search of a published mass spectral database. The results of TCL components analysis are generally accurate. However, non-TCL components identified and reported as tentatively identified compounds (TIC) are rarely verified. The retention indices (RI) of TICs may provide a means of confirmation for certain types of compounds.

Kovats retention indices (1), based on a homologous series of n-alkanes under isothermal conditions, have been widely available for many organic compounds. Lee retention indices (RI), based on a series of four polycyclic aromatic hydrocarbons (PAHs) as retention index standards, have been reported by Lee et al. (2) and Vassilaros et al. (3) for a large number of polycyclic aromatic compounds. These Lee RIs are determined using capillary columns GC operated under temperature programming conditions. Rostad and Pereira (4) reported Lee RIs determined by GC/MS for a large number of PAHs and other organic compounds of environmental interest. The purposes of this presentation are: [1] to compare the Lee RIs determined in our lab with those published by Rostad et al. and other workers for several classes of compounds, [2] to compare the Lee RIs determined in our lab run at different GC conditions for several classes of compounds, and [3] to explain the differences between our RI values and published values and their applicability for compound confirmation. The classes of compounds that are reported by Rostad et al. and our laboratories are PAHs (including N, S, and O-heterocycles), n-alkanes, primary alcohols, and fatty acids methyl esters. The RI values of additional compounds that will be reported by us in this study are Appendix IX compounds, free fatty acids, and explosives and their related compounds.

EXPERIMENTAL SECTION

Sample Preparation. Water samples were extracted at pH > 11 and then at pH < 2 with methylene chloride according to EPA Method 625 (5). Soil samples were extracted with methylene chloride in Soxhlet extractors according to EPA SW-846 Method 3540/8270 (6). Before extraction, each sample was spiked with 1.0 mL of surrogate spiking solution which contains 100 μg/mL each of acid surrogates and 50 μg/mL each of base/neutral surrogates. Methylene chloride extract was concentrated to 1 mL with Kuderna-Danish concentrator and analyzed by GC/MS.

GC/MS Analysis. Samples and standards were analyzed on an HP 5970 MSD and an HP 5988 GC/MS system. For samples run on the HP 5970, the column used was a 25m x 0.2mm i.d. HP-5 (0.33 μm coating) fused silica capillary column. For the normal ramp, the column temperature was held isothermal at 40°C for one minute and then programmed at 10°C/min to 310°C and held isothermal at this final temperature for 8-10 minutes. Under this temperature programming, chrysene elutes during the temperature ramping period, but benzo(g,h,i)perylene elutes during the isothermal period. In order to have benzo(g,h,i)perylene (the last RI standard) elute during the temperature ramping period, a slow ramp was also used. In the slow ramp, the oven temperature was programmed at 4°C/min instead of 10°C/min for the normal ramp. For samples run on the HP 5988 GC/MS, the column used was a 30m x 0.25mm i.d. DB-5MS (0.50 μm coating) fused silica capillary column (J&W Scientific, Folsom, CA). For the normal ramp, the column temperature was held isothermal at 40°C for 4 minutes and then programmed at 10°C per minute to 295°C, and held isothermal at this final temperature for 10 minutes. For the slow ramp, the oven temperature was programmed at 4°C/min to 315°C and held at this final temperature for 3 minutes. The mass spectrometer was scanned from 35 to 500 amu per half second. The extract or the standard was spiked with a mixture of six internal standards (which contains naphthalene-d8, phenanthrene-d10, and chrysene-d12 among other compounds) before GC/MS analysis according to CLP protocol (7). A forward library search was performed for

non-TCL compounds on a Wiley/NBS data base which contains 139,000 different spectra (8). Compounds were tentatively identified by library search or by elucidation of the compound structure from its mass spectrum if no match was found in the library. The retention time of the tentatively identified compound or the standard was used for the calculation of Lee RI according to the equation described in the following paragraph.

Calculation of Lee Retention Indices. The Lee retention indices are calculated according to the following equation:

$$RI = \frac{100\,(Tx - Tz)}{Tz+1 - Tz} + 100 * Z$$

Where: Tx is the retention time of compound of interest
Tz is the retention time of the preceding RI standard
Tz+1 is the retention time of the following RI standard
Z is the number of rings in the preceding RI standard

The retention index standards used are naphthalene (RI=200.00), phenanthrene (RI=300.00), chrysene (RI=400.00), and benzo(g,h,i)perylene (RI=500.00). When these compounds are not found in the sample, their retention times are calculated by adding the differences in the retention times between the first three RI standards and their corresponding deuterated internal standards in the daily calibration standard to the retention times of the corresponding internal standards in the sample. Determination of RIs for certain classes or categories of compounds (Appendix IX, fatty acid methyl esters, primary alcohols, and some PAHs) were made from standard mixtures, while others were made from actual sample extracts and, if possible, confirmed with standards.

RESULTS AND DISCUSSION

Retention indices (RI) of PAHs determined in this study for both normal and slow ramps are listed in Table 1. RIs reported by Rostad et al. (4) are also shown in Table 1 for comparison. When RIs are not available from Rostad for certain PAHs, the values from Vassilaros et al. (3) are listed for comparison. When RI values are larger than 400 (which means the compounds elute after chrysene), the values from Vassilaros, or in some cases, from Lee et al. (2), are also listed in Table 1 for comparison.

The reason that the Rostad's RIs instead of Vassilaros' and Lee's RIs are primarily used for comparison is that the former's instrumental conditions are very similar to ours. Rostad's RIs were determined by GC/MS using DB-5 column with He as the carrier gas. Vassilaros' and Lee's RIs were determined by GC using coated silica SE-52 column with H_2 as the carrier gas and glass capillary SE-52 column with He as the carrier gas, respectively.

Table 1 shows that the RI values obtained by different GC conditions (normal and slow ramps) in our lab agree very well. Our RI values also agree very well with those reported by Rostad for PAHs which elute before chrysene. For PAHs which elute after chrysene, large deviations

are found between our values and Rostad's values. This discrepancy is likely due to the fact that under the GC conditions we used for slow ramp, the last RI standard [benzo(g,h,i)perylene] is eluted during the temperature ramping period, while this probably was not so for Rostad's work. It should be noted that high reproducibility of the RI determined under different GC conditions can only be achieved for those compounds having their upper bracketing RI standard elute during the temperature ramping period. This was stressed by Lee but not by Rostad. For the GC conditions used by both Lee and Vassilaros, the last RI standard (picene) was eluted during the temperature programming period. Retention time of benzo(g,h,i)perylene was not given in Rostad's paper. However, based on the GC conditions and the lower values of RI obtained for compounds bracketed by chrysene and benzo(g,h,i)perylene, it appears that benzo(g,h,i)perylene was eluted in the isothermal period. For the PAHs which elute after chrysene, our RI values agree very well with those reported by Vassilaros or Lee with an exception of dibenz(a,h)anthracene.

Retention indices of heterocyclic PAHs determined by this study and those reported by Rostad, Vassilaros, and Lee are listed in Table 2. As shown in Table 2, our values agree very well with those reported by the previous workers. High reproducibility within our lab run at different GC conditions and good agreement between our data and the published data for PAHs and heterocyclic PAHs can be explained by the fact that the RI standards used are all PAHs, the changes in their chromatographic retention behavior under different GC conditions should be similar with other PAHs of interest. The results of this study indicate that Lee retention indices can provide a high degree of confirmation for PAHs and heterocyclic PAHs such as N-, S-, and O-heterocyclic PAHs.

Table 3 lists the retention indices of n-alkanes determined in this study for both normal and slow ramps. RIs reported by Rostad are also listed in Table 3 for comparison. As shown in Table 3, poor reproducibility was observed not only for RIs determined by different labs (ours and Rostad's), but also for RIs measured at different GC conditions in our lab. This can be explained by the fact that the changes in chromatographic behaviors are different for n-alkanes and the RI standards (which are PAH) under different GC conditions. It should be noted that highly reproducible RIs can be obtained if the samples are run on the same column and at the same conditions. The RIs given in Table 3 can be used for identification of an individual n-alkane in a series of homologous n-alkanes if the GC conditions are not drastically different from those used in this work.

In addition to PAHs and n-alkanes, other classes of compounds were also investigated. They include straight chain primary alcohols and fatty acid methyl esters. The RIs values determined by us and Rostad for these classes of compounds are listed in Tables 4 and 5. Tables 4 and 5 show that RIs of primary alcohols and fatty acid methyl esters run at different GC conditions are not very reproducible. The explanation described above for n-alkanes can be applied here also. Again, the RIs given in these tables can be used for identification of an individual compound in a series of homologs if the GC conditions used are not drastically different from those used in this study.

Lee RIs of Appendix IX compounds, n-fatty acids, and explosives and their related compounds were also determined. They are shown in Table 6 to 8. The RIs for Appendix IX compounds can be used to help the confirmation of these compounds in the samples if their standards are not analyzed. Poor reproducibility was observed for most of the Appendix IX compounds, while good reproducibility was observed for those which had the chromatographic retention behaviors similar to those of PAHs.

ACKNOWLEDGMENTS

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TABLE 1. LEE RETENTION INDICIES OF POLYCYCLIC AROMTATIC HYDROCARBONS

CAS	Compound	Rostad RI	RI from this Study	
			Normal Ramp[1]	Slow Ramp[2]
496117	1H-Indene, 2,3-dihydro-	168.87	169.04	
95136	1H-Indene	170.83	171.05	
91178	Naphthalene, decahydro-	173.31	173.01	
119642	Naphthalene, 1,2,3,4-tetrahydro-	195.47	195.21	
447530	Naphthalene, 1,2-dihydro-	195.85		
91203	Naphthalene	200.00	200.00	200.00
91576	Naphthalene, 2-methyl-	221.57	221.51	220.98
90120	Naphthalene, 1-methyl-	224.53	224.42	224.16
92524	1,1'-Biphenyl	236.59	236.34	
939275	Naphthalene, 2-ethyl-	239.27	239.06	
1127760	Naphthalene, 1-ethyl-	239.88	239.30	
581420	Naphthalene, 2,6-dimethyl-	240.89	240.42	
575417	Naphthalene, 1,3-dimethyl-	243.76	243.42	
575439	Naphthalene, 1,6-dimethyl-	244.06	243.96	
	Naphthalene, 2-ethenyl-		245.81	245.39
581408	Naphthalene, 2,3-dimethyl-	247.04	247.04	
571584	Naphthalene, 1,4-dimethyl-	247.15	246.55	
571619	Naphthalene, 1,5-dimethyl-	247.62	247.00	
208968	Acenaphthylene	248.75	248.88	248.48
573988	Naphthalene, 1,2-dimethyl-	249.67	249.53	
	Naphthalene, 1-(2-propenyl)-		253.94	253.53
83329	Acenaphthene	254.98	254.87	254.36
644086	1,1'-Biphenyl, 4-methyl-	256.12		
829265	Naphthalene, 2,3,6-trimethyl-	264.99	264.98	
2245387	Naphthalene, 1,6,7-trimethyl-	267.43	267.94	
86737	9H-Fluorene	270.77	270.57	270.28
1730376	9H-Fluorene, 1-methyl-	289.49	289.27	
85018	Phenanthrene	300.00	300.00	300.00
120127	Anthracene	301.75	301.84	301.59
605027	Naphthalene, 1-phenyl-	312.74		312.91
	Phenanthrene, 3-methyl-	319.19 [3]	319.08	318.88
	Phenanthrene, 2-methyl-	319.93 [3]		319.76
613127	Anthracene, 2-methyl-	321.47		321.16
	4H-Cyclopenta(def)phenanthrene	321.77 [3]	322.52	322.42
	Phenanthrene, 4-methyl-	322.81 [3]		322.87
832699	Phenanthrene, l-methyl-	323.79		323.67
779022	Anthracene, 9-methyl-	329.52		
35465715	Naphthalene, 2-phenyl-	330.73	330.85	330.76
	Anthracene, 9-ethenyl-		334.13	334.63
206440	Fluoranthene	344.68	344.78	344.83
129000	Pyrene	352.77	352.54	352.72

(Continued)

TABLE 1. LEE RETENTION INDICIES OF PAHs (Continued)

CAS	Compound	Rostad RI	RI from this Study: Normal Ramp[1]	RI from this Study: Slow Ramp[2]
	Benzo(a)fluorene	366.72 [3]	366.39	366.48
243174	Benzo(b)fluorene	369.17	368.66	368.93
	Pyrene, 2-methyl-	369.40 [3]	370.13	369.91
	Pyrene, 1-methyl-	373.45	373.23	373.27
604535	1,1'-Binaphthalene	385.23		
	Benzo(ghi)fluoranthene	389.92 [3]	390.83	390.82
	Cyclopenta(cd)pyrene	396.55 [3]	398.17	398.41
56553	Benz(a)anthracene	398.77	398.51	398.53
217594	Triphenylene	399.45		399.94
	Benzo(c)phenanthrene	391.24		390.89
218019	Chrysene	400.00	400.00	400.00
	1-Phenylphenanthrene	421.66 [4]		421.17
	Chrysene, 5-methyl-	420.20 [3]		420.40
612782	2,2'-Binaphthalene	421.81 423.91 [4]		424.01
	12-Methylbenz(a)anthracene			421.24
	7-Methylbenz(a)anthracene			425.90
	Benzo(b)fluoranthene	439.51 443.13 [3]		442.34
	Benzo(j)fluoranthene	443.13 [3]		442.45
207089	Benzo(k)fluoranthene	440.04 444.02 [3]		443.05
	7,12-Dimethylbenz(a)anthracene			443.90
	Benzo(a)fluoranthene			446.30
	Benzo(e)pyrene	452.29 [3]		452.22
50328	Benzo(a)pyrene	448.69 454.02 [3]		454.06
198550	Perylene	451.27 457.17 [3]		457.02
56495	3-Methylcholanthrene	462.09 468.44 [4]		468.88
193395	Indeno(1,2,3-cd)pyrene	489.49 493.24 [3]		492.36
215587	Benzo(b)triphenylene	490.13		
53703	Dibenz(a,h)anthracene	491.01 496.20 [3]		493.42
	Picene	500.00 [3]		
191242	Benzo(ghi)perylene	500.00 500.29 [3]		500.00
	Dibenzo(a,l)pyrene			540.01 [5]
	Dibenzo(a,e)pyrene			554.76 [5]
	Dibenzo(a,i)pyrene			560.34 [5]
	Dibenzo(a,h)pyrene			563.59 [5]

[1] 40°C for 1 min., 40° to 310°C @ 10°C/min

[2] 40°C for 1 min., 40° to 310°C @ 4°C/min

[3] Value from Vassilaros

[4] Value from Lee

[5] Compound eluted during isothermal period

TABLE 2. LEE RETENTION INDICIES FOR HETROCYCLIC PAHs

CAS	Compound	Rostad RI	RI from this Study: Normal Ramp	RI from this Study: Slow Ramp
	Quinoline	210.32	210.37	
230273	Benzo(h)quinoline	301.50		
260946	Acridine	303.99		
85029	Benzo(f)quinoline	307.30	306.86	
	7-Azafluoranthene	350.50 [1]	350.37	
86748	9H-Carbazole	309.22	308.63	309.24
	2-Azafluoranthene	347.39 [1]	347.15	
	Benz(c)acridine	393.41 392.60 [1]	392.06	392.11
	9,10-Anthracenedione	330.53 [2]	330.26	
4265252	Benzofuran, 2-methyl-	184.50		
132649	Dibenzofuran	259.75	259.74	
	9-Fluorenone	293.88	293.64	
11095435	Benzothiophene	201.84		
132650	Dibenzothiophene	296.03	295.85	
239350	Benzo(b)naphtho(2,1-d)thiophene	390.12 389.37 [1]	389.64	

[1] Value from Vassilaros [2] Value from Lee

TABLE 3. LEE RETENTION INDICIES FOR n-ALKANES

CAS	Compound	Rostad RI	RI from this Study: Normal Ramp	RI from this Study: Slow Ramp
111842	Nonane	140.88	138.27	144.03
124185	Decane	161.47	159.66	163.22
1120214	Undecane	182.68	180.44	183.23
112403	Dodecane	204.09	200.12	202.83
629505	Tridecane	222.87	218.83	221.55
629594	Tetradecane	240.29	236.21	239.35
629629	Pentadecane	256.75	252.61	256.12
544763	Hexadecane	272.17	268.29	272.02
629787	Heptadecane	286.86	282.99	287.19
593453	Octadecane	300.96	296.84	301.71
629925	Nonadecane	317.20	312.43	318.12
112958	Eicosane	332.62	327.63	333.60
629947	Heneicosane	347.42	342.11	348.41
629970	Docosane	361.53	356.14	362.61
638675	Tricosane	375.03	369.44	376.29
646311	Tetracosane	387.99	382.35	389.39
629992	Pentacosane	400.45	394.59	402.21
630013	Hexacosane	413.20	NA [1]	415.93
593497	Heptacosane	425.51	NA [1]	429.45
630024	Octacosane	437.68	NA [1]	442.42
630035	Nonacosane	448.93	NA [1]	454.90
638686	Triacontane	460.36	NA [1]	467.01
630046	Hentriacontane	471.96	NA [1]	478.65
544854	Dotriacontane	484.94	NA [1]	489.99
630057	Tritriacontane	499.88	NA [1]	500.99
	2,6,10-Trimethylpentadecane		275.46	279.10
	Pristane		283.84	288.01
	Phytane		298.42	303.08

[1] Compound eluted during isothermal period

TABLE 4. LEE RETENTION INDICIES FOR SOME PRIMARY ALCOHOLS

CAS	Compound	Rostad RI	RI from this Study	
			Normal Ramp	Slow Ramp
111706	1-Heptanol	155.86	154.52	157.77
111875	1-Octanol	176.31	175.63	177.62
143088	1-Nonanol	196.63	195.98	197.48
112301	1-Decanol	216.09	215.20	216.62
112425	1-Undecanol	234.41	233.42	234.77
112538	1-Dodecanol	251.68	250.63	252.06
	1-Tridecanol		266.83	268.36
112721	1-Tetradecanol	283.29	282.29	283.90
	1-Pentadecanol		296.98	298.56
36653824	1-Hexadecanol	314.03	312.09	315.14
112925	1-Octadecanol	345.48	342.84	346.29
629969	1-Eicosanol	374.56	371.04	374.80
661198	1-Docosanol	400.57	397.16	401.29

TABLE 5. LEE RETENTION INDICIES OF FATTY ACID METHYL ESTERS

CAS	Compound	Rostad RI	RI from this Study	
			Normal Ramp	Slow Ramp
111115	Octanoic acid, methyl ester	187.83	186.78	188.24
110429	Decanoic acid, methyl ester	226.04	224.56	226.16
111820	Dodecanoic acid, methyl ester	260.05	258.35	260.37
1731880	Tridecanoic acid, methyl ester	275.62	-	-
124107	Tetradecanoic acid, methyl ester	290.32	288.78	291.18
7132641	Pentadecanoic acid, methyl ester	305.23	-	-
112390	Hexadecanoic acid, methyl ester	321.34	319.52	322.66
1731926	Heptadecanoic acid, methyl ester	336.74	-	-
112618	Octadecanoic acid, methyl ester	351.38	349.48	352.84
1731948	Nonadecanoic acid, methyl ester	365.43	-	-
1120281	Eicosanoic acid, methyl ester	378.87	376.90	380.64

TABLE 6. LEE RETENTION INDICIES OF APPENDIX IX COMPOUNDS

Compound	1625-C [1]	RI from this Study: Normal Ramp	RI from this Study: Slow Ramp
Pyridine		108.15	121.47
2-Picoline	112.18	121.17	130.12
N-Nitrosomethylethylamine	116.23	124.45	132.65
Methylmethanesulfonate	125.97	131.02	137.85
N-Nitrosodiethylamine	135.55	139.17	144.23
p-Benzoquinone		143.19	147.33
Ethylmethanesulfonate	146.43	146.35	150.77
Nitrosopyrrolidine		175.18	176.52
N-Nitrosomorpholine	178.41	175.79	177.39
o-Toluidine	177.76	176.52	177.86
3-Methylphenol		175.79	178.68
Acetophenone	175.81	175.06	176.57
N-Nitrosopiperidine	188.31	184.19	185.84
a,a-Dimethylphenethylamine		195.74	195.47
2,6-Dichlorophenol		204.68	203.40
Hexachloropropene	207.47	203.65	203.60
Resorcinol		213.50	216.79
N-Nitroso-di-n-butylamine	215.58	213.63	215.35
1,4-Benzenediamine		212.86	
Safrole	219.97	218.98	219.88
Isosafrole	230.20	234.79	235.68
1,2,4,5-Tetrachlorobenzene	228.25	227.13	227.19
1-Chloronaphthalene		236.62	236.15
1,4-Naphthoquinone	241.72	241.61	241.61
m-Dinitrobenzene		247.45	248.35
Pentachlorobenzene	260.55	260.10	260.09
1-Naphthylamine	263.47	262.17	262.20
2-Naphthylamine	265.58	264.23	264.62
2,3,4,6-Tetrachlorophenol		264.80	265.40
5-Nitro-o-toluidine		272.14	272.81
Diphenylamine/N-Nitrosodiphenylamine	276.62	274.57	276.00
Diphenylhydrazine/Azobenzene	276.62	275.43	276.42
1,3,5-Trinitrobenzene		284.47	287.18
Diallate		285.04	287.02
Phenacetin	288.47	285.77	288.72
Dimethoate		290.75	292.33
4-Aminobiphenyl	294.81	293.92	295.26
Pentachloronitrobenzene		297.93	298.71
Pronamide	299.19	297.57	300.49
4-Nitroquinoline-1-oxide		330.31	330.82
Methapyrilene	339.60	334.85	337.56
Aramite		363.69	364.71
p-Dimethylaminoazobenzene		366.03	368.20
Chlorobenzilate		372.66	371.32
3,3'-Dimethylbenzidine		381.39	380.70
2-Acetylaminofluorene		391.13	390.32
7,12-Dimethylbenz(a)anthracene	430.13	NA [2]	443.82
Hexachlorophene			
3-Methylcholanthrene	453.37	NA [2]	468.69
Dibenz(a,j)acridine			487.56

[1] U.S.E.P.A. Industrial Technology Division Method 1625-C

[2] Compound eluted during isothermal period

TABLE 7. LEE RETENTION INDICIES FOR N-FATTY ACIDS

Compound	RI from this Study Normal Ramp
n-Heptanoic acid	176.75
n-Octanoic acid	198.43
n-Nonanoic acid	217.59
n-Decanoic acid	234.82
n-Undecanoic acid	249.52
n-Dodecanoic acid	264.58
n-Tridecanoic acid	278.19
n-Tetradecanoic acid	293.98
n-Pentadecanoic acid	308.82
n-Hexadecanoic acid	324.00
Hexadecenoic acid	321.82
Octadecenoic acid	350.07
n-Octadecanoic acid	352.98

TABLE 8. LEE RETENTION INDICIES OF EXPLOSIVES AND THEIR RELATED COMPOUNDS

Compound	RI from this Study Normal Ramp
Nitrobenzene	180.05
o-Nitrotoluene	194.65
m-Nitrotoluene	202.07
p-Nitrotoluene	205.47
1,3,5,7-Tetraazatri-cyclo[3.3.1.1(3.7)]decane	206.78
1,3-Dinitrobenzene	247.64
2,6-Dinitrotoluene	250.87
2,4-Dinitrotoluene	262.61
1,3,5-Trinitrobenzene	285.91
2,4,6-Trinitrotoluene	287.66
4-Amino-2,6-dinitrotoluene	321.91
2-Amino-4,6-dinitrotoluene	330.74
2,4,6-Trinitrobenzenamine	337.56
3,5-Dinitrobenzenamine	321.42

52 A QUICK PERFORMANCE-BASED HPLC METHOD FOR THE ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs)

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ABSTRACT

A quick HPLC method for the analysis of polynuclear aromatic hydrocarbons (PAHs) in multimedia samples is described. The method is based on rapid extraction, direct injection of the diluted or concentrated sample extracts, fast HPLC separation, and selective programmed fluorescence detection. The elimination of sample cleanup reduces the assay time to one hour from sample extraction to data report. A 16-min PAH separation was developed using a new HPLC column packed with 3-μm polymeric C18 column materials. Method sensitivity was found to be 20 ppb levels for soil samples and low ppt levels for water samples. UV absorbance detection was used for the quantitation of acenaphthylene and for peak confirmation. The method was applied to soil, sediment, water, waste oil, and air particulate matter, and yielded excellent agreement with certified values from standard reference materials. This method is useful for routine monitoring of PAHs and for rapid sample screening in particular. Method validation parameters in terms of precision, accuracy, sensitivity, selectivity, linearity, range, and ruggedness are documented and compared to those from official methods. The proposed method provides a quick turnaround method alternative to EPA Methods 550, 550.1, 610, 8310 and TO-13. Advantages of this method include, cost-effectiveness, reduced solvent usage, and good recovery of all PAHs including volatile ones. Method limitations and precautions are also discussed.

53 The Extraction and Analysis of Polychlorinated Biphenyls (PCB's) by SFE and GC/MS. Improvement of Net Detection Levels

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Abstract

Contaminants in soils, sediments, and solid wastes is are problem today for the general public, government labs and private industrial labs. This paper examines applying supercritical fluid extraction (SFE) systems to the detection and analysis of PCBs from an oil matrices, solid wastes, sludges, and other materials. In this work contaminants are extracted using SFE and analyzed by GC and GC/MSD. The PCB from oil matrix work was done to explore whether SFE would decrease coextractant interferences with the GC/MSD and GC/ECD analysis relative to established manual procedures -- thereby, affording lower detection levels and improved quantitation.

Introduction

The detection and analysis of PCB's in soils, sediments, fish tissue and solid wastes is a common problem today for the general public, government labs and private industrial labs. One of the necessary steps involves sampling to assess what chemicals and products are present, and to what quantitative extent. Supercritical fluid extraction, (SFE) is an expedient and cost effect means of removing chemicals from the solid waste samples as well as transformer oils, food, eggs and many other materials prior to analysis.

Experimental

SFE: A Hewlett-Packard Model 7680T was used without modification. The conditions for the experiments are described below.

1. Extraction -- pressure, 1218 psi (84 bar); extraction chamber temperature, 40 ^{O}C; density, 0.35 g/mL; extraction fluid composition, CO_2; static equilibration time, 2 minutes; dynamic extraction time, 25 minutes; extraction fluid flow rate, 3.0 mL/min; resultant thimble-volumes-swept, 28; 75 ml liquid CO_2 (@ 4 ^{O}C) flowed during dynamic extraction.

2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 40 ^{O}C; nozzle (variable restrictor) temperature, 45 ^{O}C.

3. Reconstitution (of collected extracts) -- rinse solvent, isooctane; collected fraction volume, 1.0 mL; trap temperature, 40 C; nozzle (variable restrictor) temperature, 45 C; rinse solvent flow rate, 2.0 mL/min; fraction destination, vial #n.

GC : A Hewlett-Packard Model 5890 Series II GC/ECD with splitless injection, and Hewlett-Packard HP-5 (30 m x 530 um, 0.88 um film thickness) column was used. The chromatographic system included the HP 7673 B injector.

GC/MS: A Hewlett-Packard Model 5890 Series II GC with Electronic Pressure Control (EPC), a

Hewlett-Packard 7673 Automatic Liquid Sampler with Auto 250/320 um for automated on-column injection into a 250 um ID column, and Hewlett-Packard Models 5972 and 5971 MSD were used. A Hewlett-Packard HP-5MS column (30 m x 250 um, 0.25 um film thickness) with a 5 m retention gap (250 um ID) was used; it is a low-bleed column designed specifically for operation with the MSD. Deactivated glass press-fit connectors were used to connect the retention gap to the column and polyimide resin was applied to either end of the retention gap for a firm seal.

Materials and Reagents

Solvents. For the PCB's, the supercritical fluid extraction to remove PCB's from the oil samples was done at the Little Falls site and subsequently the extracts were sent to the Scientific Instruments Division for analysis. Consequently, Pesticide grade iso-octane from Burdick and Jackson was used as the SFE reconstitution solvent at the Little Falls site; at the Scientific Instruments Division (SID), iso-octane and hexane, both OmniSolv grade from EM Science, were used in preparing standards. Also at the SID laboratory, ethyl acetate, distilled in glass from Burdick and Jackson, was used in the manual solid phase extraction (SPE) clean-up of transformer oil.

Extraction fluid. Carbon dioxide, SFE/SFC ECD grade from Air Products, Allentown, PA, was used as the bulk extraction fluid in all the supercritical fluid extractions.

Samples.

The sample of Aroclor 1260 in transformer oil was obtained from Environmental Resource Associates (ERA), Arvada, Colorado. The Aroclor in the sample had a certified concentration value of 49.2 mg/kg. Sample aliquots of 100 uL were used for each conventional manual clean-up experiment carried out at the Scientific Instruments Division site using alumina solid phase extraction cartridges: Extract-Clean ESP obtained from Alltech (Stock No. 400825, Alumina-N, 500 mg in 19 mL reservoir). (The 'ESP' cartridges, with teflon reservoirs, are provided especially for mass spectral analysis.) Additionally, in some of the SFE work done at the Little Falls site, the oil was dispersed on activated alumina and/or Chromosorb W-H.P. (80/100 mesh, Manville Products corp., Denver, CO). The alumina was obtained from Supelco, Inc., Bellefonte, PA (Alumina F-1, Catalog No. 2-0284, 80/100 mesh). The procedure outlined by Bellar and Lichtenberg (1) for activating the alumina was followed prior to its use. Where cited, filter paper disks, cored out of Whatman Qualitative filter paper, Catalog No. 1003-055, are placed at both ends of the sample.

Results and Discussion

PCB's are present throughout our environment, and cause concern from many perspectives (2). The analysis of samples containing PCB's is usually complicated by two factors (at least). PCB's are present in trace quantities, and the matrices are usually complex. Usually the matrices include many other compounds similar in polarity and chemical size. It was observed during this study (which is still in progress) that PCB's have solubility characteristics in carbon dioxide that are very similar to transformer oil components and to a lesser extent similar to fats or lipids. PCB's are very often present in the same mixture with such things as transformer oils, petroleum products and fats.

In this paper, we will present data from the selective fractionation of PCB's via supercritical fluid extraction (SFE), and the subsequent detection and analysis with the HP 7680 T SFE and the HP 5972 A MSD . The initial study involves the optimization of the SFE extraction conditions for PCB's in Transformer oil. Further work involved other matrices such as solid wastes and fish tissue. The SFE cleanup is compared to conventional cleanup such as the use of alumina cartridges and alumina admixing. Comparisons are drawn for sensitivity using both the SIM mode and Scanning modes with the SFE

cleanup. Preliminary conclusions indicate that SFE improves detection limits, and eliminates the interferences of transformer oil. Also, it appears that the SIM mode works well with such samples, and thus scanning would not be necessary. The obvious advantages of the MSD over the use of the ECD with GC will be discussed and summarized.

For some period of time, we have been selectively extracting (fractionating) cholesterol from the fats contained in various food products via SFE (3) as well as selectively extracting Vitamin A (beta carotene) from cod liver oil (Figures 1 and 2). This experiment was usually optimized for maximum selectivity and minimal time by judicious choice of temperature and density (pressure) (Figure 3).

A characteristic of supercritical fluid extraction is its amenability to fractionation: adjusting the solvent power of the extraction fluid (through density, temperature, composition) can lead to selective solvation of groups of compounds from a sample. Another approach is to superimpose selectivity on the supercritical fluid extraction process by mixing a chemically active sorbent with the sample so that some of the components extracted from the sample are preferentially bound to the sorbent -- remaining in the extraction chamber -- while others are extracted and collected. In either approach the net result is somewhat analogous to what is produced by applying large-scale column chromatography for clean-up and fractionation of complex extracts; however, the whole process is easily automated within an SFE method. Both approaches have been applied by other research groups to samples which are relevant to the problem at hand -- e.g., the nearly selective extraction of PCB's relative to fats from sea gull eggs by David et al (4) by employing an appropriately low density and the selective extraction of chlorinated pesticides from chicken fat by mixing the sample to be extracted with alumina by King et al (16). Similarly, in our work within Hewlett-Packard ( ), we have been mapping extraction conditions at which fats are largely extracted and those at which fats are largely not extracted (while other components like cholesterol and Vitamin A are). These regions are outlined in Figure 8. Note that the "Fat Band" demarcates the division into the regions -- at conditions above the band (particularly higher pressures/densities) large quantities of fats coextract with other components, and at conditions below the band (lower pressures/densities) much smaller amounts of fats coextract. Within the band, minor to bulk quantities of fat can be extracted; the level seems to be heavily influenced by the matrix. The designations of the regions outlined in Figure 9 are not technically rigorous but that diagram is a very useful empirical tool to use in designing an SFE strategy -- as demonstrated by this work on selectively extracting PCB's from an oil matrix.

One of the first published demonstrations of such experimental fractionation by supercritical carbon dioxide was by Frank and Sandra (4) in a paper where they describe the fat free extraction of PCB's from sea gull eggs. They selectively extracted PCB's away from the associated fats. At one combination of density and temperature the PCB's were extracted along with the fats (* 35 % by weight). However by reducing the temperature (constant density) it was possible to obtain the PCB extract with only a 3 % fat content.

We continued this type of exploration into the SFE of PCB's in transformer oil. Extraction of transformer oil sample was first done at conditions roughly represented by point number "1" in Figure 3 after having mixed the oil sample with alumina. This experiment was not successful, possibly due to poor reproducibility of the procedure for activating the alumina, which is empirical at best, involving many complex variables such as the origin of the alumina, particle diameter and other parameters beyond the scope of this study. This was followed by SFE with no alumina sorbent, and extracting the oil sample at the milder conditions, point "2" in Figure 3. Point 2 was chosen since a nearly fat-free extract of cholesterol had been obtained in routine experiments and demonstrations from fatty matrices with similar conditions. This is illustrated in Figure 1 where cholesterol was selectively extracted away from the triglycerides (as well as mono and di glycerides).

A comparative liquid solid cleanup of the PCB's from the oil matrix with an acid clean-up followed by extraction with ethyl acetate was carried out. The extracts from the s SFE were compared to the ethyl

acetate liquid solid extracts. Aggressive SFE conditions (point 1 in Figure 3), did not accomplish a significantly better clean-up of the sample compared to the liquid-solid clean-up. However, at the milder SFE conditions (point 2 in Figure 3), the resultant SFE extracts are noticeably less complex than those produced by the manual clean-up. This is shown by Figures 4 and 5. The results for the octachlorobiphenyl homolog series were quite similar to those of the heptachlorobiphenyl homolog series. Notice that there are still some matrix interferences contributing to the background for the hexachlorobiphenyls. This leads then to carrying out the SFE experiment with conditions indicated as zone 3 in Figure 3. One major goal will accomplished then if the SFE can selectively remove the PCB's from a transformer oil matrix and effectively lower the mass spectrometer detector minimum sensing limits to approach those of the clean standards. In this work an external standard curve was generated from 10 pg to 500 pg. A pattern for a standard solution of Aroclor 1260 could be recognized down to 5 pg injected. Quantitation was done by choosing the three largest peaks in each homolog series and summing their areas to give a total for each level of chlorination. The work demonstrated that a 5-ion SIM mode was fifteen times more sensitive than detection in scanning mode while giving as much pattern information as is needed for identification (5). This sensitivity approaches that achieved by an ECD. The MSD, used in the electron impact (EI) mode, does not have a problem with response factor variation for the different PCB congeners. Co-eluting electrophilic peaks that make it difficult to do ECD quantitation (e.g., DDT and DDE) will not affect MSD quantitation because they are not of the same mass (8).

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Figure 1. Selective SFE of Cholesterol from Fats

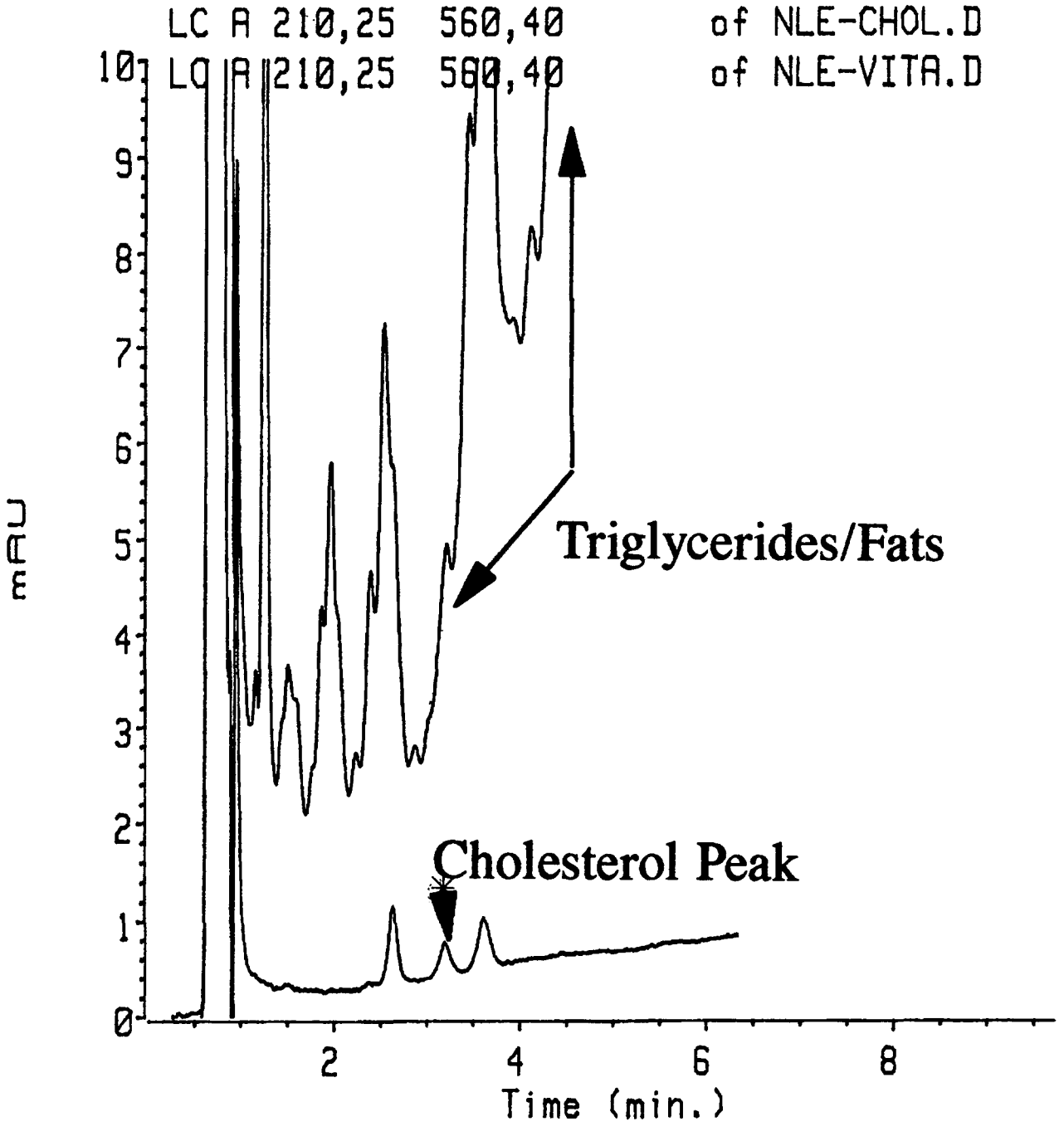


Figure 2. Selective SFE of Beta Carotene from Cod Liver Oil

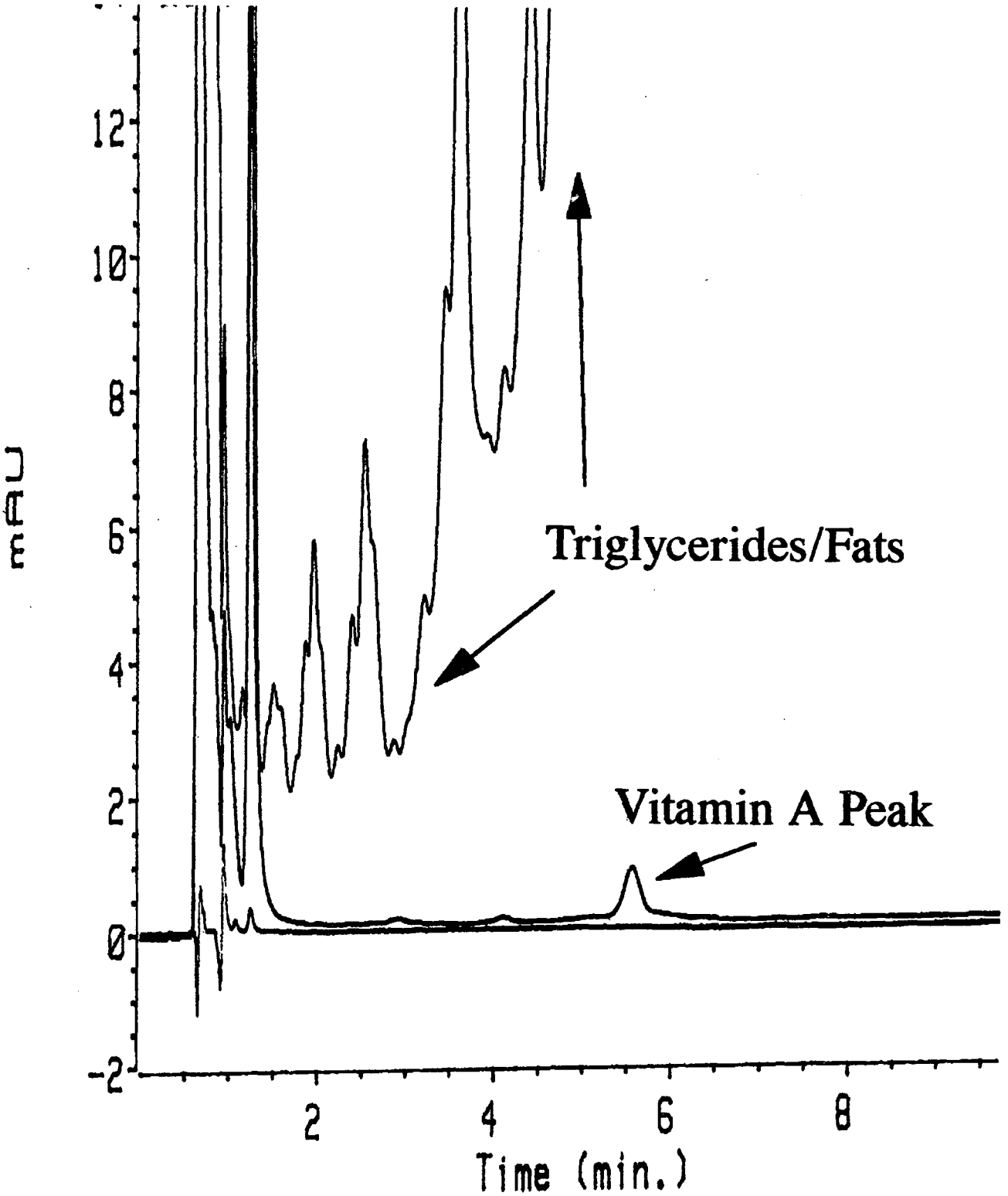


Figure 3. Density-Temperature Table for setting SFE Selectivity

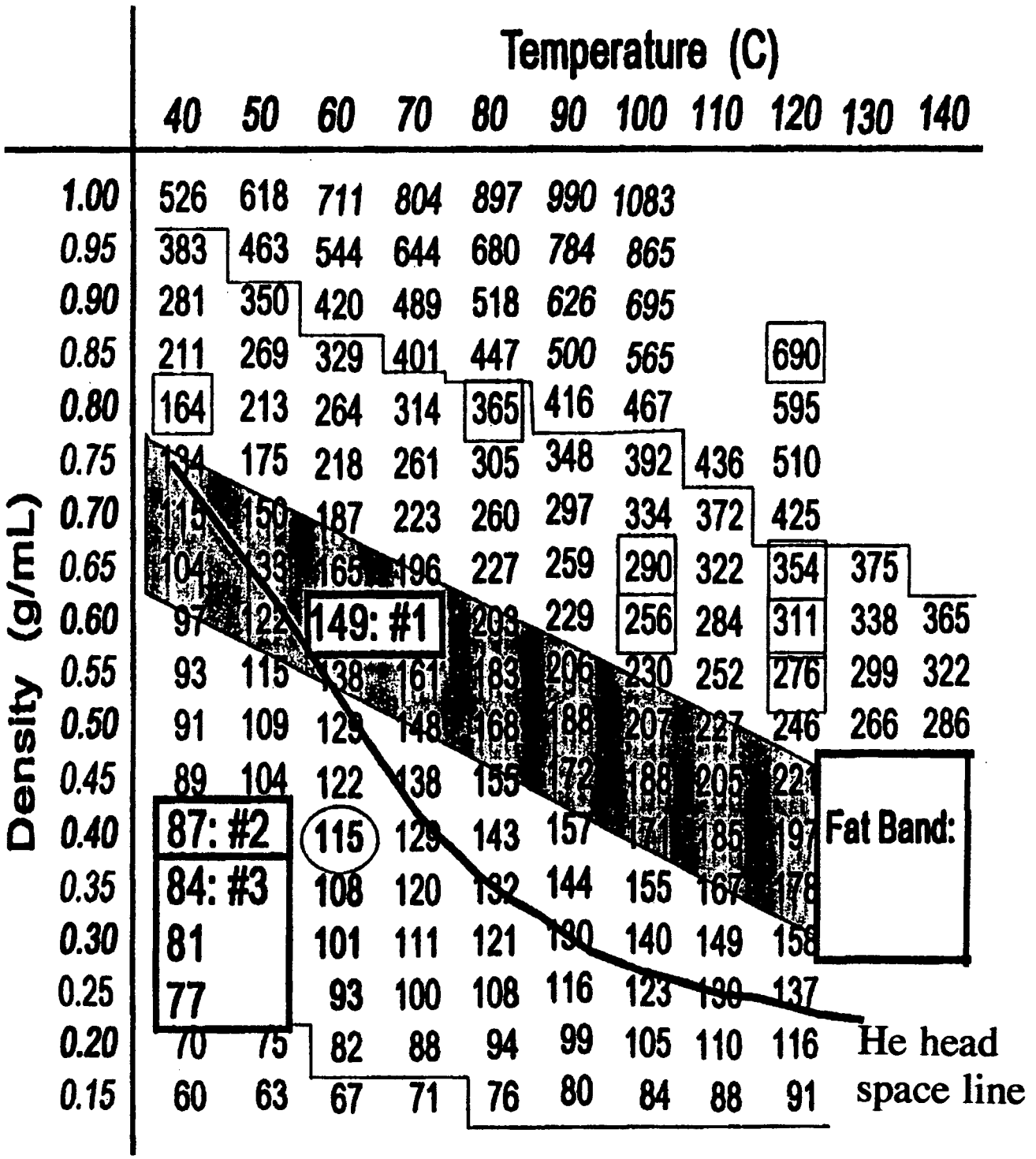


Figure 4. Comparison of SFE to Ethyl Acetate Extractoion for Hexachloro biphenyls in Aroclor 1260

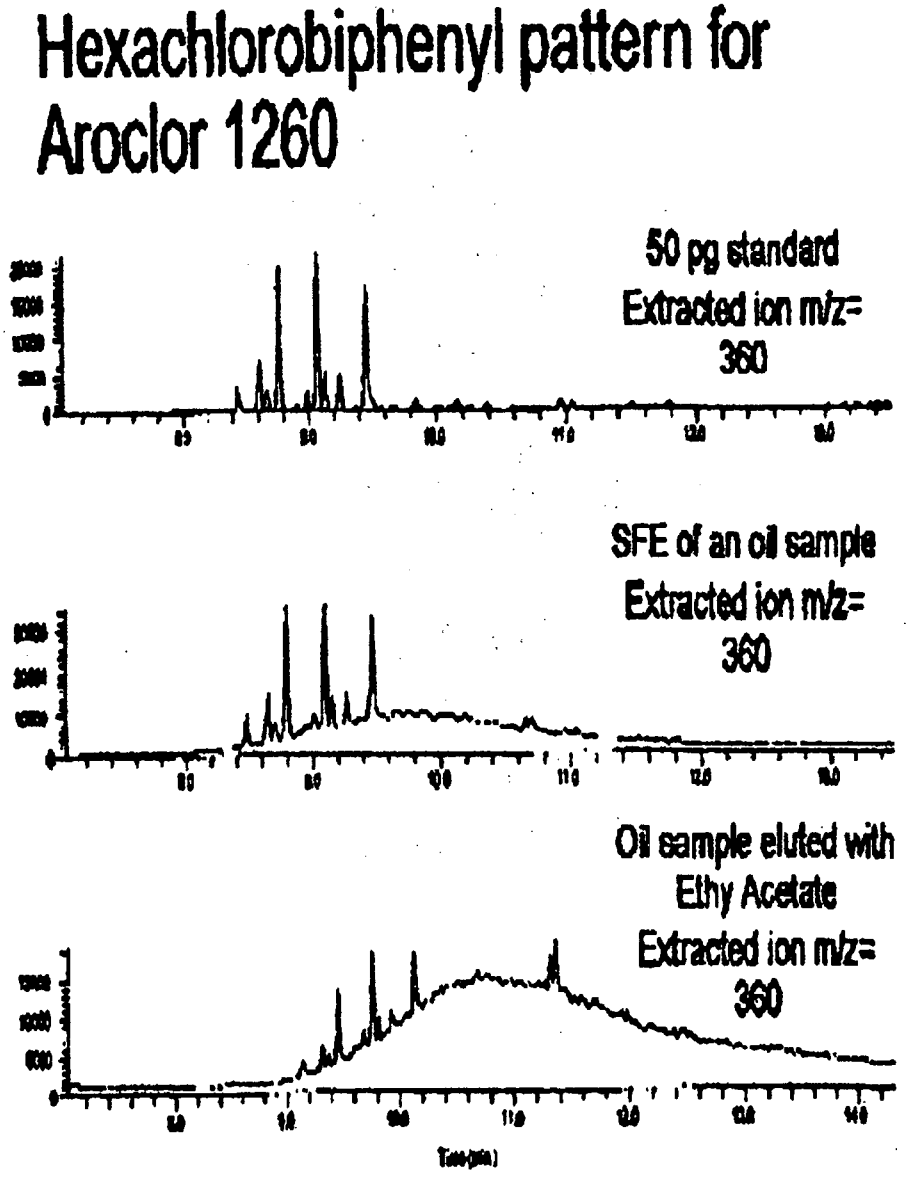
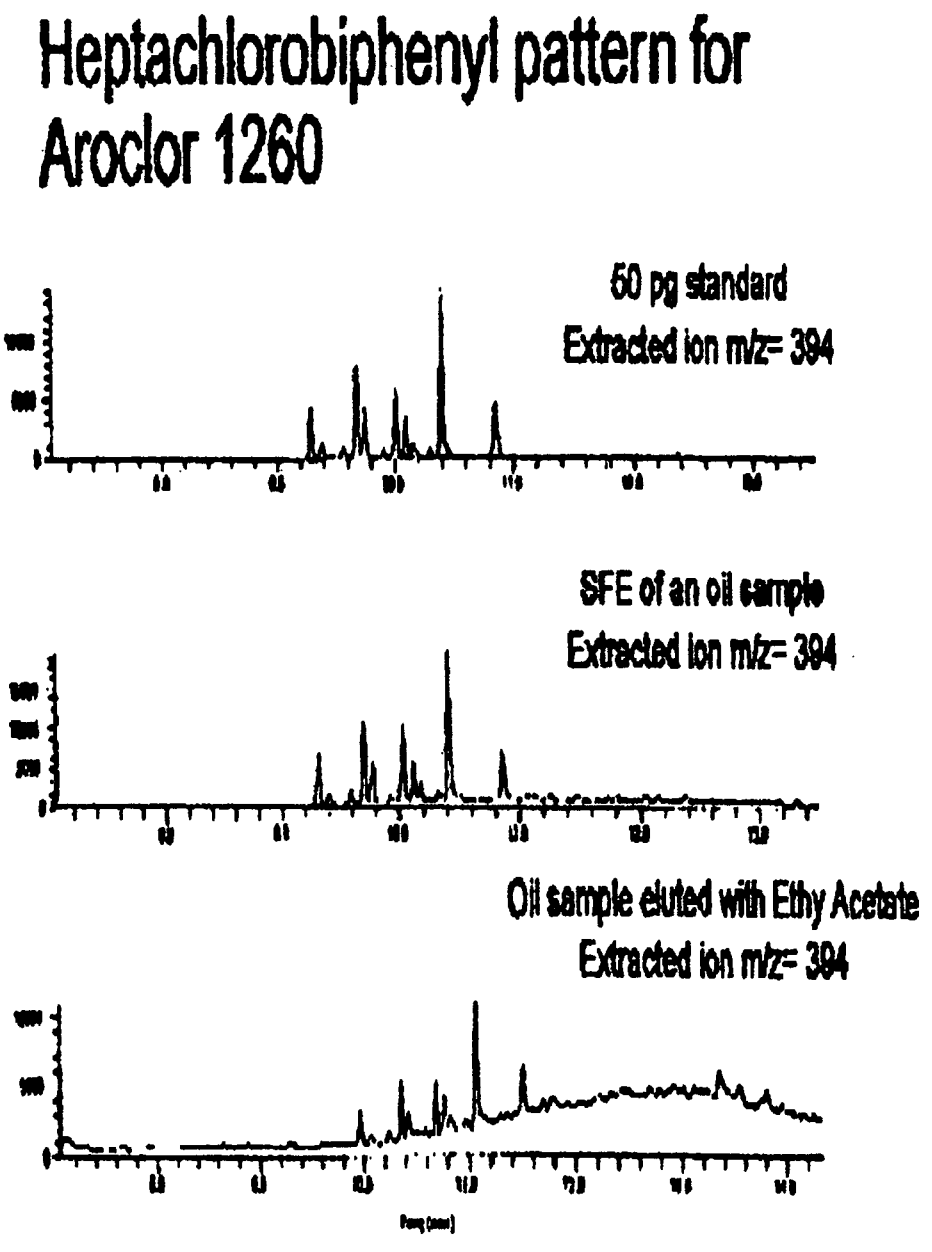


Figure 5. Comparison of SFE to Ethyl Acetate Extraction for Heptachloro biphenyls in Aroclor 1260



54 Environmental Analysis - PAH's in Solid Waste: Bridging the Automation Gap between SFE and HPLC

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ABSTRACT

The detection and analysis of contaminants in soil, sediments, and solid wastes are a common problem today for the general public, government labs and private industrial labs (1). This work with polyaromatic hydrocarbons is being undertaken as the first step towards deriving an EPA SFE method similar to the recent draft method 3560 for total petroleum hydrocarbons (TPH) (2). This present study has been in progress for some time at Hewlett-Packard. The study focused on the extraction and analysis of PAH's (polyaromatic hydrocarbons, sometimes called polynuclear aromatic hydrocarbons). There are two significantly different parts of the study. The primary element of the study has been to provide the experimental data to validate a tentative alternative to the liquid solid extraction of solid waste PAH's by SFE. It is relevant and helpful to slightly modify the standard EPA method 8310 for a couple of reasons. One simple need is to frequently use an internal standard, and often times a surrogate as relative measure of the extraction efficiency. Second, it was helpful to operate the HPLC column at a higher linear velocity than that called out in the EPA method 8310. This modification allowed increased speed and resolution. Also, with regard to the analysis part of the overall method, we made an adaptation of the tentatively optimized (final) SFE steps to better accommodate the analysis by GC and GC/MS with capillary GC columns.

INTRODUCTION

A considerable effort was directed towards the optimization of the supercritical fluid extraction steps. The primary parameters that were the temperature, the density or the pressure and the combination of density and temperature. Another parameter studied in detail was the use of modifiers or co-solvents added to the flowing extracting stream of carbon dioxide. Liquid modifiers can be added in an almost infinite number of permutations of types and amounts.

Figure 1 is an outline of the study yielding the data in this manuscript. A brief initial study re-iterated some of the HPLC method steps included in EPA Method 8310. These iterations resulted in some minor changes to optimize the time and resolution for sample throughput and robustness.

A second study (in much greater detail) reviewed the SFE extraction in light of previous studies and experimental apparatus. The optimization in this study involved two major areas in order to provide recoveries greater than 95 % for all 16 PAH's described in EPA Method 8310. The first part involved use of sub ambient solid trapping to ensure the recovery of the relatively volatile compounds. Second part of the study involved the optimization of the co-solvents or modifiers useful in recovery of the relatively large and more intractable (from solid waste)
PAH compounds.

Experimental

Materials and Reagents

Reconstitution solvents.

The reconstitution solvents dispensed by the SFE instruments varied according to the particular analyte class being extracted. Furthermore, these same solvents were used to create the internal and external standard solutions. For the polyaromatic hydrocarbons, a 50/50 v/v mixture of acetonitrile/tetrahydrofuran was used: both were HPLC grade from Burdick and Jackson.

External calibration standards.

For polyaromatic hydrocarbons, a standard mixture from Supelco, Inc. in Bellefonte PA, Polynuclear Aromatic Hydrocarbons Mixture 610-M (Catalog No. 4-8743), or alternately, Hewlett-Packard standard mix # 85-6035was used. The Supelco standards are a mixture of 16 PAH's at levels ranging from 100 to 2000 ug/mL in a 50/50 mixture of methanol/methylene chloride. The HP standard contains the same 16 PAH's at the 500 ug/mL level in acetonitrile. These standard samples were used in the automatic preparation of more concentrations by serial dilution corresponding to 1/2, to 1/50 the original concentration, using a 50/50 mixture of acetonitrile/THF as the diluent.

Extraction fluid.

Carbon dioxide, SFE/SFC ECD grade from Air Products, Allentown, PA, was used as the bulk extraction fluid in all the supercritical fluid extractions. In the PAH applications, modifiers were added to the bulk CO2 extraction fluid. In the PAH work done at the Little Falls laboratory, these were methanol, water, and methylene chloride (all, HPLC grade from Burdick and Jackson, Muskegan, Michigan), forming extraction fluid mixtures of 95/1/4 (v/v/v) CO2/methanol/water in one method and 95/1/4 (v/v/v) CO2/methanol/methylene chloride in the other.

Mobile phase solvents for liquid chromatography.

Acetonitrile and water were used; their source and purity are noted above elsewhere.

Samples.

For the work done on the PAHs from soils, spiked samples were prepared in our laboratory and also were purchased from Environmental Resource Associates (ERA), Arvada, Colorado. The following outlines the chemicals and procedure used at our Little Falls facility. First, soil from a local yard was prepared by blending 200 g soil with an equal volume of dry ice prepared from SFE/SFC ECD grade CO2 (see above) in a blender for 5 minutes, manually removing the remaining large rocks and sticks, and then sieving the cold mixture. This process produces a finely divided soil with its moisture content still intact (3). A PAH standard mixture, Supelpreme-HC PAH Mix (Catalog No. 4-8905), obtained from Supelco, Inc. (Bellefonte, PA) and having 16 PAH's at levels of 2000 ug/mL was diluted by a factor of 100 using a 50/50 mixture of acetonitrile/tetrahydrofuran (see above). One-hundred milliliters of the resultant stock solution was mixed with 100 g of the finely divided soil. The mixture was gently stirred for 3 hours until the acetonitrile and

tetrahydrofuran had evaporated. This resulted in a spike mix of 20 mg/kg of each PAH in the soil.

Supercritical fluid extraction.

For SFE, Hewlett-Packard Models 7680T and 7680A were used without modification. In applications requiring modifier addition to the bulk CO2, Hewlett-Packard Model 1050 pumps (either isocratic or quaternary models) were used. The pumps were coupled to the SFE instrument as prescribed by the manufacturer. A contributed software program controlled the SFE/modifier pump system. Figure 2 depicts a block diagram of the combination of the SFE with a modifier pump with the modular HPLC to create the "bridge" system used in an automatic sequence to maximize overall sample throughput and to minimize operator intervention, thus providing reduced overall system error (improved sample % relative standard deviation or % RSD).

Liquid chromatography.

A Hewlett-Packard Model 1050 LC equipped with an MWD diode array detector, 100 vial autosampler and quaternary gradient pump was used without modification. The separation was carried out on a Vydac C18 (25 cm x 4.6 mm, 5 um particle size) column.

Analytical Procedure,Extraction

A quantity of three grams of soil was extracted each time in applying the method to the certified spiked sample for the assay of PAH's from the soil. When screening with real samples of high concentration, sometimes only 1 gram of soil was used, admixed with an equal amount of inert material such as sand or Chromosorb W-H.P. Two similar SFE methods have been developed -- one for analysis by HPLC and one for analysis by GC. In both the HPLC- and GC-focused SFE methods, there were three extraction steps with a single fraction produced for the SFE recovery of PAH's in the final method. The purpose of Step 1 (Figure 5) was to collect more volatile PAH's. The purpose of Step 2 (Figure 6) was to collect involatile PAH's. The purpose of Step 3 (Figure 7) was to sweep modifier from the instrument and raffinate before de pressurization and to reconstitute the involatile PAH's in the same vial containing the more volatile PAH's from Step 1.

PAH SFE Method for subsequent HPLC analysis.

The following conditions for Step 1 are grouped according to function.

1. Extraction -- pressure, 1749 psi; extraction chamber temperature, 120 C; density, 0.22 g/mL; extraction fluid composition, CO2; static equilibration time, 2 minutes; dynamic extraction time, 10 minutes; extraction fluid flow rate, 2.0 mL/min; resultant thimble-volumes-swept, 12. 2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 5 C; nozzle (variable restrictor) temperature, 55 C. 3. Reconstitution (of collected extracts) -- rinse solvent, 50/50 (v/v) THF/acetonitrile; collected fraction volume, 0.8 mL; trap temperature, 60 C; nozzle (variable restrictor) temperature, 45 C; rinse solvent flow rate, 1.0 mL/min; fraction destination, vial #n.

The following conditions for Step 2 are grouped according to function.

1. Extraction -- pressure, 4899 psi; density, 0.63 g/mL; extraction chamber temperature, 120 C; extraction fluid composition, 95/1/4 (v/v/v) CO2/methanol/water; static equilibration time, 1 minutes; dynamic extraction time, 30 minutes; extraction fluid total flow rate, 4.0 mL/min; resultant thimble-volumes-swept, 25. 2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 80 C; nozzle (variable restrictor) temperature, 45 C. 3. Reconstitution (of collected extracts) -- none.

The following conditions for Step 3 are grouped according to function.

1. Extraction -- pressure, 4899 psi; density, 0.63 g/mL; extraction chamber temperature, 120 C; extraction fluid composition, CO2; static equilibration time, 5 minutes; dynamic extraction time, 10 minutes; CO2 flow rate, 4.0 mL/min; resultant thimble-volumes-swept, 8. 2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 80 C; nozzle (variable restrictor) temperature, 45 C. 3. Reconstitution (of collected extracts) -- rinse solvent, 50/50 (v/v) THF/acetonitrile; collected fraction volume, 0.8 mL; trap temperature, 80 C; nozzle (variable restrictor) temperature, 45 C; rinse solvent flow rate, 1.0 mL/min; fraction destination, vial #n.

Method for subsequent GC analysis.

The following conditions for Step 1 are grouped according to function.

1. Extraction -- pressure, 1749 psi; extraction chamber temperature, 120 C; density, 0.22 g/mL; extraction fluid composition, CO2; static equilibration time, 2 minutes; dynamic extraction time, 10 minutes; extraction fluid flow rate, 2.0 mL/min; resultant thimble-volumes-swept, 12. 2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 5 C; nozzle (variable restrictor) temperature, 55 C. 3. Reconstitution (of collected extracts) -- rinse solvent, 1/1 (v/v) methanol/methylene chloride; collected fraction volume, 0.8 mL; trap temperature, 30 C; nozzle (variable restrictor) temperature, 45 C; rinse solvent flow rate, 1.0 mL/min; fraction destination, vial #n.

The following conditions for Step 2 are grouped according to function.

1. Extraction -- pressure, 4899 psi; density, 0.63 g/mL; extraction chamber temperature, 120 C; extraction fluid composition, 95/1/4 (v/v/v) CO2/methanol/methylene chloride; static equilibration time, 1 minutes; dynamic extraction time, 30 minutes; extraction fluid total flow rate, 4.0 mL/min; resultant thimble-volumes-swept, 25. 2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 80 C; nozzle (variable restrictor) temperature, 45 C. 3. Reconstitution (of collected extracts) -- none.

The following conditions for Step 3 are grouped according to function.

1. Extraction -- pressure, 4899 psi; density, 0.63 g/mL; extraction chamber temperature, 120 C; extraction fluid composition, CO2; static equilibration time, 5 minutes; dynamic extraction time, 10 minutes; CO2 flow rate, 4.0 mL/min; resultant thimble-volumes-swept, 8. 2. Collection (during Extraction) -- trap packing, Hypersil ODS; trap temperature, 80 C; nozzle (variable restrictor) temperature, 45 C. 3. Reconstitution (of collected extracts) -- rinse solvent, 1/1 (v/v) methanol/methylene chloride; collected fraction volume, 0.8 mL; trap temperature, 30 C; nozzle (variable restrictor)

temperature, 45 C; rinse solvent flow rate, 1.0 mL/min; fraction destination, vial #n.

Liquid Chromatography

The liquid chromatographic conditions for PAH's were the following: an injection volume of 10 uL, a column oven temperature of 30 C, a water/acetonitrile mobile phase which was programmed isocratic 40 % water for 3 minutes followed by 3 different ramps to increase the acetonitrile concentration to a final value of 100 % for 3 minutes.

Results and Discussion

The extraction from solid samples of polyaromatic hydrocarbons (PAH's) is an application which has been receiving significant attention with respect to getting an acceptable, robust SFE method developed and ultimately formalized as an EPA draft method.

EPA Method 8310 describes the HPLC analysis to be used for PAH's. In this work, this method was modified slightly for the consideration of analysis time, and resolution of the 16 prescribed compounds. In order to provide chromatographic resolution of both the internal (biphenyl or bromo benzene) and surrogate (m-quaterphenyl) standards, it was found to be necessary to change the programming of the mobile phase and to operate at higher linear velocities. A representative liquid chromatographic separation is presented in Figure 3.

In developing and optimizing the SFE method, personnel from the Hewlett-Packard laboratory in Waldbronn, Germany and the Inland Consultants laboratory in Chicago, Illinois, USA have collaborated with the Hewlett-Packard Little Falls site laboratory. Additionally, the group of Dr. H.B. Lee of the National Water Research Institute, Environment Canada in Ontario, Canada further modified the method outlined here specifically to use with gas chromatography and GC/MS as the analytical techniques (4). Over the last six months, our work has been directed towards optimizing the supercritical fluid extraction method itself -- including studying the effect of temperature, density (or pressure), and, most importantly, composition of the extraction fluid. Throughout the course of developing the method, we utilized three different ways of exposing the sample in an SFE system to a modifier/CO2 solution: addition of liquid modifier into thimbles containing the samples (e.g., 1 mL liquid to 10 g soil sample), the use of premixed tanks of liquids plus CO2 (e.g., 5 weight % methanol in CO2), and the use of an external pump to meter modifier into the CO2 stream ahead of the extraction chamber. The method described here can be carried out with either premixed tanks or the external modifier pump. Without some automated means of wetting the sample directly with the modifier part way through the method, the approach of addition into the thimble often provides lower average recoveries for the whole range of PAH's studied.

The "PAH class of compounds" (listed in Table 1)includes a range of compounds that is broad with respect to volatility and molecular weight. The SFE method development described here focused on two (overlapping) groups of PAH's, with the result that each group is extracted, concentrated, and reconstituted best by different SFE conditions. We defined these as different substeps making up a full method. These groups are considered to include the relatively volatile, smaller PAH's and the less volatile,larger size (and molecular weight) PAH's. In Figure 4 the individual compounds are sorted according to size, going from smaller compounds at the left hand side to larger

ones. The recoveries are low at both ends -- the most volatile and the least volatile (largest molecules) -- with a maximum in recoveries for intermediate PAH's. In Figure 4 have plotted earlier data from a USEPA report (where the apparatus did not have the luxury of such items as sub-ambient solid trapping and modifier pumps) and added the composite data of the three laboratories participating in this methods development work. The data are outlined in Table 2.

#	Compound	#	Compound
1	Naphthalene	9	Benzo(a)anthracene
2	Acenaphthylene	10	Chrysene
3	Acenaphthene	11	Benzo(b)fluoranthene
4	Fluorene	12	Benzo(k)fluoranthene
5	Phenanthrene	13	Benzo(a)pyrene
6	Anthracene	14	Dibenzo(a,h)anthracene
7	Fluoranthene	15	Benzo(g,h,i)perylene
8	Pyrene	16	Indeno(1,2,3-cd)pyrene

Table 2. A Comparison of Recoveries of PAH's obtained in Prior Work and in This Work after Method Optimization (% Recoveries)

PAH	EPA Method-1 (11)	EPA Method-2(11)	**Mean of EPA Reports**	This Study - Little Falls	This Study -- Waldbronn	This Study -- Inland Env	**Mean of This Study**
1	40.0	50.3	**45.0**	103.4	124.0	80.0	**102.4**
2	53.1	56.4	**54.5**	84.5			**84.5**
3	80.5	87.1	**83.8**	78.8	72.0		**75.4**
4	71.4	77.3	**74.2**	119.9	117.0		**118.4**
5	98.2	90.8	**94.5**	143.3	127.0		**132.6**
6	65.7	68.2	**66.9**	50.0	1000.0		**75.0**
7	79.3	83.0	**81.1**	104.0	106.0		**105.0**
8	77.2	67.1	**72.1**	66.0	40.0	97.0	**67.8**
9	61.8	58.6	**60.2**	99.4	156.0		**127.8**
10	60.0	53.5	**56.8**	114.8	96.0	105.0	**105.3**
11	47.2	38.7	**43.0**	95.9	104.0		**100.0**
12	47.2	38.7	**43.0**	95.1	79.0		**88.0**
13	30.1	22.6	**26.5**	75.3	77.0	95.0	**87.0**
14				99.2	53.0		**76.1**
15				89.3	46.0		**67.7**
16				88.4	112.0		**100.2**
Grand Mean			**61.7**				**94.6**

In this study, the PAHs, have been divided into two groups--the early eluting ones (in the chromatography) referred to as the relatively volatile PAH's and the remaining PAH's which are larger in size and molecular weight (and more intractable for extraction in solid wastes).

The recoveries at either end of the PAH list are improved. What we believe has been happening in prior work (5,6)is that conditions appropriate for extracting and collecting intermediate and large PAH's result in the volatilization of the more volatile compounds -- e.g., temperatures are too high and extraction times are too long thereby resulting in too much expanded CO2 sweeping over and through the collected extracts. Conversely, those same extraction conditions were not aggressive enough to extract the larger PAH's -- particularly, with respect to temperature and composition. These problems were overcome by going to a multiple-step procedure using an SFE system which 1. has a solid trapping system capable of thermal operation at sub-ambient temperatures for volatile collection and high temperatures for operation with modifiers and 2. also has the capability of automatically changing the extraction fluid composition from one step to another step.

The details were outlined in the Experimental section. Briefly, part of the PAH's were extracted and recovered in the first step using pure CO2 at moderately low density and temperature and with cold trapping on an ODS trap. These were reconstituted into an autosampler vial with just 0.80 mL collected fraction volume. The rest of the PAH's were removed by a subsequent step using a mixture of CO2 with water and methanol as the extraction fluid, higher operating temperature and density in the extraction region, and a higher temperature in the trapping region with the ODS. The PAH's are not reconstituted directly after the second step. A short third step with pure CO2 (but with all other conditions as in the second step) is used to purge the system of modifier before de pressurization. The analytes recovered in the second step (and possibly, any moved during the beginning of the third step) are reconstituted in the same autosampler vial containing the first fraction -- with another 0.8 mL collected fraction volume. Therefore, all recovered analytes are merged automatically into a single fraction to be analyzed.

The data in Table 2 are plotted in Figure 4. The bar graphs show the percent recovery for the 16 EPA PAH compounds. For instance, this 1st compound is naphthalene, the last one is indeno (1,2,3-cd) pyrene and compound number 6 is anthracene.

The solid bar graphs start at a relatively low percentage and increase and then decrease again. we Two things, a solid trap which can be operated at sub ambient temperature during the extraction step and the use of modifiers, have allowed 2 significant advantages. One allows the recovery of the relatively volatile PAH compounds. The clear bar graphs represent the mean of the two labs within HP, the private environmental lab in Skokie , Illinois (7) and the environmental lab in Burlington, Ontario Canada. It can be seen that the recovery is significantly improved for all 16 PAH compounds. This is the resultant of the two separate phenomena. First, the volatiles are extracted under mild conditions and rinsed to the reconstitution vial (from the solvent trap) before the later step with more aggressive extraction conditions. Secondly, these more aggressive conditions with the modifier extract the larger less soluble (in CO2 only). During the extraction step these

compounds are precipitated on the solid trap (which is now at a substantially elevated temperature) and then rinsed into the same vial. The grand mean recovery for the 16 compounds (multiple sets of experiments in four different labs in three different countries !) is 96%. As a test of our hypothesis about the volatiles and the modifier aiding the large PAHs, we then carried out experiments which divided the 3 steps such that the reconstituted solutes from step one were analyzed, and then the extracts from steps 2 and 3 (combined) were injected into the HPLC and analyzed. In Figure 8, the results from step one are shown as solid bar graphs, while the result from the combination of steps 2 and 3 are shown as the open or clear bar graphs.
This data would appear to support the hypothesis very well.

Three are three different groups of compounds that are detected by the HPLC UV detector, with essentially 3 different relative sensitivities. The first sub group is represented by naphthalene. At the wavelength of detection called out by the EPA HPLC method 8310 (254 nanometers), the minimum detectable quantity (of the net SFE and HP analytical method) at a signal to noise ratio of 4:1 is 0.100 mg per kg (ppm weight/weight basis) for naphthalene. The most favorable compounds are represented by anthracene naphthalene. Anthracene detected at 254 nm, is being sensed virtually the lambda maximum, and so now the minimum detectable quantity, at the same signal to noise ration is 0.005 mg/kgm. Indeno(1,2,3-cd)pyrene represents the most typical type of the PAH compounds--has a minimum detectable quantity of 0.030 mg per kg. All of the PAH compounds together meet the EPA solid waste criteria for sensitivity.

Finally, it is relevant to mention an interesting observation seen by the lab at the Canadian Center for Inland Waterways in Burlington, Ontario, a branch of Environment Canada , H.B. (Bill) Lee and his coworkers. Their experiments unlike the experiments of other three labs collaborating, in this study (the Wilmington, DE HP site, the HP Germany site, and Inland Environmental Consultants in Chicago) involved the use of gas chromatography (GC/MS) for the analysis step. This brought some concern about the 4% water as one of the co-solvents. If any of the water remains in the reconstitution solution there might be a detrimental effect on the GC fused silica capillary column and the injection procedure. This lab modified the original SFE method from 1% methanol, 4% water to 1% methanol, 4% methylene chloride (with all other conditions the same). This is work which we duplicated then in our Wilmington laboratories and we found no significant difference in the overall recovery. This work is described in a separate publication .

In summary , this particular method appears robust enough to be considered for a Round Robin study such as occurred with the EPA method 3560 TPH last year.

Acknowledgment

Many people have contributed to this work by sharing ideas and results of work in progress. They include Barry Lesnik, Tom Peart, Robert Hong-You, Pat Sandra, Frank David, Jerry King, Viorica Lopez-Avila, Lee Altmayer, Werner Beckert, Steven Pyle, Robert Marsden, and Philip Wylie.

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3. Dr. Mary Ellen MacNally, Agricultural Products, Experimental Station, E402/3328B, E.I. du Pont de Nemours and Company, Wilmington, DE USA.

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7. Personal communication from John Orolin,Inland Consultants, Inc., Environmental and Engineering Services, 3921 Howard St., Skokie, IL, 60076, USA .

Figure 1 : Outline of Study

- **Verify the HPLC method**
  - speed of analysis, Resolution
  - Internal Standard (biphenyl or bromo benzene)
- **Surrogate (Quaterphenyl)**
- **Optimize SFE parameters**
  - Temperature
  - Density (pressure)
  - Modifier
  - Volatiles ,Large mw PAH's
- **Basic Parameters**
- **Modifier**
  - add to thimble
  - Pre-mixed tanks
  - On-line modifier pump
- **Recovery**
- **Reproducibility**

Figure 2 : SFE-HPLC Bridge with Modifer Pump

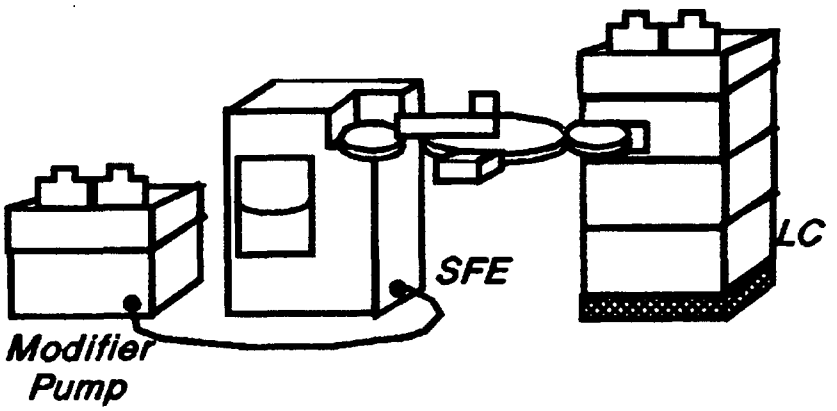


Figure 3 : EPA PAH Compounds HPLC

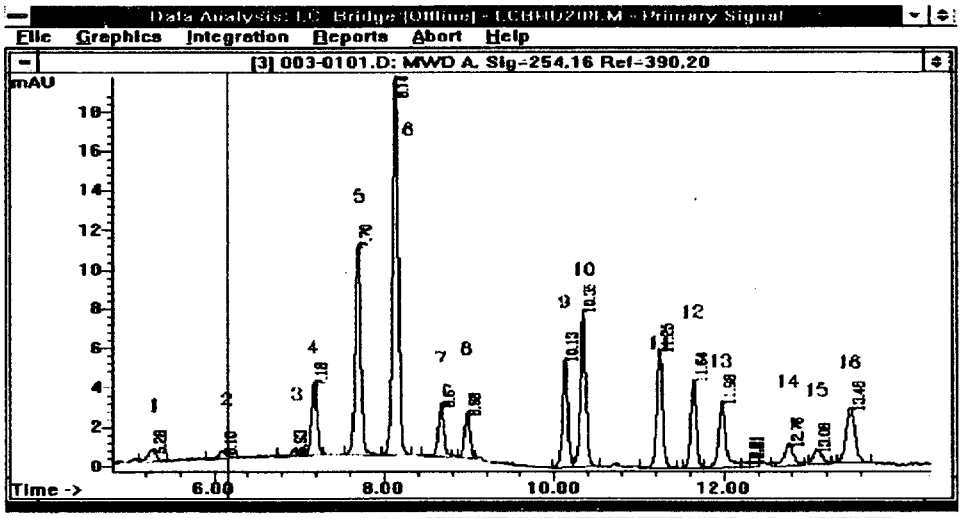


Figure 4 : Comparing HP Method to Method Without Modifier and Without Solid Subambient Trapping

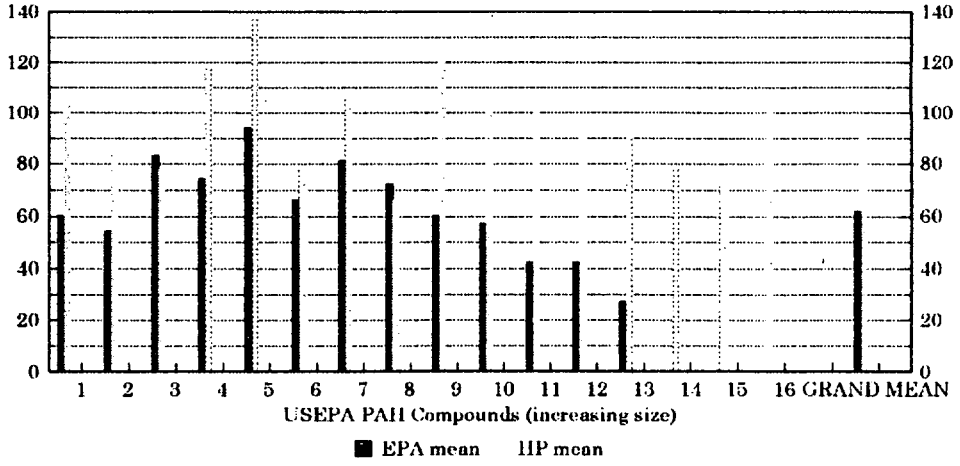


Figure 5 : SFE Conditions Step 1

Sample - 3.0 g Soil

HP7680T SFE + HP1050 Pump: Step 1

Extraction	▪ Pressure	*1749 psi*
	▪ Temperature	*120 C*
	▪ Composition	*CO2*
	▪ Static Equilib.Time	*2.0 min*
	▪ Dynamic Extn. Time	*10.0 min*
	▪ Flow Rate	*2.0 mL/min*
Collection	▪ Trap	*ODS*
	▪ Temperatures	*5 C,trap; 45 C nozzle*
Reconstitution	▪ Solvent, Fraction Vol.	*THF/ACN, 0.8 mL*
	▪ Temperatures	*60C, trap; 45 C noz*
	▪ Flow Rate	*2.0 mL/min*

Figure 6 : SFE Conditions Step 2

Sample - 3.0 g Soil

HP7680T SFE + HP1050 Pump: Step 2

Extraction	▪ Pressure	*4950 psi*
	▪ Temperature	*120 C*
	▪ Composition	*CO2 + 1% MeOH + 4 % H2O*
	▪ Static Equilib.Time	*2.0 min*
	▪ Dynamic Extn. Time	*40.0 min*
	▪ Flow Rate	*2.0 mL/min*
Collection	▪ Trap	*ODS*
	▪ Temperatures	*80 C,trap; 45 C nozzle*

Reconstitution : THIS STEP DOES NOT REQUIRE A RINSE

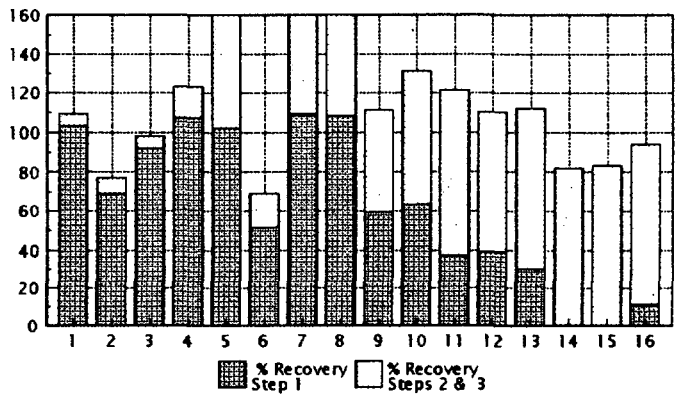
Figure 7 : SFE Conditions Step 3

Sample - 3.0 g Soil

HP7680T SFE + HP1050 Pump: Step 3

Extraction	▪ Pressure	*4950 psi*
	▪ Temperature	*120 C*
	▪ Composition	*CO2*
	▪ Static Equilib.Time	*0.5 min*
	▪ Dynamic Extn. Time	*10.0 min*
	▪ Flow Rate	*2.0 mL/min*
Collection	▪ Trap	*ODS*
	▪ Temperatures	*80 C,trap; 45 C nozzle*
Reconstitution	▪ Solvent, Fraction Vol.	*THF/ACN, 0.8 mL*
	▪ Temperatures	*60C, trap; 45 C noz*
	▪ Flow Rate	*2.0 mL/min*

Figure 8 : Separating the Variables: Recovery of the Volatile Fraction of PAH's vs. Larger PAH's



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ANALYSIS OF PCB'S IN SOIL, SEDIMENTS, AND OTHER MATRICES BY ENZYME IMMUNOASSAY

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ABSTRACT

A competitive inhibition Enzyme ImmunoAssay (EIA) for the determination of polychlorinated biphenyls (PCB's) is commercially available as the EnviroGard™ PCB Kit. Soil sample preparation can be performed in the field using disposable kit components. The test can analyze PCB's in the field in less than 30 minutes total, using no specialized equipment. Test specificity is restricted to PCB's, primarily Aroclors 1016, 1242, 1248, 1254, and 1260. The kit can be used to screen unidentified Aroclors at 4 levels from 1 to 50 ppm in soil. This method has been reviewed by the EPA Office of Solid Waste and will be proposed for inclusion in the 4000 series of screening methods in the next SW846 update. Quantitative data for soils in this concentration range can be easily obtained by standardization of the kit with the same Aroclor as in the samples (if known). Quantitative EIA analyses of river sediments were completed the same day in a portable lab on site, with a tenfold increase in sample throughput and a tenfold decrease in cost per sample compared to GC–ECD. Data for several methods and matrices are presented. These results demonstrate that EIA kits can effectively analyze for PCB's in many situations at a fraction of the cost and in a fraction of the time of standard methods.

INTRODUCTION

Reagent and Method Development

The development of the EIA for PCB's followed these steps: 1) PCB derivatives were synthesized for conjugation to proteins; 2) one of these PCB derivatives was conjugated to a carrier protein and the resulting conjugate was used to immunize animals, which then produced antibodies recognizing both the PCB derivative and PCB's; 3) a PCB derivative was conjugated to horseradish peroxidase (HRP) to make a conjugate which can be captured by anti-PCB antibodies; 4) the PCB-HRP conjugate was used to screen and select antibodies; 5) the selected system was optimized for PCB sensitivity and solvent and matrix tolerance, then characterized for specificity; 6) sample preparation

methods were developed for specific sample types; 7) these methods were validated using field samples.

PCB EIA Procedure

Figure 1 schematically illustrates the procedure used for the analysis of samples containing PCB's. In summary: 1) rabbit antibodies which recognize the PCB structure are immobilized on the walls of plastic test tubes; 2) PCB's in solvent, in the form of either standards, calibrators, or samples prepared as described below, are mixed with Assay Diluent in tubes, allowing PCB's to be captured by the immobilized antibodies (*incubation 1*). PCB's are specifically retained on the solid phase when the rest of the sample is washed away (*wash 1*); 3) PCB-enzyme conjugate is added to tubes and bound in the same manner as in step 2 (*incubation 2*). The unbound conjugate is washed away (*wash 2*) and the amount retained by the immobilized antibody is inversely proportional to the amount of PCB bound in step 2; 4) enzyme substrate and chromogen are added to the tubes for color development by the bound enzyme (*incubation 3*). The intensity of color is proportional to the amount of captured enzyme and is inversely proportional to the amount of PCB bound in step 2. Therefore, ***more color means less PCB***. Incubations are typically, but not always, 5 minutes. Washes use tap water. Sample and calibrator volumes vary with the sample type and protocol, but are generally 5, 25, or 100 µl. Incubation 1 volume is 500 µl.

Sample Preparation

Sample preparation methods are given below for several matrices. Where EIA analysis is indicated, the extract is used as described in step 2 of the EIA Procedure above (incubation 1 of Figure 1).

Soil sample preparation is summarized as follows: Weigh 5 g soil on portable balance and place in polypropylene extraction bottle, extract soil by adding 5 mL of methanol and shaking vigorously for two minutes. Filter extract and collect for storage or immediate EIA analysis. Analyze extract as described in step 2 of the EIA Procedure above. All components required for this method are commercially available in kit form.

This study used two methods of sediment sample preparation for EIA analysis. They are summarized as follows: Method 1) homogenize wet sediment, weigh 4 g onto solvent rinsed Al foil, add 10-15 g of anhydrous sodium sulfate to form a friable mixture, extract using 20 ml isopropanol with 2 minutes of sonication and 15 minutes of shaking, let settle briefly or centrifuge, then filter supernatant. Some extracts were prepared by variations of this method, all of which are similar in speed, simplicity, and ease of field use. Analyze extract as described in step 2 of the EIA Procedure above. Method 2) homogenize, Soxhlet extract (48 hours) using 1:1 acetone:hexane, exchange to cyclohexane (for GC-ECD

or storage), exchange to isopropanol for EIA. Analyze extract as described in step 2 of the EIA Procedure above.

Surface wipe sample preparation is summarized as follows: Mark surface with template, remove wipe from methanol in extraction bottle, wipe area to be analyzed, place wipe back in extraction jar and extract by vigorous shaking for 1 minute. Analyze extract as described in step 2 of the EIA Procedure above. All components required for this method are commercially available in kit form.

Water sample preparation is summarized as follows: condition glass barrel SPE column with isopropanol and reagent water, extract sample by drawing through column, air dry column, elute with isopropanol. Analyze eluate as described in step 2 of the EIA Procedure above. All components required for this method are commercially available.

RESULTS AND DISCUSSION

Test Specificity

The test response to Aroclors 1016, 1242, 1254, and 1260 is within twofold of the response for Aroclor 1248. The broad specificity of the EIA for the common moderately chlorinated Aroclors allows either screening or quantitative analysis. This specificity is relatively independent of the slight differences in protocol among the sample types described below. Biphenyl and several chlorinated ring compounds were also tested for crossreactivity in the EIA. All of these compounds demonstrated less than 0.5% crossreactivity compared to Aroclor 1248: 3,3'-dichlorobenzidine, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, biphenyl, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol. These results mean that *more than* 200 ppm of any of these compounds would be required to give the same test response as 1 ppm of Aroclor 1248. Also, *more than* 10,000 ppm of any of these compounds would be required to give the same test response as 50 ppm of Aroclor 1248.

Soil Screening

Soil screening results obtained using the kit with calibrators at 5, 10, and 50 ppm are shown in Table 1. The respective actual concentrations of these calibrator solutions are 3, 5, and 22 ppm Aroclor 1248. These values were chosen to provide 99% confidence that positive samples will be detected regardless of the Aroclor present, variations in extraction efficiency, or method imprecision for either GC or EIA. This calibration strategy biases the test slightly toward false positive results, providing greater certainty that contaminated samples will be screened out effectively. For a population of samples linearly distributed in

concentration from 1 to 100 ppm, the calculated false positive rate is less than 6%, while the calculated false negative rate is less than 0.1% for all three decision points. Several samples in Table 1 illustrate this point. For example, sample 3 is identified as ≥ 50 ppm, but is less than 50 ppm by GC (29.6 ppm). This result is expected because the actual concentration of the sample is higher than the actual 22 ppm of the 50 ppm calibrator. Table 1 shows that most of the false positive results occur in the concentration range between the middle and low calibrators, due precisely to the bias designed into the test. Prudent site screening demands that samples in this range be identified for follow-up GC analysis to ensure accurate decision making. The data of Table 1 show that the slight inherent bias of the test accomplishes this effectively. This method has been reviewed by the EPA Office of Solid Waste and will be proposed for inclusion in the 4000 series of screening methods in the next SW846 update. Another version of this kit has been developed for screening at 1 and 5 ppm in soil. Test protocol and performance characteristics are similar to the first kit.

Quantitative Soil Analysis

If the Aroclor present in the samples is known, quantitative data can easily be obtained over a wide range of concentrations. This is done by substituting for the calibrators a standard curve of the known Aroclor. Concentrations of the Aroclor in the samples are determined by comparison to the standard curve. Expansion of the range of quantitation is possible by diluting high concentration extracts and by using a more sensitive EIA protocol for levels near or below 1 ppm. Table 2 illustrates results of the latter procedure for a set of soil samples containing less than 5 ppm, compared to the GC results from 8080 analysis. Because Aroclor 1248 is recognized slightly better than Aroclor 1260, standardization on Aroclor 1260 will yield slightly higher values (as demonstrated in Table 2). Correction for this difference in crossreactivity between Aroclors 1248 and 1260 would approximately equalize the slopes of the two regression lines in Table 2. Other projects using this kit have obtained quantitative data from field samples covering a range 5 decades of concentration, from 0.1 to more than 10,000 ppm. Method precision was tested in a 9 day validation study at 3 sites using 4 field samples over a concentration range of 5 to 35 ppm, resulting in a 27% concentration coefficient of variation within site and across day and kit lot.

Quantitative Sediment Analysis

The PCB EIA kit was used for quantitative sediment analysis in two different situations. A comparison of EIA and GC-ECD was made using sediment samples from a typical Great Lakes industrial contamination site, prepared for EIA by method 2. For GC-ECD analysis, these samples

were further cleaned by gel permeation chromatography and other techniques, including sulfur removal. Correlation between the methods was good (Figure 2) over two decades of concentration, from 0.2 to 20 ppm. This result demonstrates that the EIA is able to measure PCB's at low levels in sediments when properly presented to the antibodies, despite the presence of sulfur compounds and heavy metals in these sediment extracts. Sediments which have undergone significant dechlorination may yield inaccurate results because of decreased recognition of less chlorinated congeners by the antibodies; such was not the case here. Precision in this study was good; the pooled concentration coefficient of variation (%CV) was 13% for 7 pairs of duplicates, 2 sets of 6 replicates, and 1 set of 7 replicates.

Based on the above success of method 2/EIA for quantitative sediment analysis, method 1 was developed for simpler sample preparation and EIA analysis in the field. Quantitative sediment analysis by method 1/EIA was used at other Great Lakes industrial contamination sites. Sediment cores were transported to a lab trailer on shore for sampling. Same day analysis was performed using sample preparation method 1/EIA. Performance data for the EIA are summarized in Tables 3 and 4. Correlation of EIA results with GC-ECD results was determined for a set of 41 samples containing 0.1 to 12 ppm from 3 sites; the correlation coefficient was 0.84 and the regression equation was $y = 0.63x + 0.47$ ppm. Timely on site analysis of total PCB in sediments enabled researchers to guide field sampling to ensure appropriate samples were taken for GC-ECD analysis. In addition, project managers were able to conform confidently to dredging guidelines and to guide disposal of dredge spoil. Further simplification of sediment extraction method 1 is currently under investigation.

Other Matrices

Analyses of PCB's on surfaces and in water are also possible using the same EIA kit as for the previously described applications, but with slightly modified protocols and appropriate sample preparation methods. Decisions about PCB contaminated surface remediation are often limited by the turnaround time for wipe sample analysis by GC. The PCB EIA kit has also been formatted as a wipe test kit for screening use in such situations, analogous to the previously described soil screening kit. Data from 64 field samples from three sites were used to set actual concentrations for the 10 and 100 $\mu g/100\ cm^2$ calibrators. The wipe kit design includes the same false positive bias as described above for the soil screening kit, for exactly the same reasons. Decisions are made in the same fashion as soil screening, as less than (or not less than) the decision level. For a population of samples linearly distributed in concentration from 1 to 100 $\mu g/100\ cm^2$, the calculated false positive

rate is 6 to 7%, while the calculated false negative rate is less than 0.7% for both 10 and 100 µg/100 cm^2 decision points.

PCB's in water adsorb strongly to even small amounts of particulate material. Therefore, analysis of total PCB in water requires efficient recovery of this adsorbed material. This is accomplished by the use of high throughput C18 columns which efficiently capture particulate material. These columns allow the analysis of slightly to moderately turbid field water samples with minimal reduction in flow rate. Isopropanol is used to elute the PCB's captured by the C18 from the dissolved phase and simultaneously extract the adsorbed PCB's from the trapped particles. EIA analysis is performed directly on the eluate without volume reduction. Data on the recovery of PCB spiked into water are shown in Table 5. These results demonstrate the ability of the test to detect 0.1 ppb total PCB in a small (500 ml) sample in approximately one hour using a simple sample concentration method. Preliminary data indicate a detection limit below 25 ppt in 4000 ml of water, and improvement may be possible with modest modifications of the protocol. The ultimate sensitivity of this method will depend on several factors, including sample volume, particle load, particle chemistry, etc.

CONCLUSIONS

1. Test specificity is restricted to PCB's, primarily Aroclors 1016, 1242, 1248, 1254, and 1260.
2. The test is capable of analyzing for PCB's in soil in the field in less than 30 minutes, using no specialized equipment.
3. Screening of soils containing unidentified Aroclors can be performed at 50, 10, 5, or 1 ppm, with 99% confidence of detection of contaminated samples.
4. Quantitation from 0.1 to 10,000 ppm is possible for soil samples containing an identified Aroclor.
5. Screening of surfaces contaminated with unidentified Aroclors can be performed at 10 and 100µg/100 cm^2 with 99% confidence of detection.
6. The design of the EIA accommodates significant variations in sample type and protocol, allowing the analysis of PCB's in many matrices.
7. Ongoing work with this kit includes improved sediment analysis, water analysis, oil analysis, and biological tissue analysis. Field testing and validation are proceeding for all these applications.

ACKNOWLEDGEMENT

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Table 1. Screening of 32 soils using the EnviroGard™ PCB EIA Kit. Color was read by differential photometer and interpretation of EIA result was based on comparison of optical density value to calibrator optical density value. The correctness of the EIA interpretation is indicated for each calibrator level as follows: normal = correct; italicized = false positive, bold = false negative.

Sample	Soil Type*	Aroclor Content	EnviroGard™ EIA Result Comparison to Calibrators ≤5 ppm Calibrator	≤10 ppm Calibrator	≤50 ppm Calibrator	EnviroGard™ EIA Interpretation	GC Result (ppm PCB by EPA 8080)
24	N/A	1254	No	No	No	≥50 ppm	1012
23	N/A	1254/60	No	No	**Yes**	≤50 ppm**	164
12	Loam/Clay	1260	No	No	No	≥50 ppm	73
6	Sand	1260	No	No	No	≥50 ppm	68
1	Clay	1260	No	No	No	≥50 ppm	60
10	Clay	1260	No	No	No	≥50 ppm	56
22	N/A	1242/54/60	No	No	Yes	≤50 ppm	36.6
8	Clay	1260	No	No	Yes	≤50 ppm	32
3	N/A	1254	No	*No*	*No*	≥50 ppm	29.6
18	Sand	1260	No	No	Yes	≤50 ppm	24
14	Clay	1260	No	No	Yes	≤50 ppm	15
9	Loam/Sand	1260	No	No	Yes	≤50 ppm	13
21	Clay	1242/54/60	No	No	Yes	≤50 ppm	13
16	Clay	1260	No	No	Yes	≤50 ppm	11
4	N/A	1254/60	No	*No*	Yes	≤50 ppm	6.7
20	Clay	1260	No	*No*	Yes	≤50 ppm	5
2	N/A	1254	*No*	Yes	Yes	≤10 ppm	4.7
29	N/A	1254/60	*No*	*No*	Yes	≤50 ppm	4.6
15	Clay	1260	*No*	Yes	Yes	≤10 ppm	4
25	Loam	1248/54	*No*	Yes	Yes	≤10 ppm	4
30	N/A	1254/60	*No*	*No*	Yes	≤50 ppm	3.9
27	N/A	1248/54	*No*	*No*	Yes	≤50 ppm	3
32	Loam	1248/54	Yes	Yes	Yes	≤5 ppm	2.7
13	Clay	1260	Yes	Yes	Yes	≤5 ppm	2
19	Clay	1260	Yes	Yes	Yes	≤5 ppm	1.4
26	Clay	1248/54	Yes	Yes	Yes	≤5 ppm	0.3
11	Loam/Clay	1260	Yes	Yes	Yes	≤5 ppm	0.2
28	N/A	1248/54	Yes	Yes	Yes	≤5 ppm	0.1
31	Clay	1254/60	Yes	Yes	Yes	≤5 ppm	0.1
5	N/A	1254	Yes	Yes	Yes	≤5 ppm	<0.1
7	Loam/Clay	1260	Yes	Yes	Yes	≤5 ppm	<0.1
17	Clay	1260	Yes	Yes	Yes	≤5 ppm	<0.1

* N/A = not available

** Further work indicated false negative response was due to sample matrix effect. Subsequent analysis indicated the presence of an interfering substance that prevented PCB binding to the antibody. This false negative at the highest calibrator level was not due to cross-reactivity or incomplete PCB extraction.

Table 2. Correlation of quantitative soil analysis by EIA and GC.

Sample	GC Result ppm by 8080	Lab A ppm by EIA	Lab B ppm by EIA
A	0	«0.15	«0.1
B	0	«0.15	«0.1
E	0	«0.15	«0.1
I	0.2	0.3	0.29
H	0.3	1.0	0.46
D	0.6	0.4	0.52
SS1	0.6	0.7	0.74
G	0.6	1.0	1.05
C	1.0	1.2	0.92
SS2	1.1	2.3	1.8
F	1.4	1.6	1.45
SS5	3.1	5.0	3.6
Aroclor used for standard curve		1260	1248
Regression equation data (vs. GC)			
	r^2	0.93	0.96
	slope	1.56	1.15
	Y intercept	-0.03	0.05

Table 3. Performance of sample preparation method 1 with EIA for quantitative sediment analysis.

Parameter	Performance	Comment
Detection Limit	60 ppb	Determined by repeat analysis of system blanks (n = 7); 95% confidence
Precision		Concentration %CV, based on duplicate analyses of extracts of field sediment samples. [%CV = {(mean/standard deviation) x100)]
	intraassay	7.7 %CV n = 48 pairs of duplicates
	interassay	7.9 %CV n = 52 pairs of duplicates
Spike recovery	90% of nominal	Based on detection of Aroclor 1248 spiked into clean soil, n = 8
Recovery	73±9%	Recovery of total PCB from dried SRM sediment, relative to GC-ECD result, n = 6

Table 4. Comparison of sediment analysis by PCB EIA and GC–ECD.

	Method 1/EIA	Method 2*/GC–ECD
Cost per Sample	$15	$150–300
Sample Throughput	10 per 2.5 hours	1 per 2.5 hours

* GC-ECD analysis requires Method 2 sample preparation procedure followed by gel permeation chromatography and sulfur removal.

Table 5. Recovery of Aroclor 1248 Spikes from Tap Water Samples. This water contained 0.5 mg/liter particulate material, determined gravimetrically using a 0.45 µm filter. (* reagent water blank subtracted)

ng Spike	ml	Final ng/ml	n	Recovery (mean ± SD)
50	500	0.1	3	73±29%
250	500	0.5	3	114±50%
1000	500	2.0	3	90±40%
100	4000	0.025	1	125%*

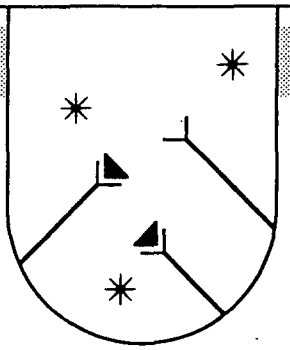
FIGURE LEGENDS

Figure 1. *Principles of the Test. Schematic depiction of the EIA for PCB's.*

Figure 2. Correlation of GC and EIA Results for Sediment Analysis. Sediments were analyzed by method 2 and EIA as described in the methods section.

Incubation 1:

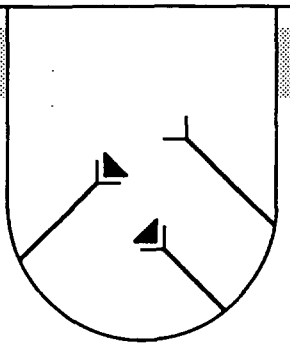
Dilution of sample or calibrator is incubated in tube containing immobilized antibodies.



▲ = PCB
✳ = Interfering Material
Y = Anti-PCB Antibody

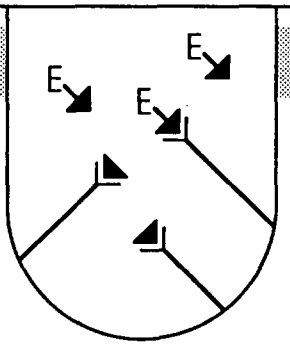
Wash 1:

Sample matrix is washed away, leaving only PCB's bound to antibodies.



Incubation 2:

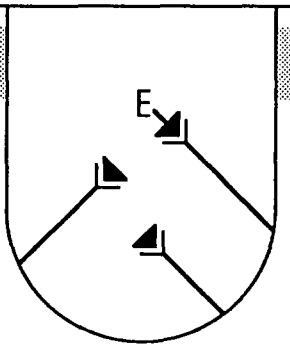
PCB-HRP binds to free anti-PCB sites on immobilized antibodies.



E = HRP
(Horse Radish Peroxidase Enzyme)

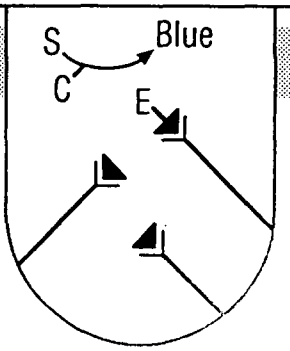
Wash 2:

Unbound PCB-HRP is washed away, leaving an amount of enzyme inversely proportional to the PCB concentration in Incubation 1.

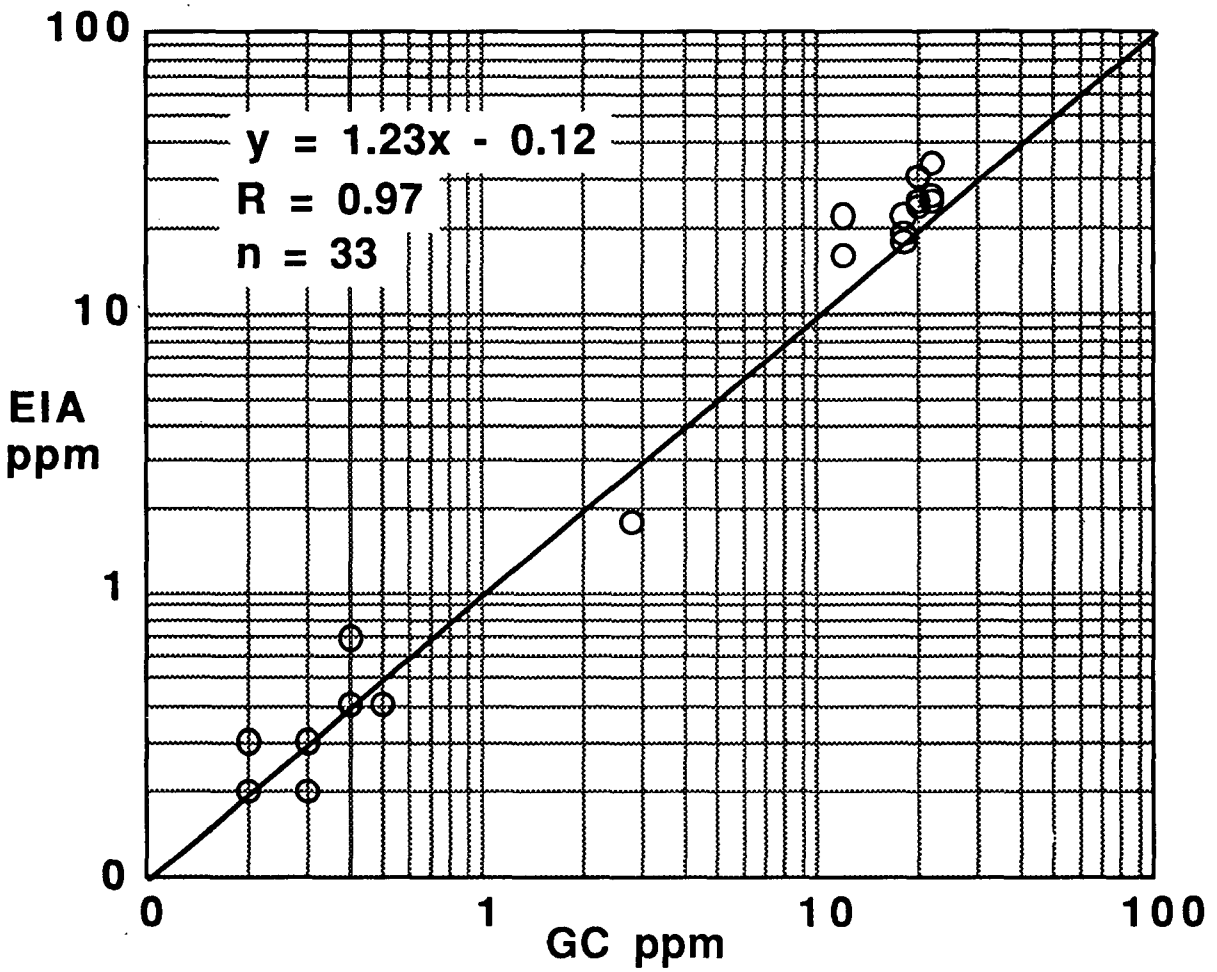


Incubation 3:

Colorless substrate and chromogen are converted to blue color in proportion to amount of bound enzyme. *Less color means more PCB*. Stop solution inactivates the HRP, changes color to yellow, and stabilizes color.



S = Substrate
C = Chromogen


100
10
1
0
EIA
ppm
y = 1.23x - 0.12
R = 0.97
n = 33
0
1
10
100
GC ppm

56 EXPLOSIVES ANALYSIS OF ATYPICAL MATRICES AND TECHNICAL ENHANCEMENTS TO U.S.EPA METHOD 8330

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ABSTRACT

The U.S. EPA Method 8330 from SW-846 is used for the determination of nitroaromatics and nitramines (including HMX, RDX, TNT, etc.) in soil and water samples by high performance liquid chromatography (HPLC). This method is being used for remedial investigation programs at former ammunition facilities throughout the United States. Variations of this method have been used by Midwest Research Institute (MRI) as the basis for analyzing more exotic matrices not addressed by the SW-846 method, including: surface wipe samples, concrete chips, plant biota, and TCLP extracts.

In order to improve data consistency, technical enhancements have been incorporated into method applications to improve overall performance and quality. These include: "pre-mixing" soil for better homogenization and analytical subsampling, performing multiple extractions for trace-level analysis of water samples using the "salting-out" technique (U.S. Army Corps of Engineers draft procedure), and enhancing chromatographic analysis with the addition of an internal standard for better qualitative identification (relative retention time) and quantization (relative response factors).

INTRODUCTION

Since 1985, MRI has performed explosives analyses for remedial investigation of sites throughout the United States using the EPA Method 8330 "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)." Although the basic method has remained the same, MRI has added several enhancements to the procedure which has improved overall method performance. In addition to analyzing soil and water samples, the method has been adapted for use with other matrices, including: surface wipes, concrete solids, TCLP extracts, and plant biota. This paper presents an overview of how this method has performed in these different applications and describes some techniques which have improved overall performance.

MATRICES

Method 8330 is a very versatile method which can be adapted to a variety of matrices. However, special applications require special techniques to achieve the most reliable results. The following paragraphs describe how this method has been applied to various matrices.

Soil and Sediment

Method 8330 specifies that soil and sediment samples be initially dried in air at room temperature or colder and protected from direct sunlight. Then the sample is ground in a solvent-rinsed (acetonitrile) mortar. MRI has found that preparing a "pre-mix" of the soil before actually taking analytical subsamples helps to assure sample homogeneity and precision of the method. The expanded procedure also uses the air-drying technique, which is then followed by grinding the soil/sediment using a solvent-rinsed laboratory burr mill to quickly reduce the particle size of the soil. Nearly all of the sample will pass through a 30-mesh screen. This step is important for several reasons: first, it allows much larger samples or an entire sample to be easily prepared for analysis, reducing the concern of inadequate composite mixing during field sample collection, and second, it provides a sample texture more conducive to further homogenization. The ground sample is collected in a glass jar and rotary tumbled to further mix the sample prior to analytical subsampling.

Table 1 shows a comparison of Method 8330 precision results for the analysis of contaminated soils. Data provided in the SW-846 methods' "Intralaboratory Precision of Method for Field-Contaminated Soil Samples," was based on a study where the method was tested by six different laboratories. These data are compared to field-contaminated samples which were analyzed by one laboratory (MRI) three separate times over an approximate one-month period. Although these data are not directly comparable because of the significant differences in analyte concentrations, the data do indicate that comparable or better precision can be achieved at trace contaminant levels using pre-mixed soil samples.

Concrete Chips

The technique used for soil/sediment preparation has been successfully used on hard clay soils and also very hard samples which would not normally be amenable to standard grinding procedures (i.e., mortar and pestle). For example, this technique was used on concrete chip samples collected from cinder block walls to determine if residual explosives remained in the concrete. The same technique, described above for the soil samples, was used to reduce the concrete chips to a powdery texture prior to analysis by Method 8330. Although none of the Method 8330 analyte list were found in these samples, method recovery and precision

were determined using spiked concrete samples. Table 2 shows precision and accuracy for this matrix; spiked soil samples, which were extracted and analyzed concurrently with the concrete samples, are also shown for comparison.

Table 1. Comparison of SW-846 Interlaboratory Precision Values with "Pre-mixed" Results for Contaminated Soils

	SW-846 data		Pre-mixed sample data	
Analyte	Concentration (μg/g)	Precision (RSD)[a]	Concentration (μg/g)	Precision (RSD)[a]
Tetryl	2.3	18	2.2	8
RDX	104 877	17 8	1.7	7
TNT	7 669	18 10	3.4	9
TNB	3 72	8 12	12.1	1

[a] Relative standard deviation.

Table 2. Matrix Spike Duplicate Recovery and Precision for Concrete and Soil Samples

		Average recovery (range)					
Matrix	Spike level (units)	HMX	RDX	TNB	Tetryl	TNT	24 DNT
Concrete Sample No. 1	2.5 μg/g	97 (±4)	97 (±8)	78 (±47)	37 (±1)	29 (±26)	69 (±27)
Concrete Sample No. 2	2.5 μg/g	99 (±4)	102 (±4)	106 (±4)	83 (±4)	95 (±3)	105 (±4)
Soil	2.5 μg/g	102 (±1)	98 (±1)	108 (±3)	94 (±10)	100 (±1)	108 (±1)

Water

The current version of Method 8330 (November 1990), is applicable to relatively high-level determinations of explosives in water samples. This method consists primarily of a "dilute-and-shoot" approach which is effective and straight-forward for samples with analyte concentrations ranging from approximately 4 μg/L (for DNB) to 44 μg/L (for tetryl). Trace-level analysis of samples with analyte concentrations as low as 0.1 μg/L require extraction and concentration of the resulting extract. MRI uses a technique based on a U.S. Army Corps of Engineer's (USACE)

draft protocol in which 400 mL of a water sample is saturated with sodium chloride salt, followed by liquid-liquid extraction of the explosive compounds into acetonitrile. This "salting-out" technique has been successfully used for many years to analyze groundwater and surface water samples from federal remediation sites.

MRI has modified and enhanced the original draft method in several ways to improve overall performance or to reduce common reagent interferences exhibited primarily at the trace levels. These changes include performing a second acetonitrile extraction of the salt-saturated aqueous sample to recover any residual explosives not collected in the first extraction and pre-cleaning the salt reagents (sodium chloride and sodium sulfate) by solvent extraction and heat. The results of these changes are shown in the following table (Table 3) where recovery and precision are shown for spiked control samples at trace level concentrations. The method has proven to be reliable and reproducible over hundreds of water samples.

Table 3. Summary of Accuracy and Precision Data for Spiked Water Samples[a,b]

Analyte	Average recovery (%)	Precision[c]	No. of determinations
HMX	96	12	5
RDX	83	20	5
2,4-DNT	53	11	5
TNT	78	8	5
TNB	85	8	5
Tetryl	76	4	5

[a] Method performance was measured by spiking clean water samples with separate extraction batches.
[b] Spike levels for the target analytes in water were 1.25 µg/L for all analytes except tetryl at 5 µg/L.
[c] s = Standard deviation of the average.

TCLP Extracts

The "salting-out" extraction technique has also been successfully used for TCLP extracts in evaluating the leachability of explosive compounds from soil. In one study, Method 8330 was used to extract highly contaminated soil samples. The same soil samples underwent the TCLP extraction procedure and a portion of the TCLP extract was analyzed using the "salting-out" procedure.

These results show that the method adequately characterized both the original soil and the resultant leachate for explosives contaminants. The extract concentrations were consistent with the original soil contamination, producing 25% to 100% of the total possible compound that would be expected based on the original soil analysis (assuming a factor of 50 to convert μg/g soil concentrations to μg/L leachate concentrations). These results are shown in Table 4 below.

Table 4. Analysis Results for RCRA Characterization Soils and TCLP Extracts

		Analyte concentration						
Matrix	Units	HMX	RDX	TNB	Tetryl	TNT	2,6-DNT	2,4-DNT
TCLP prep. blank	μg/L	< QL	< QL	< QL	< QL	< QL	< QL	< QL
Soil	μg/g	0.53	3.0	41	< QL	2600	< QL	8.3
TCLP ext.	μg/L	< QL	180	170	140	70000	< QL	130
Soil	μg/g	0.33	3.3	4.9	< QL	180	< QL	2.5
TCLP ext.	μg/L	19	150	21	< QL	3700	< QL	40
Soil	μg/g	< QL	0.34	4.3	< QL	89	< QL	3.0
TCLP ext.	μg/L	< QL	4.8	57	< QL	3000	< QL	74
Soil	μg/g	< QL	0.97	43	< QL	49	< QL	0.96
TCLP ext.	μg/L	< QL	25	1200	76	1500	< QL	25
Soil	μg/g	< QL	0.91	28	< QL	31	< QL	0.90
TCLP ext.	μg/L	< QL	20	860	65	990	< QL	22
Soil	μg/g	< QL	0.19	< QL	< QL	22	< QL	< QL
TCLP ext.	μg/L	< QL	< QL	< QL	< QL	630	< QL	< QL
QUANTITATION LIMITS: Matrix:	Units	Concentration						
Soil	μg/g	0.15	0.15	0.50	1.0	0.15	0.50	0.15
TCLP extract	μg/L	1.1	1.1	3.3	6.7	1.1	3.3	1.1

Surface Wipes

Surface wipes were analyzed using an adaptation of the soil/sediment procedure in which surface areas were wiped with acetonitrile-saturated gauze. The wipe samples were simply treated as a solid sample by adding extracting solvent to the collection jar and processing the sample the same as the Method 8330 procedure for soils. Since no explosives were found in the field samples, a spiked control was used to demonstrate recovery as shown in Table 5.

Table 5. Control Spike Recovery For Surface Wipe (Gauze) Sample

Analyte	Percent recovery (%)
HMX	75
RDX	77
TNB	80
Tetryl	87
TNT	80
2,4-DNT	75

[a] Spiked concentrations were 5 μg per gauze sample (representing a 100 cm^2 surface area).

Plant Biota

Biota samples present a more unusual sample matrix in that the explosive compounds may be chemically bound to the plant structure. As expected, the extraction technique is quite different than would normally be used in the absence of biological transformation of these contaminants. For example, one technique used for plant studies is to acid-hydrolize the plant sample, then extract the mixture with ether to recover the explosive compounds, followed by a solvent exchange and a column chromatography step. Method 8330 analysis parameters were used to measure explosive residues in the plant material.

Method performance for plants is presented in Table 6 below. Although chemical recoveries are lower than other matrices, these are reflective of the more compelx extraction procedure (which is not part of Method 8330) rather than the Method 8330 analysis procedure used to analyze the extracts. This is illustrated by the fact that similar low recoveries were found for the control samples (spiked reagent taken through the extraction procedure) reported with the biota data. It should also be noted that the plant extracts did not produce any unusual or problematic background interference for the Method 8330 chromatography.

Table 6. Blank, Control, and Matrix Spike Results (Percent Recovery)[a] for Plant Biota

Biota controls	RDX	TNB	Tetryl	TNT	2,4-DNT
Method blank	< QL	< QL	< QL	< QL	< QL
Control 1	52%	51%	78%	43%	40%
Control 2	60%	59%	79%	45%	44%
Matrix spike terrestrial Plant No. 1	57%	Interference[b]	~ 37%[c]	~ 35%[d]	37%
Matrix spike terrestrial Plant No. 2	45%	21%	~ 53%[c]	39%	43%
Root plant No. 3	49%	37%	63%	28%	35%
Root plant No. 4	54%	43%	42%	29%	38%

[a] Spike levels in control and matrix spikes were 20 μg/g for all indicated analytes.
[b] TNB recovery indeterminate due to chromatographic interference.
[c] Tetryl recoveries are estimated because the extract concentrations were near the quantitation limit.
[d] Estimated recovery for TNT due to high native level.

METHOD ENHANCEMENTS

The most significant technical improvement MRI has made to the SW-846 method has been the use of an internal standard (a chemically-similar compound which is spiked into sample extracts and standards just prior to analysis). This addition serves several important functions. First and foremost, it is used to establish relative retention time windows for qualitative identification for the Method 8330 analytes; it is relative in the sense that chromatographic retention times are normalized to the internal standard marker within each chromatogram. This technique provides a much more precise determination of close eluting compounds. For example, because the retention times for the 2,4-DNT and 2,6-DNT isomers vary by only a few seconds, normal time variances between one injection to the next can make it difficult to absolutely distinguish between the two compounds. However, when an internal standard marker is added to set relative retention time windows for these two analytes, there is an easily discernable difference. The table below (Table 7) presents a summary of how precision is dramatically improved by the use of relative retention time over normal Method 8330 retention time identification criteria. Relative percent differences decrease for all analytes when using RRT values which reduces the chance of reporting false positive results.

Table 7. Comparison of Absolute Retention Time vs. Relative Retention Time (Internal Standard) for Explosive Standards

	Average RT[a]	RPD[c]	Average RRT[b]	RPD[c]
HMX	2.8	1.4	0.137	0.73
RDX	4.1	1.7	0.199	0.50
TNB	5.4	1.3	0.264	0.38
DNB	6.5	2.0	0.317	0.95
NB	7.6	1.6	0.370	0.27
TNT	8.8	1.6	0.428	0.42
2,4-DNT	10.5	1.9	0.509	0.39
Tetryl	7.3	2.1	0.359	0.56
2,6-DNT	10.2	2.8	0.495	0.61
2-NT	12.8	2.8	0.618	0.32
4-NT	13.8	3.1	0.667	0.45
3-NT	14.8	2.9	0.715	0.28

[a] Average Retention Time (RT) in minutes.
[b] Average Relative Retention Time (RRT) = analyte RT over the internal standard RT.
[c] Precision expressed as Range Percent Difference over 20 injections and 7 different concentrations.

The internal standard also provides the advantage of improved quantitation by establishing the linear relationship between an analyte concentration and its corresponding relative response, i.e., analyte response vs. internal standard response. This technique corrects for minor fluctuations in injection volume and sample preparation volume after the internal standard is added. And finally, the internal standard can be used to monitor injection precision during automatic (auto-injector) analysis runs.

SUMMARY

Method 8330 can be adequately adapted to a wide variety of matrices, including surface wipes, solid materials, plants, and TCLP extracts. Method performance, especially precision, can be improved through more rigorous preparation of soil/sediment samples prior to extraction and by double-extracting aqueous samples. Addition of an internal standard to sample extracts just prior to analysis provides more accurate qualitative identification of target analytes and improves quantitative analysis. Method 8330 has proven itself to be a rugged and reliable test for determining trace-level explosives in environmental investigations.

57 LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY OF HIGH-MOLECULAR-WEIGHT POLYCYCLIC AROMATIC HYDROCARBONS USING THE PARTICLE BEAM INTERFACE

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Most studies of polycyclic aromatic hydrocarbons (PAH) in environmental samples have focused on PAH containing five fused rings or less (MW < 300). Because of analytical difficulties, including low vapor pressure, lack of analytical reference standards, lower sample concentration, and the large number of isomeric possibilities, the higher molecular weight PAH (MW > 300) are seldom examined. There are no standardized methods for the measurement of high-molecular-weight PAH. Despite analytical difficulties, the presence of high-molecular-weight PAH has been demonstrated in many environmental samples including carbon black, coal tar, petroleum, diesel and other air particulates, and in soils. Although the number of toxicity studies on high-molecular weight PAH are limited, several dibenzopyrenes (MW 302) are known to be highly carcinogenic.

In this work, particle beam liquid chromatography/mass spectrometry (PB LC/MS) was investigated as a means to measure high-molecular-weight PAH. Instrument performance was evaluated with 17 PAH covering the molecular weight range 300 to 450 amu. The PAH were separated by conventional high performance liquid chromatography (HPLC) using a polymeric octadecylsilica (C-18) packing (Vydac 201-TP) and gradient elution with methanol/tetrahydrofuran (THF). Instrument detection limits as measured by selected ion monitoring (SIM) on the singly charged molecular ion of each PAH were found to be 0.15 to 0.6 ng on column for PAH up to 352 amu and 2 to 4 ng on column for PAH greater than 352 amu. Linear response was observed for those PAH with molecular weight 300 to 352 amu over the concentration range 0.05 to 5.0 ug/mL. Non-linear response was observed for PAH with molecular weight greater than 352 amu over the concentration range 0.25 to 25 ug/ml. The PB electron ionization (EI) mass spectra of the PAH were found to be variable with the ion distribution ratio of the singly charged molecular to the doubly charged molecular ion being dependent on molecular weight, ion source temperature, and on concentration. Particle beam negative chemical ionization (NCI) of the PAH was also examined. Substantial signal enhancement (10 to 600 fold) was observed but found to be highly dependent on the amount of THF in the mobile phase.

Notice: Although the research described in this abstract has been funded wholly by the U.S. EPA through contract #68-CO-0049 to Lockheed, it has not been subjected to agency review. Therefore, it does not necessarily reflect the views of the agency.

58 Quantitation of Pentachlorophenol (PCP) by a Rapid Magnetic Particle-Based Solid-Phase ELISA in Water and Soil.

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ABSTRACT

Traditional testing methods for pentachlorophenol (PCP) are time consuming, expensive and require specialized instrumentation. Immunochemical assays provide methods that are sensitive, rapid, reliable, which are suitable for lab and field analysis. A magnetic particle-based ELISA for the determination of PCP in water and soil samples has been developed. Paramagnetic particles, used as the solid support, allow for precise antibody addition and superior assay kinetics. The assay procedure and detailed performance characteristics, including correlation with GC/MS and HPLC, are discussed. The method has a test range of 0.06 to 10 ppb in water, and typical within assay %CV of less than 10%. Recovery studies averaged 105%. The application of this method permits cost-effective evaluation of samples without solvent disposal and can result in savings of time and money.

INTRODUCTION

Pentachlorophenol (PCP) is used worldwide in commercial wood treatment, paper production, the leather industry (as a preservative and fungicide), and agriculture (as an insecticide and herbicide). Its extensive use has made PCP an ubiquitous environmental pollutant; the chemical has been found in water, soil, food, and air, often in high concentrations. Like many organochlorine compounds, PCP has toxic effects in humans. It is rapidly absorbed through the skin, respiratory and gastro-intestinal tract, inducing skin rashes, respiratory diseases, increased hepatic enzyme activity and renal failure.

Pentachlorophenol is one of the compounds regulated by USEPA under the NPDWR with a Maximum Contaminant Level of 1 ppb in drinking water. Under the RCRA Program (Toxicity Characteristic), the maximum concentration of PCP allowable in solid waste is 100 ppm.

The principles of enzyme linked immunosorbent assays (ELISA) have been described (Hammock and Mumma, 1980). Magnetic particle-based ELISA's have previously been described and applied to the detection of pesticide residues (Itak et al, 1993; Lawruk et al, 1993; Itak et al, 1992; Lawruk et al, 1992; Rubio et al, 1991). These ELISAs eliminate the imprecision problems that may be associated with antibody coated plates and tubes (Harrison et al, 1989; Engvall, 1980) through the covalent coupling of antibody to the magnetic particle solid-phase. The uniform dispersion of particles throughout the reaction mixture allows for rapid reaction kinetics and precise addition of antibody. The PCP magnetic-based ELISA described

in this paper combines an antibody specific for PCP with enzyme labeled PCP. The presence of PCP in a sample is visualized through a colorimetric enzymatic reaction and results are obtained by comparing the color in sample tubes to those of calibrators.

MATERIALS AND METHODS

Amine terminated superparamagnetic particles of approximately 1 um diameter were obtained from Advanced Magnetics, Inc. (Cambridge, MA). Glutaraldehyde (Sigma Chemical, St. Louis, MO). Rabbit anti-PCP serum and PCP-HRP conjugate (Ohmicron, Newtown, PA). Hydrogen peroxide and TMB (Kirkegaard & Perry Labs, Gaithersburg, MD). PCP and related compounds, as well as non-related cross-reactants (Chem Service, West Chester, PA).

The anti-PCP coupled magnetic particles were prepared by glutaraldehyde activation (Weston and Avrameas, 1971). The unbound glutaraldehyde was removed from the particles by magnetic separation and washing four times with 2-(N-morpholino) ethane sulfonic acid (MES) buffer. The PCP antiserum and the activated particles were incubated overnight at room temperature with agitation. The unreacted glutaraldehyde was quenched with glycine buffer and the covalently coupled anti-PCP particles were washed and diluted with a Tris-saline/BSA preserved buffer.

Water samples (200 uL) and horseradish peroxidase (HRP) labeled PCP (250 uL) are incubated for 30 minutes with the antibody coupled solid-phase (500 uL) (step 1). A magnetic field is applied to the magnetic solid-phase to facilate washing and removal of unbound PCP-HRP and eliminate any potential interfering substances (step 2). The enzyme substrate (hydrogen peroxide) and chromogen (3,3',5,5'-tetramethyl benzidine [TMB]) are then added and incubated for 20 minutes (step 3). The reaction is stopped with the addition of acid and the final colored product is analyzed using the RPA-I RaPID Analyzer™ by determining the absorbance at 450 nm. The observed absorbance results were compared to a linear regression line using a log-logit standard curve prepared from calibrators containing 0, 0.1, 2.0, and 10.0 ppb of PCP. If the assay is performed in the field (on-site), a battery powered photometer such as the RPA-III™ is used.

When analyzing soil samples, a simple extraction is performed prior to analysis: 10 g of soil is shaken for 30 minutes (extractions as short as 1 minute could be performed) with 20 mL of a solution of 0.5% sodium hydroxide/75% methanol/25% water (w/v/v). After settling, the sample supernatant is diluted at least 1:500 in pentachlorophenol zero standard and assayed as in the case of water samples.

RESULTS AND DISCUSSION

Figure 1 illustrates the mean standard curve for the PCP calibrators collected over 79 runs, error bars represent one standard deviation (SD). The displacement at the 0.1 ppb level is significant (86.9% B/Bo, where B/Bo is the absorbance at 450 nm observed for a sample or standard divided by the

absorbance at the zero standard). The assay sensitivity based on 90% B/Bo (Midgley et al, 1969) is 0.06 ppb.

A precision study in which surface and groundwater samples were fortified with PCP at 4 concentrations, and assayed 5 times in singlicate per assay, on five different days is shown in Table 1. Coefficients of variation (%CV) within and between day (Bookbinder and Panosian, 1986) were less than 13% and 12% respectively.

Correlation of twenty groundwater samples using values obtained by the ELISA method (y) and GC/MS EPA Method 625 (x) method is illustrated in Figure 2. The regression analysis yields a correlation of 0.980 and a slope of 1.08 between methods.

Table 2 summarizes the accuracy of the PCP ELISA. Added amounts of PCP (0.50, 1.50, 3.0, an 8.0 ppb) were recovered correctly in all cases with an average assay recovery of 105%.

Table 3 summarizes the cross-reactivity data using a variety of chlorophenol compounds. The percent cross-reactivity was determined as the amount of analogue required to achieve 90% B/Bo (Least Detectable Dose). Many non-structurally related agricultural compounds demonstrated no reactivity at concentrations up to 10,000 ppb (data not shown).

Table 4 indicates that no interferences are present from compounds commonly found in groundwater samples at concentrations much higher than usually found in those waters (American Public Health Association, 1989).

Recovery data from two different soil types (Plano loam and Sassafras sandy loam) fortified with pentachlorophenol at 5, 10, and 50 ppm is summarized in Table 5. To compare extraction efficiencies, soils were also extracted with methanol using a procedure similar to the procedure listed in materials and methods. Average recoveries of PCP for the spiked soils were 100% with NaOH/MeOH/H_2O and 78% with methanol.

To compare immunoassays results with HPLC, the same extracts prepared in the above soil recovery procedure were acidified with HCL and filtered thru 0.7 um glassfiber microfilters. Samples were analyzed by HPLC at the Air Pollution Lab of New Jersey Institute of Technology. Figure 3 shows good agreement (correlation = 0.977, slope = 0.975) between the immunoassay and HPLC methods for the twelve (12) spiked soil samples listed in Table 5.

SUMMARY

This work describes a particle-based ELISA for the detection of PCP and its performance characteristics using water and soil samples. The assay compares favorably to GC/MS and HPLC determinations, and eliminates the need for expensive instrumentation and solvent disposal. The ELISA exhibits good precision and accuracy which can provide consistent monitoring of environmental samples. Using this ELISA, fifty (50) results

can be obtained in less than one hour without the problems of variability encountered with antibody coated tubes and microtiter plates (e.g. coating variability, antibody leaching, etc.). This system is ideally suited for the adaptation to on-site monitoring of PCP in water, soil, and solid waste samples.

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Table 1

Pool Number	Pool 1	Pool 2	Pool 3	Pool 4
Replicates	5	5	5	5
Days	5	5	5	5
N	25	25	25	25
Mean (ppb)	0.51	1.67	3.16	8.63
% CV (within)	12.5	8.8	7.7	6.7
% CV (between)	11.4	8.6	1.8	3.2

Table 2

PCP added (ppb)	PCP observed (ppb)	SD (ppb)	% Recovery
0.50	0.49	0.09	98
1.50	1.63	0.17	108
3.00	3.34	0.29	111
8.00	8.43	0.71	105
Average			105

Table 3

Compound	90% B/Bo LDD (ppb)	50% B/Bo (ppb)	% Cross Reactivity
Pentachlorophenol	0.06	2.20	100
2,3,5,6-Tetrachlorophenol	0.21	4.06	54.1
2,3,3,6-Tetrachlorophenol	0.91	14.6	15.1
2,3,6-Trichlorophenol	2.44	62.9	3.4
2,3,5-Trichlorophenol	1.52	119	1.8
Tetrachloro-hydroquinone	8.7	148	1.4
2,4,6-Trichlorophenol	15.1	463	0.5
2,4,5-Trichlorophenol	21.5	574	0.4
2,3,4-Trichlorophenol	53.2	1730	0.1
2,5-Dichlorophenol	62.9	7830	0.03
2,6-Dichlorophenol	266	5990	0.04
2,3-Dichlorophenol	611	>10000	<0.02
2,4-Dichlorophenol	887	>10000	<0.02
3,5-Dichlorophenol	1670	>10000	<0.02
Hexachlorobenzene	1560	>10000	<0.02
Hexachlorocyclo-hexane	5790	>10000	<0.02
3,4-Dichlorobenzene	NR	NR	<0.02
4-Chlorophenol	NR	NR	<0.02
Pentachlorobenzene	NR	NR	<0.02
Pentachloronitro-benzene	NR	NR	<0.02

Table 4

Compound	Max. Conc. Tested	Interference
Nitrate	250 ppm	No
Copper	250 ppm	No
Nickel	250 ppm	No
Thiosulfate	250 ppm	No
Sulfite	250 ppm	No
Sulfate	10,000 ppm	No
Iron	250 ppm	No up to 50 ppm
Magnesium	250 ppm	No
Calcium	500 ppm	No
NaCl	1.0 M	No up to 0.65 M
Humic acid	250 ppm	No up to 10 ppm
Silicates	2500 ppm	No up to 1000 ppm
Zinc	250 ppm	No
Mercury (+2)	250 ppm	No
Phosphate	250 ppm	No
Manganese	250 ppm	No

Table 5

Extractant	Soil Type	PCP Spiked (ppm)	PCP Observed (ppm)	Recovery (%)
Methanol[1]	Plano loam	0	nd	---
		5	2.6	52
		10	7.7	77
		50	40.1	80
Methanol	Sassafras sandy loam	0	nd	---
		5	5.0	100
		10	8.6	86
		50	36.8	74
			Average	78
$NaOH/MeOH/H_2O$[2]	Plano loam	0	nd	---
		5	5.5	110
		10	8.8	88
		50	47.2	94
$NaOH/MeOH/H_2O$	Sassafras sandy loam	0	nd	---
		5	5.5	110
		10	10.5	105
		50	47.6	95
			Average	100

nd = below LDD of assay
1 Methanol = 100% methanol
2 $NaOH/MeOH/H_2O$ = 0.5% NaOH/75% MeOH/25% H_2O (w/v/v)

Magnetic Particle Immunoassay

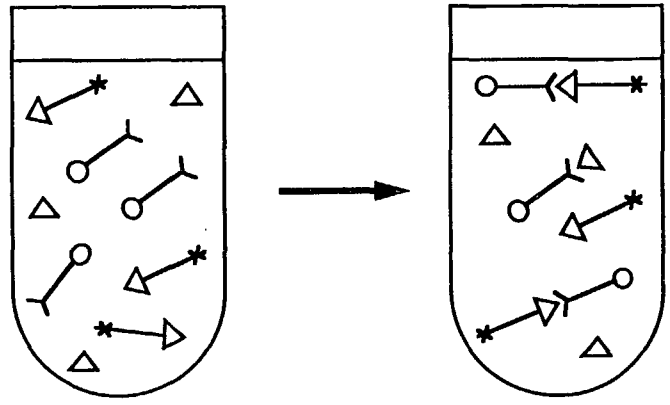
Magnetic Particle with Antibody Attached

Pesticide Conjugated with Enzyme

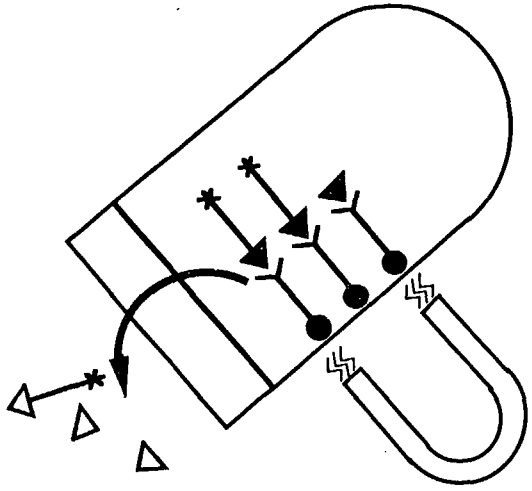
Pesticide

Chromogen/Substrate

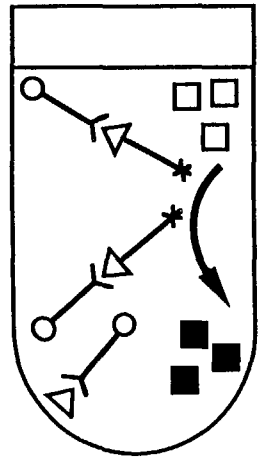
Colored Product



1. Immunological Reaction



2. Separation



3. Color Development

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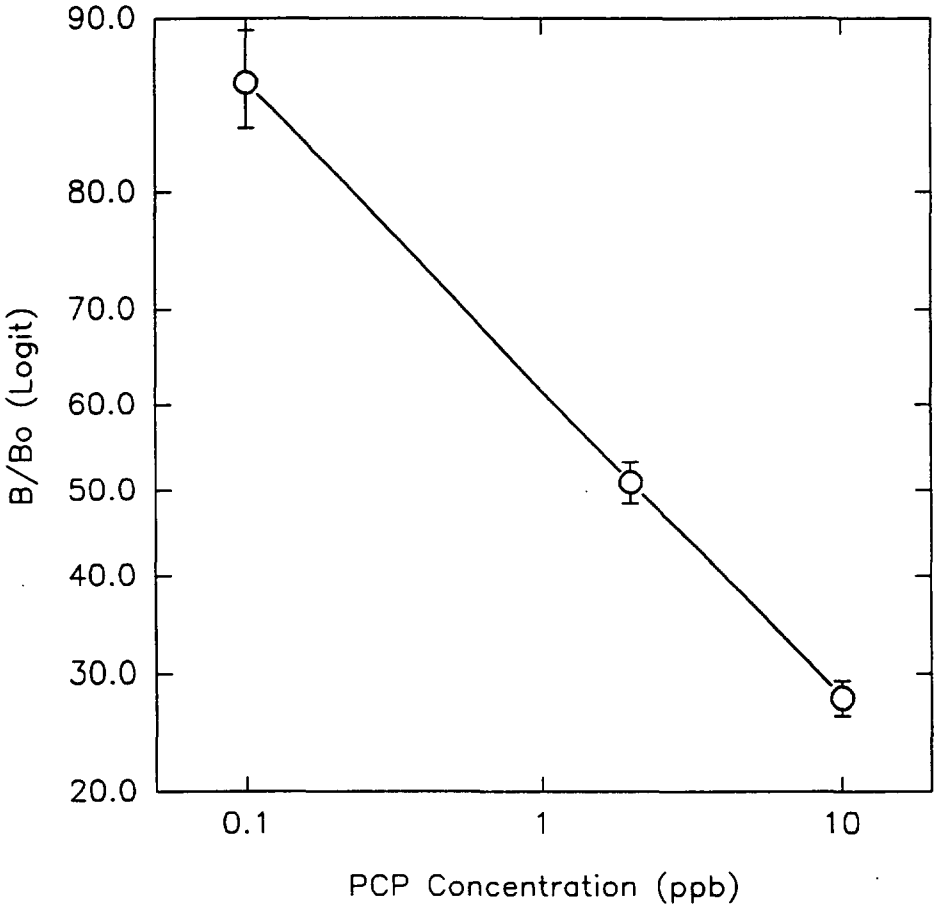

Figure 1. Dose response curve for PCP. Each point represents the mean of 79 determinations. Vertical bars indicate +/- 1 SD about the mean.

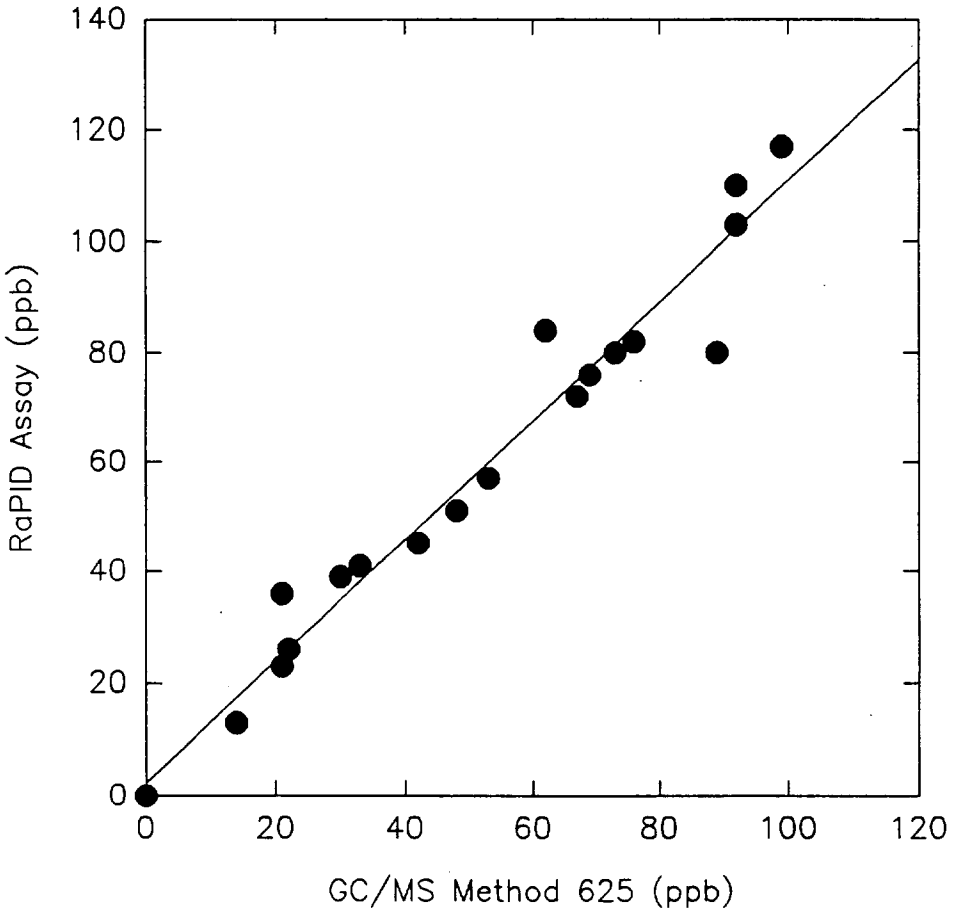

Figure 2. Correlation between PCP concentrations as determined by ELISA and GC/MS method 625, in water samples. n = 20, r = 0.980, y = 1.08 + 2.30

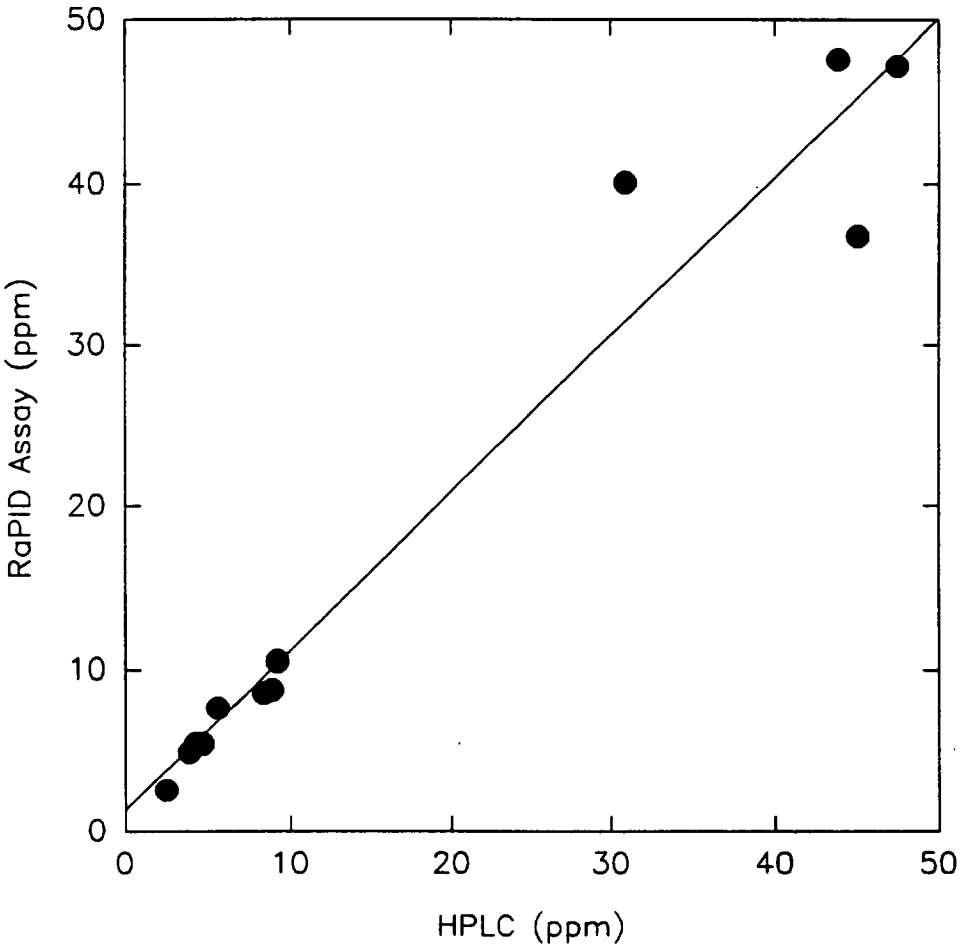

Figure 3. Correlation between PCP concentrations as determined by ELISA and HPLC in soil samples. n = 12, r = 0.977, y = 0.98 + 1.39.

59 CHROMATOGRAPHIC OPTIMIZATION FOR THE ANALYSIS OF AN EXPANDED LIST OF VOLATILE ORGANIC POLLUTANTS

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Volatile organic analysis (VOA) is one of the most common environmental test procedures for analysis of pollutants in air, water and soil. Current methodology specified in EPA methods involves concentrating the trace volatile organics onto an adsorbent material and then thermally desorbing them onto a chromatographic column. The list of target compounds to be analyzed are similar for air, water and soil matrices and there are indications that additional compounds will be added to the target compound lists in the future. When the target lists of EPA methods TO-14, 524.2, 624, 8240 and 8260 are combined, including various surrogates and internal standards, the list contains over 100 compounds. Resolution of all of these compounds in a single chromatographic analysis can be difficult if not impossible, however, through proper column selection and chromatographic optimization most compounds can be resolved.

This paper will describe a new technique for GC method development using thermodynamic retention indices and computer modeling of the chromatographic process. From the compound retention times using two different chromatographic analyses, it is possible to predict the best oven temperature and flow conditions for the target volatile compounds. This greatly simplifies the task of optimizing the GC method development, especially for complex mixtures. The application of thermodynamic retention indices will be demonstrated for the analysis of an expanded list of volatile organic compounds. Examples will be shown using the 502.2 and 624 stationary phases which are the most commonly used phases for these analyses.

60

APPLICATION OF SW-846 METHODS TO THE IDENTIFICATION OF UNUSUAL BROMINATED COMPOUNDS IN HIGH-CONCENTRATION PROCESS STREAMS.

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Abstract

This presentation reports work performed to characterize manufacturing residuals containing brominated and other organic compounds. SW-846 methods were used for analysis of volatile and semi-volatile organics and selected metals. Methods developed for the TSCA testing program were used for analysis of brominated dioxins and furans. Metals analysis was performed using ICP/MS instrumentation to utilize its superior dynamic range. However, it was found that selenium could not be reliably determined by this method because of interference from bromine isotopes of similar atomic mass. GFAA was evaluated as a specific confirmatory method for selenium in this environment. It was also noted that the use of SW-846 methods 8260 and 8270 as written may not provide the level of QC needed for complete evaluation of the volatile and semivolatile organic data. To quantify the predominant organic compounds in the samples collected, significant dilutions were required resulting in loss of some spike recovery data. The paper presents options for sample extraction and analysis which may assist in overcoming these difficulties.

Introduction

The purpose of this presentation is to describe some special challenges that were encountered in analyzing a series of high-concentration industrial wastes containing brominated compounds.

Background

A study of flame retardant manufacturing resulted in a need to sample several process waste streams containing brominated compounds. These samples were analyzed for volatile and semi-volatile organics, metals, and brominated dioxins and furans. Several aspects of this work were unusual and demonstrated issues not normally encountered in analysis of other industrial wastes or environmental media:

- Brominated dioxins and furans were suspected to be present in these samples and newly developed methods were used to identify and quantitate these species.
- It was found that bromine present in the samples interfered with the determination of selenium by ICP-MS.
- Many of the samples contained elevated concentrations of one or two semivolatile organics which made determination of other species more difficult.
- Some samples consisted of 20% NaOH, making field adjustment of pH impossible and complicating laboratory handling.

Dioxins/Furans

SW-846 Method 8290 addresses the determination of chlorinated dioxins and furans in solid wastes, but does not include their brominated analogs. Methods have been developed for these compounds [1-3] to meet the requirements of EPA's dioxin product test rule (40 CFR §766). Methods development was sponsored by the Brominated Flame Retardant Industry Panel (BFRIP). In this work, we applied these methods to industrial wastes. Some samples contained brominated diphenyl ether flame retardants, which could interfere with the determination of the furans. The methods include HPLC cleanup procedures to remove these compounds.

A typical mass of spectrum of 1,2,3,7,8-pentabromodibenzofuran is shown in Figure 1. Criteria ions used for identification of this compound are as follows:

Mass	Composition	Abundance[1]
559.608	$C_{12}H_3{}^{79}Br_4{}^{81}BrO$	0.51
561.606	$C_{12}H_3{}^{79}Br_3Br_2O$	1.00
563.604	$C_{12}H_3{}^{79}Br_2{}^{81}Br_3O$	0.98

[1] Theoretical abundance relative to peak at 561.606

Brominated compounds are immediately recognizable in a mass spectrum because the element consists of two isotopes of almost equal abundance (50.54% ^{79}Br and 49.46% ^{81}Br) giving rise to series of doublets, triplets, etc. Note that the major ions present have almost twice the mass of those which would be seen in the spectrum of the corresponding chlorinated dibenzofuran.

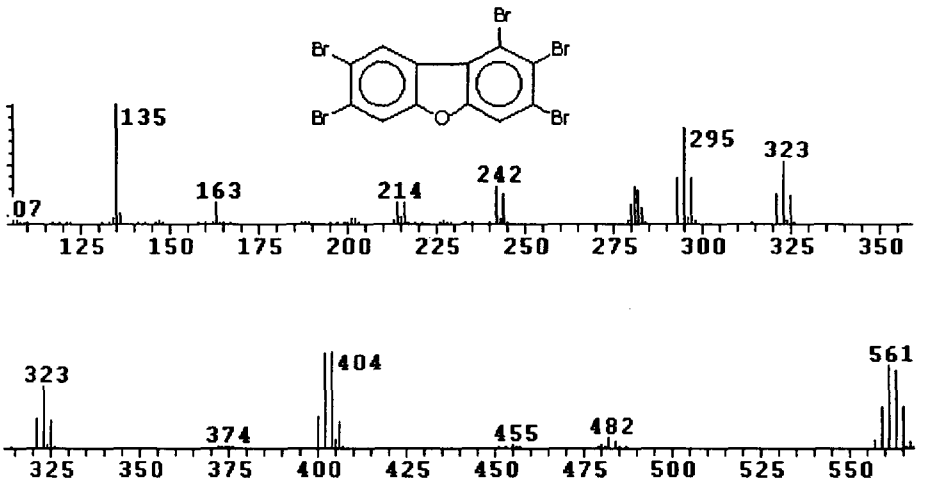

Figure 1. Mass Spectrum of 1,2,3,7,8-Pentabromodibenzofuran (*Courtesy of Mike Re, Radian Corporation*)

A unique problem encountered in the application of these methods is the fact that methylene bromide, the extraction solvent of choice, is not available commercially in the same high purity as methylene chloride. The analyst may have to purify the methylene bromide and verify that it is free of contaminants before beginning sample extractions.

ICP/MS

All of the metals included in the definition of the Toxicity Characteristic, except mercury, were quantitated using Method 6020 (ICP-MS). This method generally gives superior detection limits together with broad dynamic range. However, we found that this method cannot be applied to the determination of selenium in samples containing bromine because of mass-number interference. Selenium has six stable isotopes which span the same range as the isotopes of bromine:

Isotope	Mass	% Abundance
^{74}Se	73.9225	0.9
^{76}Se	75.9192	9.0
^{77}Se	76.9199	7.6
^{78}Se	77.9173	23.5
^{79}Br	78.9183	50.69
^{80}Se	79.9165	49.8
^{81}Br	80.9163	49.31
^{82}Se	81.8167	9.2

Initial analytical data indicated high levels of selenium in the samples. Figure 2 shows a portion of the ICP-MS spectrum of one of these samples compared with a calibration blank. Peaks which appear to represent selenium isotopes are clearly evident. A thorough review of the inputs to the flame retardant manufacturing processes revealed no sources of the metal. Additional work performed using Method 7740 (GFAA) showed no detectable levels of selenium, indicating that Method 6020 was subject to interference. However, the detection limits for Method 7740 were not as low as those found using ICP-MS instrumentation.

QA/QC issues

Several of the samples analyzed in this study contained percent levels of semivolatile organics, including solvents and solid flame retardants. Significant dilutions were required to quantify the predominant organic compounds, resulting in loss of surrogate and matrix spike recovery data. Two samples precipitated crystalline solids during initial preparation. Probe MS was used to identify these solids as tetrabromobisphenol A. Recrystallization and HPLC techniques were used to reduce the concentration of this compound so that the extract could be analyzed for other analytes present at lesser concentrations.

An alternative would be to increase the level of spiking based on preliminary screen (e.g., by GC/FID or GC/ECD) to ensure measurable recoveries even at high sample dilutions. This would be applicable to matrices where the analytes of primary interest are present in elevated concentrations in the sample. Screening analyses are in any case highly advisable when studying process waste samples.

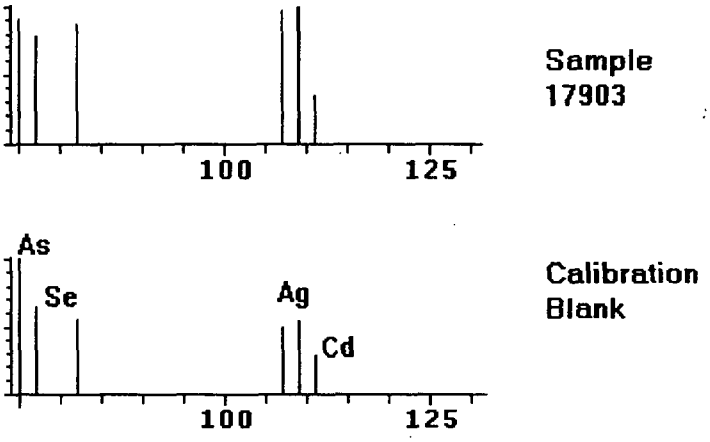

Figure 2. ICP-MS Spectrum of (*top*) a brominated sample containing no selenium, and (*bottom*) the calibration blank.

Acknowledgements

The authors wish to thank Edwin Rissmann, U.S. Environmental Protection Agency, Bruce Colby and the staff of Pacific Analytical Incorporated, Mike Re, Radian Corporation, and Siu-Fai Tsang, SAIC, for their assistance and guidance during this project.

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61 RESULTS OF LABORATORY TESTS OF THE ACCELERATED ONE-STEP™ LIQUID-LIQUID EXTRACTOR

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ABSTRACT

A series of experiments were conducted using the Corning Accelerated One-Step™ liquid-liquid extractor/concentrator for BNA and TPH analyte isolation on real samples. The results indicate the device gives comparable results to the traditional designs of continuous liquid-liquid extractors in a fraction of the time and solvent usage. The device was evaluated as a replacement for the separatory funnel liquid-liquid technique, and for the most part offers distinct advantages.

INTRODUCTION

Continuous liquid-liquid extractors play a key part in the laboratory analysis of extractable semivolatile organics such as PAHs, PCBs, chlorinated insecticides, acidic herbicides, phthalates, and a host of other pollutants from industrial wastewaters. Use of the extractors avoids formation of intractable emulsions, a common problem in the separatory funnel liquid-liquid extraction methods. Further the extractors are not prone to unexpected selective retention of target analytes or plugging due to particulates, as are the proposed solid phase extraction devices. However, the major drawback to the use of continuous liquid-liquid extractors is the 18-24 hours required for an extraction. This is particularly a problem when the sample must be made acidic, extracted, then made basic and re-extracted. A second problem is the decomposition of sensitive target analytes in the strongly basic or acidic solution during the lengthy extraction. A third, and potentially the worst problem, is the relatively large volumes of chlorinated solvents which are used and which must be either disposed or recycled at the end of the extraction.

In 1991 Corning Glass Works invented a fundamental modification of the continuous liquid-liquid extractor, by addition of a hydrophobic membrane to the bottom of the extraction chamber. The membrane allows passage of non-polar organic solvents and dissolved materials, while retaining polar and aqueous liquids. Use of the membrane eliminates the solvent pool at the bottom of the extraction chamber and renders obsolete the solvent siphon tube. The membrane serves a second function in drying the solvent as it passes through, eliminating the need for sodium sulfate drying columns after the extraction process.

Analytical Services, Inc. began testing the Accelerated One-Step™ Extractor in January, 1993. Objectives of the test experiments were to determine the amount of time necessary for extraction of analytes, determine the range of extractions which could be performed with the device, examine which solvents were compatible with the device and produce date comparing the effectiveness of the device with the liquid-liquid separatory funnel and more tradition continuous liquid-liquid extractors. The results of these test objectives and some observations of the device in use are the subject of this paper.

METHODS AND MATERIALS

BNA surrogates, matrix spike solutions and internal standards were purchased as concentrates from Supelco (Belafonte, PA) or Ultra Scientific (Kingston, RI) and were those specified in SW-846, 3rd Edition, Final Update. Methylene chloride, 1,1,2-trichlorotrifluoroethane (Freon 113™), carbon disulfide, acetone and hexane were of the highest quality available (Pesticide Residue grade or Nano-grade™) from Fisher Scientific. All volumetric measurements were performed in Class A volumetric glassware. BNA analyses were performed by EPA method 8270A, 1990 on a Hewlett-Packard 5890A, Series II GC with 5971 Mass Selective detector. The capillary column used was a Hewlett-Packard HP5-MS column. Daily QC acceptance criteria for DFTPP tuning,

SPCC, and CCC were met prior to analysis, as specified in the method. TPH analyses were performed by modified EPA method 418.1.
The extractor was cleaned prior to each use with detergent, brush and hot water, rinsed with hot water, rinsed with chromic acid solution, rinsed with hot water, rinsed twice with DI (organic free) water and allowed to air dry. Immediately before use it was rinsed with the extraction solvent. The membrane was rinsed immediately prior to use with the extraction solvent. After assembly (3 to 5 Teflon™ boiling chips were added to the concentrator flask), 50 mL of solvent was added to the extraction chamber with the stopcock closed. The sample was added to the extraction chamber, then the container rinsed with 50 mL of the extraction solvent which was added to the chamber. The surrogates and/or matrix spikes were added to the sample with a volumetric pipet followed by pH adjustment with 1:1 sulfuric acid or 10 *M* sodium hydroxide. pH was read with wide range paper. The stopcock was opened and about half of the solvent was allowed to drain into the concentrator flask. Heat was applied to the concentrator flask. Extraction times were established from the first drops of solvent to fall from the condensor into the sample. At that time the stopcock was opened and all the solvent allowed to drain into the concentrator. A distillation rate of 15 to 25 mL per minute was maintained. At the end of the extraction the stopcock was closed and the solvent concentrated to about 10 mL, at which time the heat source was removed. The apparatus was allowed to cool, then the concentrator was removed. The solvent was removed to 2 mL under nitrogen blowdown. The concentrate was quantitatively transfered to a Class A 2 mL volumetric ground glass stoppered tube which had previously been calibrated at the 1.00 mL level. The sample was reduced to 1.00 mL with nitrogen blowdown, internal standards were added and the sample sealed and shaken followed by transfer to an autosampler vial for analysis. TPH extractions were similar except there was no solvent concentration.

RESULTS AND DISCUSSION

The first set of experiments were performed by adding acid matrix spike (200 ng in methanol per method 3500) and BN surrogate (100 ng in methanol per method 3500) compounds to DI water at neutral pH and extracting them with methylene chloride for 1, 2, 4 and 16 hours. The results are in Table 1 with example plots shown in Figures 1 and 2 . The point at time 30 hours (PES) represents the results of a post-extraction spike and analysis of the surrogate mixture. Poor results were obtained for the acidic spikes (phenol, 2-chlorophenol, 4-chloro-3-methylphenol and 4-nitrophenol) as expected for pH 7. The BN surrogates (nitrobenzene -d_5, 2-fluorobiphenyl and terphenyl-d_{14}) were recovered with above 90% efficiency within 4 hours. Surprisingly pentachlorophenol was recovered in 90% efficiency in 4 hours at pH 7 (Figure 3).

Time	1	2	4	18	PES
Compound					
Phenol	35.1	61.3	58.8	69.1	194
2-Chlorophenol	18.8	43.2	37.6	40.1	172
Nitrobenzene d5	45.3	72.2	91.5	93.0	95.4
4-Cl-3-methylphenol	8.85	23.8	14.5	-	168
2-Fluorobiphenyl	56.9	75.8	90.9	90.6	99.8
4-Nitrophenol	23.2	45.2	66.7	86.3	174
Pentachlorophenol	52.9	123	175	192	195
Terphenyl d14	82.2	74.9	86.4	86.6	82.1

Table 1. Acid matrix spike compound and BN surrogate recoveries (ng) for extractions at various times (hours) at pH 7.

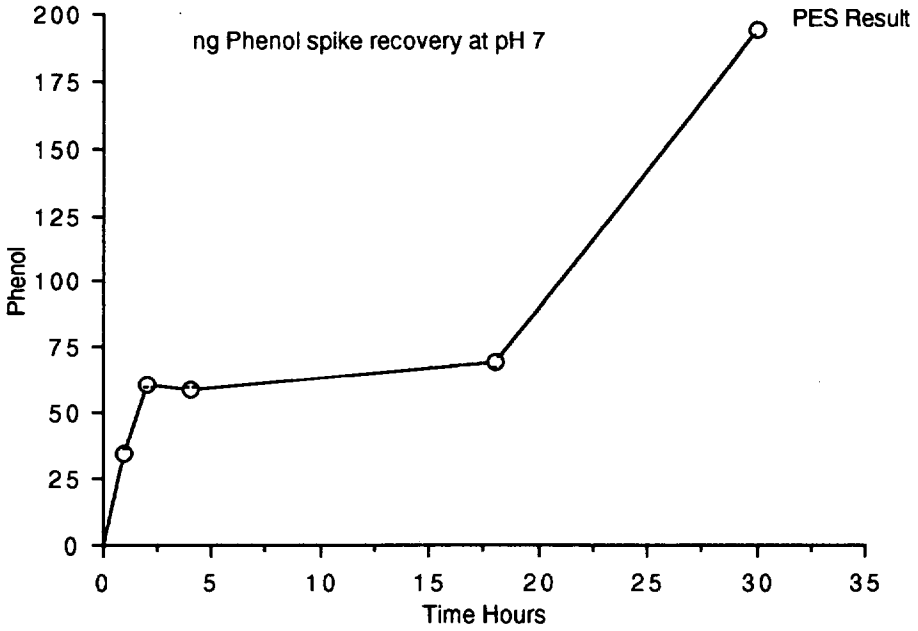

Figure 1. Phenol recovery (in ng) vs. time (hours) extracted at pH 7. The PES represents the amount of spike placed in the extractor as determined by neat analysis.

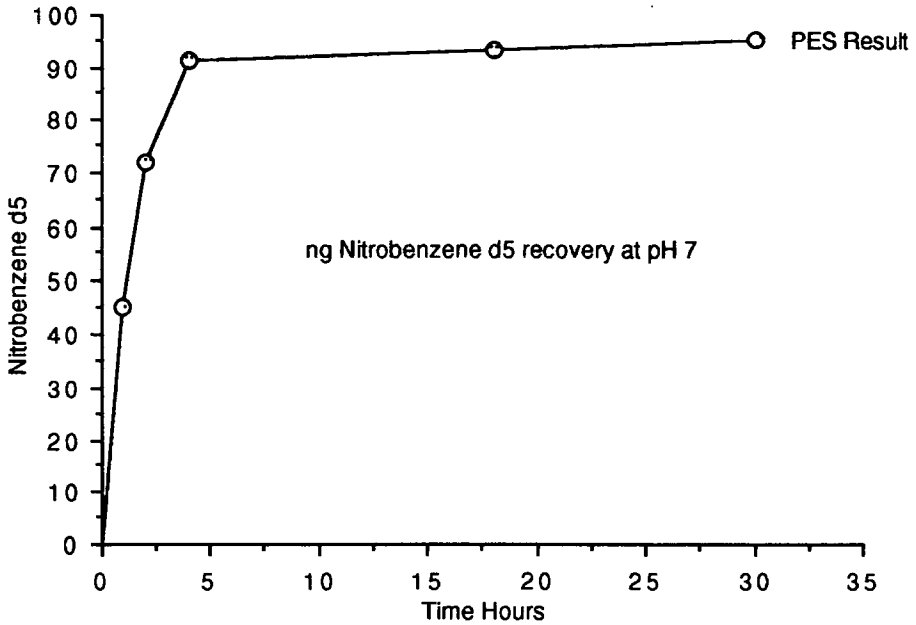

Figure 2. Nitrobenzene d_5 recovery (ng) vs. time (hours) extracted at pH 7. The PES represents the amount of spike placed in the sample as determined by neat analysis.

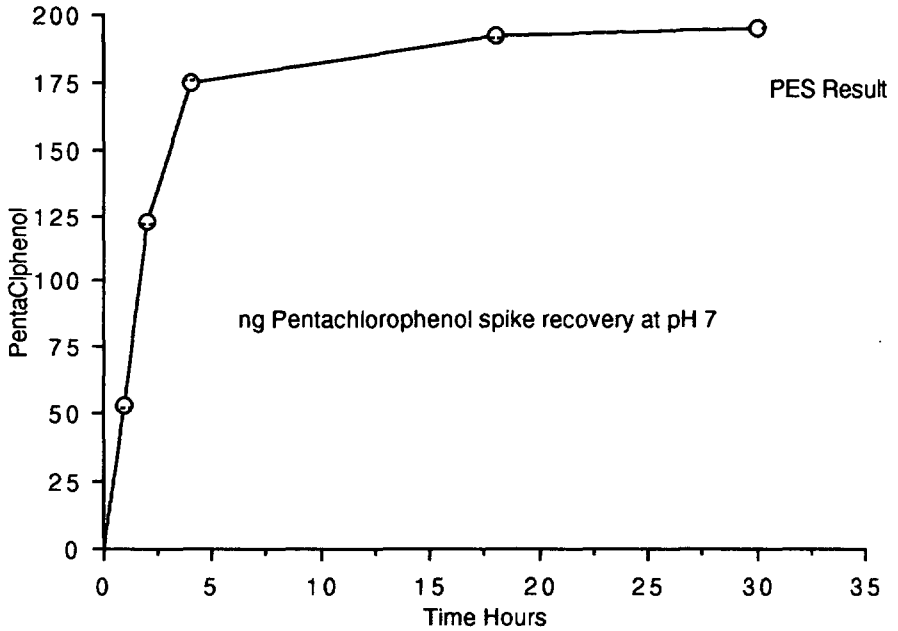

Figure 3. Pentachlorophenol recovery (ng) vs. time (hours) extracted at pH 7. The PES represents the amount of spike placed in the extractor as determined by neat analysis.

The experiment was repeated with initial acidification to pH < 2 with extraction times of 1, 2, and 4 hours. Over 80% recoveries of all phenolic compounds (Table 2.), except 4-nitrophenol, were obtained, as illustrated for phenol (Figure 4). The 4-nitrophenol results are illustrated in Figure 5. These results indicated that 4 hours extraction for each pH change would give suitable results.

Time	1	2	4	PES
Compound				
Phenol	105.7	131.9	165.2	188.4
2-Chlorophenol	127.2	144.8	165.2	185.1
Nitrobenzene d5	69.2	85.7	92.3	98.4
4-Cl-3-methylphenol	128.3	165.8	190.9	191.4
2-Fluorobiphenyl	69.9	82.0	90.1	100.7
4-Nitrophenol	94.9	146.3	162.4	210.8
Pentachlorophenol	129.1	187.1	205.7	197.0
Terphenyl d14	72.5	80.2	92.6	89.1

Table 2. Acid matrix spike compound and BN surrogate recoveries (ng) for extractions at various times (hours) at pH <2.

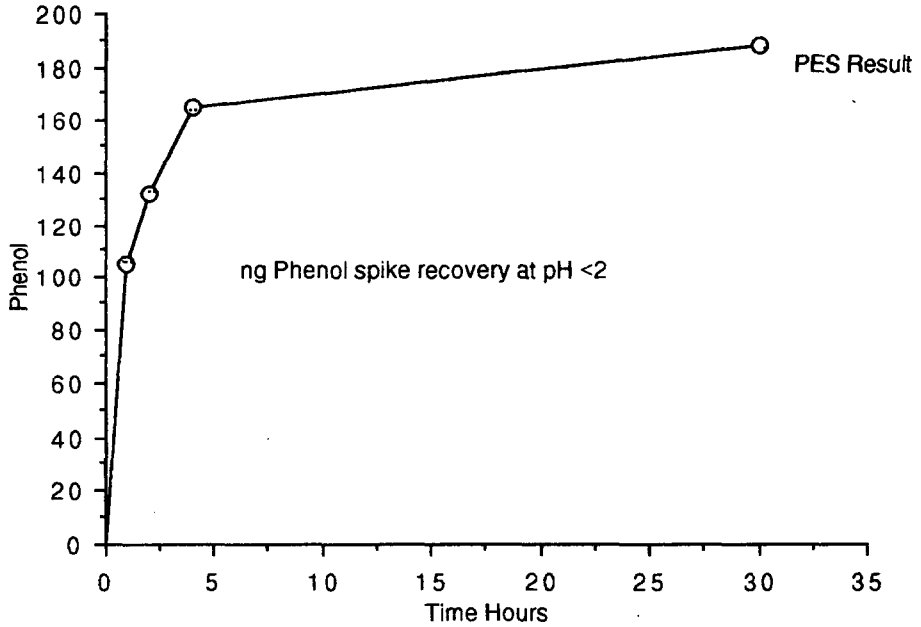

Figure 4. Phenol recovery (ng) vs. time (hours) extracted at pH <2. The PES respresents the amount of spike placed in the extractor as determined by neat analysis.

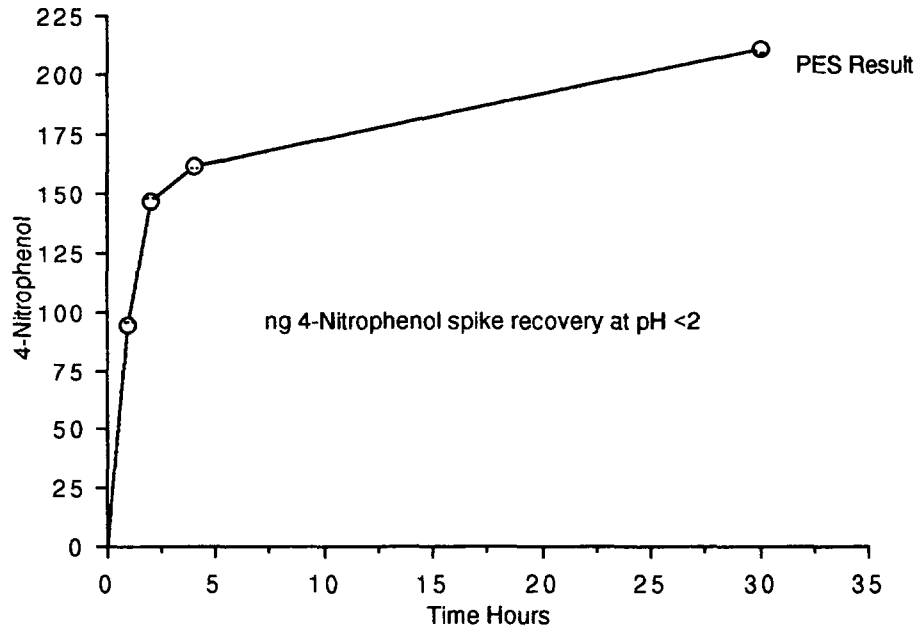

Figure 5. 4-Nitrophenol recovery (ng) vs. time (hours) extracted at pH <2. The PES respresents the amount of spike placed in the extractor as determined by neat analysis.

The extraction of TPH samples for IR analysis with Freon 113™ (1,1,2-trichlorotrifluoroethane) was examined. Spikes of the calibration standard mix (isooctane, hexadecane and chlorobenzene), were made into DI water and extracted for various times. The results are presented in Figure 6. The first three data points were collected and analyzed on one day and the 8 and 22 hour

extractions performed on another day. The results are equivalent given the ±10% acceptance criteria of the calibration curve and indicate that a 1 to 2 hour extraction time is suficient..

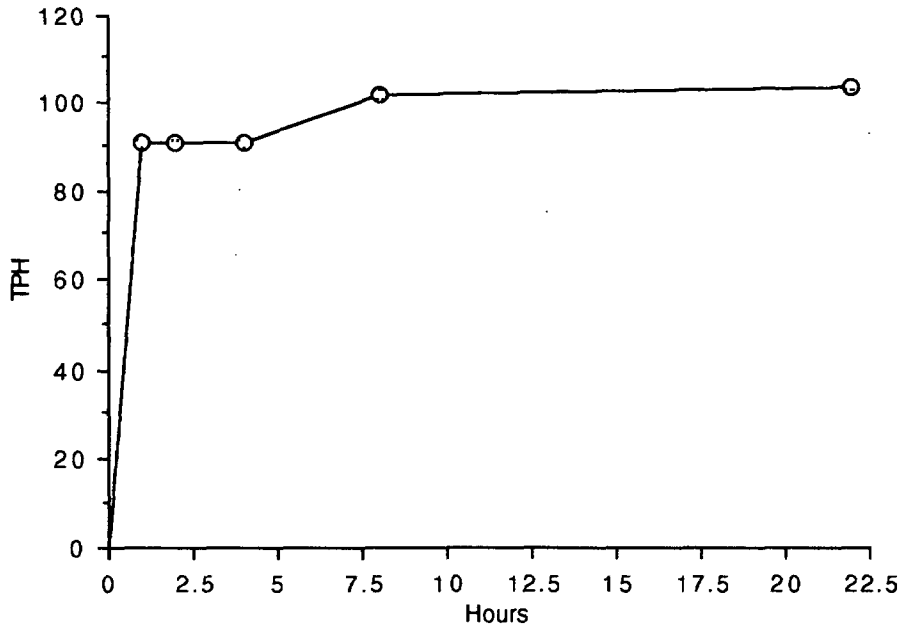

Figure 6. THP standard recovery (percentage) from DI water vs. duration (hours) of extraction using Freon 113 as the solvent.

The ability of the hydrophobic membrane to pass organic compounds was evaluated by placing 50 mL of a solvent in the extraction chamber and recording the time required to drain. The data are presented in Table 3. Most of the solvents tested passed through the membrane within the same time window, Freon 113 being marginally faster. As expected the hydrogen bonded solvent, *n*-butanol was significantly retarded. Carbon disulfide has been proposed as a possible Freon 113 replacement for the IR-TPH test, however it is not suitable for use with the Accelerated One-Step™ membrane, as shown in Table 3. Carbon disulfide is an opposite polarity compound (carbon is polarized negative and sulfur positive) as compared to the other halogenated and hydrocarbon solvents tested. These data support the observations of the lower extraction efficiency of the hydrogen bonding carbamates, amines and highly acidic phenols, such as the mono- and di-nitrophenols, as reported by Bruce (1993).

Solvent	Minutes.Seconds
Freon 113	8.45
Hexane	10.40
Benzene	16.07
Chloroform	11.43
Methylene chloride	9.55
tert-Butyl methyl ether	12.42
Acetone	10.17
n-Butanol	55.0
Carbon disulfide	< 10 mL after 55.0
Water	none after 120

Table 3. Time (minutes) for 50 mL of solvent to pass through the hydrophobic membrane of the Accelerated One-Step™.

A number of real samples were then extracted using 4 hours extraction times each for the acid and basic extractions. Two different samples, a TCLP extraction and a wastewater sample were performed as BNA matrix spike (MS) and matrix spike duplicate (MSD), as part of a normal batch of samples. The MS was extracted using the separatory funnel technique of Method 3510 with sodium sulfate drying column and Kuderna-Danish concentration, while the MSD was extracted using the One-Step™ extractor and direct concentration, followed by nitrogen blowdown. The results are presented in Table 4 and demonstrate that the One-Step™ extraction is at least as good as the separatory funnel technique of Method 3510 for normally encountered samples.

	TCLP Sample		Wastewater Sample	
Surrogate Compounds	Sep Funnel	One-Step™	Sep. Funnel	One-Step™
2-Fluorophenol	35	62	33	49
Phenol d5	28	79	25	65
Nitrobenzene d5	88	86	89	85
2-Fluorobiphenyl	75	83	82	77
2,4,6-Tribromophenol	84	89	75	81
Terphenyl d14	90	88	83	73
Matrix Spike Compounds				
Phenol	15	71	11	60
2-Chlorophenol	31	73	29	65
1,4-Dichlorobenzene	39	77	15	65
N-Nitrosodipropylamine	57	103	45	81
1,2,4-Trichlorobenzene	43	80	20	66
4-Chloro-3-methylphenol	35	86	26	85
Acenaphthene	49	88	45	79
2,4-Dinitrotoluene	42	74	42	80
4-Nitrophenol	14	74	15	75
Pentachlorophenol	48	97	39	78
Pyrene	55	83	44	77

Table 4. Comparison of percent recoveries of BNA matrix spike and surrogate compounds on the same samples using Method 3510 (separatory funnel) and the modified 3520 using the Accelerated One-Step™.

An industrial wastewater sample from a industrial cleaner formulator was analysed for acid extractables as a sample and as a matrix spike with separatory funnel extraction. Past history of the sample indicated it needed to be diluted 1:20 (50 mL sample to 950 mL DI water) to avoid swamping the GC/MS detector. The same sample at 1:20 dilution was extracted on 4 consecutive days as a BNA matrix spike with the Accelerated One-Step™. The results are presented in Table 5. The One-Step™ consistently produces higher recoveries of the more volatile compounds such as phenol, 1,2-dichlorobenzene, 2-chlorophenol and benzoic acid, while prerforming about as well as Method 3510 on the rest of the compounds.

Compounds	Sep. Funnel		Accelerated One-Step™			
Analytes	Sample	MS	MS1	MS2	MS3	MS4
1,2-Dichlorobenzene	32	32	97	97	91	65
2-Methylphenol	-	-	15	139	128	-
4-Methyl phenol	3	2	9	-	14	10
Isophorone	6	1	5	2	3	1
Benzoic acid	103	72	173	249	189	120
Naphthalene	4	3	7	8	7	5
Diethylphthalate	5	1	12	15	11	10
Di-n-butylphthalate	28	12	26	12	18	11
Bis(2-ethylhexyl)phthalate	4	3	6	7	5	1
Surrogates						
2-Fluorophenol	60	54	90	63	72	87
Phenol d5	80	74	201	176	182	168
Nitrobenzene d5	75	92	95	86	88	80
2-Fluorobiphenyl	58	47	59	49	55	35
2,4,6-Tribromophenol	177	153	157	148	146	128
Terphenyl d14	85	63	71	68	72	57
Matrix Spike Compounds						
Phenol	-	67	205	155	160	171
2-Chlorophenol	-	119	197	175	172	151
1,4-Dichlorobenzene	-	65	102	95	82	75
1,2,4-Trichlorobenzene	-	62	74	67	63	52
4-Chloro-3-methylphenol	-	162	182	177	173	165
Acenaphthene	-	53	68	57	67	44
2,4-Dinitrotoluene	-	63	77	79	82	73
4-Nitrophenol	-	48	116	119	132	131
Pentachlorophenol	-	130	88	85	94	77
Pyrene	-	47	71	63	73	47

Table 5. Comparison of recoveries of target analytes and matrix spike compounds for a strong industrial effluent processed with a separatory funnel by method 3510 and processed on 4 consecutive days with the Accelerated One-Step™ extractor. Acid compounds are spiked at the 200 ng level while BN compounds are at the 100 ng level.

A wastewater treatment plant sludge (6% solids) was extracted for BNA analysis using a continuous liquid-liquid extractor and the Accelerated One-Step™ extractor. Another portion of the same sample was diluted 1:30 with DI water and 1 L extracted using Method 3510 with a separatory funnel. The membrane of the Accelerated One-Step™ did not plug, however channeling of the solvent through the sludge was noticed. The surrogate recoveries for the three extraction techniques are presented in Table 6. Although none of the recoveries were quantitative, the Accelerated One-Step performed significantly better than the other two techniques.

	Sludge sample with 6% solids		
Surrogate Compounds	Sep Funnel	Cont. Liq-Liq	One-Step™
2-Fluorophenol	0	0	6
Phenol d5	5	14	26
Nitrobenzene d5	47	33	63
2-Fluorobiphenyl	27	31	60
2,4,6-Tribromophenol	2	3	49
Terphenyl d14	31	45	65

Table 6. Comparison of percentage suggogate recoveries of BNA separatory funnel, continuous liquid-liquid and Accelerated One-Step™ extraction of a sludge sample containing 6% solids. The separatory funnel extraction was performed on a 1:30 dilution of the sludge.

Three other wastewater samples have been extracted for BN or BNA analysis. The surrogate recoveries are presented in Table 7. In general, use of the Accelerated One-Step™ extractor gives recoveries which are comparable to those obtained using separatory funnel techniques in each respective batch.

Surrogate Compounds	41082-1	40619	40598-1
2-Fluorophenol	-	65 (56)	-
Phenol d5	-	93 (62)	-
Nitrobenzene d5	115 (121)	101 (108)	69 (73)
2-Fluorobiphenyl	105 (88)	74 (96)	69 (74)
2,4,6-Tribromophenol	-	105 (103)	-
Terphenyl d14	87 (98)	74 (79)	50 (61)

Table 7. Percentage surrogate compound recoveries for wastewater samples extracted and concentrated using the Accelerated One-Step™. Samples 41082-1 and 40598-1 were extracted for base/neutrals only. The values in parentheses are the average recoveries for the batch.

Two instances of membrane plugging were encountered. The first was a sample which contained a fine dense grit which coated the membrane and was not displaced by the methylene chloride solvent. The sample was successfully prepared by separating the solid from the liquid layer, separately extracting the solid with sonication and the liquid with the One-Step™, then combining the extracts. The second was a sample which formed a tenacious emulsion as the solvent fell from the condensor. The surface of the bubbles coated the membrane and stopped the flow of solvent through it. The sample had to be processed by continuous liquid-liquid extraction followed by removal of the large amounts of water in the extract by slurrying with sodium sulfate.

SUMMARY

The Corning Accelerated One-Step™ liquid-liquid extractor/concentrator has been shown to offer rapid extraction of target analytes with acceptable recoveries and minimal solvent usage as compared to more traditional liquid-liquid extractors. When compared to separatory funnel liquid-liquid extraction, the Accelerated One-Step™ is shown to be a viable alternate with demonstrated savings through reduced solvent usage and elimination of the drying column and Kuderna-Danish concentrator with no decrease in the recovery of most analytes.

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62 A MATCHED DUAL CAPILLARY COLUMN SYSTEM FOR PESTICIDES

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ABSTRACT

In early and existing GC pesticide analyses methods, packed columns were and are employed. The use of packed columns has, in many cases, given way to the use of Megabore (0.53 mm I.D.) columns in these methods. Many laboratories and regulatory agencies have realized that, relative to packed columns, Megabore columns offer greater reproduceability, longer lifetimes, increased resolution, and decreased overall analysis times.

Many laboratories, among them those doing pesticide analyses for the EPA and FDA, have both a high sample throughput and require quick sample turnaround times. It follows that any enhancement to the GC system that increases resolution and decreases run times will enhance the performance and profits of these laboratories. This decrease in run time becomes even more attractive if minimal to no hardware changes need be made. What follows is an experiment converting the chromatography of an EPA Contract Laboratory Program (CLP) Chlorinated Pesticide analysis currently done by two Megabore columns to an analysis utilizing two 0.32 mm I.D. columns. A reduction in run time of over 25% is realized while still maintaining the ability to use a Splitless or Megabore direct injection inlet.

INTRODUCTION

BACKGROUND

Quantitative and confirmatory qualitative information can be obtained for a list of analytes by running the analytes on two columns with significantly dissimilar stationary phases. Many state and federal regulatory agencies accept this data as conclusive. The benefit of single injection, dual column analysis is a time savings by having both quantitative and confirmatory qualitative information available from one run.

For example, from analysis of a sample using one column, tentative identification of the analyte of interest is made if its retention time matches the retention time of the standard run on that column. Quantitative confirmation the presence of that component on the column with the different stationary phase if the component's retention time also matches the standard's retention time on that column. If

components are resolved on both columns, quantitation data can be compared to insure quantitative accuracy. This technique becomes even more powerful if a selective detector is employed.

In the latest available version (OLM01.3, 2/91) of the CLP Chlorinated Pesticide Method, two 30 m x 0.53 mm I.D. columns with dissimilar stationary phases are used (DB-608, 50% phenyl 50% methyl polysiloxane; DB-1701, 14% cyanopropylphenyl, 86% methyl polysiloxane) and a selective detector (ECD) is employed in the analysis of 20 chlorinated pesticides. It was the purpose of this experiment to determine if two 0.32 mm I.D. columns of the same stationary phase type could be utilized in order to decrease the run time, while still meeting the required resolution criteria, and without changing hardware or increasing hardware costs.

INLET AND COLUMN CONNECTION CONSIDERATIONS

A number of different options were considered when designing this single injection, dual column system. Five criteria were used to evaluate certain inlet and column connection options. The inlet and column connection design had to be:

1) equal or lower in cost compared to the current low cost of a Megabore configuration--the least expensive mode,
2) adaptable to splitless or Megabore direct injectors since both injection techniques are currently in use,
3) highly inert (some analytes degrade easily when exposed to active sites) by eliminating any metal or other active sites in the sample flow path,
4) easily, reliabilly, and reproducibly installed,
5) amenable to the use of two 0.32 mm I.D. columns.

Table I is a report card of how each option scored in the above categories.

Table I

Option	Qualified	Unqualified
Graphpak Divider for Simultaneous Sampling to Two Capillary Columns (Hewlitt -Packard)	4,5	1,2,3
Injection Tee Kit for Simultaneous Analyses on Two Wide Bore Columns (Supelco)	1,3	2,4,5

Two Hole Ferrule	1,2,3,5	4
Deactivated Megabore Guard Column with a Deactivated 0.53/0.32/0.32 mm 3-Way "Y" Union	1,2,3,4,5	

To reduce activity, a deactivated, splitless liner would have been used if splitless injection mode was used. This particular experiment employed the Megabore direct injection mode as it was thought that this technique could potentially pose sample transfer and solvent front problems[1] that would not result from the use of the splitless mode (see "Inlet and Column Flow Considerations" below). A deactivated, Direct Flash Vaporization liner (J&W Scientific)--the type of liner that allows the Megabore guard column to seal into a tapered region below an expansion chamber--was used with the Megabore direct injection mode. The configuration decided upon is shown in Figure I.

COLUMN DIMENSION CONSIDERATIONS

Provided that temperature, phase ratio, stationary phase type, linear velocity, test compound, and length are kept constant--smaller diameter columns yield an increased number of theoretical plates and sharper peaks than larger diameter columns.

As a demonstration of this, two 30 meter, DB-608 columns of the same phase ratio but with differing diameters (0.53 and 0.32 mm I.D.'s) were tested under identical temperature, carrier gas, and linear velocity conditions. To simplify the mathematics, the equation used to describe the area of the Gaussian peak ideally obtained from a chromatogram was that of a triangle: Area = 1/2 Base x Height. Theoretical plates were determined using the same compound, and width was calculated using the following formula[2]:

$$w = 4t / n^{1/2}$$

where

w = width at the base of the peak
t = retention time of the peak
n = calculated theoretical plates

If the same amount is injected on each column, we will assume this amount generates the same number of area counts whether chromatographed using the 0.53 or 0.32 mm I.D. column. So if the area remains the same and the width of the peak decreases, the height of the triangle must increase.

So we can say that:

$$0.5 \times Base_{0.53} \times Height_{0.53} = 0.5 \times Base_{0.32} \times Height_{0.32}$$

or

$$Base_{0.53}/Base_{0.32} = Height_{0.32}/Height_{0.53}$$

The 0.53 mm I.D. column generated 40400 theoretical plates and the retention time of the test compound was 11.523 min., therefore the width of the base of this peak is 0.229 min. The height was set at 1 unit since we are trying to see the resulting ratio difference in height.

The 0.32 mm I.D. column generated 85100 theoretical plates and the retention time of the test compound was 11.460 min. which makes the base of the peak 0.157 min wide. Therefore, all of the above parameters remaining the same, the increase in the peak height resulting from the use of the 0.32 mm column as opposed to the 0.53 mm I.D. is approximately 1.5 for the same compound when using the triangle approximation. This figure cannot be exactly correlated to peaks of differing retention, or peaks eluting on the ramp portion of a temperature programmed run, but it does demonstrate a benificial peak height, or signal to noise increase which implies a resulting increase in system sensitivity when using a smaller, rather than a larger diameter column.

INLET AND COLUMN FLOW CONSIDERATIONS

With the above column considerations in mind, why not use 0.25 mm I.D. or smaller diameter columns in this single injection, dual column setup and really minimize run times and system sensitivity?

In order for sample transfer to occur efficiently (in a short period of time and with minimal band broadening) from a Megabore direct inlet to a column(s), their generally needs to be a minimum of 4-5 mL/min. of carrier flow through the inlet[3]. Therefore, the summed flow through the two columns must be at least 4-5 mL/min.

As demonstrated by Van Deemter curves[4], carrier gases have flow ranges for particular length, diameter, and film thickness columns in which they will yield the most efficient (greatest number of theoretical plates) chromatography. Table II shows what are considered general, effecient flow ranges for different diameter, length, and film thickness columns for components of varying retention using Helium or Hydrogen as a carrier gas[5].

Table II

Inner Diameter(mm)	He Efficient Flow Range (mL/min)	H_2 Efficient Flow range (mL/min)
0.25	0.9-1.3	1.3-1.8
0.32	1.4-2.2	2.2-2.9
0.53	4.0-6.0	6.0-7.9

Since most analysts doing the CLP Chlorinated Pesticide analysis are using Helium as a carrier gas, and since Helium's efficient flow range is lower than that of Hydrogen, Helium was considered the limiting parameter. It was selected as the carrier gas in this experiment as its lower efficient flow range could potentially cause flow problems in the Megabore inlet, or chromatography problems if it was necessary to operate above the efficient flow range to avoid inlet problems.

Allowing for the flow limitations of the Megabore inlet and the Helium carrier gas, it becomes apparent that the smallest diameter column that could be most efficiently employed in a single injection, dual column analysis is the 0.32 mm I.D. column, the efficient flow range for two columns summed being 2.8-4.4 mL/min.

If sample transfer problems from the inlet to the column exist, they would be manifested in two ways. First, if the solvent front interfered with the chromatography of the first eluting peak, it would tail, be excessively broad, and/or possibly rounded at the top, especially on the thinner film (0.25 μm) DB-1701 column. Second, if the flow through the inlet was inadequate, all peaks might tail.

ADDITIONAL COLUMN CONSIDERATIONS

There are a number of advantages, relavent to this experiment, that smaller diameter columns have over larger diameter columns of the same length and phase ratio. They produce less bleed because there is less stationary phase available to degrade. Under proper flow conditions, as demonstrated above, smaller diameter columns generally yield sharper peaks. Additionally, because there are more theoretical plates generated by smaller diameter columns, the same resolution can be achieved in a shorter period of time. This means compounds spend less time in the column and, since the width of a peak is directly related to the amount of time the compound spends in the column (the amount of time it has to diffuse longitudinally in the mobile phase), the compound suffers less from band broadening when it elutes earlier. For the same amount of analyte on column, this results in narrower, taller peaks. All of

these factors translate directly into a greater signal to noise ratio, and, more importantly, lower, more easily reached detection limits.

There are, however, relavent disadvantages of using smaller diameter columns as opposed to Megabore columns. Smaller diameter columns of the same phase ratio are generally fouled more quickly by non-volatile sample residues. This fouling can be minimized by the use of an adequate length of guard column and/or by the use of a plug of silanized glass wool in the inlet. Smaller diameters of the same phase ratio are also thought to be slightly more active than larger diameter columns because the thinner stationary phase allows the analytes more interactions with the surface of the fused silica tubing than with the thicker film Megabore columns. Also, assuming analytes are well separated from the solvent front on a 1 or 2μL injection, up to 8μL can be injected on a megabore column with a standard film thickness without significant negative chromatogrphic consequences (retention time shifts from run to run and noticeable band broadening of components). At most, only 3-4μL should be injected on the 0.32 mm I.D. dual column setup. So, if injection volumes greater than 3-4μL are normally used, the greater signal to noise generated by using a 0.32 as opposed to a 0.53 mm I.D. column would be somewhat negated.

MEETING THE RESOLUTION REQUIREMENTS

In the latest available version (OLM01.3, 2/91) of the CLP Chlorinated Pesticide Method, certain resolution requirements must be met. All components must be adequately resolved, particularly the targeted pesticides in Table III which are ordinarily difficult to resolve on the Megabore system. Acceptable resolution is defined as the depth of the valley between two adjacent peaks as being greater than or equal to 60% of the height of the shorter peak.

Table III Pesticides in CLP Resolution Check Mixture

gamma-Chlordane	Endosulfan Sulfate
Endosulfan I	Endrin Ketone
p,p'-DDE	Methoxychlor
Dieldrin	

SUMMARY

As shown in Figure 2, peak shapes and widths with a 2 μL injection for tetrachloro-m-xylene, the earliest eluting peak on both columns, and decachlorobiphenyl, the latest eluting peak on both columns, do not display symptoms that

would indicate sample transfer problems from the inlet to the column.

Figure 3 contains the compound list with the conditions under which the chromatograms in Figures 2,4-6 were generated.

Figure 4 demonstrates the chromatography of the list in Figure 3 on the DB-608, and Figure 5 shows the measured and calculated resolution of the only partially co-eluting pair on this column: alpha-Chlordane and Endosulfan I. Figure 6 demonstrates the chromatography for the compounds listed in Figure 3 on the DB-1701, and Figure 7 shows the measured and calculated resolution between the only partially coeluting pair on this column: Endosulfan Sulfate and Methoxychlor.

The GC/FID instrumentation was used for two reasons: 1) it was considered adequate to determine if the chromatography of the dual column capillary system would or would not work, and 2) a GC/dual ECD instrument was not available.
The above example chromatograms demonstrate acceptable resolution with on-column amounts in the 2-5 **nanogram** range by GC/FID. CLP Chlorinated Pesticide analysis, however, uses GC/ECD and routinely analyzes for compounds in the **picogram** range. Knowing that peak width is dependent partially on the amount of compound present, it is expected that the peaks should be narrower as there is at least 2 orders of magnitude difference in the amount on column. This difference should result in analyte resolution better than that demonstrated, especially for critical pairs.

If the system described above were to be used for routine sample analysis, it would be highly recommend that a guard column of adequate length (2-5 meters) be used in order to protect the analytical columns from non-volatile sample residues.

The dual column system using 0.32 mm I.D. columns in the CLP Chlorinated Pesticide analysis, on the surface, appears to be a viable alternative setup which would result in increased sample throughput and greater profits. Also, more samples could be run between quality control checks as their analysis is required every 12 hours as opposed to every so many samples. Detection limits should be more easily achieved by using the smaller diameter columns as they result in an increased signal to noise ratio of analytes.

The overall cost of the dual column setup would be less as column price is directly proportional to column diameter. The dual 0.32 mm I.D. setup could be used in either the Megabore or splitless injection mode. In this particular

CLP protocol, as with most EPA methodology, substitution of columns is **explicitly** allowed. Section 2.2.1 says *"Equivalent columns may be employed if they meet the requirements for resolution, initial calibration, and calibration verification..."* If a capillary system such as this is proven effective for pesticide analysis, PCB analysis should follow easily as identification is accomplished on a pattern recognition basis, and quantitation should not change from whatever mode laboratories are currently using.

Future experiments might include: single injection sample splitting into three dissimiliar stationary phase 0.25 mm I.D. columns; use of hydrogen as a carrier as opposed to helium on the system described above; an investigation into the significance of using the thinner film capillaries on sensitive compound degredation at the 10-100 picogram level using GC/ECD; and the investigation of other Megabore and capillary dual column methods that could be adapted to this dual column setup, or dual column setups with other types of stationary phases. The possibility of using shorter capillaries that would still generate the same number of theoretical plates as a Megabore column could also be investigated.

1. Jennings, W. *Analytical Gas Chromatography;* Academic Press, San Diego, California, 1987; p 10.

2. Rood, D. *A Practical Guide to the Care, Maintenance, and Troubleshooting of Capillary Gas Chromatographic Systems;* Huthig Buch Verlag GmbH, Heidelberg, 1991; p 109-113.

3. Rood, D., Ibid.; p 108.

4. Jennings, W. Ibid.; p 111-151.

5. Rood, D., Ibid.; p 32.

Figure 1

INSTRUMENT CONFIGURATION

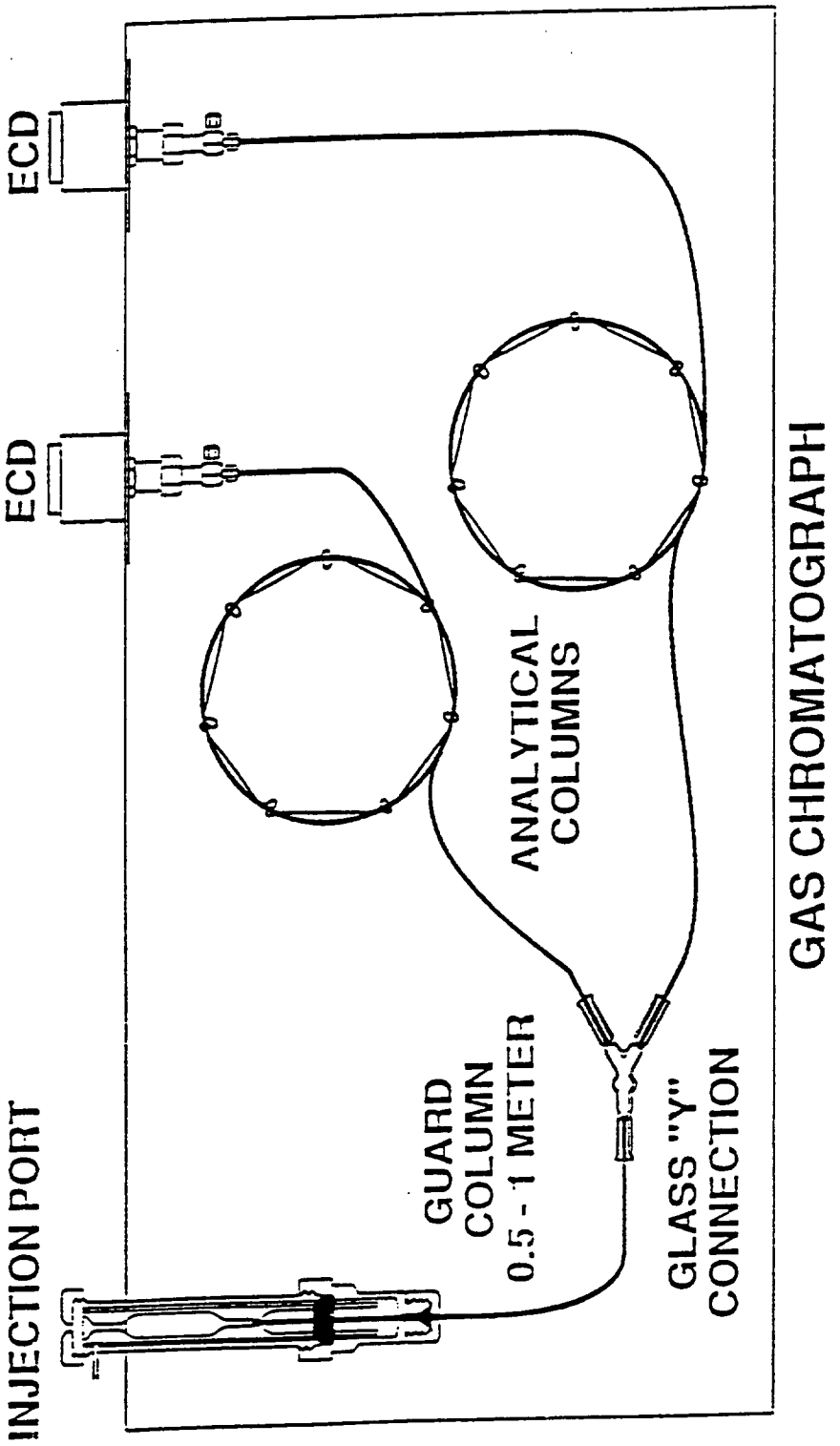
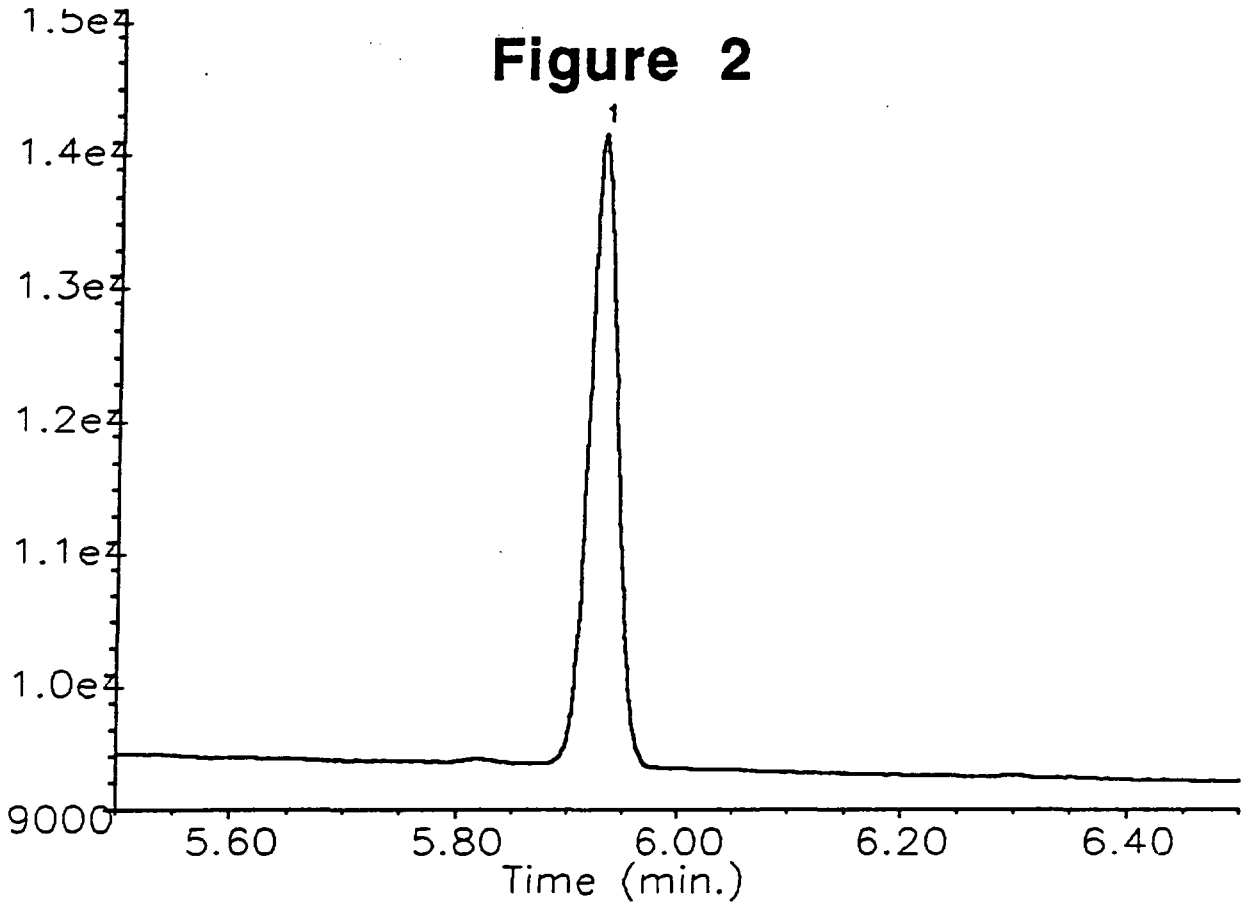


Figure 2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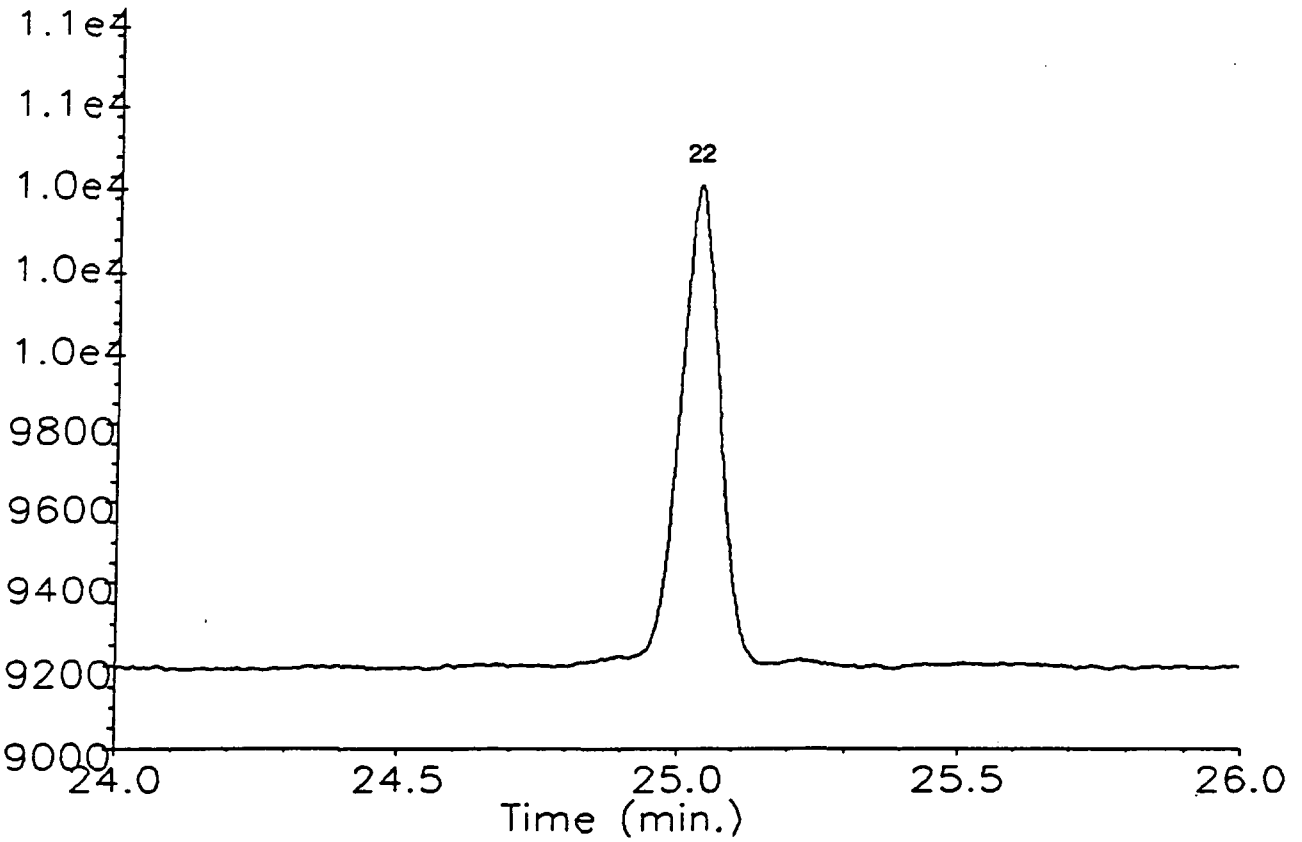
6.00
6.20
6.40
Time (min.)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1.0e4
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9600
9400
9200
9000
22
24.0
24.5
25.0
25.5
26.0
Time (min.)

Figure 3

Column:	DB-608 30m x 0.32 mm I.D., 0.5µm J&W Scientific P/N 123-1730
Column:	DB-1701 30m x 0.32 mm I.D., 0.25 µm J&W Scientific P/N 123-0732
Carrier:	Helium at 48 cm/sec (measured at 150°C)
Oven:	110°C for 0.5 min 110-140°C at 20°/min 140-235°C at 9°/min 235°C for 4.5 min 235-280°C at 15°C/min 280°C for 6 min
Injector:	Megabore direct, 250°C, 2µL Direct Flash Vaporization Liner 2-5 ng each component
Conector:	2 m x 0.53 mm I.D. deactivated guard column 0.53/0.32/0.32, 3-way "Y" union
Detector:	FID, 280°C Nitrogen make-up gas at 30 mL/min

1. Tetrachloro-m-Xylene
2. alpha-BHC
3. gamma-BHC
4. beta-BHC
5. Heptachlor
6. delta-BHC
7. Aldrin
8. Heptachlor Epoxide
9. gamma-Chlordane
10. alpha-Chlordane
11. Endosulfan I
12. p, p'-DDE
13. Dieldrin
14. Endrin
15. p,p'-DDD
16. Endosulfan II
17. p,p'-DDT
18. Endrin Aldehyde
19. Endosulfan Sulfate
20. Methoxychlor
21. Endrin Ketone
22. Decachlorobiphenyl
23. Unknown

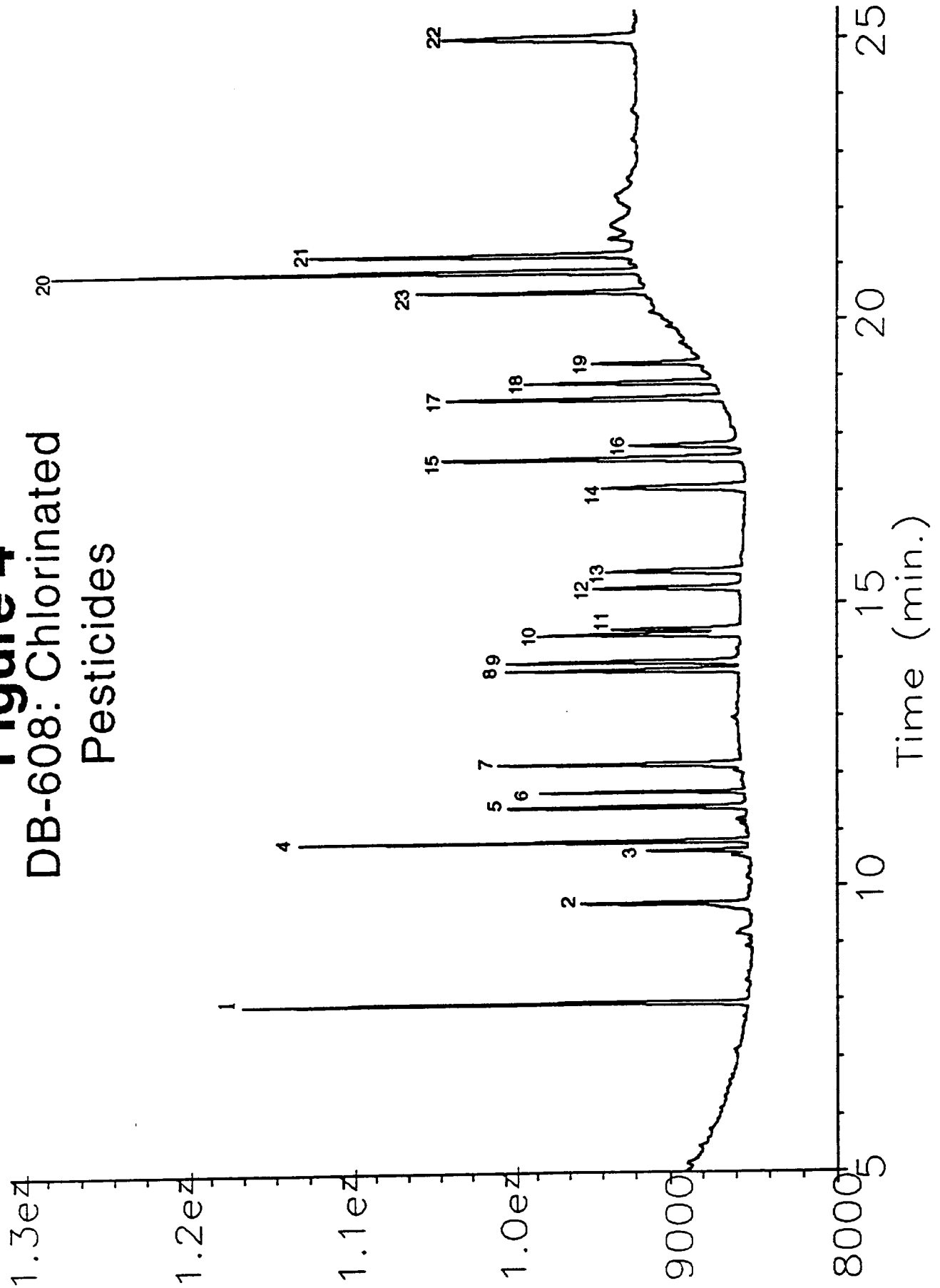


Figure 4
DB-608: Chlorinated Pesticides

Figure 5

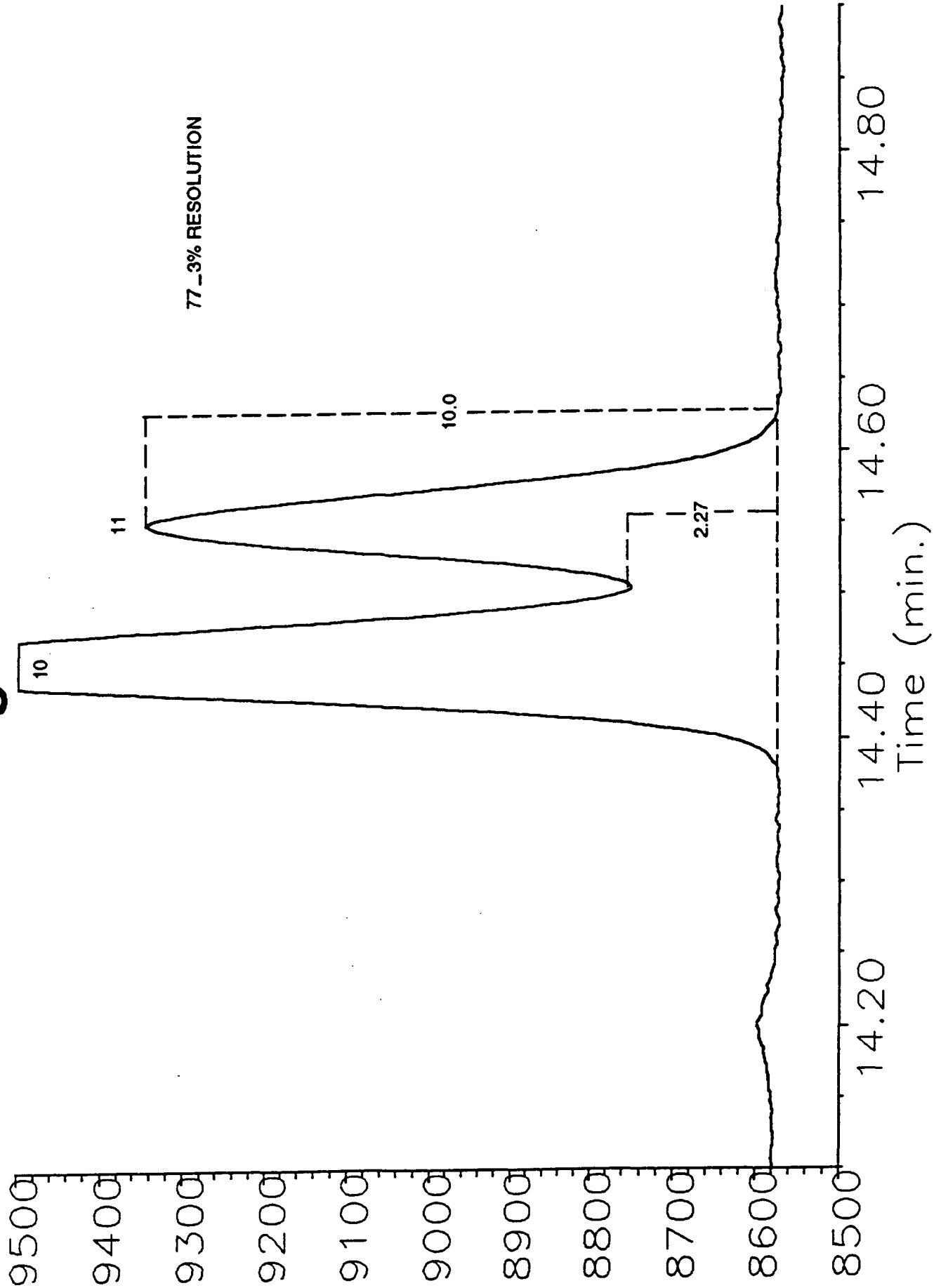

77_3% RESOLUTION
10
11
10.0
2.27
9500
9400
9300
9200
9100
9000
8900
8800
8700
8600
8500
14.20
14.40
14.60
14.80
Time (min.)

Figure 6
DB-1701: Chlorinated Pesticides

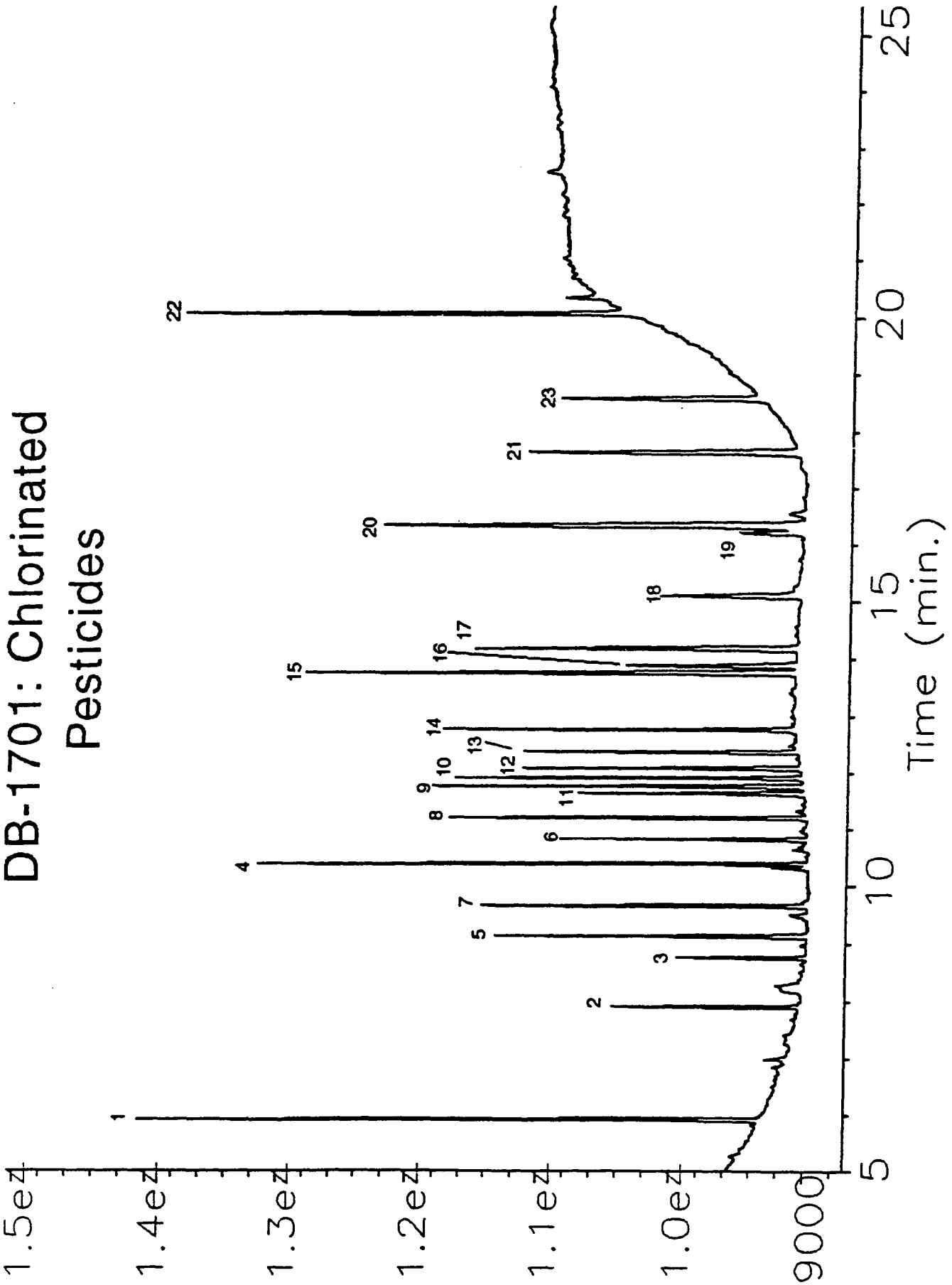
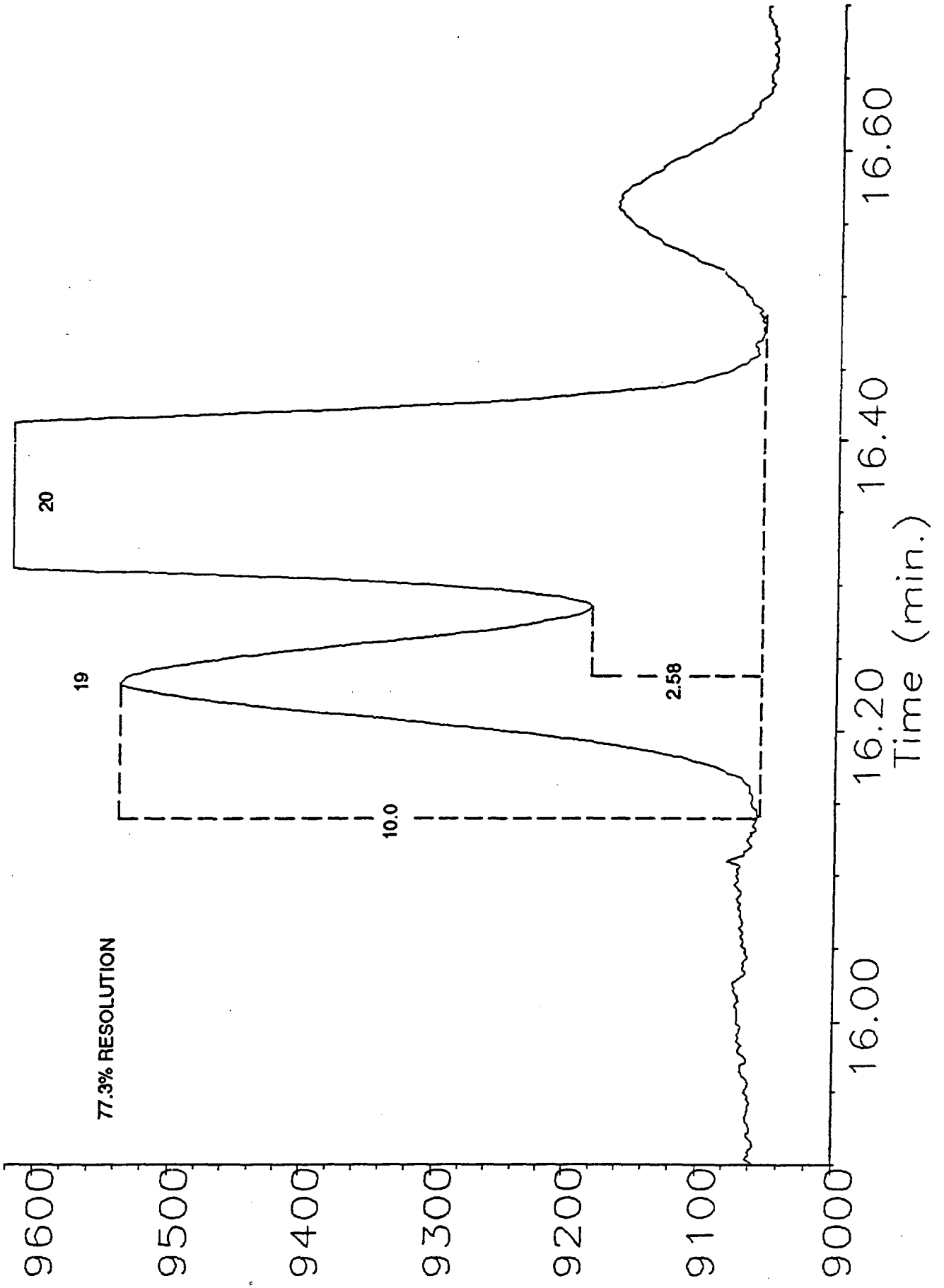


Figure 7


20
19
10.0
2.58
77.3% RESOLUTION
9600
9500
9400
9300
9200
9100
9000
16.00
16.20
16.40
16.60
Time (min.)

63 PERFORMANCE DATA FOR THE ANALYSIS OF PHENOLS, NITROAROMATICS, CYCLIC KETONES, HALOETHERS AND CHLORINATED HYDROCARBONS

Siu-Fai Tsang, Nellie Chau, and Paul Marsden, SAIC, San Diego, CA 92121 and Barry Lesnik, Organics Methods Program Manager, OSW/EPA 22403

The U.S. EPA, Office of Solid Waste (OSW) is responsible for providing reliable, robust analytical methods with documented performance. This mission requires that the OSW regularly evaluate developments in analytical technologies that could improve the measurement of chemicals regulated under the Resource Conservation and Recovery Act (RCRA). Whenever modifications to existing methods are proposed by research scientists, government laboratories, commercial laboratories, or instrument manufacturers, the Methods Section of the OSW compares them with existing SW-846 methods. If a technique is promising, single- or multi-laboratory method studies are conducted to document method performance.

This report provides performance data for the analysis of phenols [Method 8041], nitroaromatics and cyclic ketones [Method 8091], haloethers [Method 8111], and chlorinated hydrocarbons [Method 8121A] using capillary gas chromatography (GC). Target analytes were extracted from spiked soil using Method 3540 (Soxhlet) and analyzed with 0.53 mm id a DB-5 capillary column. Phenols were analyzed with and without derivatization using diazomethane. Initial conditions for some chromatographic separations were derived from reports presented by the Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV) during the 1990 and 1991 Symposia.

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RAPID CONFIRMATION OF NITROAROMATICS AND NITRAMINES USING UV DIODE ARRAY SPECTRAL COMPARISON

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ABSTRACT

The present proposed SW846 method for the determination of nitroaromatics and nitramines, designated EPA 8330, requires a second column confirmation for any positive identification from the primary analysis. Since this confirmation is sequential to the primary analysis it results in additional turnaround time for an already complex determination. By comparing spectral data collected using a diode array detector the confirmation can be accomplished with a single analytical run.

Spectra from the UV range of 200-400 nm are collected for each peak within the retention windows determined by a standard curve run prior to sample analysis. These spectra are stored electronically for comparison to the standard curve spectra in the method library. Peaks of interest may also be checked for peak purity by comparing spectra from the leading edge, apex, and downslope of each peak. Criteria for confirmation are established by comparing spectral integrity over the range of the standards run for calibration.

This technique presents a three-dimensional approach to analyte determination and reduces the total time of analysis. Some of the remaining problems associated with a second column confirmation, such as nonresolution of all the analytes and interferences which do not appear in the primary analysis, can also be eliminated or reduced.

65 The Effect of GPC Cleanup of Semivolatile Extracts on GC/MS Analysis.

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ABSTRACT

Gel Permeation Chromatography (GPC) is a size exclusion type of chromatography which efficiently removes high boiling materials that may interfere with the analysis of target compounds in semivolatile extracts. Currently, the use of GPC to clean up environmental soil samples is required under the USEPA Contract Laboratory Program (CLP) Statement of Work. The purpose of this study was to evaluate the effects of GPC clean up on GC/MS performance in order to justify the cleanup of all samples wit difficult matrices by GPC prior to analysis. Potting soil was chosen as the subject matrix due to the high level of organic interferences found in this matrix. A sample was split into two portions both of which were extracted by USEPA SW-846 Method 3550. One extract was then cleaned up using GPC. Each extract was then injected four times on a Hewlett-Packard GC/MS. In order to monitor the performance of the GC/MS system, a standar containing all of the semivolatile Priority Pollutant List compounds at a concentration of 50 ppm was injected before and after each sample. The degradation of the system was monitored by measuring the decrease in response factors against the number of injections of the potting soil extracts. Results were compared for the GPC extract versus the non-GPC extract. The response factors dropped drastically for five acid compounds 2,4-dinitrophenol, 4-nitrophenol, pentachlorophenol, 2,4,6-trichlorophenol and 4,6-dinitro-2-methylphenol after only one or two injections of the non GPC extract. However, the response factors for these compounds were much more stable even after four injections of the GPC extract. A similar tren was observed for the internal standards, which are used to monitor system performance. This loss of system sensitivity after injecting the non-GPC extract can be explained by an increase of active sites in the injector port caused by the buildup of high molecular weight compounds in the injector liner and on the stainless steel seal. Although the experiment i very simple, the results make the utility of GPC cleanup evident and therefore justify the extra time and effort spent in adding this step to semivolatile sample preparation.

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EVALUATION OF THE ENSYS PAH-RISc® TEST KIT

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ABSTRACT

A polynuclear aromatic hydrocarbon field screening method, utilizing enzyme-linked immunosorbent assay techniques, was recently evaluated. The validation study was conducted to evaluate the performance and assess the utility of this method for use in field screening activities at hazardous waste sites. Design criteria included analysis of field samples, analysis of well-characterized reference materials, test kit response to various soil types (including analyte-spiked soils), and a general performance evaluation using selected soil types with varying PAH concentrations.

INTRODUCTION

The authors recently conducted a validation study for an Enzyme-Linked Immunosorbent Assay (ELISA) field-screening test method, PAH-RISc®. This semiquantitative chromogenic analytical method, developed by Ensys, Inc., Research Triangle Park, NC, was evaluated for use in the determination of Polynuclear Aromatic Hydrocarbons (PAHs) in environmental soil and sediment samples. The experimental design and interpretation of results obtained are described below.

BACKGROUND

Field Screening

Field screening for contaminants has applications in a wide variety of situations (1), from collecting real-time data relating to worker safety to monitoring plume boundaries resulting from materials spills. Low cost, rapid-turnaround sample analysis is beneficial to site characterization and assessment, as well. Sampling locations of possible interest and local "hot-spots" may be identified quickly, aiding in the selection of samples to be collected for subsequent CLP analysis. Other considerations such as remediation efforts and effluent compliance may also be monitored.

The need for rapid, reliable, semiquantitative methods for measuring environmental contaminants has resulted in the introduction and development of new technologies. In addition, laboratory-based analytical methods such as GC/MS and HPLC, among others, are finding increased use in field applications (2).

One novel field screening method gaining regulatory acceptance utilizes immunoassay-based testing (3). Immunoassay techniques have been used for more than 15 years in medical and clinical settings. This technology has received Agency approval for a few classes of analytes (4), and is currently being applied to the detection of PCBs, petroleum hydrocarbons, and pentachlorophenol. One of the earlier environmental applications in which this technology was used was in the detection of pesticides and pesticide residues (5).

Enzyme-Linked Immunosorbent Assays

Immunochemical analysis is a well-established clinical diagnostic technique which is gaining wider acceptance in other areas. In the field of environmental analysis, antibodies have been or are being developed for

a number of contaminants. All these antibodies are of animal origin, but advances in monoclonal preparation have yielded *in-vitro* propagation methods.

In order to obtain antibodies of the desired specificity, an immunological response must first be generated in the host. Typically, the target analyte, or hapten, is derivatized to produce a "handle" for use in attachment to a macromolecule. Historically, proteins such as bovine albumin have been used as the carrier. This step is essential because direct injection of the analyte, due to its small mass (on a biological scale), would result in detoxification by the animal's liver. In order to be recognized as an antigen, or immunogen, by the immune system, a foreign substance must have a mass which is large on a molecular scale (>10,000 Da). When injected into the host animal these immunogens cause the animal's immune system to generate antibodies in response to the foreign substance. The hapten is then bound to an enzyme, such as horseradish peroxidase, to form an enzyme-conjugate. The conjugated compound is used as the chromogenic reagent in this test.

After the antibodies are extracted from the host, they are sorted based on sensitivity and specificity to the hapten. In the polyclonal method, the above steps are repeated until a desired quantity of antibody is obtained. The test kit used in this study utilizes a monoclonal preparation of the desired antibodies using hybridoma technology, in which antibody-producing (spleen) cells are fused with myeloma cells. The resulting progeny cells are able to produce relatively large amounts of the specified antibody.

In a typical test kit, antibodies of the desired specificity are then immobilized on a solid substrate such as a small test tube. A predetermined amount of sample, possibly containing analyte, is extracted with a suitable solvent. An aliquot of extract and a fixed amount of enzyme-conjugate are added to the antibody tube and allowed to incubate for a given period of time. Competition between the analyte and enzyme-conjugate for a limited number of antibody binding sites results in binding of the haptens in proportion to their relative concentrations. Unreacted haptens are washed from the tube and two color development reagents added. These reagents react with the bound enzyme-conjugate, producing a depth of color proportional to the amount of enzyme-conjugate bound. The "intensity" of color, compared photometrically to a calibration solution containing analyte, is inversely proportional to the amount of analyte present in the original sample.

This test method utilizes ten-fold serial dilutions of the solvent extract for comparison with a 1 ppm calibration standard prepared in the same manner as the samples. A comparative photometer measures the difference in absorbance between the sample and the standard, and uses the difference measurement rather than the parametric value for quantitation.

EXPERIMENTAL DESIGN

Four main design parameters were selected for this validation study, including analyses of 30 samples for comparison with CLP-generated data, analysis of four "worst-case" Superfund-class reference samples, false-positive and then false-negative (1 ppm spike level) reaction to soil types, and a general reliability/performance test using a given soil type spiked with varying amounts of analyte. Given a fixed number of test kits, the key design criterium was to conduct a comprehensive yet conclusive set of experiments.

Polynuclear aromatic hydrocarbons are a class of compounds which have one or more aromatic rings, generally in conjugation. The majority of common PAHs contain three, four or five rings, may have alkyl- or aryl- groups bound to them, and the rings themselves may be heterocyclic. One important three-ringed PAH is phenanthrene, because it has a physical structure which resembles the skeleton of many other PAH compounds.

Table I PAH RISc® Soil Test Sensitivity to PAH Compounds

Number of Rings	PAH Compound	Concentration Necessary to Result in Positive Test (ppm)*
2 rings	Naphthalene	200
3 rings	Acenaphthene	8.1
	Acenaphthylene	7.5
	Phenanthrene	1.0
	Anthracene	0.81
	Fluorene	1.5
4 rings	Benzo[*a*]anthracene	1.6
	Chrysene	1.2
	Fluoranthene	1.4
	Pyrene	3.5
5 rings	Benzo[*b*]fluoranthene	4.6
	Benzo[*k*]fluoranthene	9.4
	Benzo[*a*]pyrene	8.3
	Dibenzo[*a,h*]anthracene	>200
6 rings	Indeno[*1,2,3-cd*]pyrene	11
	Benzo[*g,h,i*]perylene	>200

* Samples with stated concentration will give positive result greater than 95% of the time when tested at stated concentration level.

The antibody used by this test kit was developed to target, or key, phenanthrene. According to the manufacturer, the kit is designed such that concentration of phenanthrene necessary to result in a positive test is 1 ppm (6). With the exception of anthracene, which is detectable at 0.81 ppm, the test is less sensitive to other PAHs. The concentrations necessary to produce a positive result range from 1.2 ppm for chrysene to 200 ppm for naphthalene. A list of several PAH compounds (SW-846 Method 8310 Target List) and their respective detection limits has been provided by the vendor (Table I). The reported sensitivities have been used as

scaling factors in some sections of this report. For example, to produce an equivalent response using naphthalene rather than phenanthrene as the target analyte, 200-times more naphthalene (on a mass basis) is required. This relationship will be further investigated in a later section.

Phase I: Analysis of Field Samples

Several issues were raised during the initial design of the validation study, the most obvious of these being the evaluation of the test kit with respect to the manufacturer's claim:

> *This method correctly identifies 95% of samples that are PAH-free and those containing 1 ppm or 10 ppm of PAHs. A sample that develops less color than the standard is interpreted as positive. It contains PAHs. A sample that develops more color than the standard is interpreted as negative. It contains less than 1 ppm or 10 ppm PAHs.*

To substantiate this claim, 30 samples were selected from the Manchester Environmental Laboratory (MEL) soils storage facility. These samples were analyzed previously using either GC/MS (tentatively identified compounds excluded but noted) or HPLC methodology; total PAH values (16 analytes) ranged from zero (non-detect) to >182 ppm. Soil types ranged from weathered sand to dark loamy humus.

Phase II: Analysis of Reference Samples

Four well-characterized reference samples were selected for use in this study. These samples have been independently analyzed by a number of laboratories and are representative of materials present at various preremediated Superfund sites. The matrices range from marine sediment to composited hazardous waste. All samples contain a variety of contaminants, including pesticides, PCBs, and in one case, tributyl tin. Clearly, potential interferents are present in these samples. A scheme in which three analysts conduct the analyses, with one analyst performing the tests in duplicate, provides an empirical estimate of both precision and accuracy.

Phase III: Reaction to Soil Types

Soil compositions vary greatly on a regional basis. Extractable humic components, among many others, have the potential to negatively affect the performance of the test kit. Analysis of soils of various compositions would provide information necessary to estimate the effect of soil type on test kit reliability. To that end, 11 samples collected from different soil horizons throughout Washington state by the US Geological Service were analyzed. The PAH content of each of these library soils has been previously determined to be below the detection limit of the test kit. Therefore, any positive test result(s) could be attributed to what have been termed "relatively unremarkable" contaminants, which possess structural features similar to those of phenanthrene (7).

PAH compounds adsorbed onto soil surfaces may resist methanol extraction and the degree of adsorption may be dependent on the nature of the soil. In order to investigate this effect, a subset of the library soils was selected and the soils fortified, or spiked, with 1 ppm phenanthrene. This quality control measure was used to qualitatively estimate the distribution of phenanthrene between the soil matrix and the methanol extract.

Phase IV: Reliability/Performance Evaluation

A set of samples consisting of weathered, sandy soil was composited for use in this phase of the validation study. Each of the samples were previously confirmed to be PAH-free. Eight spiking levels were used, ranging from 0.1 to 10.0 ppm normanlized to the phenanthrene response. For the spike, a three-component mixture containing a three, four and five ringed PAH - phenanthrene, pyrene and benzo[*k*]fluoranthene - was prepared. The relative amount of each component was scaled based on the sensitivity of the test kit to the individual components.

The objective of this set of measurements was to provide an estimate of error with respect to false positive results below the detection limit as well as false negative results for samples with PAH concentrations above the detection limit.

It was also hoped that these measurements would provide insight relating to test kit response for mixtures of PAHs. Because the assay utilizes competitive binding of the antibody-antigen for detection of the analyte, we were interested in determining whether the presence of one PAH would affect the sensitivity of the test to another PAH. Rather than having only one PAH competing with the enzyme conjugate for antibody binding sites, there could be two or more competitors. There is no *a priori* reason to believe that the test response may be calculated using a simple weighted average concentration of the individual PAHs and the stated test sensitivities to each.

RESULTS AND DISCUSSION

This experiment was conducted under relatively ideal conditions. Three experienced chemists performed several trial analyses in order to gain familiarity with the kit. Work was performed at the laboratory benchtop in a controlled environment (temperature, humidity, etc.). Quality control/quality assurance, as specified through personal communications and training by the manufacturer, included analysis of method blanks, regular pipet delivery calibration verification, and rejection of analytical sequences in which the relative absorbance of replicate calibration standards varied by more than 0.2 absorbance units. The analytical instructions supplied with the kit and QA/QC guidelines provided by the manufacturer were followed without exception.

The laboratory results reported for the GC/MS and HPLC data were generated in accordance with full QA/QC requirements following USEPA CLP and SW-846 protocols. All data reported have been validated. To maintain client confidentiality, any unnecessary site-specific references have been omitted.

One set of measurements was made to evaluate the response of the comparative photometer. A series of five spiked-blank solutions were prepared in duplicate, with concentrations of 0.5, 0.75, 1.0, 1.25 and 1.5 ppm phenanthrene. Within each set, the 1.0 ppm was treated as the calibration standard. Aliquots of these solutions were withdrawn and processed as if they were actual soil extract. The absorbance of each solution was measured and recorded. The resulting "calibration" curve was determined through a linear least-squares fit of absorbance vs. concentration. The results are illustrated in Figure I.

From the data, it appears as though the instrument response is linear around the zero (difference) absorbance. However, the slope is relatively small - therefore variations in absorbance affect the apparent sample

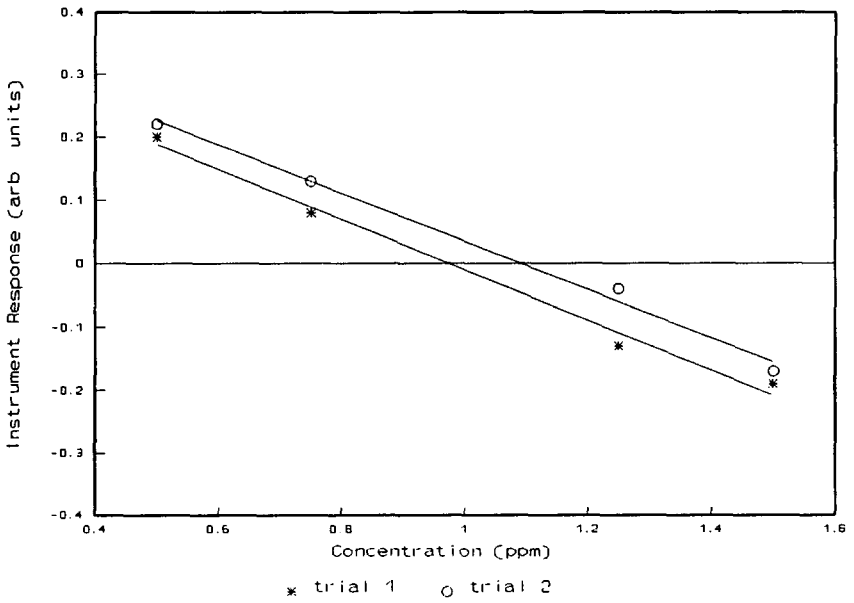

Figure 1 Instrument Response

concentrations. Instrument readings near zero must be interpreted cautiously.

Phase I: Thirty soil samples were selected for ELISA-PAH analysis. No attempt was made to target the one or ten ppm concentration levels; this portion of the study was designed to emulate characterization of samples in the field. These samples were previously extracted (EPA Method 3540) and characterized for base/neutral/acid extractable compounds (BNAs, including PAHs; EPA Method 625), volatile organic analytes (VOAs; EPA Method 624), metals (ICP-AES, EPA-CLP Method 200.8), and pesticides/polychlorinated biphenyls (pest/PCBs; GC/ECD, EPA Method 8080). In addition to quantifying total PAH content and relative amounts of the individual compounds, the supporting analyses were used to characterize the soil matrices and identify potential interferences. The results are shown in Tables II and III.

In Table II, the total PAH concentration for each sample is compared with the ELISA results. False-positive and false-negative results are indicated by "+" or "-", respectively. Results from GC/MS analysis of sample 2361 indicated the presence methyl-phenanthrenes at 3 ppm. Although the associated data were qualified "NJ" to indicate "there is evidence that the analyte is present, the associated numerical result is an estimate", the levels apparently present would be sufficient to yield positive identification at 1 ppm. This result slightly increases the accuracy rates (indicated in parenthesis). The estimated accuracy for the ELISA test, based analysis of the thirty samples, was 86.7% (90%) at 1 ppm and 73.3% at 10 ppm. The frequency of false-positive results at 1 ppm was 13.3% (10%), with no false-negatives. The frequency of false- positive results at 10 ppm was 20%, and false-negatives, 6.7%. One sample, selected randomly, was analyzed in duplicate.

Table II Analysis of Field Samples / Total PAH Content

	1 ppm Test		10 ppm test			False +/-	
Sample ID	<1	>1	<10	>10	Lab Result (ppm)	Evaluation @ 1 ppm	Evaluation @ 10 ppm
4005		*		*	0.2	+	+
4006				*	12.2		
4007				*	16.0		
4010	*				0.0		
4659	*				0.5		
4300		*		*	8.7		+
4301				*	147.7		
4302				*	182.3		
4303		*		*	4.4		+
4640		*		*	0.2	+	+
2107	*				0.0		
2358				*	85.4		
2358D				*	85.4		
2359				*	28.5		
2360	*		*		0.3		
2361		*			0.6	+[1]	
2362	*		*		0.0		
2363		*		*	1.8		+
2364		*	*		3.4		
2365		*	*		6.7		
2366	*		*		0.9		
2368				*	43.2		
2369				*	72.8		
2370		*		*	1.3		+
2371		*	*		0.3	+	
2372	*		*		0.4		
2373			*		27.9		-
2374	*		*		0.0		

Table II Analysis of Field Samples / Total PAH Content

	1 ppm Test		10 ppm test			False +/-	
Sample ID	<1	>1	<10	>10	Lab Result (ppm)	Evaluation @ 1 ppm	Evaluation @ 10 ppm
2375			*		16.4		
2376	*		*		0.4		
2377		*	*		9.5		
† *Tentatively identified compounds list indicates methyl-phenanthrenes present at 3 ppm*							

Table III Analysis of Field Samples / Normalized PAH Content

	1 ppm Test		10 ppm test			False +/-	
Sample ID	<1	>1	<10	>10	Normalized Lab Result (ppm)	Evaluation @ 1 ppm	Evaluation @ 10 ppm
4005		*		*	0.1	+	+
4006				*	8.1		+
4007				*	9.0		+
4010	*				0.0		
4659	*				0.2		
4300		*		*	5.2		+
4301				*	56.9		
4302				*	73.2		
4303		*		*	0.1	+	+
4640		*		*	0.0	+	+
2107	*				0.0		
2358				*	47.3		
2358D				*	47.3		
2359				*	11.5		
2360	*		*		0.2		
2361		*			0.5	+†	
2362	*		*		0.0		
2363		*		*	1.2		+
2364		*	*		1.7		
2365		*	*		3.6		

Table III Analysis of Field Samples / Normalized PAH Content

	1 ppm Test		10 ppm test			False +/-	
Sample ID	<1	>1	<10	>10	Normalized Lab Result (ppm)	Evaluation @ 1 ppm	Evaluation @ 10 ppm
2366	*		*		0.6		
2368				*	27.5		
2369				*	49.2		
2370		*		*	0.8	+	+
2371		*	*		0.1	+	
2372	*		*		0.2		
2373			*		13.5		-
2374	*		*		0.0		
2375			*		6.4		
2376	*		*		0.2		
2377		*	*		2.8		

[1] Tentatively identified compounds list indicates methyl-phenanthrenes present at 3 ppm

Table III shows the comparison of normalized PAH concentrations with the ELISA results. As mentioned previously, the sensitivity of the test varies with different PAH compounds. In order to account for this effect, each PAH concentration was normalized by dividing its actual value by that concentration required to produce a positive result at 1 ppm (phenanthrene = 1). This was done to minimize any bias introduced into the test by anti-PAH specificity. A critical assumption is that the manufacturer-provided list of PAH sensitivities are valid in the presence of two or more PAH compounds. Sensitivity to the methyl-phenanthrenes tentatively identified in sample 2361 is not known, but was assumed to be similar to that of phenanthrene. As in the previous data set, estimated accuracies including any contribution from the methyl-phenanthrenes are enclosed in parenthesis. The estimated accuracy was 80% (83.3%) at 1 ppm and 70% at 10 ppm. The frequency of false-positive results at 1 ppm was 20% (16.7%), with no false-negatives. At 10 ppm, the frequency of false-positive results was 26.6%, and false-negatives, 3.3%.

The results using total and normalized PAH concentration values are similar. If samples with PAH concentrations exclusively near 1 and 10 ppm had been used, a greater discrepancy would have been observed. The majority of these samples contained levels of PAHs separated from either test kit detection level. This demonstrates the need to apply the screening test judiciously, with operator intervention/interpretation applied to those samples near either limit.

Phase II: Four soil reference samples were analyzed by three different analysts, with one analysis performed in duplicate ("D" in Table IV), to illustrate the variation introduced by different analysts and also the duplicate precision. Comparison of the data is shown in Table IV. There was considerable variation in the results, apparently due to the presence

of interferents, including compounds to which the ELISA test exhibits cross-reactivity. The summary in Table IV lists the total and normalized PAH concentrations.

These samples were selected because they present a real challenge to the ELISA test. They are each representative of the types of materials found at Superfund sites. Prior to analysis, the samples were sieved and homogenized. Non-representative material was removed, but an effort was made to preserve the physical character of the original sample. A brief summary of each soil follows.

Sequim Bay: This matrix is typical of marine or lower-wetlands sediment, with corresponding levels of marine salts. The consistency was similar to water-saturated silt. Although the concentration of various contaminants were each less than 1 ppm, a large number of different compounds were present. This particular reference sample has been independently characterized as many as 50 different times. Some of the compounds present were:

Phenol - 0.24 ppm; 4-methyl phenol - 0.24 ppm; pentachlorophenol - 0.42 ppm; biphenyl - 0.79 ppm; methylnaphthalenes - 0.25 ppm; tributyl tin chloride - 0.11 ppm; halophenyl phenyl ethers - 0.4 ppm; tetrachloroguicol - 0.47 ppm

Table IV Analysis of Reference Samples

		1 ppm test		10 ppm test		100 ppm test		GC/MS Results	
Sample ID	Trial	<1	>1	<10	>10	<100	>100	Lab Result (ppm)	Normalized Lab Result (ppm)
Sequim Bay - marine sediment - low levels of many pesticides, chloro-benzenes, phthalates	1			*		*		1.73	<0.1
	2		*		*		*	1.73	<0.1
	3		*		*	*		1.73	<0.1
	3D		*		*		*	1.73	<0.1
H.I. BSRM #XX - Composite soil - PCBs: 130 ppm - Lead: 5000 ppm - contains slag/ash	1			*		*		18.3	12.1
	2		*	*		*		18.3	12.1
	3		*		*		*	18.3	12.1
	3D		*		*		*	18.3	12.1
RTC Sample #XXX - PCP: 2190 ppm - substituted naphthalenes: 2300 ppm	1				*		*	8611	5764
	2		*	*		*		8611	5764
	3		*		*		*	8611	5764
	3D		*		*		*	8611	5764
Soils Bldg 0003 - Isophorone: 4.4ppm (dimethyl hexanone)	1			*		*		24.8	12.4
	2		*	*		*		24.8	12.4
	3		*		*		*	24.8	12.4
	3D		*		*		*	24.8	12.4

As indicated in Table IV, the actual PAH concentration was less than 2 ppm. When normalized based on specificity to individual PAH compounds, the apparent PAH concentration was less than 0.1 ppm. Three of four ELISA analyses indicated that the PAH concentration was greater than 10 ppm, and two tests yielded results greater than 100 ppm. Clearly, materials were present which respond to the test in a similar manner as do PAHs, and exhibit a strong interference. Unfortunately, no clear pattern was apparent in the spurious results. The test did appear to yield either correct or false-positive results at the 1 ppm level, depending on which set of lab results were considered.

HI BSRM #XX: This bulk site reference material composite sample was manufactured from soils collected at a Superfund site by the USEPA in Region 10 and known to contain PAHs and PCBs. The matrix consisted largely of marine sediments and silt, although there is a significant amount of ash, slag and related fallout originating from the operation of a secondary smelter for many years. Other man-made debris and residue include cinders, brick material and sandblasting waste from ship refinishing. Local "hot-spots" resulting from wood and pole treating and indiscriminate dumping of waste oils and electrical transformer/capacitor dielectric contributed PCBs and PAHs to the BSRM.

The reference sample exhibited a fairly high degree of matrix inhomogeneity on both the macroscopic and microscopic level. A concerted effort was made to homogenize the sample prior to analysis. The variability is reflected, in part, by the standard deviations associated with the analytical results:

Lead - 5480 ± 2620 ppm; Arsenic - 37.8 ± 7.3 ppm; Total PAHs (7 carcinogenic PAHs identified in MTCA) - 18.3 ± 4.6 ppm; Total PCBs - 127 ± 39 ppm.

A comparison of the sample results is shown in Table IV. All ELISA analyses at the 1 ppm level correlate with the laboratory data. The first two trials produced identical results at 10 and 100 ppm (true-negatives), but disagree with the duplicate analyses performed by the third analyst. The duplicate analyses were self-consistent. Because the duplicate analyses were performed using the same soil-extract, sample inhomogeneity rather than ELISA precision may have contributed to the disparity.

RTC Sample #XXX: This sample was prepared under contract to the EPA as part of a RCRA study and made available for use in this study. Laboratory analyses were performed for both total metals and BNA compounds. The levels of sodium, potassium, nickel and total PAHs were relatively high. Some of the analytes present at significant levels were:

Chromium - 16100 ppm; Phenanthrene - 2430 ppm; fluoranthene - 1840 ppm; pentachlorophenol - 2190 ppm; methyl-naphthalenes - 200 ppm; carbazole - 81 ppm;

Of the reference samples, this was the most highly contaminated. All ELISA results indicated PAHs present at 1 ppm. One analysis yielded false-negative results at 10 and 100 ppm. This analysis is clearly in error; with the levels of contaminants known to be present, it seems unlikely that normal experimental or method uncertainties were the cause. Since the 10 and 100 ppm results were

generated using serial dilution of the 1 ppm extract, we believe their inaccuracy may be attributed to dilution error.

Soils Building 003: This sample was also a composite soil manufactured from materials which had collected in a soils laboratory over a period of time. A large number of assorted samples of varying origin were blended, with aliquots withdrawn for waste disposal characterization. Some of the material was dated and all had been stored at room temperature. Microbial and oxidative decomposition were expected to have yielded a variety of degradation products of the PAHs and other contaminants. Subsequent analysis showed that with the exception of 4.4 ppm isophorone (dimethyl hexanone), the composition of contaminants was due predominately to PAHs, with total and normalized concentrations of 24.8 and 12.4 ppm, respectively. The matrix of the composite soil sample included clay, silt, sand and loam.

All ELISA results indicated PAHs present at the 1 ppm level. Two replicates yielded false-negative results at 10 ppm. Duplicate analysis yielded correct results at 10 ppm, but false positive results at 100 ppm. No simple explanation can be offered for this disparity.

Phase III: Eleven soil samples collected from various soil horizons across Washington state were analyzed using the ELISA method. The soils were previously determined to contain undetectable amounts of PAH compounds. The purpose of this phase of the experiment was to determine the effect of soil type with respect to false-positive ELISA results.

Analysis of these soils yielded negative results in each case. On this basis, soil type did not appear to negatively impact the accuracy of the test with respect to false-positive results.

Four soils from this set were spiked with PAH to provide an estimate of false-negative results with respect to soil type. These soils were primarily clay/silt with a fair amount of humic or loamy material. A 10-gram aliquot of each soil was spiked directly with phenanthrene to give a final concentration of 1 ppm, allowed to weather at room temperature for 24 hours, extracted, and analyzed in duplicate. This method was preferred to that in which the extract is spiked because adsorption of phenanthrene on the soil surface is a potential physical interference. Resistance to methanol-extraction would result in a negative bias and, therefore, false-negative results. Phenanthrene was selected for use as the spike on the basis of ELISA sensitivity, and to reduce any possible cross-reactivity questions which may arise from the use of a mixed-PAH spike. The results are shown in Table V.

Results from the spiking study show a high frequency (75%) of false-negative results, indicative of the inability of the methanol extraction fluid to completely liberate the phenanthrene from the matrix. Although it is reasonable to expect that the methanol-based extraction is not 100% efficient, these results yield an unacceptable percentage of false-negative results. The bias built into the ELISA test did not appear to be able to provide a large enough margin of uncertainty in this case. Because a CLP-quality extraction and analysis was not performed, it was not possible to estimate the actual efficiency of the extraction using the ELISA method.

These limitations should be compared with those generally encountered during laboratory-based analysis. Standard CLP soxhlet extraction

involves refluxing the solid sample for a minimum of 18 hours in boiling solvent. Even then, extraction efficiency may only approach 80% or so. Matrix spike analysis generally involves adding the spike compound to the extraction solvent rather than to the soil itself. Obviously, no weathering of the PAH/soil occurs. However, this does not change the fact that the kit was unable to detect PAH at 1 ppm in soil.

Table V Reaction To Soil Types

	1 ppm test		10 ppm test		Spike result	
Sample ID	<1 ppm	>1 ppm	<10 ppm	>10 ppm	phenanthrene 1 ppm	Soil description
8114	*		*		n/a	yellow brn sandy loam
8123	*		*		n/a	pale brn silty loam
8129	*		*		n/a	brn silty loam
8136	*		*		n/a	pale brn sand
8142	*		*		n/a	pale brn sand
8500	*		*		n/a	drk brn silt loam
8500 S	*		*		-	"
8501	*		*		n/a	drk brn gry sandy loam
8501 S	*		*		-	"
8506	*		*		n/a	lake sediments
8512	*		*		n/a	lt brn coarse loam sand
8512 S		*	*			"
8513	*		*		n/a	drk brn stony silt loam
8513 S	*		*		-	"
8107	*		*		n/a	lt grey silty clay

Two papers previously published by the manufacturer described spiking studies performed during validation of their PCB and pentachlorophenol immunoassay methods (8-9). In each case the extracts, rather than the native soils, were spiked. A similar study reported poor extraction efficiency for PCBs spiked directly onto the soil (10). We felt it important and more procedurally valid to spike and then weather the soil.

Phase IV: Another spiking study was performed to estimate reliability of the ELISA method as a function of analyte concentration. Sandy, weathered soil previously determined to be PAH-free was divided into 57 - 10 gram aliquots, spiked directly, and allowed to interact for one hour.

A spiking solution was prepared using a three, four and five ring PAH compound - phenanthrene (3), pyrene (4) and benzo[*k*] fluoranthene (5) - such that their relative, *normalized* contributions on a mass basis to the spike cocktail were equivalent. Using the 1 ppm spike as an example, a solution was prepared such that 0.33 ppm of phenanthrene would be added to the soil. The same contributions were desired from the four and five-

ringed compounds, but the test is less sensitive to them. Since 3.5 ppm of pyrene is required to produce the same response as 1 ppm phenanthrene, 3.5 times more pyrene was used (3.5×0.33). Similarly, the test is 9.4 times less sensitive to the benzo-compound, so 9.4×0.33 ppm benzo[*k*]fluoranthene was used. Calculation shows that the total PAH concentration in the spiked soil was actually 4.6 ppm. A similar scheme was used in the preparation of the soils at the other spiking levels. With the exception of the blank sample, which was analyzed once in duplicate, seven replicates were analyzed in duplicate at each of 0.1, 0.5, 0.8, 1.0, 1.5, 2.0, 5.0, and 10.0 ppm (normalized) concentrations. Seven extractions were performed at each level, and each extract analyzed in duplicate. The results for normalized and total PAH concentrations are shown in Tables VI(a) and VI(b), respectively; agreement of estimated error rates for the different spike levels is coincidental.

Table VI(a) Reliability Test - Normalized Concentrations

Normalized Value (ppm)	0.0	0.1	0.5	0.8	1.0	1.5	2.0	5.0	10.0
Estimated Rate of False Positives (%)	0.0	0.0	78.5	78.5	-	-	-	-	-
Estimated Rate of False Negatives (%)	-	-	-	-	21.5	0.0	0.0	0.0	0.0

Table VI(b) Reliability Test - Actual Concentrations

True Value (ppm)	0.0	0.46	2.32	3.71	4.63	6.9	9.3	23.2	46.3
Estimated Rate of False Positives (%)	0.0	0.0	-	-	-	-	-	-	-
Estimated Rate of False Negatives (%)	-	-	21.5	21.5	21.5	0.0	0.0	0.0	0.0

Three false-positive results were observed at both the 0.5 and 0.8 ppm levels. The 0.5 ppm trial was repeated (extraction and analyses), and the results were identical to those obtained in the first trial. Three false-negative results were observed at the 1 ppm level. No false-negative results were seen above 1 ppm.

The total PAH results showed a high rate of false-negatives. This data would seem to indicate that normalizing the PAH concentration based on sensitivity of the anti-PAH to the various PAH compounds is somewhat valid. Also, the discrepancy between the spike recoveries in Phase V and Phase VI is attributed to the difference in soil matrices. More PAH was extracted from the sandy soil than from the loamy soil. This further supports the conclusion that adsorption may introduce a low bias into the test results.

CONCLUSION

It was the intent of this validation study to investigate and evaluate the performance of the Ensys PAH-RISc• test kit. The goal was to conduct a comprehensive set of experiments while working under the constraint of a predetermined number of available test kits.

This immunoassay test method performed favorably, although not quite as well, as claimed by the manufacturer. It does appear to have the potential to be used as a field screening tool, provided that the limitations of its use be borne in mind.

The primary caveat is that this kit should be used by personnel capable of proper interpretion of the results from a scientific standpoint. A negative result at 1 ppm does not necessarily indicate that less than 1 ppm of PAH contamination exists. Relatively high concentrations of particularly carcinogenic PAHs, such as benzo[a]pyrene, may be present on-site at levels which are well above 1 ppm but below the levels necessary to generate a positive test response. The sensitivity of the test kit to the various compounds must be borne in mind when interpreting the results. PAH-extractability may introduce low-bias at 1 ppm; the implications of this must be considered when concentrations of PAHs are near the 1 ppm level.

Also, proper soil sampling is a scientific technique. In order to obtain accurate, representative results using this test kit, the operator should follow appropriate soil collection methods.

Any samples which generate positive results, as well as a percentage of those which test negative, should be submitted for subsequent confirmational analysis by classical analytical methodology.

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DISCLAIMER

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67 RESULTS OF ANALYTICAL FIELD TRIALS FOR PCBs USING AN IMMUNOASSAY TECHNIQUE

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The use of immunoassays (IA) for field screening of environmental samples has increased dramatically over the past few years. Their utilization in remedial investigation and monitoring has gained widespread acceptance due in large part to the efforts of the US EPA to demonstrate the technology and begin the process of promulgating methods in which IA methodology is incorporated.

As part of the Superfund Innovative Technology Evaluation (SITE) program, the EnviroGard™ PCB Test Kit (Millipore Corp., Bedford, MA) was evaluated as a field screening method for identifying soil samples containing less than 10 mg/kg PCB. As part of the field screening activities, the SITE demonstration contractor (PRC Environmental Management, Inc., Kansas City, Kansas) standardized the IA with Aroclor 1242 (the major PCB contaminant at the site) and assessed the IA's utility in quantitating the level of PCB contamination. The screening results, which have been published in the SITE Technical Evaluation Report (TER), were consistent with the assay's performance claim of less than 5% false negatives (0/96 in the actual demonstration). To assess the accuracy of the EnviroGard PCB test kit, 89 samples that were quantitated using the IA with Aroclor 1242 standards, were compared to values obtained by GC/ECD analysis (SW846-8081). The correlation coefficient (r^2) for this data set was 0.45. Six of the 89 samples, all with high (>300 mg/kg) PCB levels, skewed the data so that when they were removed (i.e., N = 83), r^2 increased to 0.87. However, when only samples with GC/MS values of ≤ 100 mg/kg were considered, r^2 dropped to 0.33. Zero to 100 mg/kg, which encompasses most regulatory contamination limits, is the approximate dynamic range of the IA: Quantitation of levels higher than 100 mg/kg normally requires sample extract dilution. The high degree of scatter that was reported in the TER might be attributed to the imprecision associated with the field screening procedure: Analyses were performed in a non-laboratory environment, no reference (e.g., performance evaluation) samples were included, all results were based on single determinations, and the analyst, although competent, was only marginally trained in IA methodology. In order to determine if improving the method precision will improve its accuracy, the SITE demonstration samples will be reanalyzed under more rigorous, laboratory conditions.

If no improvement in accuracy is seen, it would suggest that IA technology, at least in terms of PCB analysis, might be limited to screening applications. On the other hand, if upgrading the analytical data quality and running the method under controlled laboratory conditions improve the IA's accuracy (i.e., $r^2 \geq 0.8$) in the 0 - 100 mg/kg range, it may be possible to bring many of the advantages of this innovative technology to quantitative analyses.

Data from the reanalysis will be presented and compared to the results obtained during the field demonstration. Based on the reanalysis, recommendations with regard to the scope and limitations of PCB immunoassay will be made.

68 IMPORTANT FACTORS IN ENHANCING SUPERCRITICAL FLUID EXTRACTION EFFICIENCIES FOR ENVIRONMENTAL APPLICATIONS

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ABSTRACT - Poster Presentation

Supercritical fluid extraction (SFE) has a broad range of applicability, especially with regards to environmental matrices. SFE has achieved a significant amount of attention due to the benefits of eliminating toxic, liquid solvent usage, reduction in sample preparation time and an increase in the overall analytical reliability of determinations. On-line SFE/GC-MS is a powerful technique to accurately analyze and quantitate environmental analytes. In addition, the off-line transfer of SFE effluents to collection vials adds a considerable amount of flexibility in characterizing complex matrices since a full complement of analytical tools can be used (i.e., GC, LC, IR, NMR and UV). Moreover, the advantages of SFE can be further augmented by the use of automation for greater sample throughput which can be especially important for environmental applications.

Examples will be presented showing the use of SFE/GC-MS and FID methodologies for the determination of different target analytes in environmental matrices, such as polynuclear aromatic hydrocarbons (PAHs), total petroleum hydrocarbons and pesticides in the soil. The discussion will also focus on the experimental verification of optimized SFE variables to achieve efficient and quantitative extractions of the target analytes in environmental solids. An example is shown in Table 1 where an off-line SFE/GC comparison was made between the extraction of PAHs from soil at different pressures, indicating that higher pressures were necessary for the complete recovery of the PAHs, especially the four and five ring PAHs.

Table 1

Compound	EPA Method 8270 Acceptance Range (ppm)	Concentration Levels (ppm) 250 atm	350 atm	450 atm
Naphthalene	24.2-40.6	23	23	25
Acenaphthylene	14.7-23.5	20	*	22
Acenaphthene	527-737	566	601	614
Fluorene	414-570	445	471	458
Phenanthrene	1270-1966	1682	1978	1911
Anthracene	373-471	357	439	400
Fluoranthene	1060-1500	1028	1459	1571
Pyrene	744-1322	703	1153	1269
Benzo(a)Anthracene	214-290	74	235	284
Chrysene	271-323	74	251	314
Benzo(b,k)-Fluoranthene	130-174	<1.0	107	155
Benzo(a)Pyrene	80.1-114.3	<1.0	64	89

INORGANICS

69 EVALUATION OF A RAPID STEAM-DISTILLATION PROCEDURE FOR THE EXTRACTION OF CYANIDE FROM LIQUID AND SOLID WASTES

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Cyanide in waste occurs as free cyanide (CN^- or HCN) or in complexes with metal ions. Depending on the thermodynamic stability and kinetic lability of the complexed forms, they may or may not be toxic to aquatic organisms if leached into surface water. For the estimation of potential water pollution, two operationally defined cyanide determinations are often performed on wastes. Total cyanide is usually determined by air-purged refluxing of the waste acidified with dilute sulfuric acid in the presence of magnesium chloride catalyst (*1*). The volatilized HCN is trapped in an alkaline scrubber solution and determined by one of a variety of methods. Strongly complexed cyanide (e.g., ferricyanide and ferrocyanide) is often determined by a second air-purged reflux after oxidation of other cyanide forms with alkaline hypochlorite. The presumed-toxic "cyanide amenable to chlorination" is determined by difference (*1*). An alternate estimation of the more toxic cyanide species can be made by the "weak-acid dissociable cyanide" procedure, which utilizes air-purged refluxing to liberate HCN from a sample containing zinc and buffered at pH 4.5. Under these conditions, iron cyanide complexes do not generate HCN (*2*).

All of the above procedures for the measurement of total cyanide and the estimation of the more toxic cyanide fraction are problematic. In addition to being prone to numerous interferences, they all rely on the air-purged reflux for the liberation of HCN. The reflux requires a minimum of about 90 minutes per sample. The procedures prescribed in SW-846 require a large reflux apparatus that precludes the simultaneous refluxing of several samples. None of the procedures have been validated for the determination of cyanide in solid waste. An alkaline extraction procedure for such samples is provided in SW-846, but recoveries are poor (*3*).

A steam-distillation procedure for the liberation of HCN from samples containing free and complexed cyanide will be described in this presentation. The method is rapid (< 15 minutes per sample) and provides good cyanide recovery from synthetic samples. Statistical analysis of the effect of various experimental parameters will be presented. Results for liquid and solid wastes using steam distillation will be compared to standard methods of analysis.

REFERENCES

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(3) "Cyanide Extraction Procedure for Solids and Oils," Method 9011, *Test Methods for Evaluating Solid Wastes (SW-846)*, U.S. Environmental Protection Agency, Washington, D.C., November 1990.

Notice: Although the research described in this presentation was conducted in part by the U.S. Environmental Protection Agency, it has not been subjected to Agency review. Therefore, it does not reflect the views of the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

70 ABSTRACT

A METHOD EVALUATION STUDY FOR THE ANALYSIS FOR HEXAVALENT CHROMIUM IN SOLID SAMPLES USING A MODIFIED ALKALINE DIGESTION PROCEDURE AND COLORIMETRIC DETERMINATION

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ABSTRACT

The difference between the levels of hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) in environmental samples is important from a human health concern due to the significantly greater toxicity of Cr(VI) compared to Cr(III). Consequently, knowledge of the chemical speciation and distribution of these two valence states of chromium in solid matrices is essential for adequate characterization and risk assessment of sites containing elevated levels of chromium. While current approved analytical methodologies exist to successfully differentiate between the 3^+ and 6^+ valence states in the liquid (aqueous) medium, there is currently no approved method for the determination of total Cr(VI) in the solid medium. An alkaline digestion method (Method 3060) appeared in the SW846 2nd Edition as a preparatory method for Cr(VI) analysis in soils. However, subsequent research and evaluation of the method in 1986 resulted in Method 3060 being omitted from SW846 3rd Edition due to a lack of predictability in environmental samples relating to oxidation of Cr(III) and/or reduction of Cr(VI). More than a thousand field samples and the results of a recently completed method evaluation study (MES) have demonstrated significant improvement over Method 3060 (SW846 2nd Edition). The MES which is the focus of this presentation, was divided into four distinct portions with the objective of showing that the modified Method 3060 is predictable and reliable within the constraints of the sample types evaluated. These include: (1) sample homogenization, (2) spiking studies using Cr(III) and Cr(VI), (3) a comparison of the modified Method 3060 to Method 3060 and (4) a mass balance study to determine the ultimate fate of Cr(VI) spikes with respect to chromium oxidation and/or reduction. Nine different types of solid matrices were selected for testing, ranging from quartz sand to chromite ore processing residues. All samples were characterized for auxiliary parameters including total organic carbon (TOC), total sulfides, pH, oxidation/reduction potential (ORP), and percent solids. The results of the study indicate that good matrix spike recoveries (76-115%) and duplicate precision were achieved in non-reducing samples using the modified alkaline digestion (Method 3060)/colorimetric technique (Method 7196A). In contrast, for highly reducing samples (e.g., anoxic sediments), zero percent Cr(VI) matrix spikes were obtained. For these samples, auxiliary characterization parameters and mass balance results demonstrated that such samples are not capable of maintaining a Cr(VI) matrix spike in the 6^+ valence state either in the laboratory or in the environmental settings from which they were collected. Spiking studies using soluble forms of Cr(III) indicate that less than 1% oxidation of Cr(III) to Cr(VI) is possible on the freshly precipitated Cr(III) that forms during the alkaline digestion, which should not hinder an accurate characterization of Cr(VI) in non-reducing solid matrices. A more difficult challenge for analytical chemists who use this method will be to avoid the interpretation that poor spike recoveries automatically mean that the method does not yield acceptable results.

71 THE ANALYSIS OF REDUCING SOILS FOR HEXAVALENT CHROMIUM

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ABSTRACT

The Second Edition of SW-846 contained a method (3060, 7196) for the determination of hexavalent chromium in soil. The method did not perform adequately for reducing soils and was dropped from later editions of SW-846. A need to analyze soil samples for hexavalent chromium exists; this paper presents a method suitable for reducing soils. The Second Edition method worked under two conditions: 1) the soil contained hexavalent chromium, or 2) the soil did not contain hexavalent chromium and was non-reducing. The Second Edition method failed the matrix spike recovery test if the soil did not contain hexavalent chromium and was reducing. The method given in this presentation uses capillary electrophoresis (CE), passes the matrix spike recovery test for reducing and non-reducing soils, and has a method detection limit of 4 mg Cr(VI) per kg soil (dry weight basis). This CE method is presently used in our laboratory for the determination of hexavalent chromium in soil.

INTRODUCTION

Previously presented methods and subsequent variations for the determination of hexavalent chromium, Cr(VI), in soil (for example, SW-846, Second Edition, Method 3060, 7196) have given acceptable results if Cr(VI) is present in the soil or the soil is non-reducing. Many of the methods fail a spike recovery quality assurance, QA, test if Cr(VI) is not present in the soil and the soil is reducing. Experience with actual samples indicates that the previous methods failed often and that a need existed for a new method to determine Cr(VI) in reducing soils.

This method determines the concentration of Cr(VI) in soil samples. The range is from 0.5 to 500 ppm (mg of Cr(VI) per kg of soil). This method determines easily extracted Cr(VI) from friable soil and other similar solid or semi-solid matrices, but is not acceptable for oily sludge, bricks, and other similar matrices. This method tolerates colored interferences in the soil and passes QA tests for soils which contain reducing agents.

The data quality objectives are: 1) The result of the measurement is the concentration of Cr(VI) in the soil sample expressed in units of mg/kg on a dry weight basis. 2) The desired detection limit is 4 mg/kg (dry weight) or better. The actual detection limit based on preliminary measurements for this method appears

in the Method Performance section. 3) The desired matrix spike recovery is 75% or better. The control limits for the matrix spike based on preliminary measurements appear in the Control Limits section. 4) A frequent use of the result of this method is to decide whether the concentration of Cr(VI) in a soil sample is equal or greater than an action level.

Summarizing the method: extract soluble Cr(VI) from the soil by using an alkaline solution, separate Cr(VI) from interferences in the extract by capillary electrophoresis, and measure Cr(VI) directly by absorbance at 270 nm. The extracting solution is alkaline to inhibit reduction of Cr(VI) by any reducing agents present in the soil.

Interferences are any soluble substances in the soil absorbing at 270 nm and co-migrating with Cr(VI). Any reducing agent in the soil capable of reducing Cr(VI) in alkaline solution, assuming such an agent and Cr(VI) co-exist in the soil when the soil was sampled, will be a negative interference. Any unfilled binding sites (mineral or organic) in the soil, assuming such sites co-exist with available Cr(VI) in the soil at the time of sampling, will be a negative interference. The usual reducing agents found in natural soils do not reduce Cr(VI) in alkaline solutions in the time frame of this method.

APPARATUS AND MATERIALS

1. Capillary electrophoresis (CE) with electromigration injection, absorbance detector at 270 nm, and a device to flush the capillary between runs. A number of instruments are commercially available. The instrument used to gather the data in the Method Performance section was: ISCO Model 3850 Electropherograph; uncoated silica, 60 cm, 50 μm ID capillary; detector at 270 nm, 0.002 absorbance range, 0.10 seconds rise time; voltage at 15 kilovolts, negative polarity (the injector end is negative); injection by electromigration, 5 seconds at 2 kV.

2. Integrator or Strip Chart Recorder.

3. 40 mL sample vials with lids.

4. Disposable Pasteur pipettes with cotton or tissue wrapped tips.

5. pH paper.

6. Micropipettes, adjustable, 10- to 100-μL and 100- to 1000-μL.

7. Volumetric flasks, 100 mL.

REAGENTS AND CHEMICALS

1. Extraction Solution: 0.1 gram sodium acetate, 0.04 gram alkyl trimethylammonium bromide (Sigma M-7635 or equivalent), 0.1 mL of 10 N sodium hydroxide, all diluted to 100 mL with deionized water.

2. 10 N NaOH: Dissolve 40 grams sodium hydroxide pellets in 50 mL deionized water. Dilute to 100 mL with deionized water.

3. 1 N NaOH: Dilute 10 mL of above 10 N NaOH to 100 mL with deionized water.

4. Dry reagent grade potassium dichromate ($K_2Cr_2O_7$).

5. Cr(VI) Calibration Stock Solution, 2000 mg Cr(VI) per liter of solution: Dissolve 0.566 gram potassium dichromate and 0.1 gram sodium acetate in 50 mL deionized water. Dilute to 100 mL with deionized water.

6. Cr(VI) Calibration Standards: Dilute the following volumes of Cr(VI) calibration stock solution to 100 mL with Extraction Solution:

[Cr(VI)],(mg Cr(VI)/L soln)	Stock,(μL)
0	0
1	50
3	150
5	250
10	500
20	1000
30	1500
50	2500

7. Dry sand known to be free of Cr(VI).

8. Method Standard Stock Solution: Dissolve 0.283 grams of potassium dichromate and 0.1 gram of sodium acetate in 50 mL of deionized water, dilute to 100 mL with deionized water to make stock solution with a concentration of 1000 mg Cr(VI) per liter of solution. Prepare this solution using a separate source of potassium dichromate than the Calibration Stock Solution in Step 5 above, and keep it as independent as possible from the Calibration Standards.

QC SAMPLES

The definitions of recommended QC samples are:

1. Method Blank: a sample of sand known to be free of Cr(VI) put through the same steps as a regular soil sample.

2. Matrix Spike: an amount of the Cr(VI) Calibration Stock Solution added to a replicate of a soil sample at the appropriate step (see Analytical Procedure section: Sample Preparation) and analyzed as a regular soil sample.

3. Matrix Spike Duplicate: an amount (as above) of the Cr(VI) solution added to a second replicate of a soil sample to give the same increase in concentration as the above matrix spike, and analyzed as above.

4. Method Standard: an independent check sample of sand known to be free of Cr(VI) spiked (as above) with Method Standard Stock Solution to give 40 mg Cr(VI)/kg sand (or other amount as specified in a QA project plan) and put through the same steps as a regular soil sample.

SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

Collect soil samples using standard field procedures. Since the Cr(VI) and other interfering substances may be unstable in the disturbed soil, analyze the samples as soon as possible after sample collection. Do not add preservatives to the sample. Holding time studies were not conducted.

ANALYTICAL PROCEDURE

1. SAMPLE PREPARATION

Tare a 40 mL wide-mouth glass vial (as commonly used for VOA analysis) and transfer approximately 20 grams of the sample into the vial. Measure and record the actual sample weight. Add the extraction fluid to the sample in the vial, 15 mL or enough to make a free-flowing slurry, and mix the solid and liquid phases by shaking. Calculate and record the actual volume of extraction fluid using the measured weight and the density of the fluid. Test the pH of the slurry immediately and, if necessary, adjust the pH with 10 N NaOH to greater than 8.5. For matrix spike and matrix spike duplicate samples, add the spike to the sample after the pH is adjusted. Experience showed that analysis should be completed within two hours after adding the extraction solution to prevent loss of Cr(VI).

2. INSTRUMENT

Set up the CE instrument with electromigration injection according to the manufacturer's instructions. Use extraction fluid to fill both reservoir cups.

3. CALIBRATION

Analyze each of the calibration standards. Flush the capillary between standards with three drops of extraction fluid.

Construct a calibration curve. Initial trials indicated the correlation coefficient was 0.995 or greater over a range of zero to 50 mg/L.

4. SPIKING PROCEDURE

Calculate the amount of spike (S) to add to the sample as follows:

Let "D" equal the desired increase in concentration of Cr(VI) due to the added spike to the soil sample, in units of mg Cr(VI)/kg soil, dry weight basis.

Then,

$$S = \frac{V * 1{,}000{,}000}{\frac{V * 2000}{D * W * F} - 1}$$

where:

S = the volume of calibration stock solution (which is 2000 mg Cr(VI) per liter) added as a spike to the soil sample, in units of μL,

V = the volume of extraction fluid added to the soil sample, in units of L,

1,000,000 = the units conversion factor to convert the units of S from L to μL,

2000 = the concentration of the calibration stock solution in units of mg Cr(VI)/L,

D = the desired concentration increase, in units of mg Cr(VI)/kg, dry weight basis,

W = the weight of the soil sample in the vial, "as is", in units of kg, wet weight basis, and

F = the unitless fraction of dry material in the soil sample.

Add the spike, S (μL), to the sample at the appropriate step given above, and mix thoroughly by shaking.

5. ANALYSIS

Draw about 100 μL of the liquid from the slurry through a tissue or cotton-tip into a Pasteur pipet and transfer the clear liquid into the sample cup in the CE instrument. Inject the sample by electromigration into the instrument using a 5-second injection time. Apply the CE voltage and record the absorbance measured at 270 nm with a chromatographic integrator or stripchart recorder. For most samples, the Cr(VI) absorbance peak occurs at about two minutes. The retention time depends on the concentration of the buffer, the flush history of the capillary, the temperature, and the voltage.

Since other electrophoretic peaks appear in the electrophoreogram and the capillary becomes coated with contamination when running regular soil samples, flush the capillary before every injection using three drops of 1.0 N NaOH, followed by six drops DI water, and finally six drops of extraction fluid. Indications of inadequate flushing are shifts in retention time, ghost peaks, and broad peaks. A small peak observed at the correct time window should be confirmed with another injection after flushing the capillary.

CALCULATIONS

1. Calculate the result, H, as follows:

$$H\ (\text{mg Cr(VI) /kg soil, dry}) = \frac{C\ (\text{mg Cr(VI) / L soln}) * V\ (\text{L soln})}{W\ (\text{kg soil, as is}) * F\ (\text{unitless, solids in soil})}$$

where:

H = the measured concentration of Cr(VI) in the soil, dry weight basis, in units of mg/kg,

C = the concentration of Cr(VI) measured in the extraction fluid, taken from the detector response and the calibration graph, in units of mg/L,

V = the volume of extraction fluid added to the soil sample in units of L,

W = the weight of the soil sample in the vial, "as is" or "wet weight", in units of kg,

F = the unitless fraction of dry material in the soil sample.

2. Calculate the spike recovery for the matrix spike and the matrix spike duplicate as follows:

$$\% \text{ Recovery (spike)} = 100 * R/(H + D)$$

where:

% Recovery (spike) = the matrix spike recovery in units of percent, dry weight basis,

H = the measured unspiked sample result given above, in units of mg/kg, dry weight basis,

D = the increase in concentration of Cr(VI) in the sample due to the spike added, in units of mg/kg, dry weight basis,

R = the measured spiked sample result, obtained using the same expression as H above, in units of mg/kg, dry weight basis.

3. Calculate the method standard recovery as follows:

$$\% \text{ Recovery (standard)} = (H / STD) * 100$$

where:

% Recovery (standard) = percent recovery of the method standard in units of percent, dry weight basis,

H = the measured sample result given above, in units of mg/kg, dry weight basis, and

STD = the actual or true value of the concentration of Cr(VI) in the standard sample, in units of mg/kg dry weight basis. The default value of STD was set to 40, but may be changed to meet project objectives specified in a QA project plan.

4. Calculate the percent relative standard deviation of the matrix spike and the matrix spike duplicate (the two replicate samples may have different weights, but each must have the same increase in concentration due to the spike, see Analytical Procedures section: Spiking Procedures) as follows:

$$\%RSD = sqrt(2) * abs(MS - MSD) / (MS + MSD)$$

where:

%RSD = percent relative standard deviation in units of percent,

sqrt(2) = the square root of 2,

abs(X) = the absolute value of X,

MS = the measured result for the matrix spike sample, obtained as H above, in units of mg/kg dry weight basis, and

MSD = the measured result for the matrix spike duplicate sample, as MS above.

CONTROL LIMITS

Using the data given in the Results Section, the 95% confidence interval for the control limit for the percent recovery of the method standard and the matrix spike was from 60% to 140%. This assumes the method standard and the matrix spike behave the same.

The 95% control limits of the percent relative standard deviation of the lab matrix spike and the lab matrix spike duplicate were: lower limit = 5%, upper limit = 10%.

When conducting field spiking, note that field spiked samples are potentially unstable, since Cr(VI) and reducing agents could co-exist indefinitely only in a completely dry soil spiked with a dry substance.

METHOD PERFORMANCE

The following is a summary of results for a number of different matrices using this method. All following values were the result of seven separate replicate samples analyzed in one batch. All values are in units of mg Cr(VI) per kg soil, dry weight basis. All entries in the following tables were calculated using the expressions specified above, except the MDL which followed 40 CFR Part 136 Appendix B. The naming and data reporting conventions are:

Av.Obs. the average observed value,

n=7 indicates seven replicate samples were used to determine the reported value,

A%R the average percent recovery,

MDL the detection limit,

df the degrees of freedom of the reported value,

AL%RSD the average laboratory percent relative standard deviation.

1. Fertilite (tm) "Top Soil", UPC# 7270140030, Hyponex Corporation, 14111 Scottslawn Road, Marysville, Ohio 43041. (This soil failed QA using the previous methods.)

Spike Added	Av.Obs.(n=7)	A%R(n=7)	MDL(df=6)	AL%RSD(df=6)
0	non-detect	-	-	-
10.3	8.4	84.1	3.2	11.9
102.8	96.9	94.3	-	4.5

2. U.S. EPA Synthetic Soil Matrix, Risk Reduction Engineering Laboratory, Release Control Branch, Edison, New Jersey 08837-3079. (This soil passed QA using previous methods.)

Spike Added	Av.Obs.(n=7)	A%R(n=7)	MDL(df=6)	AL%RSD(df=6)
0	non-detect	-	-	-
4.0	4.3	106.5	4.3	32.5
40.0	53.4	133.5	-	9.2

3. The above Synthetic Soil Matrix fortified with 2% glucose by weight. (This soil failed QA using previous methods.)

Spike Added	Av.Obs.(n=7)	A%R(n=7)	MDL(df=6)	AL%RSD(df=6)
0	non-detect	-	-	-
4.0	6.4	161.	4.3	21.9
40.0	27.0	67.5	-	8.9

4. Loess, underlying material obtained from road cut on Interstate 70 between the 57th Street exit and the 61st Street overpass, Section 11, T11S, R24E, Wyandotte County, Kansas. (This soil passed QA using previous methods.)

Spike Added	Av.Obs.(n=7)	A%R(n=7)	MDL(df=6)	AL%RSD(df=6)
0	non-detect	-	-	-
5.52	4.2	75.9	0.55	4.8
55.2	52.7	95.5	-	2.8

SUMMARY

The above text is an abridged version of the SOP used in our laboratory for the analysis of soil samples for hexavalent chromium. The throughput for one person using this method is 20 to 30 samples per day. This compares with a throughput of 2 to 3 samples per day using the older method. Analysts familiar with both methods prefer the CE method. Background reading for this method includes: 1) P. Jandik et al., "Electrophoretic Capillary Ion Analysis: Origins, Principles, and Applications." LC-GC 9 634-645, 1991, and 2) J. E. McLean & B. E. Bledsoe, "Behavior of Metals in Soils." EPA/540/S-92/018.

72 FACTORS AFFECTING SAMPLE THROUGHPUT FOR AN ICP-OES SYSTEM WITH A SEGMENTED-ARRAY CCD DETECTOR

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Introduction

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a fast, economical technique commonly employed for the determination of metals in a variety of environmental matrices. Advances in optics and detection systems for ICP-OES have led to instruments that have new capabilities and better performance (1, 2). In this work we examine the potential to increase sample throughput by evaluating the factors that may be varied versus the data quality objectives for the analysis. We will characterize several of the ICP performance characteristics and evaluate several real applications for potential time savings.

Data quality objectives (DQOs) are critical in evaluating the performance that must be achieved with an ICP-OES method. DQOs that will be particularly important in evaluating sample throughput are detection limits, accuracy requirements, precision, and dynamic range. If these are well-characterized for a particular analytical situation then potential sacrifices can be identified and judicious choices made in pursuing sample throughput increases.

Several ICP-OES instrumental factors will affect the DQOs and analysis time. These factors were investigated to quantitate the magnitude of each effect. Integration time will affect both the detection limits and precision of an analysis. Fifteen elements representing the full wavelength range were studied and showed that increasing the integration for each replicate will improve both detection limits and precision. The greatest improvement is for elements with transitions below 350 nm where photon shot noise is the predominant source of noise affecting the signal and background.

Background correction can remove spurious radiation from the desired signal by comparison with an off-line measurement. If background correction is done simultaneously, rather than sequentially, detection limits can be improved for elements with transitions above 250 nm and exceed detection limits without background correction above 350 nm. These transitions take place in a region of the spectrum dominated by flicker noise, which can be partially removed by the correlation in simultaneous background correction.

In a complex sample, background correction may be even further improved by the use of a multivariate correction procedure such as Multicomponent Spectral Fitting (MSF) (3). MSF uses the full spectrum to create a model of peak shapes used in correcting the analytical signal. Figure 1 demonstrates the magnitude of improvement that can be expected with different types of background correction procedures. MSF improves the detection limit beyond that which can be achieved without background correction.

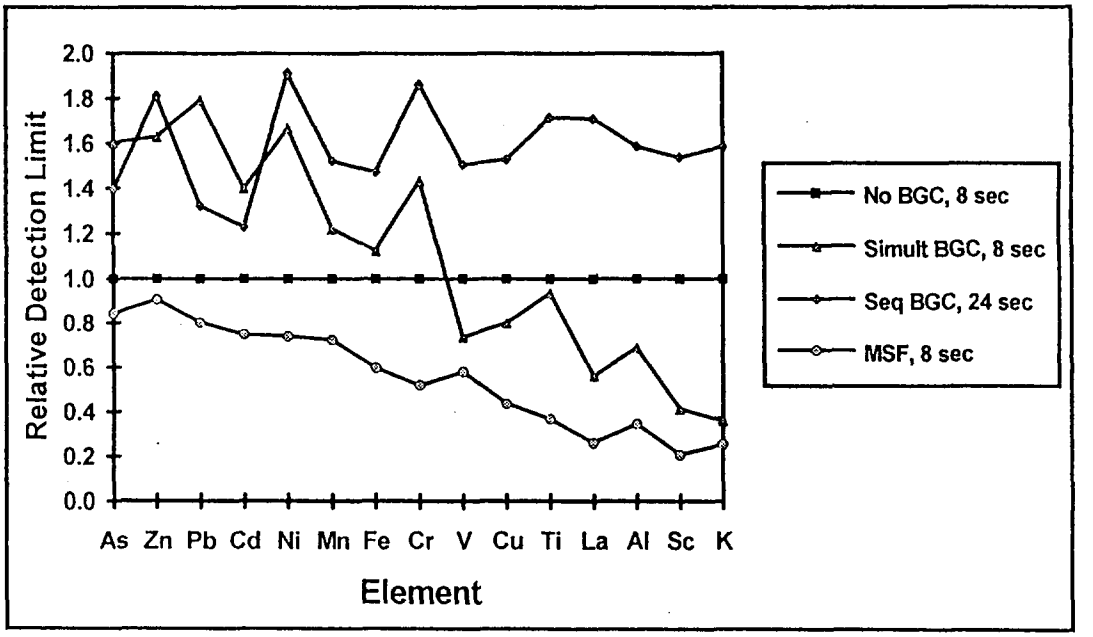

Figure 1. Effect of Background Correction on Detection Limits

Three applications were studied to demonstrate the practical application of the decision-making process. The first application is to increase the sample throughput for a wear metals trend analysis (WMTA) requiring moderate detection levels for 16 elements. An oil additive and trace analysis (OATA) requires lower detection limits and precision better than 1%. Finally a TCLP analysis for 7 elements extracted into an acetic acid buffered matrix was examined. Table I lists the data quality objectives for the three analytical situations.

Table I
Data Quality Objectives of
Three ICP-OES Applications

	WMTA	OATA	TCLP
No. Elements	16	16	7 (14 lines)
No. Reads/Sample	1	2	3
Detection Limits (mg/L)	0.01-0.5	0.001-0.1	< 0.1 x MCL
Accuracy	±10%	-	±10%
Precision (RSD)	3%	< 1%	3%
LDR (orders/elem.)	3	4-5	4-5
Rinse Out (orders)	3	LDR to 3x DL	LDR to 3x DL

Results

After careful evaluation of the various instrumental factors the WMTA was speeded up to allow the analysis of a standard, blank, and 20 samples in 13.5 minutes. Including a QC check sample every fifth sample, 98 samples can be analyzed in 1 hour. The average precision obtained at concentrations above 50x the detection limit were 1.4% RSD.

The OATA speed was increased to analyze 35 samples per hour. For low concentration samples an analysis time of 2 minutes was necessary to meet the DQOs, but when concentrations approach 20 mg/kg the analysis time can be reduced to 1.2 minutes/sample.

Two emission lines were monitored for each TCLP element to add confirmation information to the analysis. The analysis was performed in less than one minute with 65 samples per hour analysis rate, including the QC checks. If the ICP periodic table is monitored to evaluate the sample for other possible contaminants the analysis is still performed in less than 2 minutes per sample.

Summary

Advances in ICP-OES technology have provided the base for improvements in sample throughput. ICP-OES factors have been evaluated to demonstrate the relationship with sample throughput and the concepts applied to three real-world applications. In all cases the analyses were speeded and the sample throughput increased significantly. The principles examined can be applied to other situations to evaluate the potential for time savings.

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73 DESIGN, PERFORMANCE, AND ENVIRONMENTAL APPLICATIONS OF AN ICP ARRAY DETECTOR SPECTROMETER

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This paper will describe and evaluate a new kind of ICP-optical emission spectrometer — one utilizing a mega-pixel, two dimensional, solid state array detector. With more than one million individual detector elements, the array captures a high resolution electronic photograph of the complete UV-visible emission spectrum. All elements in the periodic table that emit UV-visible light in an ICP discharge can be detected and quantified at any number and any combination of wavelengths. This capability enables rapid qualitative and semiquantitative screening of unknown samples, an application that will be discussed in detail especially as it pertains to waste analysis. In addition, rigorous quantitative analysis of water and waste will be demonstrated to the quality control standards established by the Contract Laboratory Program.

74 VARIABILITY IN TCLP METALS RESULTS FROM STABILIZED WASTES

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ABSTRACT

The purpose of this multi-laboratory study was to identify variables in Toxicity Characteristics Leaching Procedure (TCLP) and subsequent analysis and to recommend standard protocols to improve inter-laboratory precision. The TCLP, together with subsequent digestion and instrumentation methods, allow choices of laboratory practices. The choices made by individual laboratories contribute to inter-laboratory variability. For instance, TCLP allows extraction of any particle size less than 3/8 inch, and any extraction time from 16 to 20 hours. Additionally, choices made about specific digestion methods and instrument methods may also allow further inter-laboratory variation.

For analyzing TCLP metals, a laboratory can choose from any appropriate digestion or instrument procedures. For example, lead can be analyzed either by graphite furnace atomic absorption (GFAA) spectroscopy (Method 7421) or inductively coupled plasma (ICP) atomic emission spectroscopy (Method 6010). The digestion procedure associated with each analysis is Method 3020 for GFAA or Method 3010 for ICP. Inevitably, there are differences between the methods, and there is variability within each method. Individual waste matrices can also add variability to the results.

The goal of improving inter-laboratory precision therefore required identifying and quantitating variables that lead to differences in TCLP results. The approach taken in this study was to have each participating laboratory analyze a "tailor made" proficiency sample so that inter-laboratory and intra-laboratory variability could be measured. Existing QA/QC data from proficiency samples and standard reference materials were also examined. The results from round robin analyses and the recommendations for analytical protocols are discussed.

75 AMALGAMATION CVAA TO IMPROVE THE DETECTION LIMIT OF MERCURY IN ENVIRONMENTAL SAMPLES

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Introduction

Mercury is of continuing interest in the environment due to its persistence and toxicity. Mercury determination has traditionally been performed using cold vapor generation coupled with atomic absorption (CVAA) to achieve a detection limit of 200 ng/L (ppt) in a prepared sample. Each sample is handled individually and the technique is very labor and time intensive. Manual sample handling may also expose the sample to additional sources of contamination, increasing the variability in the results obtained with the technique.

Flow injection techniques (FI), where reagents are mixed with the digested sample automatically, provide several advantages. The samples are isolated from atmospheric and handling contamination. The volume of sample necessary to generate the signal is greatly reduced, which also reduces the consumption of reagents and waste generated from the process. Interferences are reduced because the mercury vapor is separated from the mixture very quickly, limiting the time for adverse reactions to occur. The sample throughput is increased and the procedure can run unattended (1).

Although FI can significantly improve the quality and ease of a classical mercury determination, lower detection limits would also be useful. Coupling FI with newer light sources, such as the EDL System 2 can lower the detection limit to 60 ng/L for routine analyses. However, research into bioaccumulation of mercury and naturally occurring marine levels require the establishment of still lower detection levels. This work describes the development of a FI system coupled with preconcentration of mercury by amalgamation to reduce mercury detection limits to 2 ng/L for an 8.5-mL sample size (2).

Figure 1 shows the FI system coupled to the amalgamation accessory for mercury preconcentration. Mercury vapor is generated in the mixing manifold and separated in the gas-liquid separator. The mercury vapor is trapped on a gold/platinum gauze and held there until a sufficient amount is deposited. The deposition is halted and the gauze heated to release the mercury as a concentrated plug into the absorption cell of the atomic absorption spectrometer, where the absorbance is measured and quantitated.

Results

Figure 2 compares the signals obtained for 1000 ng/L mercury with and without amalgamation preconcentration. The method detection limit, measured using the procedure in CFR, Part 136 Appendix B, was found to be 2 ng/L for an 8.5-mL sample and 60 seconds of deposition time. This represents the detection of 17 pg of mercury on an absolute basis. Larger samples and longer deposition times might decrease the detection limit, but eventually reagent and handling contamination are going to limit further improvement.

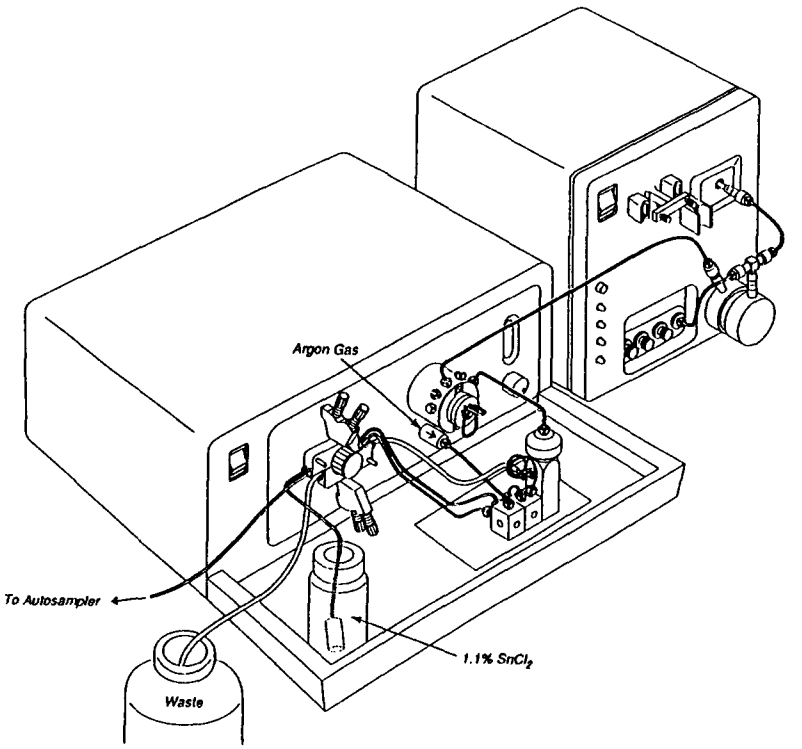

Figure 1. FI Mercury Amalgamation System

The mercury vapor is channeled through the FI valve to the amalgamation system. This controlled vapor deposition technique reduces sample carryover and improves precision. The precision for replicate samples was 2.5% RSD at 20 ng/L of mercury.

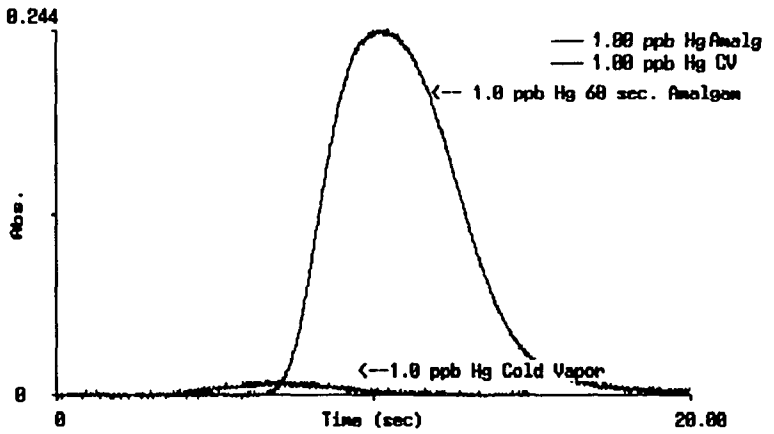

Figure 2. Mercury Signals With and Without Amalgamation

Summary

The system described in this work provides several advantages for the determination of mercury compared to conventional CVAA batch analysis. The detection limit using amalgamation is reduced to levels that allow the study of marine and estuary ecosystems. The addition of reagents is automatic and the sample throughput is improved to allow the determination of 30 samples per hour in unattended operation.

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76 THE DEVELOPMENT OF EPA TOTAL MERCURY METHOD USING COLD VAPOR FLUORESCENCE MERCURY DETECTION SYSTEMS. THE MERCURY METHOD WILL BE USED FOR THE ANALYSES OF MERCURY IN WATER, WASTEWATER, SEA WATER AND RELATED MATRICES.

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ABSTRACT:

The U.S. Environmental Protection Agency (USEPA) is developing a method for the determination of total mercury found in water and sediment at the part per trillion (ppt) level. The total mercury method has an estimated method detection limit (MDL) of 5 ppt to 20 ppt of mercury. The MDL is made possible by digesting the sample using bromide/bromate reagent followed by detection of elemental mercury by cold vapor atomic fluorescence spectrometry at 253.7 nm

INTRODUCTION:

Methylmercury poisoning of humans and cats in Japan known as "Minamata" disease (1950-1970) was caused by the consumption of mercury (10 to 24 parts per million [ppm]) contaminated fish. This environmental catastrophe marked the beginning of a world-wide concern that mercury may be a global pollution problem. The history, hazards, and concerns about mercury pollution were documented by 1972[1]. The Minamata Bay tragedy led to independent investigations of the Great Lakes region by the United States and Canada. These studies found high levels of mercury in fish. From these early studies, it became apparent that a standardized mercury method was needed for the exchange of mercury data between the two countries. Jacobs et al[2] in 1960 introduced the oxidation/digestion of biological samples by wet digestion. The wet digestion technique of mercury samples using potassium permanganate and sulfuric acid gained acceptance in Canada and United States. The Canadian government made strides to standardize this approach. The credit for developing wet digestion and the cold vapor (flameless) atomic absorption technique is credited to the Canadian team Hatch and Ott[3]. However, their approach to digestion of mercury samples varied from the Jacobs' approach. This variation of sample digestion and a lack of standardization of methodology created data compatibility problems between countries. The Canadian government elected to standardize on one of these sample digestion techniques. By 1970 the cold vapor technique and the permanganate sulfuric acid oxidation/digestion was accepted by the Fisheries Research Board of Canada and Federal Water Quality Administration (FWQA) as provisional methods with minor differences in sample digestion. The United States reviewed the

results of the Canadian methods, then provided the Water Pollution Control Agency (WPCA, 1970) a provisional method for mercury analysis.

The USEPA, established in 1971, took over the responsibilities of the WPCA. The USEPA, Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) continued the research on the WPCA provisional cold vapor method. The USEPA, EMSL-Cincinnati proceeded to standardize the method. The EPA's method development protocol required a feasibility study and single laboratory validation study. The method feasibility study was conducted by J.F. Kopp, M.C. Longbottom, and L.B. Lobring.[4] These researchers used an experimental design that included the analysis of known interferences (chloride, sulfide, organics) and other variables (digestion, heat, time). The result of this research in 1972 lead to the development of the optimized "Cold Vapor" USEPA Mercury Method 245.1 for mercury-total[5] that was completed in 1976 and revised in 1983. The USEPA adopted an extensive method validation policy and then proceeded to confirm the single operator precision by expanding to multi-laboratory confirmation. The USEPA, EMSL-Cincinnati, Quality Assurance Branch conducted a nation-wide validation study. This study validated the USEPA Mercury Method 245.1 that produces data of known quality at the part per billion (ppb) level. However, new regulatory demands are now being made to detect mercury at the parts per trillion (ppt) level. These regulatory demands are a result of new consensus among researchers[6,7,8,9] over growing mercury pollution of the aquatic food chain.

There are at least 23 states with existing fish consumption advisories for mercury and numerous USEPA Superfund sites with significant mercury contamination of soils, ground and surface waters. The fish advisories and the need to monitor trace level mercury migration from Superfund sites has prompted many requests for a mercury method able to detect mercury at the ppt level. To protect the aquatic environment, many states are now implementing monitoring and enforcement of National Pollutant Discharge Elimination System (NPDES) permits established by water quality-based effluent limitations. The effluent limitation for mercury uses a bioaccumulation factor in the equation that has resulted in permit values being set below the USEPA Method 245.1 detection limit for total mercury. The current USEPA Method 245.1 has a detection limit for mercury of .2 μg-Hg/L (.2 ppb) in water. This current MDL is too high to satisfy monitoring requirements as established by the USEPA and state water quality-based effluent limitations requirements. A mercury method with a low detection limit (20 to 2 ppt) is desired for the determination of mercury in natural waters. This would support studies that are attempting to define probable sources of mercury contamination in the aquatic food chain. There is a study being proposed for the Florida Everglades that will require ppt detection limits.

The State of Florida has determined that many sport fish caught in the South Florida Everglades are contaminated with high levels (0.5 to 4 ppm) of mercury. This has caused a fish advisory to be issued for the Florida Everglades. The search for the cause of mercury contamination is hampered by a mercury method having a detection limit of 0.2 ppb. This detection limit is too high for ambient water analysis where mercury levels are expected to be in the low ppt level. The State of Florida is located in USEPA Region 4. The USEPA,

Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-Cincinnati) received a request to support USEPA, Region 4, by providing methods development and quality assurance resources for the Everglades study. Region 4 will provide a plan of study for the Everglades ecosystem[10]. The study of the Everglades will require methods that can measure mercury below the ambient levels found in nature.

The current EPA Mercury Method 245.1 may be applied to many sample types (industrial and domestic). Although it is a rugged method, it suffers from interferences that absorb UV radiation that can cause a positive bias. There are two ways to overcome these interferences and lower the detection limits:

(a) The atomic fluorescence of mercury is independent of UV absorption interferences. Atomic fluorescence detects mercury by emission rather than by absorption. Since emission is inherently more sensitive than atomic absorption, it is expected that detection limits may be lowered to parts per trillion (ppt, ng/L) range.

(b) Interferences may be eliminated by pre-concentration of mercury on gold amalgam. Gas vapors containing interferences pass through the instrument before the mercury analysis. The gold/mercury amalgam trap is heated, releasing the mercury vapor for analysis by atomic fluorescence detector. This increases mercury sensitivity by producing a highly concentrated peak.

EXPERIMENTAL:

A statistically-based experimental design or chemometric approach as described by Deming and Morgan (1987)[11] was selected for the evaluation of the mercury method. The chemometric experimental approach was applied to this mercury method to speed the process of method evaluation. The chemometric approach is dynamic (modifiable) and recursive (experiments may be repeated). During the execution of the experiments an evaluation of each "phase" of an experiment is required. When a modification of the experiment was required, it was strongly supported by the statistical evidence. The experimental design consisted of the following phases:

Phase 1 -Familiarization Study.
Phase 2 -Automated Instrument Optimization Study.
Phase 3 -Automated Instrument Linearity Study.
Phase 4 -Mercury Precision and Recovery Study.
Phase 5 -Instrument Stability Study.
Phase 6 -Initial Interference Study.
Phase 7 -Sample Preservation Study.
Phase 8 -Single Laboratory Validation Study.
Phase 9 -Establish Instrument Control Charts.
Phase 10 - Establish Clean Room Protocol.

The instrument selected for the study is a QuesTron "PSA" Automated Mercury Analyzer (Merc 22). This instrument offers a complete system containing Autosampler, Gold amalgam pre-concentrator, fluorescence detector, an IBM compatible USEPA Contract Laboratory Program (CLP) quality control software program and data acquisition system.

The automated instrument is generally configured as shown below. The gold amalgam accessory for the instrument system is not shown in this configuration. The gold amalgam accessory will be evaluated during the ruggedness testing portion of the method development and is not part of the scope of this experimentation.

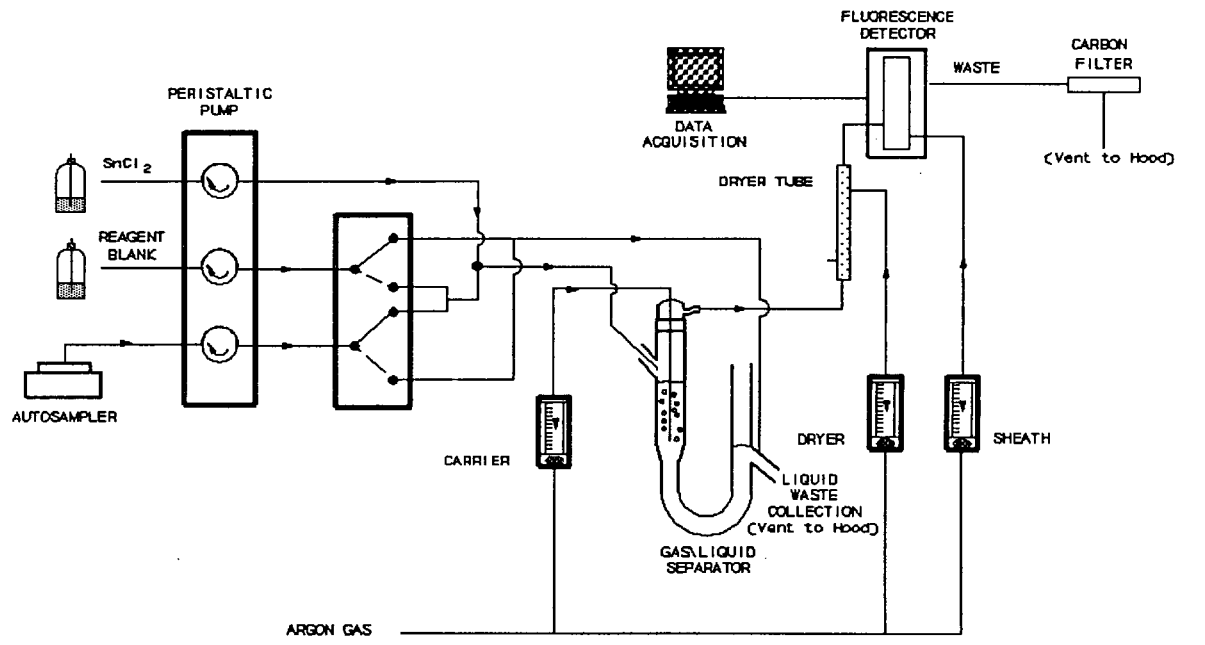

FIGURE 1: PSA AUTOMATED MERCURY FLUORESCENCE SYSTEM

RESULTS:

Instrument Optimization:

In the familiarization and optimization phase of the experiments, the mercury analyzer was optimized for maximum sensitivity and/or signal-to-noise ratio. The use of Simplex optimization was investigated using the carrier gas and sheath gas flow rates as selected variables. A Simplex program written in BASIC was used for algorithm computations. The optimized flow rates calculated by the program were 156 mL/min for the sheath gas and 329 mL/min for the carrier gas, although there was some evidence from the Simplex convergence behavior that the two variables were not interactive. The timing sequences on the hydride generator, which define the analytical cycle, were also optimized manually to obtain good peak shapes. Work continued on the evaluation and optimization of instrument performance and assessment of sample preparation procedures.

Improvements were made on the system to increase precision and sensitivity. The rotameters for the carrier, sheath, and dryer tube gas were replaced by new rotameters from PS Analytical. The new rotameters for the carrier and sheath gas flows were modified to a lower and more practical range. The dryer tube rotameter was modified to allow much higher flows to remove moisture from the sample more effectively. The sensitivity of the instrument was also increased over 30% upon replacement of the worn dryer tube element. After these changes were made, a check on the precision of the instrument was performed. The system was calibrated once an hour for seven hours and the slope of the curve was monitored as an indication of the instrument drift. The RSD of the slope over the day was 3.6%, a noticeable improvement over earlier drift that ranged from about 10-20%.

Before conducting any detailed analytical benchmark studies, it was decided to optimize the instrumentation with respect to maximizing the slope of the sensitivity curve, while maintaining acceptable precision, accuracy and peak shape dynamics. As only two user-adjustable variables were considered to have a critical effect on the analytical performance of the instrument, namely the carrier and sheath gas flow rates, it was not considered necessary to use a simplex optimization process. The experiment consisted of running two repetitions of a 3^2-factorial design. Each repetition was conducted on a separate day to find out the day-to-day reproducibility of the system. The order of the experiments within each repetition was randomized. The levels of carrier gas flow chosen for the experiment were 200, 350 and 500 mL/min, while the sheath gas flow rates chosen were 0, 350 and 700 mL/min. For each experiment, the instrument was calibrated using a calibration blank and three calibration standards (50, 100 and 150 ng/L). Using this calibration curve, the instrument was then used to determine three test concentrations (25, 75 and 125 ng/L). The output variables recorded for each experiment were the maximum peak height for the 50 ng/L calibration concentration, the slope of the calibration line, the correlation of the calibration line and the estimates provided by the system for each of the three test concentrations. The results of the experiments are summarized in Table 1 below.

TABLE 1: DATA FROM OPTIMIZATION EXPERIMENTS

Carrier mL/min	Sheath mL/min	Day	Peak Height	Slope	r	25 ng/L	75 ng/L	125 ng/L
200	0	1	146.2	2.24	1.0000	24.4	75.5	****
200	0	2	164.6	2.52	1.0000	24.1	****	****
200	350	1	101.3	1.52	0.9999	26.4	79.4	118.7
200	350	2	108.4	1.68	1.0000	24.6	77.1	****
200	700	1	63.1	0.95	0.9998	25.1	75.7	124.8
200	700	2	71.6	1.04	0.9997	23.6	74.2	125.6
350	0	1	106.8	1.60	1.0000	25.1	75.3	****
350	0	2	118.6	1.86	1.0000	24.3	71.4	****
350	350	1	84.5	1.27	0.9998	24.8	73.5	122.8
350	350	2	93.7	1.38	0.9999	23.2	74.2	120.9
350	700	1	61.3	0.91	0.9999	22.9	76.5	127.5
350	700	2	68.2	1.01	0.9996	25.8	76.0	127.1
500	0	1	76.4	1.13	0.9999	24.2	73.5	126.5
500	0	2	93.6	1.39	1.0000	23.5	71.7	119.8
500	350	1	68.0	0.97	0.9998	21.5	71.4	118.6
500	350	2	68.5	1.11	0.9999	24.4	74.0	125.1
500	700	1	48.8	0.71	0.9999	24.5	76.2	126.4
500	700	2	54.3	0.82	1.0000	25.8	75.4	125.0

****Test concentration signal off-scale r correlation coefficient

For the (500,0) run on day 1, two duplicates of each calibration and test concentration were run through the system. However, it was decided that running duplicates for all factor setting combinations would be too time consuming. All of the remaining runs were based on just one sample of each of the calibration and test concentrations. To equalize the underlying variance, only the numbers for the first of the duplicates on the first run were used. The calibration curve, correlation coefficient and estimates for the test concentrations were computed manually from the peak heights produced by the instrument.

To characterize the accuracy of the readings of the three test concentrations, the absolute percent deviation from the true concentration was used. Originally a multivariate analysis of variance (MANOVA) was proposed for the analysis of the data. However, the missing values in Table 1 meant that only thirteen observations could be used in the MANOVA. Individual statistical analyses were, therefore, run using the response variables, calibration slope and percent deviation for each of the three sample concentrations. Peak height was not included because it provides similar information as the slope of the calibration line. The correlation coefficient was omitted because the calibration line was almost always a perfect fit (r values ranging from 0.9996 to 1.0000). Type III sums of squares were used because it could not be assumed that interaction effects were insignificant. The day was included in the analysis because it was of interest to know whether the performance of the system changed from day to day. Table 2 contains the F-statistics and p-values for each of the four response variables for the factors carrier gas flow, sheath gas flow, the interaction term between the two and the day. This information shows that the accuracy of the system does not change significantly when the flow levels are varied. However, the slope of the calibration line differs significantly based on all of the independent variables in the model.

TABLE 2: OPTIMIZATION TEST STATISTICS

Dependent Variable	Source of Error	F-statistic	Degrees of Freedom	p-value
Slope of Calibration Line	Model	153.02	9,8	0.0001
	Carrier Gas	203.71	2,8	0.0001
	Sheath Gas	392.61	2,8	0.0001
	Carrier - Sheath	35.53	4,8	0.0001
	Day	42.44	1,8	0.0002
Absolute Percentage Error (25 ng/L)	Model	0.43	9,8	0.8867
	Carrier Gas	0.39	2,8	0.6924
	Sheath Gas	0.46	2,8	0.6471
	Carrier - Sheath	0.54	4,8	0.7129
	Day	0.00	1,8	0.9714
Absolute Percentage Error (50 ng/L)	Model	0.73	9,7	0.6765
	Carrier Gas	0.16	2,7	0.8566
	Sheath Gas	1.28	2,7	0.3350
	Carrier - Sheath	0.91	4,7	0.5083
	Day	0.11	1,7	0.7495
Absolute Percentage Error (125 ng/L)	Model	0.86	7,5	0.5876
	Carrier Gas	0.22	2,5	0.8067
	Sheath Gas	2.33	2,5	0.1928
	Carrier - Sheath	0.82	2,5	0.4903
	Day	0.05	1,5	0.8262

Inspection of the data in Table 1 shows that the slope of the line increases as either the carrier flow or sheath flow is lowered. Unfortunately, the peak shape produced by the system at the lower gas flows is not of an acceptable shape for routine measurements and although higher slopes would maximize the detection power of the system it also would compromise the robustness of the measurement process. The experimental results clearly show that the calibration line slope is inversely related to the carrier and sheath gas flow rates. The flow rates selected for continuing work were, therefore, based on the lowest values of the gas flows that were consistent with the provision of reasonable peak shapes. These experiments have indicated that adjustment of the flow rates within the limits employed here has no effect on the overall accuracy of the system. The flow settings for the system were selected based on a compromise between these two parameters. The final results of the optimized instrument setting are in Table 3 below. These optimized settings and procedures were held constant for the remaining experiments.

TABLE 3: EXPERIMENTAL CONDITIONS FOR SINGLE LABORATORY VALIDATION

Fluorescence Instrument Condition Instrument

PSA *Merlin* Series AFS

Flow rate, blank	8.00 mL/min	Delay time	10 s
Flow rate, $SnCl_2$	3.00 mL/min	Rise time	25 s
Flow rate, sample	8.00 mL/min	Analysis time	30 s
Carrier gas rate	0.35 L/min	Memory time	60 s
Sheath gas rate	0.70 L/min		
Drier tube gas rate	3.00 L/min		

INSTRUMENT PERFORMANCE BENCHMARKS

As part of the familiarization phase of the project, initial assessments of the instrument detection limit (IDL) and analytical precision were made. Precision evaluated as relative standard deviation (n=10) was estimated at 100, 150, and 200 ng/L concentration levels to be 4.2, 1.6 and 0.9%, respectively. The IDL was evaluated using three different variations in sample preparation. All three initial assessments yielded an IDL of around 3 ng/L, where the IDL was defined as that concentration giving an analytical signal equal to three times the standard deviation of the blank signal.

Once the instrument settings were optimized and improvements to the system had been made the instrument performance was assessed in more detail. The IDL was determined to be 0.8 ng/L. Short term precision was measured by running ten replicates of an inorganic mercury standard at 10, 50, and 100X the IDL and digested using the bromate/bromide technique. The RSD of the instrument response at each concentration was 2.3, 1.3, and 0.79% respectively. The short term precision experiment was repeated using an organic mercury standard at the same concentrations. The RSD at 10, 50, and 100X the IDL were 2.1, 1.1, and 1.0% respectively. Instrument stability was determined by measuring the long term

precision of the analysis of a mid-level mercury standard over the course of one work day. The RSD of seven separate analyses over six hours was 1.2%. A control chart that represents the day to day long term stability of the instrument was constructed by plotting the sensitivity slopes for twenty-five calibration curves produced between 8/13/92 and 10/14/92. The average slope over the two month period was 0.914 with an RSD of 6.9%. All slopes were within three standard deviations of the average, indicating no excessive drift in the system.

COMPARISON OF SAMPLE DIGESTION METHODS

Two methods for sample digestion were assessed to determine which should be recommended for the proposed EPA Method. The standard EPA type digestion defined in Method 245.1 using $KMnO_4/K_2S_2O_8$, and a semi-automated method for total mercury is being evaluated for acceptance as an official USEPA method. This method is used routinely by the Yorkshire Water Authority (YWA) in the United Kingdom[12]. In the YWA method, a sample aliquot is digested using free bromine reagent, resulting in the break down of the commonly occurring organomercury species to mercury(II)[13,14]. Elemental mercury vapor is generated from the digested sample by reduction with stannous chloride and is purged from solution by a carrier stream of argon. The mercury vapor is determined by atomic fluorescence spectrometry at 253.7 nm[15]. The proposed method procedure is simplified and summarized as follows:

(1) Transfer 35-40 mL of sample to a 50-mL tared container.

(2) Add 5 mL (1+1) hydrochloric acid and 1 mL 0.1N potassium bromate/potassium bromide.

(3) Allow samples to stand for at least fifteen minutes before analysis.

(4) If the yellow color does not persist after fifteen minutes, add more $KBrO_3/KBr$ solution.

(5) Add 12% (w/v) hydroxylamine hydrochloride (NH_2OH-HCl) at a conc. of 6.0 μL per 10 mL of the sample, to eliminate the excess bromine until yellow color disappears.

(6) Turn on the automated instrument/detector and allow to stabilize.

(7) The sample enters gas/liquid separator with $SnCl_2$ to form mercury vapor.

(8) The vapor is analyzed by cold vapor atomic fluorescence spectrometry.

Each digestion procedure was optimized for reagent volume and final dilution. Sample containers for digestion and analysis were also evaluated. The original EPA Method 245.1 utilizes glass BOD bottles. Some initial studies for this work were done in glass volumetric flasks. The difficulty in using glass containers for sample digestion is that their capital cost can be prohibitive for disposable use and they must be cleaned using a rigorous and time consuming wash regimen if

they are to be reused. At ng/L detection levels any contamination from the sample container becomes a crucial issue. To reduce the risk of contamination, disposable polypropylene sample containers for digestion and immediate analysis were introduced. Initially, the digestion procedures were experimented with using inorganic standards in deionized water to determine the stability of mercury in each digestion matrix. Early studies showed that both procedures processed the mercury standards equally well. The effects of heat on the performance of the permanganate method were also initially tested with inorganic and organic standard solutions in deionized water. No significant difference in recovery was observed between heated and non-heated samples (Table 3). The importance of the heating step for the permanganate method became apparent when more complex matrices were studied. The current methods using permanganate require that additional reagents be added to digest adequately samples high in chloride concentrations. This complicates the analysis procedure since it requires the preparation of a separate blank for samples treated with additional reagents.

To compare the permanganate method with the bromate method in high concomitant chloride conditions, an artificial seawater with an estimated chloride content of 18,000 ppm was used as a sample matrix. Three aliquots of artificial seawater were spiked to a concentration of 100 ng/L with either 100% inorganic mercury, 50:50 inorganic/organic mercury, or 100% organic mercury. Two samples of each spike were digested and analyzed for each digestion procedure. The permanganate method was tested both with and without heating. The average recoveries for the inorganic, 50:50, and organic mercury spiked samples using the bromate digestion were 93.8, 92.1, and 90.4% respectively with close agreement between replicates. For the permanganate digestion using heating, average recoveries were 95.3, 85.6, and 81.4% respectively with a high relative percent difference between replicates. Repeating the permanganate digestion without heating yielded recoveries of 108.6, 83.3, and 62.1% for the inorganic, 50:50, and organic spiked samples also with high RPDs between replicates.

TABLE 3: COMPARISON OF BROMATE AND PERMANGANATE DIGESTION RECOVERIES (100 NG/L INORGANIC, 50:50, AND ORGANIC MERCURY) IN ARTIFICIAL SEAWATER

	% Recovery/(RPD)		
	Bromate	Permanganate with Heat	Permanganate no Heat
Inorganic	93.8 (0.43)	95.3 (6.7)	108.6 (4.2)
50:50	92.1 (2.3)	85.6 (5.1)	83.3 (12.9)
Organic	90.4 (0.11)	81.4 (18.7)	62.1 (5.6)

Several advantages were found using the bromate digestion. It provided better accuracy and precision and increased sensitivity about the permanganate method. The bromate method also is preferable because it requires less reagents and can be performed at ambient temperature in a shorter amount of time. Specifically for saline matrices, the bromate digestion does not require further additions of

reagents or supplemental standard preparation to complete the digestion, thus eliminating this time consuming procedure that is necessary for the permanganate digestion. From the evaluation of these data it was decided to incorporate the bromate digestion into the experimental development of the method.

INTERFERENCE STUDIES:

Studies of the affects of chloride on the recovery of mercury using the bromate digestion and the permanganate digestion techniques were performed. It was noticed upon heating that the samples lost the purple permanganate color and formed a brown precipitate. This was not observed in the standards that were heated. A noticeable difference in sensitivity was observed between the digestion procedures. Slopes of calibration standard curves prepared with bromate digestion ranged from 0.9 to 1.0 and a 100 ppt sample had a peak height of about 100, whereas slopes for the permanganate digestion ranged from 0.5 to 0.6 and the peak height of the 100 ppt sample was about 60. The bromate digestion appears to be superior to the permanganate digestion in sensitivity, accuracy and precision and is faster and easier to perform.

Further interference studies (Table 4) were performed using the bromate digestion only. Potential interferences from sample matrices containing fluoride, sulfate, nitrate, phosphate, gold, silver, or a mixture of calcium, copper, lead, manganese, barium and iron were evaluated. Recoveries for matrices of fluoride up to 100 ppm and phosphate up to 1000 ppm were over 93%. The composite sample containing 1 ppm of Cu, Pb, Mn, Ba, and 10 ppm of Ca and Fe had 100% recovery. The samples used for preparing the sulfate and nitrate matrices were too high in residual background mercury to analyze. The determination of mercury in a 1 ppm gold matrix had a pronounced interference that was thought to be from a reaction of mercury vapor combining with gold from the sample matrix in the gas/liquid separator during analysis. A sample matrix containing silver at 1 ppm also exhibited this effect, but to a lesser extreme. Potential interferences from volatile organic compounds were also evaluated using the bromate digestion. Recoveries were 100% for sample matrices containing up to 50 ppb chloroform or 500 ppb toluene.

Table 4: Interference Study

Interferent	Level	Recovery
Fluoride	50ppm	98.2%
	100ppm	101.4%
Sulfate[1]	100ppm	115.4%
	500ppm	197.6%
Nitrate[1]	100ppm	151.5%
Phosphate	100ppm	93.0%
	500ppm	97.0%
	1000ppm	100.3%
Gold[2]	1ppm	76.1%
Silver[2]	1ppm	182.2%
Composite:		101.6%
Ca	10ppm	
Cu	1ppm	
Pb	1ppm	
Mn	1ppm	
Ba	1ppm	
Fe	10ppm	
Chloroform	5ppb	98.9%
	25ppb	102.1%
	50ppb	102.6%
Toluene	50ppb	100.9%
	250ppb	101.9%
	500ppb	99.1%

[1] Sulfate and nitrate solutions obtained from an outside source contained high levels of mercury.

[2] Chemical Interference

ppm = mg/L ppb = μg/L

SINGLE LABORATORY VALIDATION:

The single lab validation study was completed. Precision and accuracy data were generated and the linear range of the method was determined to be 25 μg/L. Recoveries for duplicate samples fortified at 25, 50 and 100 ng/L and precision for six replicate samples fortified at 50 ng/L were determined for each of the six aqueous matrices selected for the study. The Trade Effluents (T&E) primary effluent matrix yielded lower recoveries than the other matrices and the recoveries also had a higher standard deviation. Matrix interference was suspected in this case, so a standard additions curve was constructed using this matrix. The curve generated showed no interference from the matrix. Some laboratories have claimed difficulty when using the bromate-bromide digestion procedure for samples high in organics. Further studies with the T&E matrix are planned using a modification of the digestion procedure similar to one for trade effluents described by Yorkshire Water Authority in the United Kingdom. This procedure uses more vigorous digestion conditions.

DISCUSSION:

The determination of total mercury by automated cold vapor atomic fluorescence spectrometry has a linear range approximately 2 ng-Hg/L to 25 μg-Hg/L. The MDLs as calculated are as follows:

METHOD DETECTION LIMITS FOR MERCURY

MATRIX	ng/L
Reagent water	1.8
Florida marsh water	3.3
Synthetic seawater	2.6

The digestion procedures evaluated seem equivalent except sea water where the bromide/bromate reagent tends to perform better than the permanganate procedure. The statistical approach requires that the interferant studies should be resumed. This will include field testing of many kinds of sample matrix and ruggedness testing.

The gold amalgam accessory may be useful when dealing with certain kinds of interferences (organics and inorganics) not yet identified. Interferences may be eliminated by preconcentration of mercury on gold. Gas vapors containing interferences are passed through the instrument before analyzing mercury. The gold/mercury amalgam trap is heated to release the mercury for cold vapor atomic detection analysis. The gold amalgam accessory would be inserted between the mercury vapor generator and the fluorescence detector. The future of this accessory will be evaluated during short-term and long-term stability studies. These studies are needed for this accessory before its inclusion in an official USEPA method for Total Mercury.

ACKNOWLEDGEMENTS

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DETERMINATION OF TETRAETHYLLEAD IN GROUND WATER

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Abstract: A chemical analysis method for determining tetraethyllead (TEL) in ground water has been devised based on purge and trap GC/MS. It incorporates TEL-d_{20} as an internal standard and naphthalene-d_8 as a surrogate. The method detection limit (MDL) has been calculated as 2.1 µg/L and recoveries averaged 102 percent.

INTRODUCTION

Organic lead compounds constitute the largest single application of industrial organometallic chemistry. Of those generated commercially, tetraethyllead (TEL), an octane-boosting agent, has been produced in the largest quantity. DOT classifies TEL as a Class B poison. TEL has a strong affinity for lipids and is known to affect the central nervous system causing symptoms such as fatigue, ataxia, psychosis and convulsions. Due to the quantities produced and its highly toxic nature, TEL is a potentially significant threat to the environment.

At present there are no "official" TEL analysis methods. The most common approach to inferring TEL levels, especially those presumably associated with leaking underground gasoline tanks, is to determine "organic lead" via solvent extraction using xylene followed by reaction iodine, then tri-capryl methyl ammonium chloride in methyl isobutyl ketone (MIBK); finally, elemental lead is determined using flame AA. The detection limit using this method is only about 100 µg/L and it is nonspecific.

Because tetraethyllead has a vapor pressure exceeding that of naphthalene, it is amenable to analysis using a purge and trap gas chromatography based analysis system.

METHOD SUMMARY

A 25 mL aliquot of ground water is spiked to 50 µg/L each with tetraethyllead-d_{20} and naphthalene-d_8. It is then subjected to GC/MS analysis using conditions equivalent to those identified in Method 8260. The GC/MS is calibrated with standard solutions containing 10, 20, 50, 100 and 200 µg/L of TEL and naphthalene-d_8, plus 50 µg/L of TEL-d_{20}. All quantitation and quality control are performed per Method 8260 except that TEL-d_{20} is used as the internal standard and naphthalene-d_8 is the surrogate.

EXPERIMENTAL

Data were acquired using an OI purge and trap interfaced to a Fisons MD800 GC/MS using a 20-to-1 split where the transfer line connects to the head of the GC column. A 60 m x 0.32 mm ID, 1.8 micron film DB-624 column was employed using a temperature

program which included a 4 min initial hold at 40 °C, then a program of 8 °C/min to 200 °C and a final hold of 10 min. This arrangement provided good performance without the added complexity of cryogenic trapping. All data reduction and report generation was performed using the Lab-Base data system.

Neat TEL was obtained from Ethyl Corporation, TEL-d_{20} was obtained from Merck Isotopes (Merck stock is now available from Cambridge Isotopes), and naphthalene-d_8 was obtained from Cambridge Isotopes. An MDL study was carried out using seven laboratory water samples spiked at 5 µg/L. Approximately 60 field samples from a site suspected to involve TEL contamination were analyzed. Matrix and matrix spike duplicates were all spiked to 50 µg/L.

RESULTS AND DISCUSSION

Mass chromatograms showing the elution of TEL, TEL-d_{20} and naphthalene-d_8 are given in Figure 1 for a 50 µg/L standard solution. Peaks shapes are good and retention times are reproducible. Mass spectra for TEL and TEL-d_{20} are shown in Figure 2. Masses chosen of quantitation were 295 for TEL and 310 for TEL-d_{20}.

In performing the initial analyses it was noted that both TEL and TEL-d_{20} were apparently being lost over time as they sat in the autosampler. Initial suspicions were that the TEL was decomposing. This was difficult to justify, however, because TEL could be detected in ground water samples which most likely were many years old. Subsequent review of the data suggested that ethyl groups were exchanging between labeled and natural TEL. If a TEL/TEL-d_{20} spiked sample was allowed to stand for several hours, spectra for TEL-d_{15}, TEL-d_{10} and TEL-d_5 would start to appear. This exchange process was not significant when samples were allowed to stand less than an hour prior to initiating the purge cycle. Consequently, all samples were purged immediately after spiking.

A typical calibration curve is shown in Figure 3. Response factors are constant to within 25% RSD, but a marked tendency for the response factor to increase with increasing concentrations of TEL was noted. Consequently, calibration via linear regression is recommended if accurate results are more important than strict adherence to SW-846 protocol.

Matrix spikes and matrix spike duplicates using field samples yielded an average recovery of 102% and an average difference of 1.5% based on three sets of data. The method detection limit study provided a calculated MDL of 2.1 µg/L.

TEL was detected in field samples even when they were very highly contaminated. The example shown in Figure 4 is for a well water sample with 32 µg/L of TEL. The primary reason TEL can be measured interference-free in samples like these is due to the high masses used for quantitation.

Figure 3 - TETRAETHYLLEAD CALIBRATION CURVE

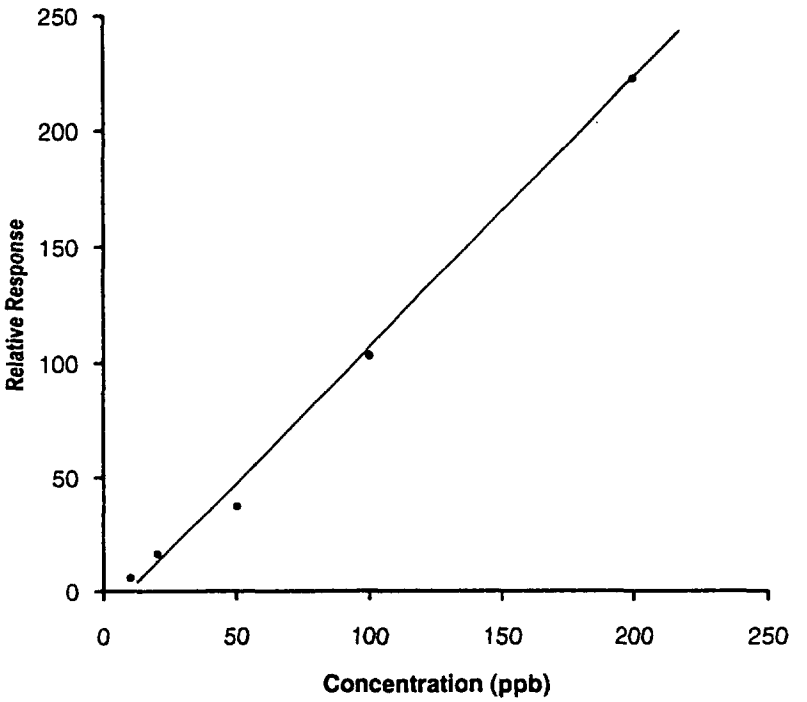
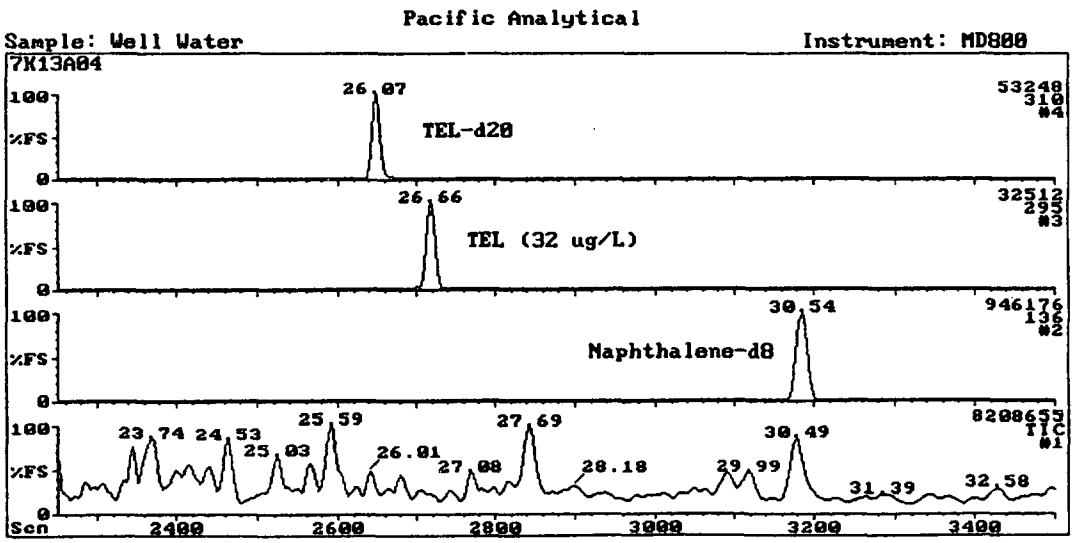


Figure 4 - TETRAETHYL LEAD IN GROUND WATER



SUMMARY

Purge and Trap GC/MS is a viable technique for determining tetraethyllead in ground water. It can be both accurate and precise if care is taken to avoid ethyl group exchange between labeled internal standard and natural material.

Figure 1 - TETRAETHYLLEAD STANDARD

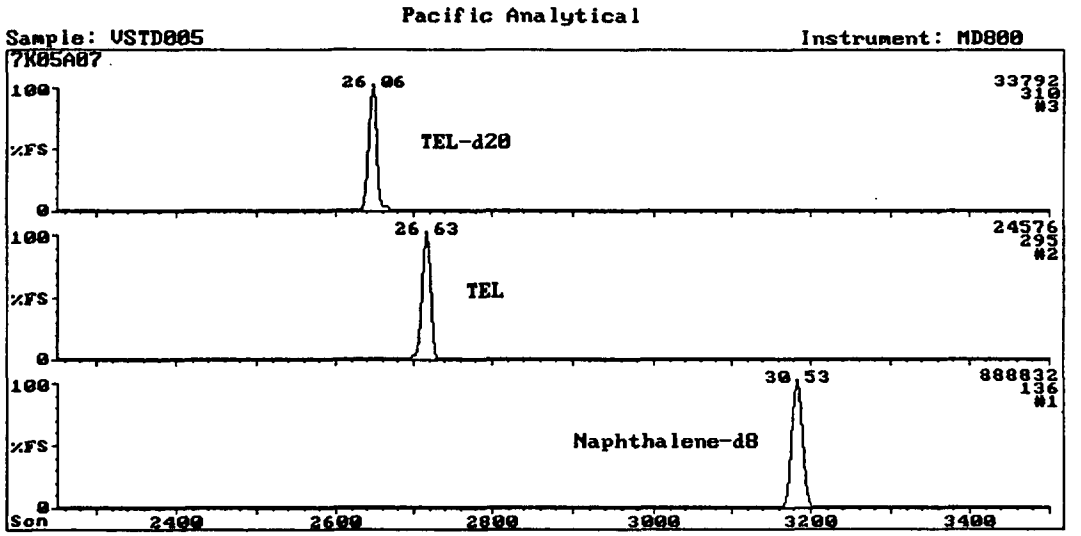
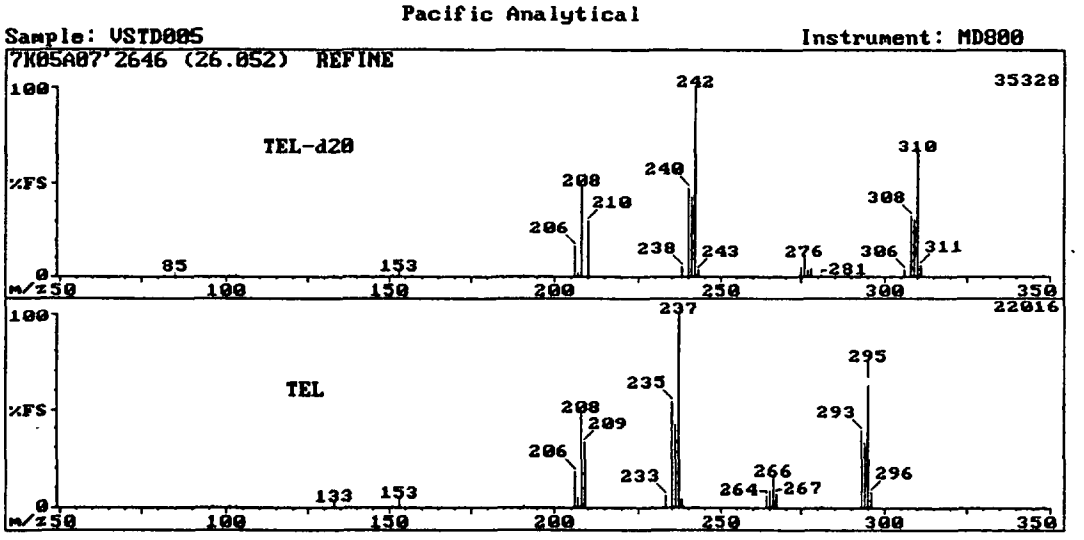


Figure 2 - TETRAETHYLLEAD MASS SPECTRA



78 USE OF A TELEPHONE SERVICE AND DATABASE TO PROVIDE GUIDANCE AND INCREASE PUBLIC INVOLVEMENT IN OSW METHODS

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ABSTRACT

The Methods Section of EPA's Office of Solid Waste (OSW) is responsible for approving and issuing methods used to evaluate solid waste and determine whether the waste is hazardous under RCRA. These methods are contained in EPA's methods manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", also known as SW-846. Individuals in the Methods Section have specific areas of responsibility for these methods, including organic, inorganic, miscellaneous, and characteristic test methods. Each member receives many inquiries and comments regarding method status, selection, performance, and detection capabilities. The number of inquiries (particularly phone calls) is often overwhelming and, in order to fully answer a question, more than one member of the Methods Section is frequently involved.

The Methods Section, therefore, identified a need to more efficiently respond to inquiries and to document the transmission of the information for future reference. In order to accomplish this task, the OSW Methods Section established a telephone service known as the Methods Information Communication Exchange (MICE) Service. Using a voice-mail system, MICE is set up to contain informational messages of the most commonly asked methods questions and record questions and comments from callers regarding technical difficulties or issues regarding the use of the SW-846 manual. After compiling the incoming messages for one day, the calls are sorted and distributed to appropriate technical staff members for a telephone response. Each response is summarized, categorized, and entered into a computer database on a periodic basis so that internal reports can be sent to the OSW Methods Section.

Once categorized and entered into the database, the resulting call responses and any issues raised are used internally at the Agency to document typographical errors in the manual and recurring technical problems with a particular method. The data are also used to record ideas and comments for possible directions of future analytical research and manual expansion. The MICE Service voice-mail system has received up to 821 calls and responded to 349 individuals requesting information in one 4 week period.

EXTRACTION OF METAL IONS FROM SOLID MATRICES BY COMPLEXATION SFE

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ABSTRACT

Complexation combined with solvent extraction has been widely used to extract metal ions from various matrices. Despite its good performance, this technique is usually time and labor intensive. Since we have been working on SFE techniques for other classes of compounds, we undertook a feasibility study to determine whether SFE could be used to extract metal ions from solid matrices. We knew from work published by Wai and coworkers that metal complexes formed with fluorinated complexing agents such as bis(trifluoroethyl)dithiocarbamate (FDDC) are soluble in supercritical carbon dioxide; thus, we were expecting that these complexes could be extracted by SFE. Experiments were performed to derivatize the metal ions with FDDC, extract the complexes by SFE, and then analyze the extracts by gas chromatography with atomic emission detection. Data will be presented on the extraction of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Co^{2+} from spiked filter paper and spiked soil by complexation SFE and then on the analysis of the complexes by gas chromatography with atomic emission detection.

80 MICROWAVE SAMPLE PREPARATION FOR MERCURY ANALYSIS VIA COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

Mercury contamination in the environment has become an increasing concern due to the toxicity of this element. The volatility of elemental mercury and organomercury compounds requires precautions be taken to avoid losses during sample preparation.

Microwave acid digestion of environmental samples inside sealed vessels is an EPA approved method for metals analysis by AA and ICP spectroscopy. This study will describe microwave digestion methodology required for mercury analysis via cold vapor AAS.

Analytical results obtained following microwave digestion of standard reference materials and real world samples spiked with organomercury standards will be presented. Microwave sample preparation methods for SRM 1575 Pine Needles, US EPA Fish, US EPA Dried Sludge, effluent municipal wastewater, waste motor oil and mixed solvent fuel will be described.

STUDY OF EPA METHOD 300.0: APPLICATION TO HAZARDOUS WASTE ANALYSIS

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ABSTRACT:

One of the first rules of using chemical analysis in the chemical waste industry is that standard analytical methodology must be employed. The second rule is that even if a standard method is used, it must be verified. Analytical data are used to determine proper disposal, secure information that may then be used in litigation, etc. So it is important to get the right answer and be able to prove it.

This work is a study of EPA Method 300.0 ion chromatography method for anions. The method has been certified under ASTM method D4327. Two commercial columns were studied for selectivity accuracy and precision. The effectiveness of EPA Method 300.0 was studied using standard reference materials.

Several samples of hazardous waste were examined. Of particular interest are halogenated organic solvent sample containing high amounts of chloride, fluoride, and bromide. Prior to anion determination, these sample were digested using a combustion bomb. Residues were taken up with an aqueous bicarbonate medium and the samples analyzed. Halide values are used in determining the feasibility of hazardous waste disposal and recycling. Furthermore, the cost of disposal is directly dependent upon the halogen concentration of the waste. Bromide containing waste are more expensive to incinerate than chloride containing waste.

INTRODUCTION:

Characterization of a waste as hazardous is performed by regulatory agencies, including EPA, OSHA, and DOT. Generally hazardous waste is either corrosive, reactive, toxic, or flammable. Once a hazardous waste is generated, it must be properly managed. Proper management includes the cost effective, safe, and legal disposal of the waste. However, to accomplish this, the content of the waste must be known accurately. For example, whether a waste is incinerated and how it is incinerated depends on the individual concentrations and total concentration of the halogens in the waste.

Because of this and of possible litigation considerations, it is important to use standard analytical methodology. But even if standard analytical methodology is used, it is still important to be able to show that accurate results are being achieved. Accurate results are gnerally obtained with standard methods such as EPA method 300.

Ion chromatography is widely used for the analysis of environmental samples (Ref. 1-3). The most common method for anion determinations in ion chromatography is EPA Method 300.0. The method has been certified as ASTM Method D4327. The method is based on ion exchange chromatography and therefore, is largely sample independent and rugged. The ion exchange column acts as a buffer to the sample as it is injected. Thus, retention times of sample peaks are much more constant (matrix independent) than other forms of chromatography when a variety of sample are injected.

This work examines the accuracy and precision of the method for organic solvent digests. Two different analytical columns are compared.

EXPERIMENTAL:

The ion chromatograph used in this work was a Dionex 4000i equipped with a AMMS™ suppressor and conductivity detection. The regenerant was 25 mM sulfuric acid at 2.8 mL/min flow. A 25 uL loop was used. Except for a standard digest material used for column comparison, the normal Method 300.0 eluant concentration and flow rate was decreased to increase resolution of the anions: The eluant concentration was 0.9 mM Na_2CO_3 / 0.85 mM $NaHCO_3$ and the flow rate was 1.5 mL/min. All reagents were analytical or reagent grade.

Two different analytical columns were used in this study: Dionex HPIC AS4A™, 250 x 4 mm and Sarasep AN300™ 100 x 7.5 mm. The two columns are designed to operate under identical eluant concentrations and flow rates. No changes were made in the instrumentation. Each column was equipped with a 5 cm guard column available from their respective companies.

All samples and standards were prepared with bomb calorimeter (Ref. 4) digestion (PARR Model 1261 calorimeter). Approximately 0.5 g of a representative (homogenized) sample was accurately weighed into a capsule. Some samples are not highly combustible. If necessary for combustion, 0.2 - 0.5 g of halogen-free kerosene was added to the capsule. All weights were recorded to 3 decimal places. To a clean bomb 10 mL of 5% aqueous $NaHCO_3$ was added, coating the internal surface of the bomb. The capsule was placed in the bomb seat. A Ni alloy wire was tied to the ignition electrodes. If the sample was liquid, the wire was placed close the sample, and if solid, the wire touched the sample. The PARR cover was screwed tight and about 30 psi of oxygen was charged to the bomb. After combustion, the bomb was shaken. The solution and 3 rinses were made up to 50 mL. The sample was filtered 0.45 micron filter prior to injection into the ion chromatograph.

RESULTS AND DISCUSSION:

Digest of sodium salt standards. The selectivity of two commercial columns were compared under identical separation conditions specified by method 300.0. A liquid standard containing 10 - 50 ppm of sodium salts of fluoride, chloride, bromide, nitrate, and sulfate were digested and injected into the chromatograph. The results are shown in Figures 1 and 2. Figure 1 shows that for the AS4A column, fluoride is non-retained and elutes in the water dip. Other materials such as non-ionic organics and cation are also non-retained and elutes with fluoride. Counter ions are suppressed by the AMMS and will not affect quantification of fluoride provided the capacity is not exceeded. No study has been published on the effect of non-ionic organics on quantification.

Figure 2 shows exactly the same separation on an AN300 column. The selectivity is identical expect that the peak window is retained. Non-retained material is elutes well before the fluoride peak. Normally a water dip would elute first, but in this case the digest contains material that gives a positive peak. A unknown positive peak eluting with fluoride will give a false positive result. It is unknown what causes the positive peak or whether it is present in all digests.

Digests of Standard Reference Materials. Several organic standard reference materials (SRM) were obtained from the National Institute of Standards and Technology (NIST) and Environments Resource Associates (ERA) (see Table 1). The samples contains elemental bromine, fluorine, chlorine, and sulfur; however ions generated in the digest were bromide fluoride, chloride, and sulfate.

The results of the ion chromatography analysis are shown in Table 2. The data are a compilation of the injection of individual SRMs listed in Table 1. The data show that the two commercial column gave virtually identical results. The concentrations obtained were all within the accepted range of elemental

concentrations reported for the SRMs.

Note the precision of the method, measured over a eight day period, was < 5%.

Digests of Hazardous Waste Samples. Three actual hazardous waste samples were obtained from generator companies. When the sample is received, the generator also provides a profile of the elemental composition. The types sample received can range from pesticides, oil, organic flux, The samples were digested and analyzed by ion chromatography using the two columns. The results, reported as elemental wt/wt percent, are shown in Table 3. All of the samples were also spiked with a known concentration of each ion. The recovery of the standard spikes ranged from 90 - 113%. While the precision of the analyses were < 5%.

The peak was sharper and higher for bromide with the AS4A column. Therefore, under identical conditions, limit of quantification (LOQ), was 0.2% for the AS4A column and was 0.5% for the AN300 column. On the other hand, the AN300 column produced sharper peaks for fluoride (LOQ 0.2%) and chloride (LOQ 0.2%).

All other results were comparable for the two columns.

Table 1. SRM for Ion Chromatography.

Digest Ion Generated	SRM
Fluoride	Spex Lot # W5-378
Bromide	NIST #3184
Sulfate	NIST #2684A
Chloride	ERA #03042

Table 2.
ANALYTICAL RESULTS OF STANDARD REFERENCE MATERIALS ON TWO DIFFERENT COLUMNS

Sample	ANIONS IN PPM							
	Cl^-		Br^-		SO_4^{2-}		F^-	
	AS4A	AN300	AS4A	AN300	AS4A	AN300	AS4A	AN300
Standard Reference Materials (NIST) from Environment Resource Associates	255	236	1012	1012	8.41	8.32	1.57	1.35
	246	246	--	--	8.20	8.32	1.70	1.51

Table 3. ANALYTICAL IC RESULTS ON TWO DIFFERENT COLUMNS

Sample	ANIONS IN PERCENTAGE							
	Cl^-		Br^-		F^-		SO_4^{2-}	
	AS4A	AN300	AS4A	AN300	AS4A	AN300	AS4A	AN300
Rinse water containing oil and DDT	<0.5 *94%	0.38 *96%	<0.2 *107%	<0.4 *108%	<0.6 *97%	<0.2 *99%	2.89 *95%	2.79 *94%
% Error	--	3.8	--	--	--	--	3.2	3.9
DY-90	<0.5 *92%	0.437 *94%	<0.2 *108%	<0.4 *109%	<0.6 *99%	<0.2 *105%	<0.6 *92%	<0.6 *95%
% Error	--	--	--	--	--	--	--	--
Organic Flux	2.03 *106%	2.18 *112%	<0.2 *108%	<0.4 *111%	<0.6 *102%	<0.2 *109%	<0.6 *113%	<0.6 *108%
% Error	2.3	2.6	--	--	--	--	--	--

* % Accuarcy

ACKNOWLEDGEMENTS:

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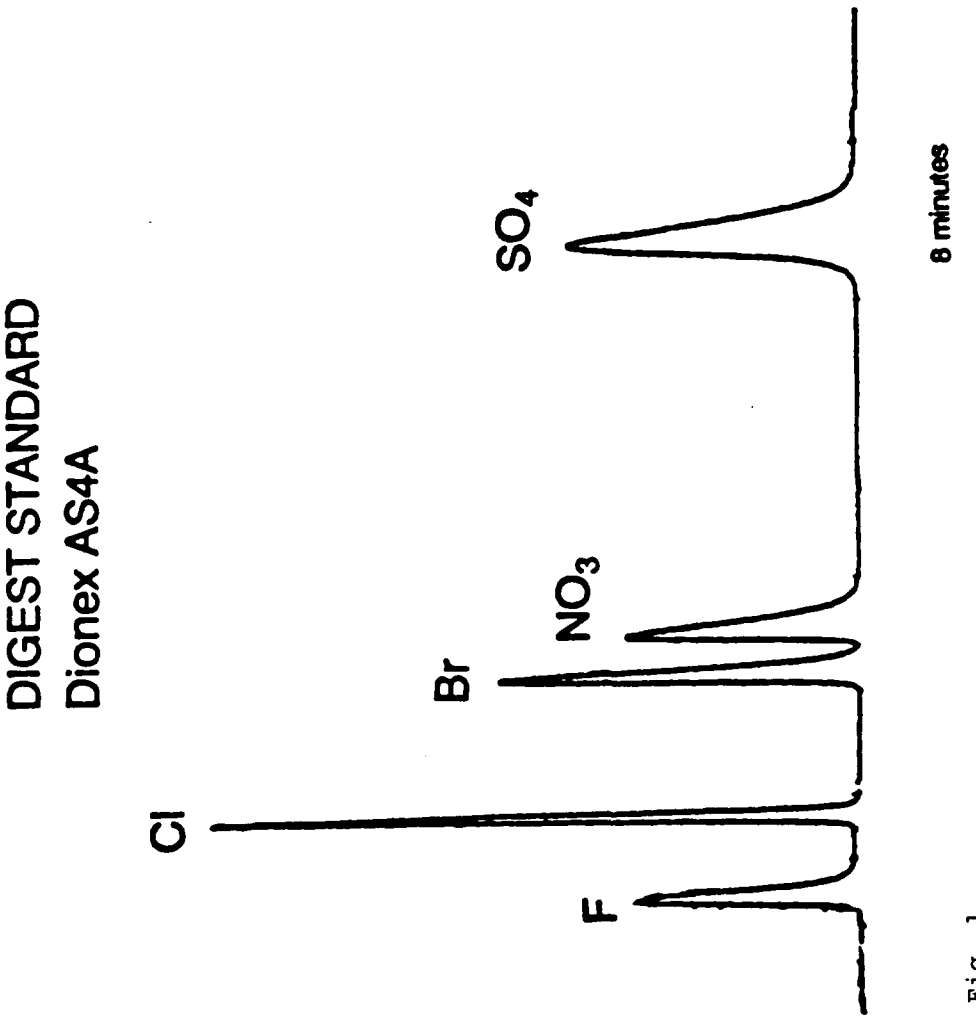

Fig. 1

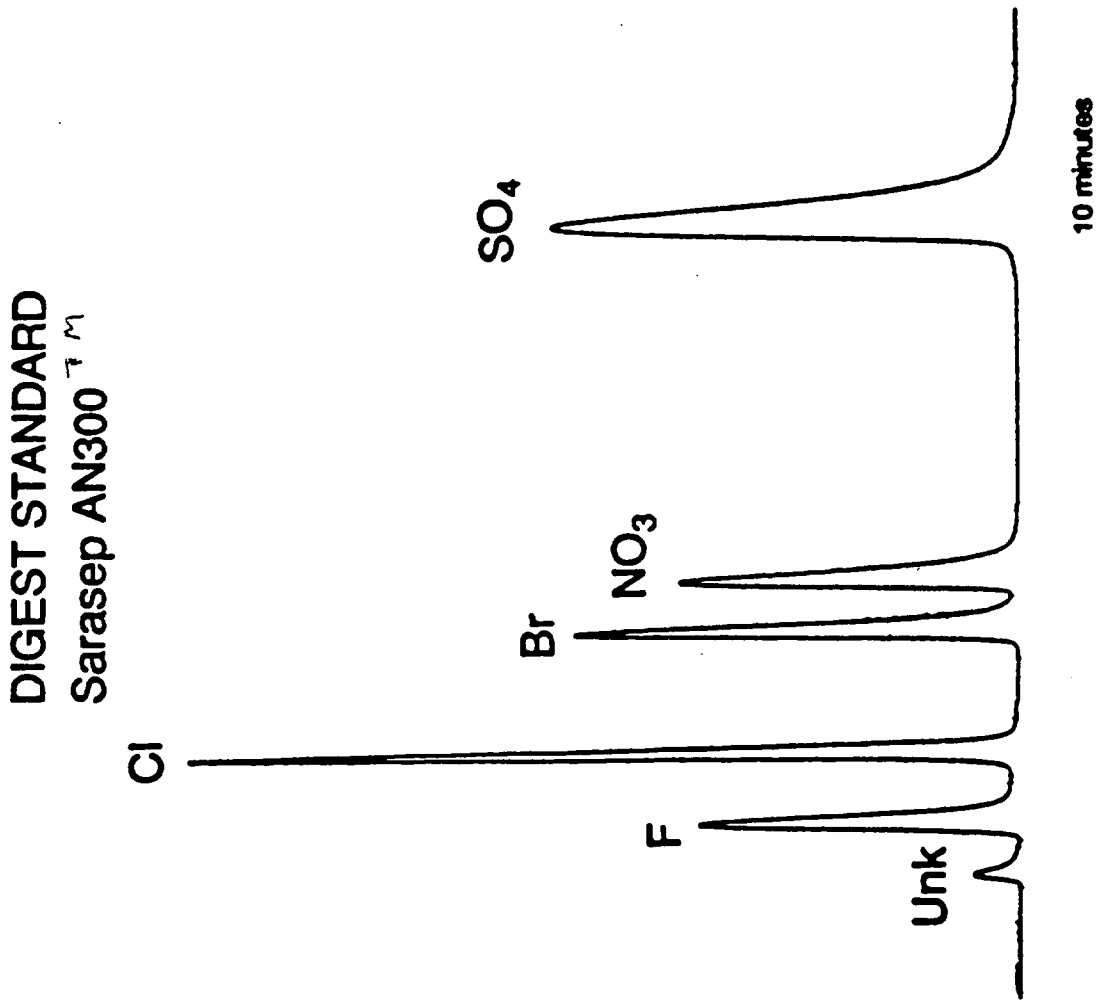

Fig. 2

The Effects of Size Reduction Techniques on TCLP analysis of Solidified Mixed Wastes

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The Rocky Flats Plant (RFP) is presently engaged in research and development activities for the stabilization of mixed wastes. Two stabilization technologies (microwave melting and polymer encapsulation) are being developed to process various waste forms produced at RFP. At the Nevada Test Site storage facility one of the acceptance criteria for low level mixed waste is passing the Toxicity Characteristic Leaching Procedure (TCLP).

The microwave melting and polymer encapsulation processes rely, at least partially, on a physical separation of toxic metals from the environment via formation of a monolith containing the mixed waste. The most important step, but least specified, in the TCLP analysis of these types of waste forms is size reduction.

This paper is a study of the effects of several different approaches for size reduction of the products of the above mentioned waste stabilization processes. Inductively Coupled Plasma Atomic Emission analysis results for several TCLP metals are presented to prove how the size reduction step drastically affects the TCLP analysis results. Also presented are results that show how the three stabilization techniques respond differently to the size reduction step of the TCLP analysis.

AIR AND GROUNDWATER

CANISTER ANALYSIS BY USING GAS CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETER

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Summa®-passivated canisters used for the collection of air samples have distinct advantages over tenex and charcoal tubes since the whole air sample is collected with long storage stabilities and allows for multiple and flexible analysis schemes to be used.

When very low detection limits are required, pressurization of the canister is generally required which must use specialized and expensive sampling devices which will pressurize the canister above atmospheric pressure. A simpler approach and the preferred one is to do the sampling in evacuated canisters using inexpensive flow controllers and sample up to atmospheric pressure. Clean humidified air is when added in the laboratory to bring the pressure above atmosphere and the sample is when concentrated cryogenically before analysis. Addition of humidified air dilutes the sample and raises the detection limits and therefore places sensitivity demands on the instrumentation when low detection limits are required.

A gas chromatography/high resolution mass spectrometer has always offered better sensitivity and selectivity when low resolution quadrople instruments. Operating at resolution of 3000 in full scan-mode has quite a number of distinct advantages in highly contaminated air samples since due to the high resolutions used. it is possible to detect target analysis even in the presence of high background contaminants. We have found that several modifications are required in sample introduction to prevent high voltage flashovers to occur. The sensitivity and selectivity of the approach is indeed improved and the results will be presented.

AN EFFECTIVE MOISTURE CONTROL SOLUTION FOR THE GC/MS DETERMINATION OF VOCS IN CANISTER SAMPLES COLLECTED AT SUPERFUND SITES

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ABSTRACT

EPA Compendium Method TO-14[1] has become the preferred guidance method for the sampling and analysis of volatile organic compounds (VOCs) in ambient air samples . A Contract Laboratory Program (CLP) protocol[2] for the analysis of air samples at Superfund sites, which is based on TO-14, has recently been drafted by the USEPA . Like TO-14, the CLP draft protocol recommends cryogenic preconcentration of the air sample followed by thermal desorption into a chromatographic system. Because moisture in the air sample is cryogenically preconcentrated along with the VOCs, it will also delivered into the chromatographic system during themal desorption. The moisture can adversely affect chromatography and/or detector sensitivity and reliability. Therefore, unless the moisture in the sample is removed or significantly reduced, sample size must be limited with consequent limitations to method sensitivity. Compendium Method TO-14 and the proposed CLP analytical protocol recommend a Nafion dryer for moisture removal. However, this technique limits the method to non-polar analytes and introduces potential carryover and reproducibility problems. Because many polar VOCs are of great interest to the EPA, a canister analysis procedure that allows these analytes to be determined with acceptable precision and accuracy should be preferred over an approach that eliminates that possibility. This paper decscribes a commercially available system that effectively controls moisture in large volume air samples, thereby allowing both non-polar and polar VOCs to be measured at very low concentration levels with acceptable precision and accuracy.

INTRODUCTION

In response to CERCLA and SARA mandates for assessment of potential air emissions and air quality impacts of toxic contaminants before and during Superfund site remediations, the USEPA's Analytical Operations Branch (AOB) within the Hazardous Site Evaluation Division (HSED) of athe Office of Emergency and Remedial Response (OERR) has drafted a CLP SOW for the analysis of air samples collected at Superfund sites. One of the four analytical protocols which has been drafted for the proposed CLP air program involves the determination of VOCs in whole air samples collected in passivated stainless-steel canisters. The CLP draft protocol is based on Compendium Method TO-14 and expands the target compound list from 41 to 61 analytes, including several polar VOCs. Air samples are collected in 6-L canisters, 500 mL of which is preconcentrated by collection on a cryogenically cooled trap, revolatilized and backflushed onto a capillary GC column for separation, and quantitated with a mass spectrometer operated in the full-scan mode. The full-scan mode is required in order to tentatively identify non-target or unknown responses.

The CLP draft protocol recommends removal of excessive moisture from the sample gas stream with a Nafion® dryer, if applicable. Excessive moisture can cause the cryotrap or GC capillary column head to plug with ice, degrade chromatographic resolution, especially of the early eluting gases, and cause MS source overpressure. However, use of a Nafion® dryer as a moisture reduction technique limits quantitative determinations to non-polar VOCs only, because polar VOC compounds are coincidentally removed, or partially removed, from the sample stream. Because the protocol requires a 500 mL sample to be analyzed, a Nafion® dryer will have to be employed for most environmental air samples. Analysis of sample volumes greater than 100 mL generally requires moisture reduction. Unfortunately the proposed target compound list does contain several polar VOCs. This apparent conflict is not clearly addressed by the protocol.

This paper presents results of a preliminary evaluation of an Entech Model 2000 preconcentrator interfaced to a Hewlett-Packard 5890 gas chromatograph (GC)/Finnigan Incos 50 mass spectrometer (MS). The analytical system can reliably measure VOC concentration levels as low as 0.1 ppbV while avoiding the typical problems caused by the introduction of excessive moisture into the analytical system. At the same time, the preconcentrator system allows both non-polar and polar VOCs to be determined for target and unknown compounds alike. The components and operating configurations of the system are described and the results of system performance and method detection limit (MDL) studies are also presented.

EXPERIMENTAL

Canister Cleaning and Leak Checking

To determine ambient air VOC concentrations with accepable precision and accuracy at ppbV and sub-ppbV concentration levels, it is imperative that the laboratory establish the cleanliness and integrity of each sampling canister. ESE's laboratory in Gainesville, Florida, utilizes an Entech Model 3000 Canister Conditioning System for cleaning and leak checking canisters prior to sampling and analysis.

Canister leak checking is performed prior to canister cleaning. The canisters are connected to the system manifold via 1/4-inch stainless-steel tubing and the canister valves are left closed. A high vacuum pump is engaged and the vacuum pressure is monitored using an in-line pirani gauge (0-2000 mtorr sensor). If a significant leak exists, it will manifest itself by not allowing the system to quickly evacuate to approximately 0.3 torr, and/or the system pressure will quickly rise once the high vacuum pump is disengaged. Quick disconnects are situated between each canister and the manifold to allow easy isolation of individual canisters which may have leaking valves. After the repetitive fill/evacuate cycling is completed, the high vacuum pump is used for final canister evacuation. Leaks will not allow the canisters to achieve a vacuum reading of approximately 0.5 torr.

Four to eight 6-liter canisters are cleaned simultaneously over a 4-hour period through automatic, unattended cycling between canister filling and evacuation modes. Each of the canisters is heated to 100°C for the duration of the cleaning process. A rough-vacuum oilless diaphragm pump cycles between eight 8-minute fillings and eight 8-minute evacuations. Nitrogen vent gas from a liquid nitrogen tank is used for the fill gas and a humidification chamber containing ASTM Type II HPLC grade water is used to add

moisture to the fill gas in order to assist in the displacement of VOCs from the interior surface of the canisters. In the fill mode the canisters are pressurized to about 25 psig. After completion of eight cycles with the low-vacuum pump, the canisters are evacuted with a high-vacuum oil-based pump for about 75 minutes to an absolute pressure of 0.5 torr, which is measured by an in-line pirani gauge. A cryogenic trap containing liquid nitrogen is placed between the pump and the system controller to keep oil vapor out of the system.

At the completion of the cleaning cycle, the canisters are pressurized to 30 psig with humidified nitrogen and analyzed by GC/MS. No target analyte should be detectable at or above the lowest calibration standard (0.1 ppbV for this study). After analysis, each canister is re-evacuated to 0.5 torr.

Standards Preparation

Working calibration standards were prepared in canisters at a minimum of five concentration levels in the range of 0.1 - 15 ppbV. These working standards were prepared from stock calibration mixtures containing approximately 100 ppbV of each of the target analytes in dry nitrogen in high pressure (2000 psi) cylinders. These calibration mixtures were purchased from Scott Specialty Gases and are certified to $\pm$ 5 % for each of the VOCs.

The working calibration standards were generated by dynamic flow dilutions of the purchased mixtures with cleaned, zero grade nitrogen humidified with ASTM Type II HPLC-grade water. ESE utilizes an Entech Model 4560 Dynamic Dilution System for this process. This system utilizes up to six mass flow controllers for simultaneous blending from multiple cylinders. Canisters are filled to 15-25 psig. Newly prepared calibration standards are allowed to equilibrate at least 24 hours.

The 40 compounds listed in Compendium Method TO-14 (ethyl toluene was not included) were evaluated for this paper.

Instrumental Analysis

Canister samples are analyzed with an Entech Model 2000 automated VOC cryogenic preconcentrator equipped with an Entech 2016 16-position autosampler manifold and interfaced to a HP 5890 GC/ Finnigan INCOS 50 MS operated in the full scan mode (m/e 35 to 270 amu). Since the preconcentrator system is under software control (IBM compatible), a QA/QC report is a standard feature for documentation of actual run conditions.

Canisters are attached to the manifold with 1/8 inch stainless-steel tubing. A leak check of the system is then performed. Sample flow is set under mass flow control to 150 mL/min. to give an integrated total volume of 1000 mL. Both subambient and pressurized samples can be analyzed because the system employs a mechanical pump to draw samples across the preconcentor. The internal standards, bromochloromethane, 1,4-difluorobenzene, and d5-chlorobenzene, are also added to each analysis at 150 mL/min. to a total volume of 100 mL. All rotary valves and transfer lines exposed to the sample matrix are heated at 70-100°C.

The Entech preconcentrator is configured with a 3-stage trapping approach which allows a large sample volume to be concentrated and the moisture and carbon dioxide removed without significant loss of non-polar or polar VOCs. Entech refers to the technique as microscale purge and trap because it is based on classical purge and trap principles. (15-20 µL of water is purged with 30-40 mL of nitrogen instead of 5000 µL being purged with 400 mL of nitrogen.) The first stage is a high-volume cryogenic trap (1/8-inch nickel tube containing glass beads) cooled during sampling to -150 °C with liquid nitrogen. After cryotraping 1000 mL of air sample, the first stage trap is heated rapidly to room temperature and slowly purged with about mL of nitrogen to transfer the trapped VOCs to a second stage trap (1/8-inch nickel tube) containing hydrophobic Tenax TA held at 0°C. Only the amount of water vapor that can saturate 30-40 mL of nitrogen (.7 - .9 µL) will be delivered to the second stage Tenax trap. Carbon dioxide and some the water will not be trapped by the Tenax. The second stage trap is then heated to 170°C and backflushed with helium to a third stage megabore focusing trap cooled with liquid nitrogen to -150°C. After heating and backflushing of the second stage trap is complete, the third stage trap is then very rapidly heated to above 100°C to allow a rapid injection of the VOCs onto the GC analytical column.

The target analytes are separated on a DB-1 fused silica capillary column, 75 m x 0.32 mm I.D., with a 1 micron film thickness. The chromatographic run is started at 35°C and held for 5 min. A subambient starting temperature is not required because of the rapid transfer of VOCs from the preconcentrator's third stage megabore focusing trap of the Entech preconcentrator to the head of the GC column. Sharp peaks with 2-5 sec. widths are maintained, even for early eluting compounds. The column is then temperature programmed at 6°C/min. to 180°C and then at 7.5°C/min. to 225°C. The scan rate is approximately 3 scans/sec. The total run time for preconcentration of the sample and chromatographic separation is approximately 60 min. Figure 1 shows a mass chromaogram of a 1 ppbV standard of target VOCs.

The MS scan rate is approximately 3 scans/sec. The Incos 50 turbomolecular source pump draws about 170 L/min. This pumping rate effectively prevents source pressure increases from any residual sample moisture.

System Performance and Method Detection Limit (MDL) Studies

The reproducibility and linerarity of the analytical system were evaluated over a two-week period. Eight calibration standards and a blank were prepared as described above in separate 6-liter canisters. The blank canister was prepared with humidified zero grade nitrogen. The calibration standards contained the 40 compounds listed in Method TO-14 and were prepared at concentration levels of 0.1, 0.25, 0.5, 1, 2, 5, 10, and 15 ppbV. Another canister containing the three internal standards was also prepared. All canisters were attached to the autosampler manifold and analyzed, after instrument tuning, as described above. Internal standards were added to each analysis at 5 ppbV. The canisters were analyzed three times, with a week between analytical runs. Each analytical sequence lasted about 9 hours after tuning. Initial canister pressures ranged from 10 to15 psig for the first day's run, from 1 to 2 psig for the second day's run, and from -1 to -2 psig for the last day's run.

In addition to the reproducibility study described above, an MDL study was performed. Lower limits of detection for the target compounds were estimated for each instrument

by determining the method detection limits (MDLs) as specified by the U.S. Environmental Protection Agency (U.S. EPA).[3] Nine canisters samples were prepared at about 0.5 ppbV for each of the target compounds used the standards preparation system described above. The nine replicate samples were then analyzed and quantitated against a calibration curve containg eight standards ranging from 0.1 to 15 ppbV. The compound responses divided by the appropriate internal standard response were plotted against concentration. The MDL for each target compound is calculated by multiplying the standard deviation of the seven replicate concentration measurements by the appropriate one-sided t-value corresponding to n - 1 (8) degress of freedom. The corresponding t-value for seven measurements is 2.897.

RESULTS AND DISCUSSION

The reproducibility, or precision, of the analytical system was evaluated by comparing the responses of the target compounds and their corresponding internal standards over the three analysis days at different calibration standard concentrations. In addition compound retention time variability was evaluated. Table 1 summarizes response and retention data for vinyl chloride, benzene, and hexachlorobutadiene (HCBD) at 0.1, 1 and 10 ppbV. These compounds represent low boiling (vinyl chloride = -13.4°C), middle boiling (benzene = 80.1°C, and high boiling (HCBD = 215°C) VOCs, respectively. For each of the three compounds listed in Table 1, the relative stardard deviations (RSDs) of the absolute responses for the three analysis days over the three concentration levels averaged less than 6 percent . The relative response factors (RRFs) averaged less than 5 percent. The RSDs of the absolute responses of each of the internal standards for the three analysis days and within each analysis day over the three concentration levels averaged less than 5 percent. Retention times had ranges no greater than .03 minutes for the three compounds. Response and retention time reproducibility for the other target VOCs were also very good.

Table 2 summarizes calibration data for vinyl chloride, benzene, and HCBD on the second analysis day. The compound responses were very linear over the 0.1 to 2.0 ppbV range, as measured by either a linear regression curve or the %RSD of the RRFs.

Table 3 lists the calculated MDLs for this study. The calculated MDLs averaged 0.11 ppbV for all the TO-14 compounds. Seven of the calculated MDLs were less than 10% of the 0.5 ppbV nominal concentration analyzed. This indicates that the replicate analysis for those compounds should have been targeted at a lower concentration (probably 0.25 ppbV). The 0.1 ppbV responses for all the TO-14 compounds were well above background noise, in the range of 10 - 80,000 area counts. Compound responses were very linear over the 0.1 - 2 ppbV range and generally approached a quadratic fit across the full calibration range (0.1 - 15 ppbV).

Polar VOCs

Although this paper does not discuss experimental results for polar VOC determinations using the analytical system described above, preliminary analysis of eight polar VOCs of interest have been good. The compounds that are currently being investigated are those listed in the CLP draft protocol target compound list. They include acetone, acetonitrile, acrolein, acrylonitrile, methyl ethyl ketone, methyl isobutyl ketone, methyl methacrylate, and vinyl acetate. Other polar analytes will also be examined.

Several limited studies have been performed elsewhere that have examined the stability of selected polar compounds in canisters. There is sufficient evidence to indicate that some polar VOCs are unstable in canisters if held over extended periods due to canister and/or matrix effects. However, considerable experimentation is still needed, especially at low concentration levels.

SUMMARY

Routine measurement of non-polar and polar ambient VOCs at ppbV and sub-ppbV levels by GC/MS-SCAN can be acheived with acceptable precision and accuracy if sample moisture is effectively reduced. This has been demonstrated with a analytical system comprised of an Entech preconcentrator, a Hewlett-Packard GC, and a Finnigan MS.

ACKNOWLEDGEMENTS

The authors thank Norm Staubly for his laboratory assistance.

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Table 1: Area Response and Retention Time Reproducibility of Selected VOCS

	Pressurized 2/17/93			Atmospheric 2/23/93			Sub-Atmospheric 3/04/93		
	VC	Bzn	HCBD	VC	Bzn	HCBD	VC	Bzn	HCBD
10 ppbV									
Resp. ($x10^3$)	2058	2379	883	2067	2256	910	1996	2195	843
IS Resp. ($x10^3$)	764	2078	1665	702	1947	1610	732	1978	1582
RRF	1.35	0.57	0.27	1.47	0.58	0.28	1.36	0.56	0.27
Ret. Time	4.03	10.16	28.11	4.02	10.15	28.11	4.03	10.16	28.12
1 ppbV									
Resp. ($x10^3$)	278	302	124	271	279	111	290	300	106
IS Resp. ($x10^3$)	808	2143	1652	762	2000	1577	788	2094	1614
RRF	1.72	0.70	0.38	1.77	0.70	0.35	1.84	0.72	0.33
Ret. Time	4.03	10.15	28.11	4.04	10.16	28.11	4.03	10.16	28.11
0.1 ppbV									
Resp. ($x10^3$)	29.7	27.1	13.5	27.9	26.1	13.8	31.3	29.8	14.8
IS Resp. ($x10^3$)	739	1968	1479	724	1894	1440	748	1985	1551
RRF	2.01	0.69	0.46	1.93	0.63	0.48	2.09	0.75	0.48
Ret. Time	4.02	10.15	28.10	4.02	10.14	28.09	4.02	10.15	28.11

Table 2: Calibration and MDL Results for Selected VOCs

Calibration:

Standard (ppbV)	VINYL CHLORIDE Response	RRF	BENZENE Response	RRF	HCBD Response	RRF
2	515511	1.67	575498	0.700	219910	0.340
1	270598	1.77	279430	0.699	111351	0.353
0.5	141763	1.93	132341	0.672	51646	0.355
0.25	74681	2.03	68616	0.733	27152	0.371
0.1	27932	1.89	26112	0.652	13810	0.461
0	0	-	3248	-	254	-
L.R. Corr. Coeff. =	0.9995		0.9993		0.9997	
y-Intercept =	6895		-5397		264	
Average RRF =	1.86		0.691		0.376	
%RSD of RRFs =	7.5		4.5		13	

Table 3: Calculated MDLs of TO-14 Compounds

Compound	MDL (ppbV)
Dichlorodifluoromethane	0.10
Chloromethane	0.12
1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.15
Vinyl chloride	0.07
Bromomethane	0.09
Chloroethane	0.04
Trichlorofluoromethane	0.12
1,1-Dichloroethene	0.11
Methylene chloride	0.40
1,1,2-Trichloro-1,1,1-trifluoroethane	0.20
cis-1,2-Dichloroethene	0.07
1,1-Dichloroethane	0.07
Chloroform	0.06
1,2-Dichloroethane	0.06
1,1,1-Trichloroethane	0.29
Benzene	0.03
Carbon tetrachloride	0.03
1,2-Dichloropropane	0.09
Trichloroethene	0.04
cis-1,3-Dichloropropene	0.09
trans-1,3-Dichloropropene	0.12
1,1,2-Trichloroethane	0.10
Toluene	0.07
1,2-Dibromoethane	0.11
Tetrachloroethene	0.06
Chlorobenzene	0.04
Ethylbenzene	0.06
m,p-Xylenes	0.14
Styrene	0.03
1,1,2,2-Tetrachloroethane	0.30
o-Xylene	0.04
1,3,5-Trimethylbenzene	0.06
1,2,4-Trimethylbenzene	0.13
Benzyl chloride	0.30
1,3-Dichlorobenzene	0.05
1,4-Dichlorobenzene	0.06
1,2-Dichlorobenzene	0.04
1,2,4-Trichlorobenzene	0.08
Hexachlorobutadiene	0.09
Average MDL =	0.11

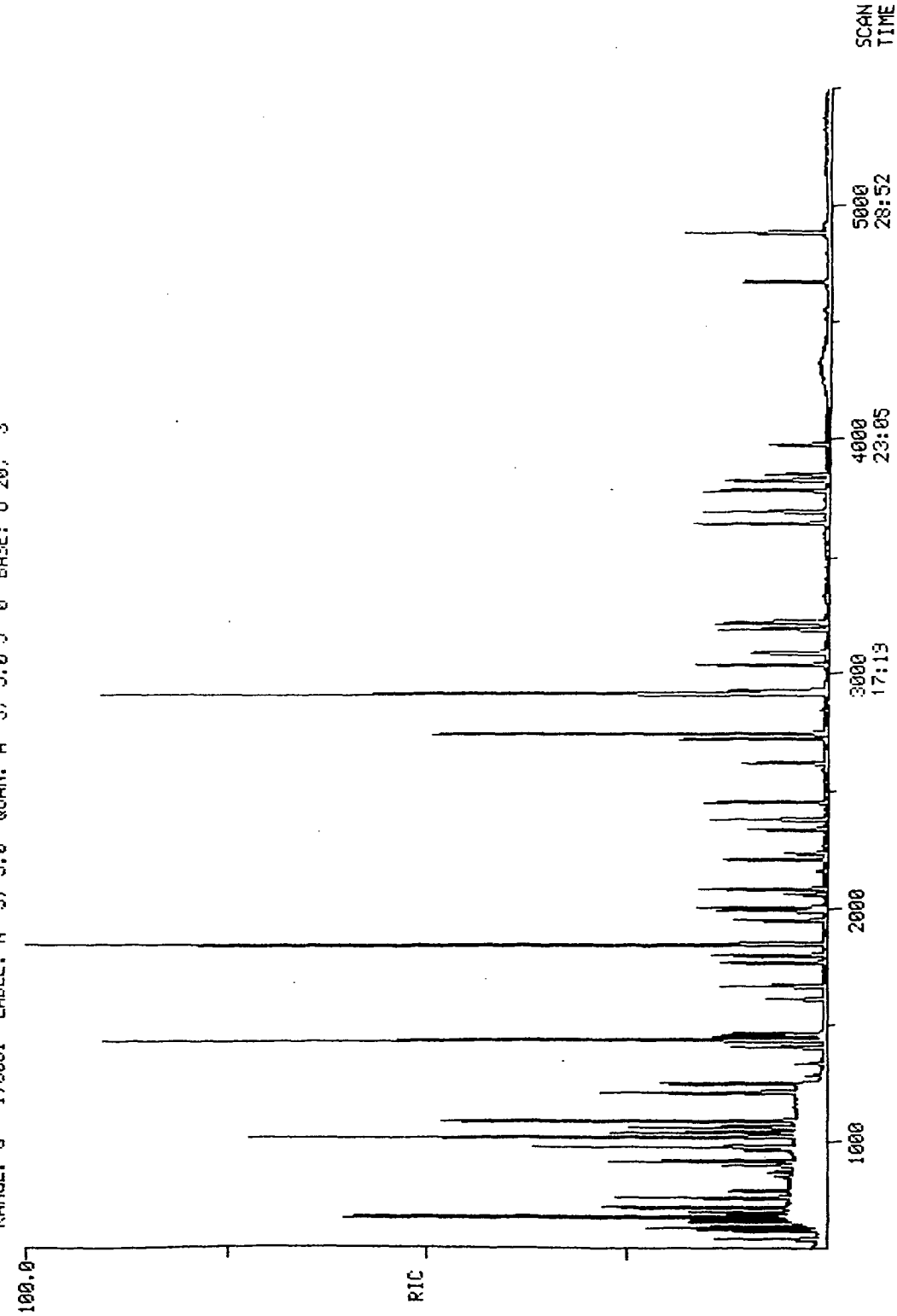

Figure 1 Mass Chromatogram of a Canister VOC Standard

SELECTION CRITERIA FOR GROUND-WATER MONITORING WELL CONSTRUCTION MATERIALS

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ABSTRACT

This presentation discusses a regulatory perspective on the selection of ground-water monitoring well casing materials for hazardous and solid waste disposal facilities that must comply with the Resource Conservation and Recovery Act requirements. The primary focus will center on EPA's current recommendations for selecting well casing materials, with special consideration given to regulatory requirements, data quality objectives, common types of well casing materials and their physical and chemical characteristics, and geochemical considerations. A table summarizing the recommended selection criteria and a series of case studies will also be presented.

AUTO-GC DESIGN AND OPERATION FOR REMOTE UNATTENDED VOC DETERMINATIONS

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ABSTRACT

Recent emphasis on the design considerations for ozone precursor analytical systems using gas chromatography has focused on the practical and logistical difficulties of using liquCid cryogen for trapping volatile organics. Conventional approaches to the problems of trapping species in the range of C_2 to C_{10} require liquid nitrogen for cold-trapping and for sub-ambient operation of the chromatographic oven. Liquid nitrogen is not only expensive, but difficult to supply in a reliable fashion for long-term unattended operation at remote locations.

A system has been developed and evaluated for the on-line ambient detection of hydrocarbon ozone precursors that does not use liquid cryogen. This novel chromatographic approach has been used to optimize the separation of C_2 to C_{10} compounds using a pressure switching facility. Such a chromatography system has the added benefit of stabilizing the column system resulting in improved retention time reproducibility. This is consistent with the requirements of a robust, stable system capable of long-term unattended operation.

INTRODUCTION

U.S. Environmental Protection Agency, namely carbon monoxide, sulfur oxides, nitrogen oxides, ozone, particulate matter less than 10 microns in size, and airborne lead. Though EPA has promulgated these levels for some time, a number of urban areas in the United States continue to be unable to bring their normal levels into compliance with EPA regulatory levels. This "non-attainment" problem is especially acute with respect to ozone. There are 23 cities in the U.S. that are considered non-compliant with ozone regulations.

In order to address this problem, the 1990 Clean Air Act Amendments (CAAA) required that EPA develop an ozone abatement strategy based not only on the chemical species itself (i.e., ozone), but based as well on hydrocarbon precursors of ozone that react with sunlight and nitrogen oxides to form the unhealthful, ozone-rich, summer's haze so prevalent in urban areas.

In order to limit the release of low molecular weight hydrocarbon precursors into ambient air, it is necessary to determine the hydrocarbon source. Therefore, an instrumental approach has been developed permitting the automatic collection and chromatography of C_2 to C_{10} hydrocarbons from ambient air.

INSTRUMENTAL DESIGN

This system is based on the Perkin-Elmer ATD-400 Automatic Thermal Desorption instrument that has a Peltier-cooled adsorbent trap. After being electrically cooled to -30 oC, ambient air is

drawn through the trap. Following a predetermined sampling time, the trap is automatically connected to the Perkin-Elmer 8700 gas chromatograph via a 6-port valve, and the trap is programmably heated at 40 oC/sec; hydrocarbons are flashed off the adsorbent and onto a capillary GC column.

Chromatographic separation is multi-dimensional, i.e., a combination of a PLOT column for the extremely volatile low molecular weight compounds and a BP1 boiling point column for the higher molecular weight species. All the organic analytes from the trap are transferred to the BP1 column. For the first 13 to 14 minutes, the effluent from the BP1 column is directed onto the $Al_2O_3.Na_2SO_4$ PLOT column. Thus early eluting poorly resolved components from the first column are transferred for further chromatographic separation on the PLOT column. After 13 to 14 minutes, the effluent from the BP1 column is switched (using the Deans system) directly to a 2nd FID. Higher boiling, well-resolved components are analyzed on this second detector and are prevented from contaminating the PLOT column. For the remainder of the analysis, components elute simultaneously on both columns. However, as each peak only elutes on one or the other column, and not on both columns, data handling is not complex. This system is illustrated in Figure 1.

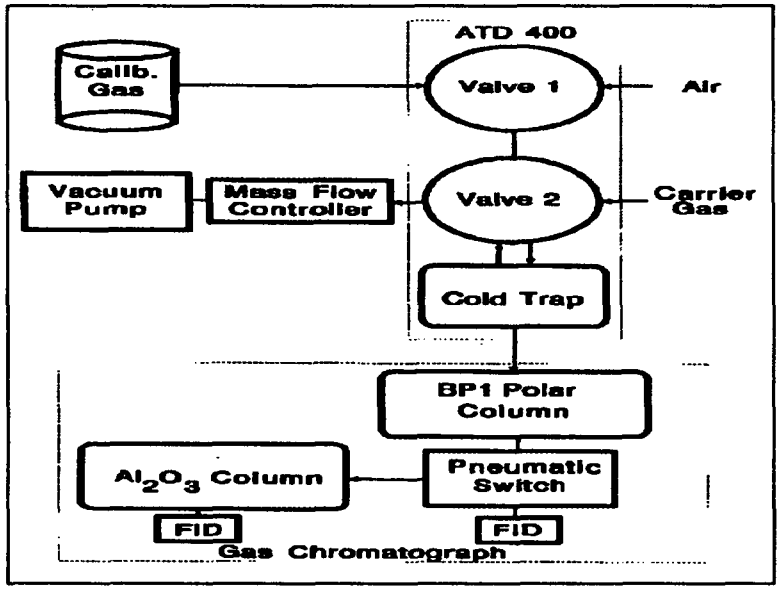

Figure 1: Schematic diagram of ambient air monitoring system.

The resulting chromatographic output comes from two GC detectors, one for the PLOT column, and a second for the BP1 column. Figure 2 shows a typical GC output for a 55-component standard.

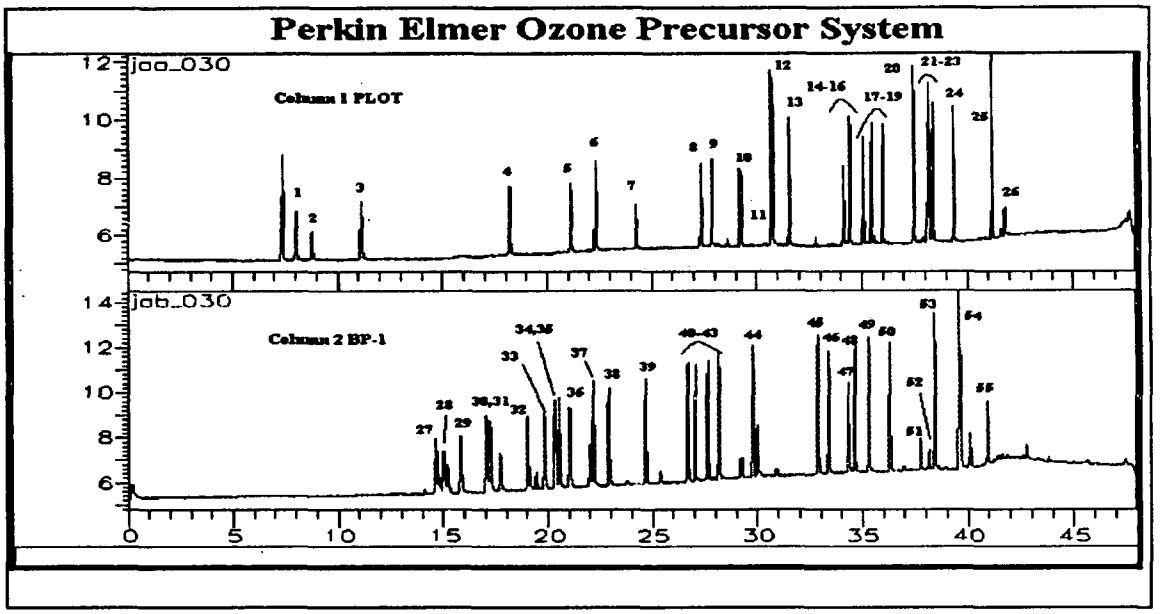

Figure 2: Multidimensional chromatographic output from ambient air monitoring system.

Peak identities are shown in Table 1.

VOCS Chromatographed on PLOT Column			
01	Ethane	15	Cyclopentene
02	Ethylene	16	Trans-2-pentene
03	Propane	17	3-Methyl-1-butene
04	Propene	18	1-Pentene
05	Isobutane	19	cis-2-Pentene
06	n-Butane	20	2,2-Dimethylbutane
07	Acetylene	21	3-Methylpentane
08	trans-2-Butene	22	2-Methylpentane
09	1-Butene	23	2,3-Dimethylbutane
10	cis-2-Butene	24	Isoprene
11	Cyclopentane	25	4-Methyl-1-pentene
12	Isopentane	26	2-Methyl-1-pentene
13	n-Pentane		
14	2-Methyl-2-butene		

VOCs Chromatographed on BP1 Column			
27	n-Hexane	42	2-Methylheptane
28	trans-2-Hexene	43	3-Methylheptane
29	cis-2-Hexene	44	n-Octane
30	Methylcyclopentane	45	Ethylbenzene
31	2,4-Dimethylpentane	46	p-Xylene
32	Benzene	47	2-Methylheptane
33	Cyclohexane	48	3-Methylheptane
34	2-Methylhexane	49	n-Nonane
35	2,3-Dimethylpentane	50	Isopropylbenzene
36	3-Methylhexane	51	n-Propylbenzene
37	2,2,4-Trimethylpentane	52	a-Pinene
38	n-Heptane	53	1,3,5-Trimethylbenzene
39	Methylcyclohexane	54	b-Pinene
40	2,3,4-Trimethylpentane	55	1,2,4-Trimethylbenzene
41	Toluene		

Table 1: Identification of chromatographic peaks in Figure 2.

The advantages of this instrumental system are that the 55 compounds of interest are separated cleanly, and without the use of liquid nitrogen. Neither the VOC collection (using the Peltier-cooled trap) nor the chromatography (which starts at 40 oC) require liquid nitrogen.

In defining the limits of this system, questions naturally arise concerning trap breakthrough volume and overall detection limits. Figure 3 below shows three of the key C_2 compounds, introduced to the system at 16 to 19 ng in absolute amounts. After introduction of the three hydrocarbons, zero grade bottled air was drawn through the Peltier-cooled trap and the organic-laden adsorbent. The trap was then heated to release the three VOCs for chromatography. As shown, acetylene response began to fall off only above 600 mL of air volume. Therefore, 600 mL of air was chosen as the sample size for analysis.

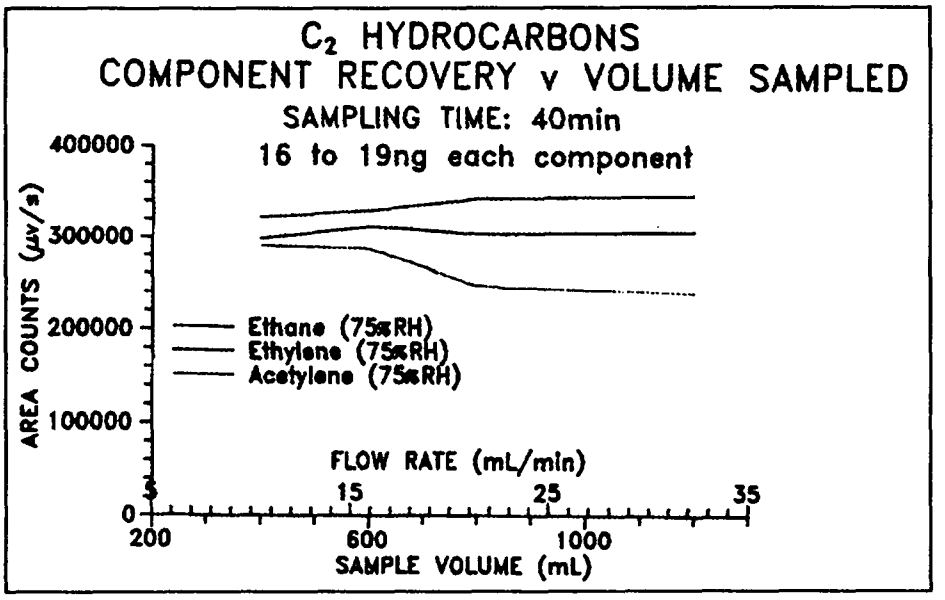

Figure 3: Determination of air volume breakthrough values for acetylene, ethylene and ethane.

That modest sample size notwithstanding, Figure 4 shows that this system achieves low level quantitation levels well within the part-per-trillion range. Methyl cyclohexane, the second labeled peak, has been quantified at 0.06 ppb.

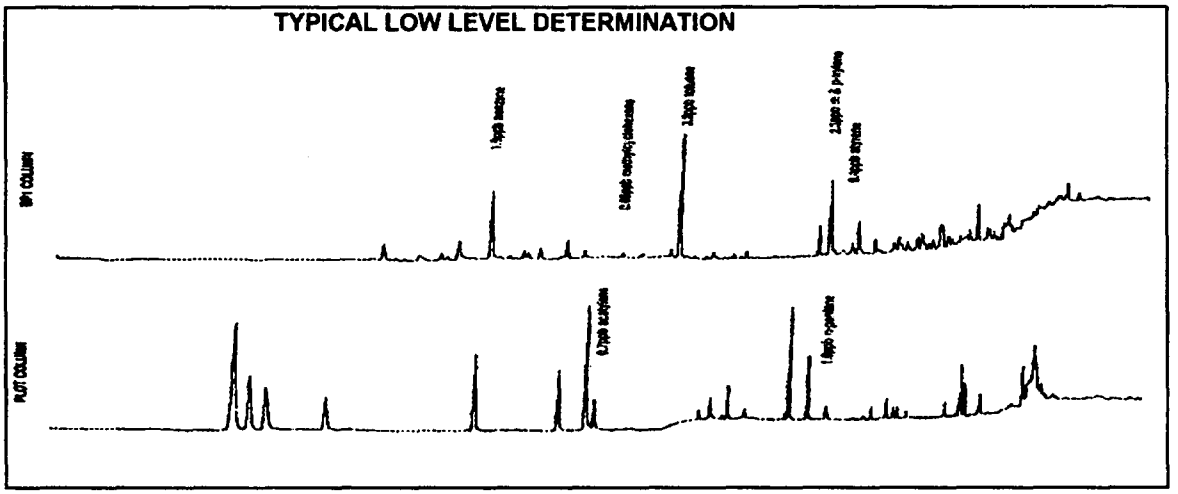

Figure 4: Illustration of low quantitation levels achievable with air monitoring system.

As an example of how this system can be used, consider Figure 5. In this chart, concentrations of three VOCs, namely isobutane, n-butane and ethane (based on ppb of carbon), in laboratory ambient air have been determined over a 24 hour period. Note that the X axis is based on a starting time of 9:00 AM, i.e., the first series of bars is at 9:00 AM, the second at 10:00 AM, etc.

At 6:00 PM, there is a dramatic increase in isobutane. This is when the evening laboratory cleaning crew begins their work, and one can speculate that the isobutane and n-butane rise might be due to the cleaning reagents they use, specifically if isobutane is a propellant in one of their spray cans. The butane data, along with charts derived from other hydrocarbon data, is presented in Figures 5 to 8.

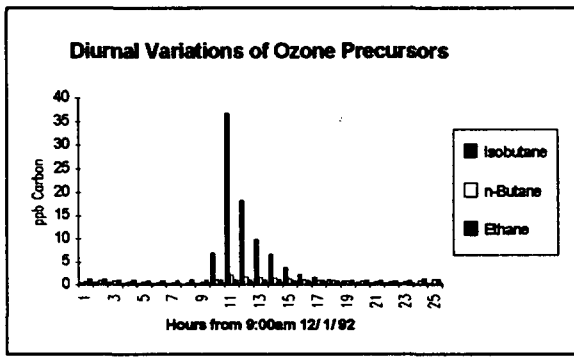

Fig. 5: Concentration of butanes and ethane over 24 hour period.

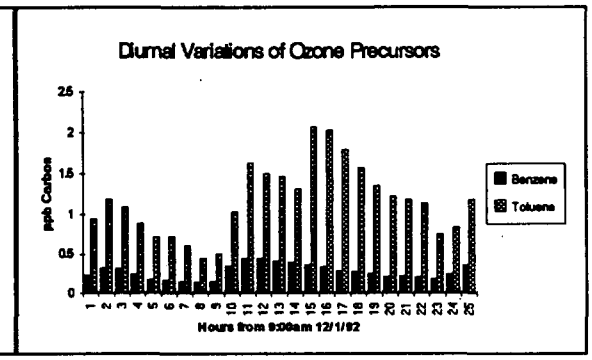

Fig. 6: Concentration of benzene and toluene

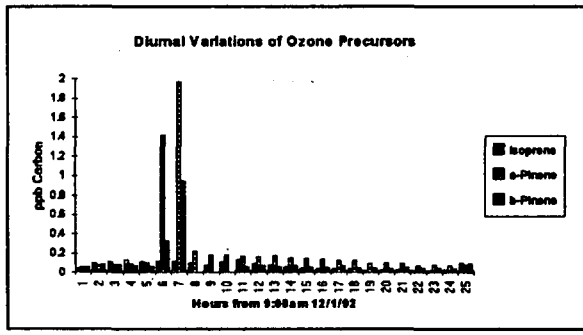

Fig. 7: Concentration of nonane and decane over 24 hours.

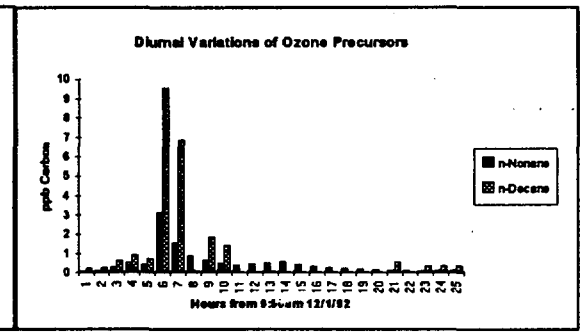

Figure 8: Concentration of isoprene and two pinenes over 24 hours

It is interesting to compare the four charts, even if explanations for the data are not readily apparent. As noted above, the butanes might be explained as a propellant used in a spray can. However, no similar explanation for the presence of nonane, decane, isoprene and the pinenes readily comes to mind, other than that the engineering laboratory in which this instrument is located is adjacent to a major roadway. Investigations to determine the source of these chemicals continue.

It should also be noted that an intrinsic part of this ambient air monitoring system is the ability to not only collect data at a remote site, but also to transmit information on the status of the instrument operation and reports on the collected data to a central operation. Using personal computers, modem telecommunications software such as PC-Anywhere, and Perkin-Elmer Turbochrom 3 chromatographic data handling software, the status of the ambient air monitoring system can be evaluated, raw data can be examined, and summary reports generated for transmission to a central operation where they can be combined with reports from other stations. Raw data files, because of their size, would likely be collected once per week during routine visits to the monitoring site. Chromatographic run and summary reports could be collected several times a day as needed.

SUMMARY

There are unique advantages to an ambient air monitoring system such as that described above. First and foremost, the system routinely operates unattended. The instrument used to collect data for this paper has been in continuous operation for over 1500 hours, and has consumed only 1 tank of hydrogen. No liquid nitrogen was required and zero grade air is generated using a laboratory compressor. Secondly, even though the instrument operates unattended, through the use of appropriate data handling and remote operation software, reports on instrument operation and chromatographic results can be collected as often as necessary.

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