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ORGANICS

44 Methods for the Determination of Volatile Organic Compounds in Soil Samples

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Methodology for the determination of volatile organic compounds (VOCs) in soil and some other solid matrices has traditionally been fraught with problems. Sample integrity is jeopardized when samples are manipulated to introduce internal standards or surrogates, or when the sample is exposed to the atmosphere while being transferred to the extraction device. There has also been a problem with the incomplete extraction of the VOCs from the solid matrices. Recently, instrument manufacturers have developed analytical equipment specifically designed to efficiently extract VOCs from a variety of solid matrices, while preserving the integrity of the original sample. Evaluations of two such units, the Dynatech PTA-30 W/S and the Tekmar Model 7000 Equilibrium Headspace Analyzer, are described for the determination of a broad spectrum of organic compounds contained in several soil types. For comparison purposes, similar analyses were performed with both systems according to Method 8260. Problems such as excessive amounts of water vapor interfering with the reproducibility of the gas chromatographic retention times are addressed. For both evaluations, several types of matrices were fortified and analyzed. The same gas chromatograph equipped with a wide-bore capillary column, and the same ion trap detector were used for separation and measurement in both studies. The features of each instrument, accuracies, precisions, and method detection limits are discussed for representative VOCs.

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CONCENTRATION OF WATER SOLUBLE VOLATILE ORGANIC COMPOUNDS FROM AQUEOUS SAMPLES BY AZEOTROPIC MICRODISTILLATION

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ABSTRACT

Methanol and other similar volatile organic compounds in zero headspace extracts and other aqueous matrices can be analyzed by azeotropic microdistillation, followed by gas chromatographic separation and detection. The method detection limits for methanol, 1-butanol and 2-methyl-1-propanol are at least an order of magnitude below the current Land Disposal treatment standards using the Toxicity Characteristic Leaching Procedure (TCLP).

A microdistillation system was developed to address the limitations of direct sample injection, purge-and-trap and other azeotropic distillation systems. Sample volume requirements range from 10 to 40 ml. The concentration factors range from 90 to 250 (depending on the analyte) with a 40 ml sample. The total distillation time is approximately five minutes. Typical detection limits are between 5 and 15 $\mu g/l$ when the distillate is analyzed by gas chromatography with flame ionization detection.

Aliquots of zero headspace extraction fluid and ground water were spiked with methanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 1,4-dioxane, acetonitrile, propionitrile, acrolein, acrylonitrile and ethyl acetate at 0.10 mg/l and 0.75 mg/l. Each aliquot was distilled and analyzed in duplicate during a 10-day period. Accuracy and precision were determined. System bias for most compounds was less than 15% (i.e., the average percent recovery was between 85-115%). The relative standard deviation for percent recovery for most compounds was also less than 15%. The microdistillation was most effective for the alcohols.

INTRODUCTION

The Hazardous and Solid Waste Amendments of 1984 amended RCRA by banning all land disposal of untreated hazardous waste within $5^1/_2$ years after passage on May 8, 1990. The basic purpose of the land disposal restrictions is to discourage activities that involve placing untreated wastes in or on the land when a better treatment or destruction alternative exists. Under the land disposal restrictions (40 CFR part 268.41) for spent solvents, methanol has a treatment standard of 0.25 mg/l for wastewaters containing spent solvents and 0.75 mg/l for all other spent solvent wastes in the waste extract using zero headspace extraction (ZHE). To date there are no EPA-approved methods for methanol that have detection limits below these treatment standards. The effect of this situation is that residues from the treatment of solvent wastes and multi-source leachate wastewaters cannot presently be certified to meet the corresponding treatment standards and thus cannot be landfilled.

This paper presents the development of an aqueous sample concentration, cleanup and analysis method with a detection limit lower than the spent solvent treatment standards

for methanol. The total sample handling time from the start of distillation to the completion of analysis is less than one-half hour. The initial experimental parameters were derived from a method for the azeotropic distillation of water soluble volatile organic compounds (1,2). This method is based on the fractional distillation of compounds which form azeotropes with water.* When distilling a 40 ml aqueous sample, or ZHE extract, total distillation time, including warm-up, is five minutes. GC run time is approximately 17 minutes. The distillate is free from nonvolatile organic and inorganic interferences. These nonvolatile components may degrade gas chromatographic performance and shorten the life of the GC column.

INSTRUMENTATION, EQUIPMENT AND SUPPLIES

Gas Chromatograph/Data System
    Hewlett Packard 5890 equipped with a flame ionization detector, Macintosh IIci (Apple) with LabView (National Instruments) and GC Integrator & Workmate (WillStein) software.
Gas Chromatography Columns
    Quantitation: DB-Wax, 30 m X 0.53 mm I.D., 1.0 micron film thickness
    Confirmation: DB-1, 30 m X 0.53 mm I.D., 1.5 micron film thickness
Hardware
    Wadsworth MicroVOC^3 System$^®$, Shamrock Glass (see Figure 5.)
    Round bottom flask, 100 ml , 14/20 joint
    Fractionation column, 14/20 joint, 1.6 cm O.D., 1.3 cm I.D., 60 cm in length, Shamrock Glass (see Figure 3.)
    Pipe insulation, polyurethane foam, $1^1/2$" O.D., $5/8$" I.D., 55 cm in length
    Glass beads, 5 mm O.D.
    Keck clamps, for 14/20 ground glass joint, Shamrock Glass
    Glass reducing union, 14/20 ground glass joint to 6 mm O.D. tube, Shamrock Glass (see Figure 4.)
    Stainless steel reducing union, $1/16$" to $1/4$"
    Air condenser, Teflon$^®$ tubing, $1/16$" O.D., $1/32$" I.D. (40 cm in length)
    GC autosampler vials
    Autosampler vial inserts, 100 μl, calibrated
    Graduated cylinder, 50 ml
    Support stand with rod, 1 meter
    Three-finger clamp
    Heating mantle, Glas-Col, 115 volts, 230 watts, STM 400
    Temperature controller, Glas-Col PL115-Cordtrol, 115 volts, 600 watts
    Porous carbon boiling chips, VWR cat # 26397-409
Reagents and Standards
    Ethanol, Everpure, 200 proof
    Methanol, B&J Brand, purity 99.9%
    1-Propanol, Baxter, purity 99%
    2-Methyl-1-propanol, Aldrich, purity 99.9%
    1-Butanol, Aldrich, purity 99.8%
    1,4 Dioxane, Aldrich
    Acetonitrile, Aldrich, purity 99.9%

* Note: Methanol does not form an azeotrope with water; nevertheless it can be effectively distilled with this method.

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Propionitrile, Aldrich, purity 99%
Acrolein, Aldrich, purity 97%
Acrylonitrile, JT Baker, purity 99%
Ethyl Acetate, Aldrich, purity 99%
Reagent water, deionized
Zero headspace extraction fluid: Refer to Method 1311 of the Federal Register Vol 55
    No. 126, Friday, June 29, 1990, pg 26986-26998

BACKGROUND

The goal was to develop a sample preparation/introduction system which when combined with GC-FID analysis would provide methanol method detection limits (MDL) below 0.1 mg/l, use less than 100 ml of sample and require less than 30 minutes of sample preparation. Reaching the MDL goal would require a concentration factor of approximately 30. Concentration factor is the ratio of the analyte concentration in the collected distillate fraction to that in the original sample.

Many physical parameters were investigated, such as the sample volume, boil/reflux rate, total distillation time and volume of distillate collected. The physical design characteristics of the distillation system itself were investigated. Several distillation/condenser designs were used: a commercial modified Nielson-Kryger and two miniaturized Nielson-Kryger (Peters) systems. Several alternate overflow systems were studied: the straight tube, notched, flared, wick and hoop systems (3). In addition, a completely redesigned capillary condenser was developed. The capillary condenser system was later refined into a more rugged form, the Wadsworth MicroVOC[3]. Two chemical parameters were also studied: analyte concentration and matrix. Table 1 lists the parameters that were studied.

<p align="center">Table 1.   Distillation Parameters Investigated</p>

Physical	
sample volume	10 to 1000 ml
boil/reflux rate	2 to 7 ml/min
distillation time	5 to 120 minutes
distillate volume collected	2 µl to 20 ml
Physical design	
Fractionation column	Vigreux, glass bead, sand, glass wool, Rashig ring, spinning band
Distillation system design	
collection chamber volume	1 to 20 ml
condenser height/cooling surfaces	15 to 60 cm, cooling coil, baffles
overflow design	Peters/Dow, straight, notched, flared, side drain, wick, hoop
overflow tube inside diameter	2 to 10 mm
overflow tube height	2 to 35 mm
capillary condenser	
Wadsworth MicroVOC[3]	
Chemical	
analyte concentration	0.025 to 10 mg/l
matrix	ground water, ZHE extract

<p align="center">II-4</p>

Modified Nielson - Kryger condenser

Initial experiments employed a commercially available modified Nielson - Kryger (N-K) condenser from Ace Glass (3). Its design was similar to that described by Peters (2) except with larger dimensions and sample removal through a stopcock was used rather than a syringe (Figure 1). The N-K collection chamber volume was larger; 20 ml vs 1 ml. Factorial design experiments* indicated that 70% recovery and an estimated detection limit in the mid ppb range could be obtained for methanol with a distillation time of one hour using a one liter sample aliquot. Azeotropic distillation appeared to be the right process. However, this large scale system was not practical because of the long distillation time and large sample volume requirement. Many miniaturized condenser overflow systems were investigated (3). Most miniaturized systems were more practical than the modified Nielson-Kryger system, but none produced a concentration factor greater than 20. Examination of fundamental distillation principles led to a radical change in condenser design.
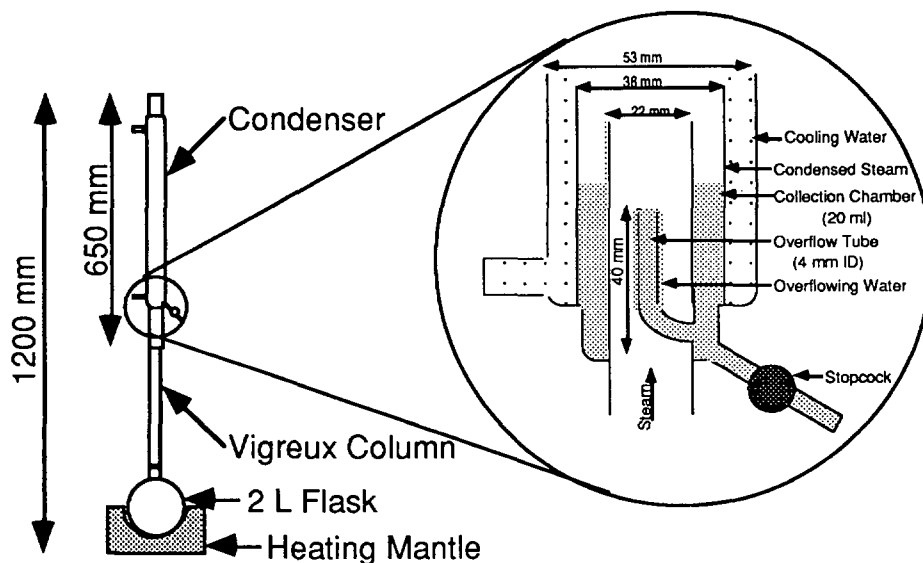
Figure 1.   Modified Nielson-Kryger Condenser Distillation System

ANALYSIS

EPA SW-846 Method 8015 (modified) was used for analyzing the concentrated aqueous samples. The analytical conditions are summarized in Table 2.

The instrument detection limit (IDL) was calculated to be 0.15 ng using 10 2 μl injections of a 0.10 mg/l standard. IDL = $(t_{n-1,99\%})$(Std Dev) = (2.821)(0.0528) = **0.15 ng**. A special note of caution regarding the GC temperature program is in order. Even though methanol and most other analytes elute relatively early, the GC column temperature must be ramped high enough and held long enough to remove all water from the capillary column. Retention time shifts may result if the water is not eluted from the column.

* Note: Factorial design is a statistical procedure which facilitates optimization of several parameters at the same time. Precision estimates can also be obtained.

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Since methanol is a common laboratory solvent it is difficult to obtain methanol-free water. One deionized water system contaminated reagent water with methanol. Also, airborne methanol can be absorbed by water in open containers.

Table 2.   Analysis Parameters

quantitation column	DB-Wax	external & internal standardization	
confirmation column	DB-1	carrier gas	helium
instrument calibration range	0.2 to 2000 ng	carrier gas flow	2.5 ml/min.
response factor %RSD	<15%	detector	FID
continuing calibration		detector temperature	230°C
response factor %D	<10%	hydrogen flow	37 ml/min.
injection volume	2 µl	air flow	426 ml/min.
injection type	splitless	make-up gas	nitrogen
injection port temperature	180°C	make-up gas flow	30 ml/min.
temperature program	30°C for 5 min., 5°C/min. to 70°C, 20°C/min to 150°C		

PROTOTYPE VOC[3]

Previous N-K distillation systems had not met the goals described above. A new condenser design improved both the concentration factor and the simplicity of the distillation system. The capillary condenser, an early prototype of the VOC[3], is shown in Figure 2. The fractionation column and condenser were very simple and inexpensive to make. The system consisted of a sample flask, fractionation column packed with glass beads (35 cm length), capillary column (0.53 mm I.D. and 35 cm length) and microcollection vial.

The capillary tube was normally water-cooled. The first 10 to 100 µl of distillate were collected in the micro vial. When 100 µl of distillate were collected a concentration factor of 80 was achieved in a 7-8 minute distillation. The methanol absolute recovery was 20%. The method detection limit of methanol in reagent water was 0.018 mg/l.

Figure 2. Capillary Condenser

Various types of fractionation columns were studied. Glass and Teflon® tubes were packed with sand, glass wool, Rashig rings and glass beads. A spinning band fractionation column was also studied. Small increases in distillation efficiency (relative to glass beads) were found with some fractionation column types, but the columns were either more difficult to clean or mechanically complex. Thus, the glass bead fractionation

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column was chosen as the best compromise between ease of use and distillation efficiency.

WADSWORTH MICROVOC[3]

The Wadsworth MicroVOC[3] is a rugged version of the capillary condenser system constructed from standard glass, stainless steel and Teflon® components. VOC[3] is an acronym for Volatile Organic Compound Concentration and Cleanup. The glass bead fractionation column is constructed from glass tubing with standard 14/20 ground glass joints (Figure 3). The air condenser consists of three parts (Figure 4): a custom glass reducing union which converts from the ground glass joint to $1/4''$ glass tube, a stainless steel reducing union which joins the $1/4''$ glass tube to a Teflon® tube and a Teflon® tube ($1/16''$ O.D., $1/32''$ I.D.) which was substituted for the 0.53 mm capillary column used in the prototype. The complete system is shown in Figure 5. The total system cost is about $300 with glassware comprising less than $70.

This microdistillation system more effectively concentrates methanol (and other alcohols) than the previous prototypes. The concentration factors range from 100 to 250 depending on analyte. The absolute analyte recoveries range from 20% to 60% (Table 3). The microdistillation system is more effective than purge-and-trap or other azeotropic distillation systems even though the absolute percent recovery is significantly less than 100%. Relative recoveries, calculated by using standards which are also distilled, average 99%.

Table 3. Analyte Concentration and Recovery

Analyte	CAS number	Typical Concentration Factor*	Typical Absolute Recovery*	Average Relative Recovery
Methanol	67-56-1	140	35%	100%
1-Propanol	71-23-8	240	60%	92%
2-Methyl-1-propanol	78-83-1	250	63%	86%
1-Butanol	104-51-8	250	63%	89%
1,4 Dioxane	123-91-1	150	38%	100%
Acetonitrile	75-05-8	200	50%	101%
Propionitrile	107-12-0	200	50%	96%
Acrolein	107-02-8	100	20%	99%
Acrylonitrile	107-13-1	100	20%	116%
Ethyl acetate	141-78-6	100	20%	114%

* When a 40 ml sample aliquot is used and the first 100 µl of distillate are collected.

Method Summary

The azeotropic microdistillation method is summarized in Figure 6. A 40 ml aliquot of sample is transferred to a round bottom flask. Boiling chips and internal standard(s) are added to the sample. Matrix spike compounds are added when appropriate. The distillation apparatus is assembled using Keck clamps at both ground glass joints after insuring that the fractionation column and air condenser are completely dry. The sample

14/20 Ground Glass Joint

Glass beads

Indentations

14/20 Ground Glass Joint
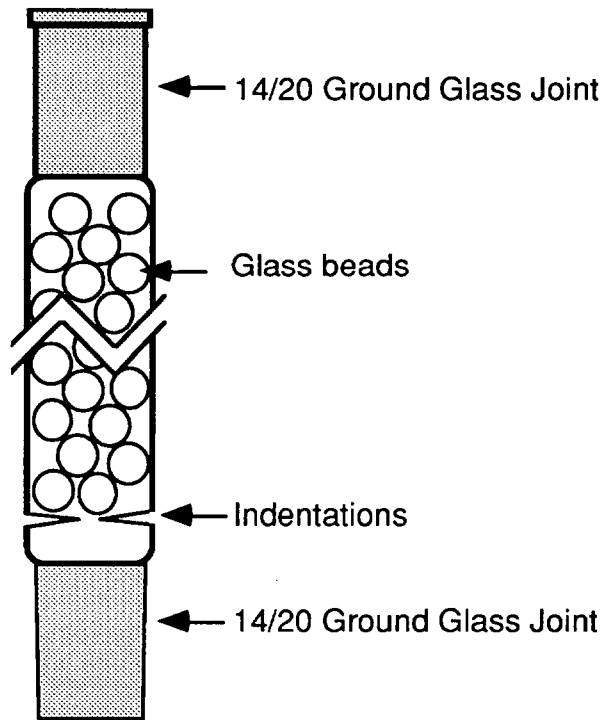
Figure 3. Fractionation column

$\frac{1}{16}$" OD Teflon® Tube

Stainless Steel
Reducing Union

$\frac{1}{4}$" to $\frac{1}{16}$"

6 mm OD Tube

Glass Reducing Union

14/20 Ground Glass Joint
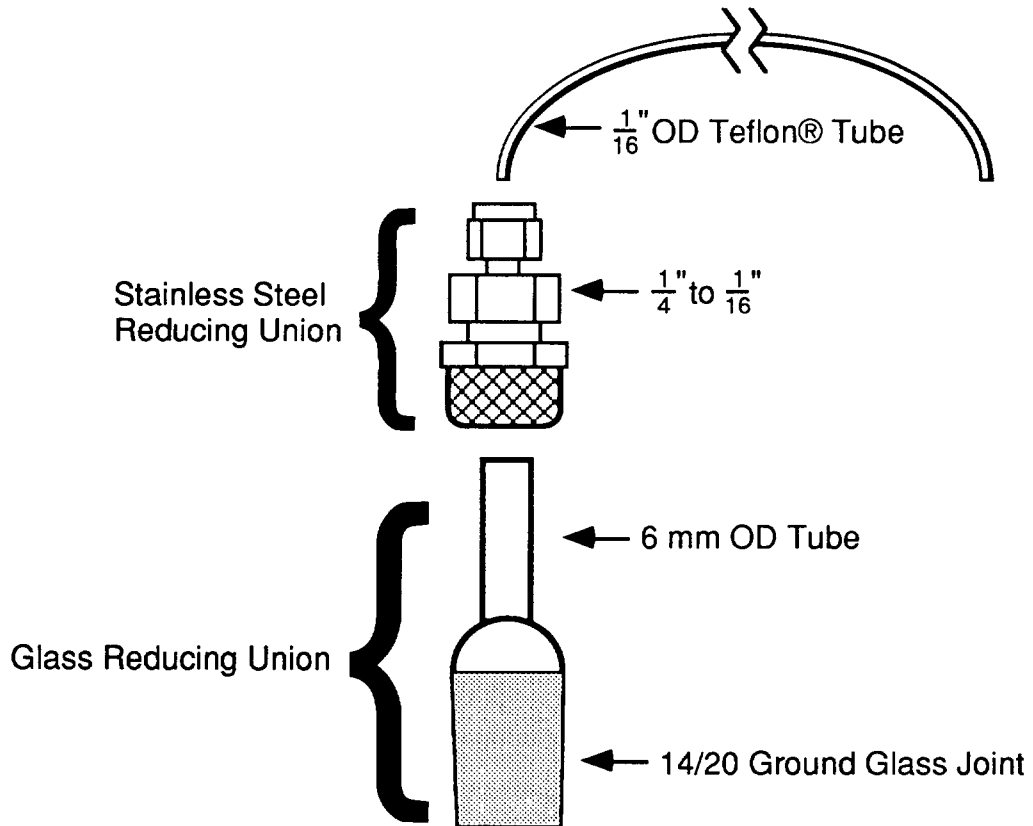
Figure 4.   Air condenser

II-8
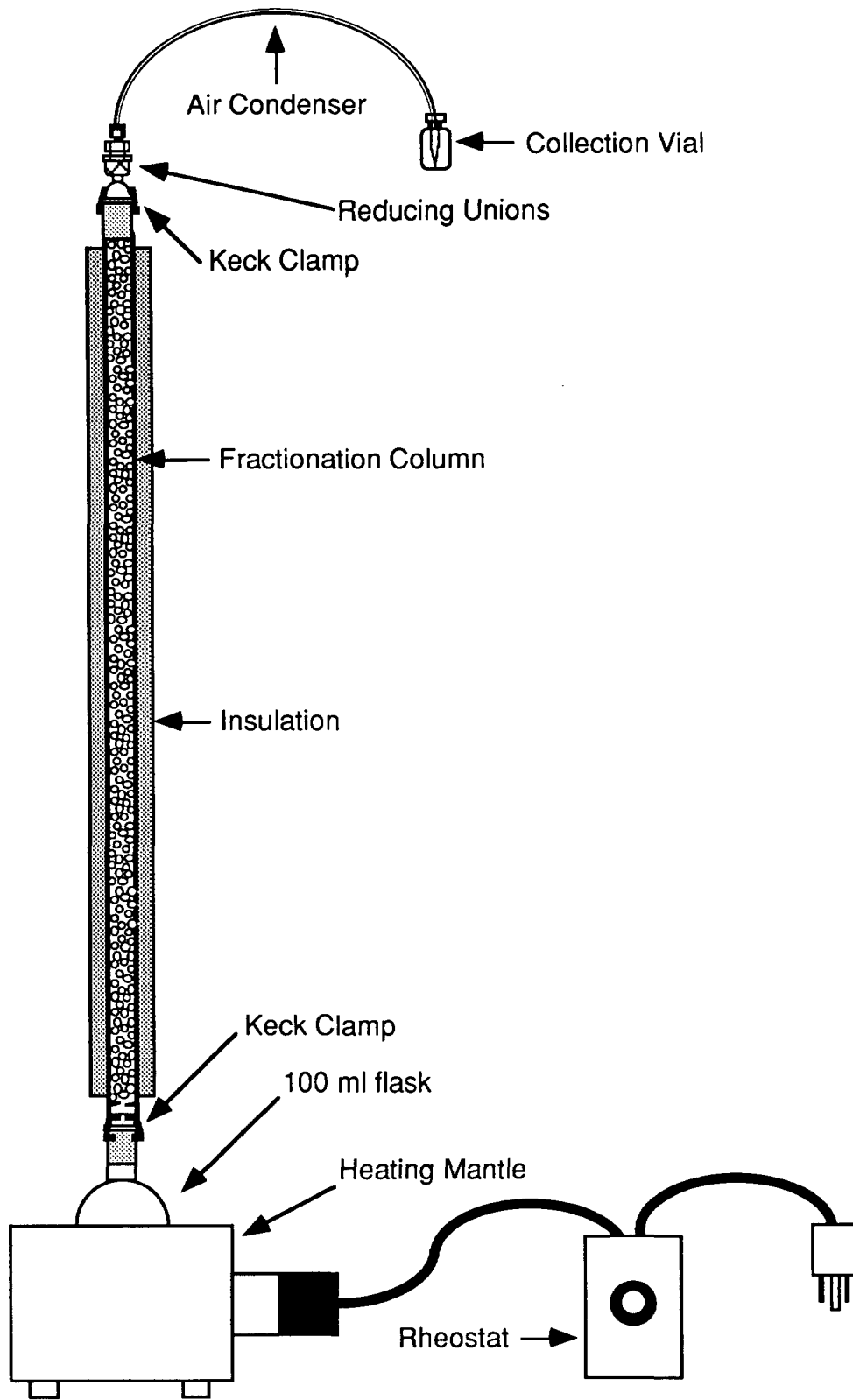
Figure 5.   Micro distillation system

is heated to the boiling point (2-3 minute warm-up) and held at a boil for 2 minutes. The first 100 μl of distillate are collected in a microvial for analysis by GC-FID. All calibration standards are distilled in the same manner as samples to compensate for system bias since the absolute recoveries of analytes are typically 50%. This calibration procedure is analogous to purge-and-trap calibration procedures.

TECHNIQUE COMPARISONS

Four sample introduction/preparation techniques were compared to this microdistillation for low molecular weight alcohols such as methanol (Table 4). Direct sample injection did not provide adequate analyte detection limits because there was no concentration step. In addition, direct sample injection deposited nonvolatile sample constituents in the chromatographic system, which degraded performance. This was particularly true for zero headspace extracts. Purge-and-trap sample introduction did not meet the detection limit requirements because the analytes were very water soluble and thus difficult to purge. Absolute analyte recovery was very low, (typically <1%) and highly variable.

Two modified Nielson-Kryger (N-K) azeotropic distillation systems have been used. A large scale N-K system (5) did provide adequate analyte detection limits but required one liter of sample and a one hour distillation. The one liter sample requirement was problematic since ZHE extraction produced only a few hundred milliliters. Also, the precision of methanol recovery was poor (40% RSD). A small scale N-K system (3) did not meet the detection limit (concentration factor) requirement. However, only a small sample aliquot was required and the distillation time was short relative to the large scale N-K system.

Figure 6
Method Summary

The microdistillation system presented in this paper has the highest actual concentration factor and lowest analyte detection limits of these five sample introduction/preparation techniques. Sample volume requirements and equipment cost are low and preparation time is short.

METHOD VALIDATION

A method validation study following the guidelines specified in the EPA Test Method Equivalency Petitions guidance manual (4) was performed. A data summary of the aqueous matrix study for samples spiked at two concentration levels is presented below.

Two sample matrices were studied: ground water and ZHE extraction fluid. The ground water was taken from a residential drinking water well. It was high in calcium, magnesium and iron content. The ZHE extraction fluid was prepared from reagents with low methanol content. Appropriate amounts of each matrix were spiked with each of the compounds listed in Table 5. The spiking concentrations were 0.10 mg/l for the low concentration spike and 0.75 mg/l for the high concentration spike. Both matrices contained low concentrations of methanol. Unspiked aliquots of each matrix were

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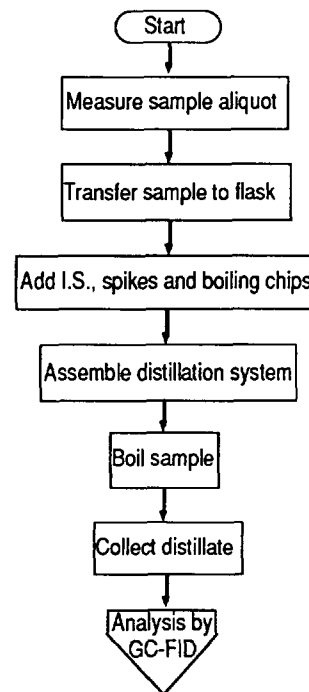
processed and analyzed to allow the percent recoveries to be corrected for the "native" analyte concentrations.

Each spiked matrix was subsequently shaken briefly (with minimal headspace) to homogenize it. Each spiked and unspiked matrix was divided into sample aliquots and stored in glass 40 ml VOA bottles with Teflon® lined caps at 4°C with zero headspace. Each day for 10 consecutive working days each matrix was distilled six times: two unspiked samples, two low concentration spikes and two high concentration spikes. A total of 12 "samples" were distilled each day. All calibration standards were distilled in the same manner as the samples to automatically compensate for system bias. An internal standard (ethanol) was used to improve precision. Analysis of Variance (ANOVA) was used to estimate method accuracy (bias) and precision.

Table 4.   Technique Comparison

Method*	Theoretical Concentration Factor	Absolute % Recovery	Actual Concentration Factor	Method Detection Limit mg/l	Sample Preparation Time minutes	Sample Volume ml
Direct sample injection	1	100	1	2	0	0.002
Purge-and-trap	2500**	1	25	0.1	10	5
Nielson-Kryger (5)	350	40	150	0.05†	60	1000
Nielson-Kryger (3)	8	100	8	0.3	10	40
Wadsworth MicroVOC[3]	**400**	**50**	**200**	**0.01**	**5**	**40**

Notes and Equations:

*   Assume a 2 µl injection into the GC-FID for comparison purposes.
**   The purge-and-trap TCF assumes a 2 µl final sample volume to be consistent with the injection volumes used by the other techniques.
†   The methanol recovery precision is low so the method detection limit is not improved as much as expected based on the actual concentration factor.

$$\text{Theoretical concentration factor (TCF)} = \frac{\text{original sample volume}}{\text{final prepared sample volume}}$$

$$\text{Absolute \% Recovery} = \frac{\text{amount of analyte in prepared "sample"}}{\text{amount of analyte in original sample}} \cdot 100$$

$$\text{Actual Concentration Factor} = \text{TCF} \cdot (\text{Absolute \%Recovery} / 100)$$

$$\text{Method Detection Limit (estimated)} = \frac{\text{Direct Inject DL}}{\text{Actual Concentration Factor}} \cdot \text{Sample prep precision}$$

The method detection limits (MDL) for both matrices are shown in Table 5. The detection limit was calculated from two different data sets. The one-day detection limit was derived from seven replicate analyses performed on the same day. The 10-day

detection limit was derived from the equivalency study data and consisted of 20 replicates spread over 10 days. The one-day MDL is often much lower than the 10-day MDL. This is expected since day-to-day reproducibility is usually not as good as same-day reproducibility. In addition, the distillates from the one-day ground water detection limit study were analyzed on a less sensitive GC. The detection limits remained essentially unchanged. This indicates that in this study the precision of the distillation is the limiting factor for method detection limits. Thus, using a less sensitive detector will not necessarily raise the method detection limit. Regardless of the GC used for analysis, the methanol, 2-methyl-1-propanol and 1-butanol method detection limits are well below current land disposal treatment standards.

Table 5.   Target Analytes

Analyte	Method Detection Limit* (mg/l)				
	Ground Water			ZHE Fluid	
	1 day[1]	1 day[2]	10 day[1]	1 day[1]	10 day[1]
Methanol	0.008	0.014	0.021	0.008	0.028
1-Propanol	0.007	0.005	0.017	0.018	0.024
2-Methyl-1-propanol	0.005	0.007	0.029	0.004	0.029
1-Butanol	0.002	0.009	0.018	0.004	0.027
1,4 Dioxane	0.007	0.012	0.026	0.018	0.042
Acetonitrile	0.004	0.005	0.022	0.030	0.027
Propionitrile	0.002	0.005	0.037	0.011	0.029
Acrolein	0.012	-	0.082	0.019	0.080
Acrylonitrile	0.010	0.021	0.10	0.014	0.092
Ethyl acetate	0.011	0.020	0.11	0.015	0.089

* Microdistillation with modified 8015 analysis.
[1] GC number 1, nominal instrument detection limit 0.1 mg/l
[2] GC number 2, nominal instrument detection limit 0.5 to 1.0 mg/l

The method may be extended to 2-butanone, 2-propanol and acetone, but these compounds were not included in this study.

The results of the equivalency study are summarized in Tables 6 and 7. No outlying data points were found in any of the data sets. The day effect was significant for some data subsets. Day effect is statistically significant when the precision within days is much better than the precision between days. This is a normal situation for analytical procedures. The bias column in Tables 6 and 7 shows the 95% confidence interval of analyte fraction recovered. A value of 1 corresponds to 100% recovery. The lower bound for precision is the lower limit of the 95% confidence interval of the true variance (of analyte recovery). The EPA has used 0.25 as an example maximum (4).

Figures 7 and 8 graphically present the bias data of Tables 6 and 7. The 95% confidence intervals (CI) of analyte percent recovered are plotted for both low and high spike levels. Most 95% CIs are small and near 100% recovery. This indicates that both accuracy (bias) and precision are good.

Overall the method is very effective for concentration and cleanup of the two aqueous matrices studied. **The alcohols exhibited excellent accuracy (bias) and precision.** The nitrile results were also quite good. The method is not as effective for acrolein,

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acrylonitrile and ethyl acetate although it may be adequate for some uses. Ethanol was not a good internal standard for these three compounds. A more appropriate internal standard may solve most of the precision problems associated with these compounds.

Table 6. EPA Equivalency Study-Analysis of Variance (ANOVA) Results for ZHE Fluid

Analyte	Low Concentration				High Concentration			
	Outliers	Day effect	Bias	Lower bound for Precision	Outliers	Day effect	Bias	Lower bound for Precision
Methanol	No	No	1.02-1.12	0.007	No	Yes	0.97-1.06	0.003
1-Propanol	No	Yes	0.92-1.04	0.006	No	No	0.87-0.92	0.002
2-Methyl-1-propanol	No	No	0.81-0.92	0.008	No	No	0.77-0.87	0.007
1-Butanol	No	Yes	0.82-0.95	0.007	No	No	0.83-0.90	0.003
1,4 Dioxane	No	No	0.95-1.10	0.017	No	Yes	0.97-1.06	0.003
Acetonitrile	No	Yes	1.04-1.17	0.007	No	No	0.90-1.00	0.007
Propionitrile	No	No	0.94-1.05	0.008	No	No	0.83-0.97	0.015
Acrolein	No	Yes	0.89-1.28	0.059	No	No	0.70-1.03	0.080
Acrylonitrile	No	No	1.06-1.40	0.082	No	No	0.84-1.21	0.096
Ethyl acetate	No	Yes	0.97-1.41	0.072	No	No	0.87-1.28	0.123

Table 7. EPA Equivalency Study-Analysis of Variance (ANOVA) Results for Ground Water

Analyte	Low Concentration				High Concentration			
	Outliers	Day effect	Bias	Lower bound for Precision	Outliers	Day effect	Bias	Lower bound for Precision
Methanol	No	No	0.90-0.98	0.004	No	No	0.91-0.98	0.003
1-Propanol	No	Yes	0.87-0.95	0.003	No	No	0.88-0.94	0.003
2-Methyl-1-propanol	No	Yes	0.80-0.94	0.008	No	Yes	0.82-0.96	0.008
1-Butanol	No	Yes	0.82-0.91	0.003	No	Yes	0.85-0.95	0.004
1,4 Dioxane	No	No	0.92-1.01	0.006	No	Yes	0.94-1.04	0.004
Acetonitrile	No	Yes	0.99-1.10	0.005	No	Yes	0.87-0.97	0.004
Propionitrile	No	Yes	0.93-1.12	0.013	No	Yes	0.81-0.98	0.010
Acrolein	No	Yes	1.00-1.39	0.063	No	No	0.71-0.89	0.015
Acrylonitrile	No	Yes	1.18-1.68	0.098	No	Yes	0.82-1.06	0.024
Ethyl acetate	No	Yes	1.07-1.63	0.117	No	Yes	0.77-1.08	0.032

LIMITING FACTORS

The method is most effective for water soluble compounds having a boiling point low enough that the distillate is enriched in the target compounds relative to the original sample. The precision with which the distillate is collected significantly affects overall method precision. The distillation rate also affects method performance. System and reagent contamination must be kept to a minimum. The type and condition of fractionation column affect the recovery of the target analytes. Although the microdistillation removes many nonvolatile and semivolatile interferences, it does not remove interferences from nontarget water soluble volatile organic compounds. Absolute analyte recovery ranges from 20 to 65%. Although the recovery is significantly less than 100%, the bias is consistent and the results can be corrected to account for this limitation

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using internal standards and calibration procedures similar to the purge-and-trap technique.
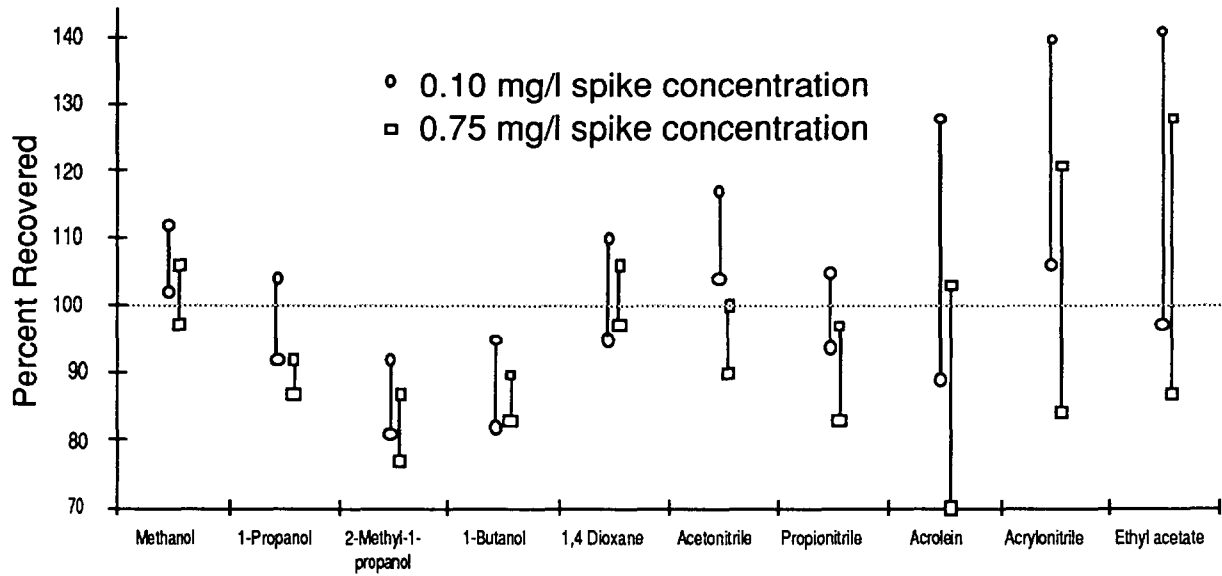
Figure 7   EPA Equivalency Study-Bias Results for Zero Headspace Extraction Fluid
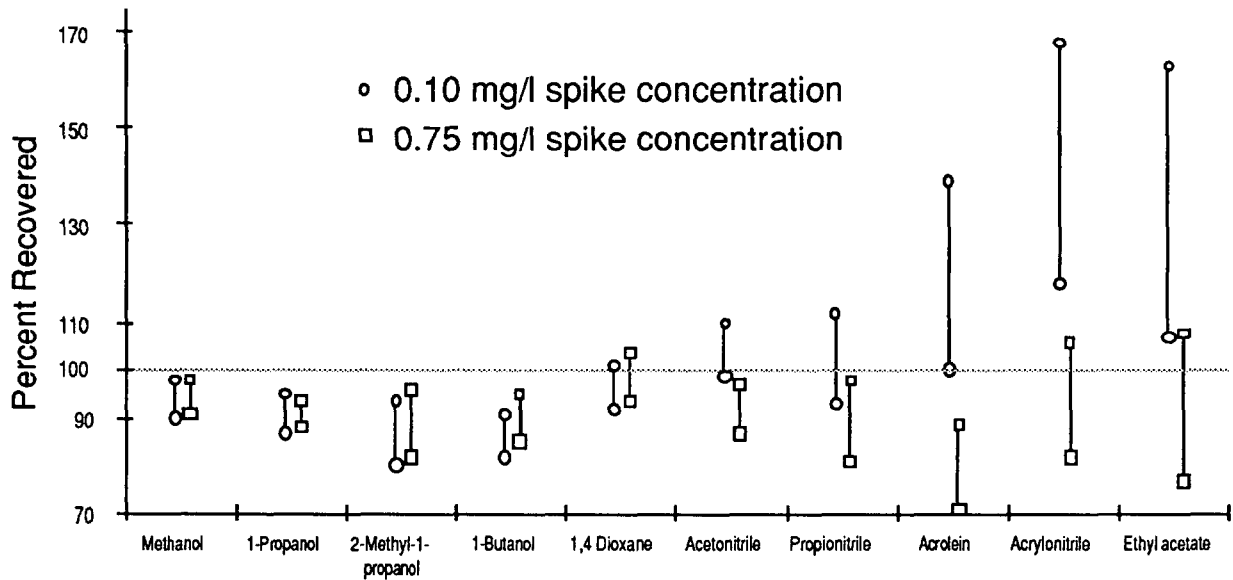
Figure 8   EPA Equivalency Study-Bias Results for Ground Water

The target analyte must be sufficiently volatile to be distilled from the aqueous sample. Significant enrichment of the analyte in the distillate (relative to the original sample) only occurs when the vapors released from the boiling water have a higher analyte to water ratio than the original sample. This happens when the analyte forms an azeotrope with water which is > 50% analyte. If the azeotrope is < 50% analyte no enrichment of the vapors will take place in the fractionation column. Some low boiling analytes such as

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methanol do not form an azeotrope with water but still are effectively concentrated by this system. In general this method is most effective for compounds that have boiling points below that of water. However, some butanols have boiling points higher than water but form azeotropes that boil at less than 100°C. This method appears to work for such compounds. It does not work for compounds such as 2-ethoxyethanol which form an azeotrope that is predominantly water.

The precision with which the distillate is collected significantly affects method precision. We recommend collecting the **FIRST** 100 µl of distillate. This seems to be a reasonable compromise between maximum concentration factor and ease of handling. The first few µl will contain the highest concentration of analyte; however, it is very difficult to manually collect this small fraction in a reproducible manner. Larger volumes such as 1 ml can be collected. However, this significantly reduces the method concentration factor. The volume collected should be 100 ± 20 µl. An internal standard (added prior to distillation) should be used to help compensate for these small variations in volume in the same manner that an internal standard compensates for purge-and-trap, chromatographic and detection variations.

The distillation rate also affects method performance. If the distillation rate is significantly higher than 2 ml/minute the fractionation column may not function efficiently. The analyte enrichment in the distillate may be reduced. If the distillation rate is too slow the distillate will not reach the air condenser or the distillation may take too much time.

System and reagent contamination must be kept to a minimum. The specific maximum contaminant concentration varies according to the quantitation limit required. Methanol and acetone are common contaminants in deionized water, reagents and laboratory air. If either of these compounds are target analytes, special laboratory practices may be necessary. Some water deionizers actually increase the amount of methanol and other potential target compounds in the laboratory water system. High purity reagents may also be necessary, particularly in the preparation of ZHE extraction fluid.

The type and condition of fractionation column affect the recovery of the target analytes. For best reproducibility and efficiency, the fractionation column, reducing unions and air condenser must be completely dry before use. Only 50 µl of water in the condenser can seriously reduce the analyte concentration in the distillate. Therefore, the entire distillation apparatus should be oven-dried before use.

Although the microdistillation removes many nonvolatile and semivolatile interferences, it does not remove interferences from nontarget water soluble volatile organic compounds. Nonvolatile sample components will not be distilled and thus will not be introduced into the GC. Most semivolatile components will also be eliminated or greatly reduced. This greatly reduces contamination of the injection port and GC column. Many water soluble volatile organic compounds may be collected in the distillate. Some of them may be difficult to resolve chromatographically. For example methanol, 2-butanone and 2-methyl-2-propanol elute very closely on a polyethylene glycol stationary phase (J&W DB-Wax). Such interferences may require different GC columns and/or detectors to resolve.

The method bias due to low analyte recoveries can be corrected by using an internal standard and distilling all calibration standards. This is similar to purge-and-trap

procedures except that the microdistillation system is not directly interfaced to the GC at present.

CONCLUSION

Methanol and other water soluble volatile organic compounds in zero headspace extracts and other aqueous matrices can be analyzed by azeotropic microdistillation, followed by gas chromatographic separation and detection. The method detection limits for methanol, 1-butanol and 2-methyl-1-propanol are much less than the current land disposal treatment standards.

This microdistillation system (Wadsworth MicroVOC[3]) addresses the shortcomings of direct sample injection, purge-and-trap and other azeotropic distillation systems. Small sample aliquots are required (40 ml). Analyte concentration factors are about two orders of magnitude when a 40 ml sample aliquot is used. The total distillation time is five minutes. Typical detection limits are between 5 and 15 µg/l when the distillate is analyzed by gas chromatography with flame ionization detection. The cost of the complete system is less than $300 with glassware comprising less than $70 of the total cost.

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POLLUTION REDUCTION IN THE LABORATORY THROUGH THE USE OF SMALLER INITIAL SAMPLE SIZE

by

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1.0 INTRODUCTION

Since the first of EPA's wastewater analysis methods were put forth in 1976, the environmentally sensitive chemical, methylene chloride, has been the solvent specified for extracting semivolatile organic compounds (BNA's) from aqueous media. Present methods for determining BNA's in aqueous samples use about 500 mL of methylene chloride ($MeCl_2$) for each 1 L sample exclusive of that required for GPC. Of this, only one mL is retained for analysis; the rest is either lost to the atmosphere during handling or disposed of by a waste removal firm.

Because $MeCl_2$ is on most of EPA's lists of undesirable chemicals, reducing the amount required by EPA's own analytical methods seems highly desirable. The first attempt to do this was noted in Method 525, a method for determining BNA's in drinking water where analyte removal from the sample is accomplished by adsorption in a "SEP" cartridge or disk.

Although SEP technology seems unlikely to be directly applicable to complex samples such as those associated with industrial discharges or those from test wells, one aspect of Method 525 is important. This is the fact that the GC/MS calibration curve is pushed downward from the typical 10 nG/uL low point to 0.1 nG/uL. The significance of this is that it should be possible to use a smaller initial sample size, on the order of 100 mL, yet retain the existing 1 mL final volume and still be well within the calibration range of the GC/MS equipment. This should make it possible to reduce the amount of $MeCl_2$ required by about a factor of ten.

Further, by calibrating to the existing method's high point, the effective dynamic range is increased by an order of magnitude. This should result in fewer sample extracts requiring dilution and reanalysis. Clearly this would save on analytical costs. Perhaps less clear is the savings which should result from being able to predict analytical effort more accurately due to reducing the uncertainty in the time and effort associated with reruns.

There are several minor benefits associated with using 100 mL water samples. These include reduced sampling and shipping costs, smaller, i.e., less expensive glassware and general improvements associated with improved space utilization. Such improvements, while significant in a conventional laboratory, are much more important in a mobile/field laboratory environment.

The purpose of the activity reported here was to evaluate the possibility of using smaller initial sample size, 100 mL versus 1000 mL, for the analysis of semivolatile organic compounds in aqueous waste samples. For the purpose of these experiments, a 100 mL continuous liquid-liquid extractor was designed and fabricated. It was then used to prepare seven spiked clean water samples for method detection limit assessment and five spiked field samples (provided by ICF Technology Inc., Las Vegas) for analyte recovery assessment. The quantities of solvent used in preparing the samples were recorded for comparison to those used with the standard 1000 mL extractor design.

2.0   EXPERIMENTAL

CONTINUOUS LIQUID-LIQUID EXTRACTOR DESIGNS

A set of 100 mL continuous liquid-liquid extractors (CLLE) were fabricated according to the design shown in Figure 2.1. To use them, 25 mL of methylene chloride (MeCl$_2$) is added to the CLLE and another 25 mL, to a 50 mL round bottom flask (RB) which is attached and used as the collector. A 100 mL aliquot of water sample is then added to the CLLE. Spikes are added to the water at this point. The water is then acidified with 2 mL of six N sulfuric acid, the condenser is placed on top of the extractor and the solvent in the RB is heated to boiling for 18 to 24 hours.
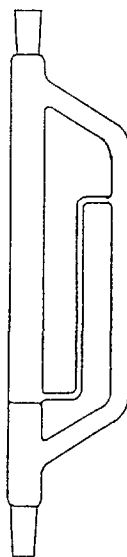
Figure 2.1 - 100 mL Continuous Liquid-Liquid Extractor.

GC/MS CONDITIONS

The instrument used to collect the data in this study was a VG Trio-1. This is a current generation instrument which provides better sensitivity than older instruments. Acquisition parameters were equivalent to those specified in the CLP 10/89 Low Concentration Water Method for Semivolatiles. The instrument was calibrated for each target analyte using a 5-point linear (regression) calibration curve. Concentrations of the calibration solutions ranged from one to 100 ng/uL; 1 uL injections were used in all cases.

A method detection limit (MDL) study was carried out using seven clean water samples spiked to 30 ug/L with each target analyte with CLLE design A and 10 ug/L with CLLE design B. MDLs were calculated from data acquired on both instruments. Percent recoveries were also calculated from the calculated concentration values for the five spiked field samples.

3.0 RESULTS AND DISCUSSION

SOLVENT USAGE

Solvent usage, identical for both CLLE designs, is summarized in Table 3.1. The quantities of methylene chloride ($MeCl_2$) were recorded for both the CLLE and RB charge volumes and the glassware washing volumes. The washing volumes were included because they are of significant magnitude and because the washing cycle is a true part of the analysis. For comparison purposes, the solvent volumes use with 1000 mL CLLEs is also included in Table 3.1. Also included in the table is the volume of solvent used to clean up the K-D apparatus.

TABLE 3.1 - METHYLENE CHLORIDE USAGE

Usage	100 mL CLLE	1000 mL CLLE
CLLE Charge	25 mL	250
RB Charge	25	250
CLLE Cleanup	75	225
RB Cleanup	30	150
K-D Cleanup	100	100
Total	255 mL	975 mL

As can be seen, the charge volumes used win the CLLEs and the RB collector are directly proportional to the volumes

of sample extracted. Thus, by going from 1000 mL to 100 mL, there is a savings of 90 percent in $MeCl_2$ usage.

The wash volumes for the CLLE and RB however, are not proportional to sample volume. This is because the washing process must clean the surface area of the glass and the ratio between the two devices in terms of surface area is on the order of 0.3-to-1. This correlates well with the $MeCl_2$ usage of 0.28-to-1.

It is important to note that both CLLE sizes result in an extract which must be concentrated via Kuderna-Danish (K-D). The wash volume for the K-D is remains unchanged with sample size because the K-D apparatus, in particular the Snyder column, is the same size in both cases. In principle it should be possible to decrease the size of the Snyder column but in practice this may be difficult due to fabrication difficulties.

The overall reduction in $MeCl_2$ achieved by going to 100 mL initial sample size and 100 mL CLLEs is 82.2 percent excluding the K-D. It drops to a savings of 73.8 percent when the K-D is included.

CONTINUOUS LIQUID-LIQUID EXTRACTOR DESIGN

Two significant behavior characteristics were noted during the extraction process. First there was a tendency for the RB to go dry. This results in target analytes being volatilized and driven up into the solvent vapor return arm where they condense. When dry RBs were noted, the extracts were discarded and an additional sample aliquot prepared, this time with less heat applied to the RB. The second problem resulted when insufficient heat was applied to the RB to maintain solvent condensation in the condenser. When this happened, solvent condensed in the solvent return arm of the CLLE and the sample was not extracted. This second problem was harder to monitor than the first because it was dependant on laboratory temperature. This tended to change due to the day/night settings on the thermostat which result in the lab becoming rather cool on cold winter nights. When the lab temperature drops, the volume of hot solvent needed to keep solvent condensation taking place in the condenser and not in the transfer arm becomes larger.

Both of the above problems could be overcome by using a 100 mL RB for the collector and charging it with 50, rather than 25 mL of $MeCl_2$. This however, would result in a significant increase in solvent usage.

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INSTRUMENT CALIBRATION

The VG Trio-1 was readily calibrated across the one to 100 ng/uL range. Most of the polar compounds were detected in the 1 ng/uL injection. Exceptions were Benzoic acid, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4,6-Dinitro-2-methylphenol and Pentachlorophenol.

METHOD DETECTION LIMITS AND SPIKE RECOVERIES

Method detection limits (MDLs) were calculated for each analyte based on the seven spiked clean water samples. The MDLs were not as low as had been anticipated when calculated from data acquired from all seven runs. They ranged from about 20 to 30 ug/L for most analytes. Problems were most significant with the highly polar analytes and the reactive analytes. These included Benzoic acid, Hexachlorocyclopentadiene, 2,4-Dinitrophenol and 4-Chloroanaline.

TABLE 3.2 - METHOD DETECTION LIMITS (ug/L)

Analyte	7 Sample Data	4 Sample Data
Phenol	39.1	2.8
bis(-2-Chloroethyl)Ether	29.6	2.2
2-Chlorophenol	29.9	3.0
Benzyl Alcohol	31.5	3.6
2-Methylphenol	29.3	4.8
bis(2-Chloroisopropyl)Ether	23.0	7.2
4-Methylphenol	27.4	5.6
N-Nitroso-Di-n-Propylamine	16.3	17.4
Hexachloroethane	29.3	4.6
Nitrobenzene	26.3	2.6
Isophorone	23.5	1.4
2-Nitrophenol	21.8	2.0
2,4-Dimethylphenol	10.8	8.7
Benzoic Acid	nd	nd
bis(2-Chloroethoxy)Methane	35.4	3.7
2,4-Dichlorophenol	23.1	5.4
1,2,4-Trichlorobenzene	26.7	6.6
Naphthalene	26.4	2.9
4-Chloroaniline	nd	nd
Hexachlorobutadiene	27.8	10.0
4-Chloro-3-Methylphenol	24.8	3.4
2-Methylnaphthalene	23.9	3.5
Hexachlorocyclopentadiene	nd	nd
2,4,6-Trichlorophenol	18.6	8.7
2,4,5-Trichlorophenol	20.0	2.4
2-Chloronaphthalene	22.9	2.1
2-Nitroaniline	17.6	2.7

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Dimethyl Phthalate	29.3	5.6
Acenaphthylene	29.6	3.3
2,6-Dinitrotoluene	16.9	4.8
3-Nitroaniline	16.1	10.8
Acenaphthene	30.0	2.6
2,4-Dinitrophenol	nd	nd
4-Nitrophenol	16.8	9.4
Dibenzofuran	22.8	4.6
2,4-Dinitrotoluene	15.2	6.0
Diethylphthalate	28.3	6.4
4-Chlorophenyl-phenylether	29.0	14.3
Fluorene	29.6	4.3
4-Nitroaniline	18.7	17.8
4,6-Dinitro-2-Methylphenol	8.5	11.4
N-Nitrosodiphenylamine	32.8	25.4
4-Bromophenyl-phenylether	27.3	5.0
Hexachlorobenzene	15.0	6.6
Pentachlorophenol	8.9	5.6
Phenanthrene	27.8	4.5
Anthracene	25.1	4.7
Di-n-Butylphthalate	32.9	29.0
Fluoranthene	31.6	13.8
Pyrene	33.0	12.0
Butylbenzylphthalate	29.8	18.1
3,3'-Dichlorobenzidine	14.4	14.3
Benzo(a)anthracene	34.0	10.8
Chrysene	32.1	7.5
bis(2-Ethylhexyl)phthalate	37.2	31.4
Di-n-Octylphthalate	36.9	31.3
Benzo(b)fluoranthene	37.6	31.8
Benzo(k)fluoranthene	46.0	36.3
Benzo(a)pyrene	24.0	10.5
Indeno(1,2,3-cd)pyrene	28.8	15.1
Dibenz(a,h)anthracene	29.2	18.2
Benzo(g,h,i)perylene	25.1	8.1
1,3-Dichlorobenzene	25.9	5.9
1,4-Dichlorobenzene	26.7	4.1
1,2-Dichlorobenzene	27.1	4.0
avg	26.0	9.4

The higher than anticipated MDLs are believed to result from the operational problems with the extractors (see above). The reason for this conclusion is that the recoveries for the target analytes in three of the seven samples was quite low (less than 40 percent). Further, the recoveries were particularly low for the more polar compounds. This suggests that there may have been problems with incomplete extraction caused by the low night time lab temperature.

If it is assumed that the three low recovery extracts are the result of a circumventible problem and MDLs are recalculated based on four, rather than seven samples, the MDL values are much closer to those anticipated (4 Sample data in Table 3.2) with an average of 9.4 ug/L.

Results from the five field samples spiked in duplicate were used to calculate mean percent recoveries (Table 3.3). The percent recoveries averaged between 65 and 80 percent which seems reasonable.

TABLE 3.3 - PERCENT RECOVERIES

Analyte	Avg %R
Phenol	47.8
bis(-2-Chloroethyl)Ether	71.2
2-Chlorophenol	54.0
Benzyl Alcohol	83.5
2-Methylphenol	52.5
bis(2-Chloroisopropyl)Ether	73.1
4-Methylphenol	51.1
N-Nitroso-Di-n-Propylamine	73.3
Hexachloroethane	72.0
Nitrobenzene	69.8
Isophorone	81.3
2-Nitrophenol	55.2
2,4-Dimethylphenol	45.8
Benzoic Acid	54.6
bis(2-Chloroethoxy)Methane	63.5
2,4-Dichlorophenol	56.1
1,2,4-Trichlorobenzene	78.0
Naphthalene	73.7
4-Chloroaniline	nd
Hexachlorobutadiene	73.9
4-Chloro-3-Methylphenol	62.7
2-Methylnaphthalene	74.1
Hexachlorocyclopentadiene	nd
2,4,6-Trichlorophenol	60.1
2,4,5-Trichlorophenol	59.8
2-Chloronaphthalene	76.1
2-Nitroaniline	92.4
Dimethyl Phthalate	83.6
Acenaphthylene	77.7
2,6-Dinitrotoluene	85.7
3-Nitroaniline	51.7
Acenaphthene	73.6
2,4-Dinitrophenol	79.7
4-Nitrophenol	70.3
Dibenzofuran	79.7
2,4-Dinitrotoluene	86.4

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Diethylphthalate	87.6
4-Chlorophenyl-phenylether	80.7
Fluorene	69.9
4-Nitroaniline	72.9
4,6-Dinitro-2-Methylphenol	75.9
N-Nitrosodiphenylamine	50.8
4-Bromophenyl-phenylether	89.8
Hexachlorobenzene	87.1
Pentachlorophenol	82.5
Phenanthrene	87.1
Anthracene	95.2
Di-n-Butylphthalate	90.5
Fluoranthene	89.3
Pyrene	73.6
Butylbenzylphthalate	76.8
3,3'-Dichlorobenzidine	2.7
Benzo(a)anthracene	83.8
Chrysene	82.5
bis(2-Ethylhexyl)phthalate	84.2
Di-n-Octylphthalate	87.0
Benzo(b)fluoranthene	80.8
Benzo(k)fluoranthene	80.7
Benzo(a)pyrene	70.6
Indeno(1,2,3-cd)pyrene	76.4
Dibenz(a,h)anthracene	78.5
Benzo(g,h,i)perylene	71.9
1,3-Dichlorobenzene	69.7
1,4-Dichlorobenzene	70.3
1,2-Dichlorobenzene	72.5
Nitrobenzene-d5	85.4
2-Fluorobiphenyl	74.2
Terphenyl-d14	72.4
Phenol-d5	48.4
2-Fluorophenol	59.7
2,4,6-Tribromophenol	80.0
2-Chlorophenol-d4	33.0
1,2-Dichlorobenzene-d4	<u>77.2</u>
Avg	72.8

4.0 CONCLUSIONS

The experiments described are promising in terms of reducing pollution associated with environmental sample preparation. The technique of using a smaller initial sample size in conjunction with calibrating the GC/MS to a lower concentration provided a reduction of approximately 75 percent in the amount of Methylene chloride required to perform an extraction. The quality of the analytical results was approximately equivalent to that achieved with

the traditional 1 L sample and extractor but a new design
is recommended to increase the ruggedness of the ruggedness
of the experimental design.

47 EXTRACTION OF PHENOLIC COMPOUNDS FROM WATER SAMPLES USING STYRENE-DIVINYLBENZENE SPE DISKS

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ABSTRACT

Phenolic compounds, especially the more polar ones, can be difficult to extract from water samples using solid phase extraction with C18 functional silica as the particulate. The cause of low recoveries is almost certainly unfavorable partitioning between the C18 and water, resulting in rather low breakthrough volumes and recoveries. Our research has shown that the use of pH adjustment and heavy salting, along with low sample volumes, can help the situation by altering the partitioning, but another solution is a different solid phase particulate.

Styrene-divinlybenzene particles were incorporated into 47 mm solid phase extraction disks and used to extract a variety of phenolic compounds from water samples. To preserve the high flow rates that make solid phase extraction disks so attractive, small particles (3-10 um) were used to preserve the fast kinetics seen with the usual 8 um C18 silica.

This presentation will briefly discuss the basics of extracting phenols from water using SPE disks, followed by the details and results of our research. The preliminary conclusion is that the resin disks do have some advantages over C18 disks for the extraction of phenols, and perhaps other polar compounds, from water samples.

INTRODUCTION

One of the more significant trends in environmental sample preparation is the replacement of liquid/liquid extraction (LLE) with liquid/solid extraction (LSE), also called solid phase extraction (SPE), for concentrating semi- and non-volatiles from aqueous samples. Although LSE works very well for extracting most analytes of environmental significance, low recoveries are expected for the more

polar, water-soluble analytes, such as certain phenols. This is expected, since LSE and LLE use very similar mechanisms and low recoveries of water-soluble compounds are well known in LLE.

Partition ratios between the organic phase and the aqueous phase govern the percentage of analyte extracted in both LLE and LSE, where it is convenient to think of the organic portion of the particle as being analogous to the solvent in LLE. For hydrophobic, water-insoluble compounds, such as PAH's, PCB's, and many other pollutants, the partition ratio is overwhelmingly in favor of the organic phase, resulting in good recoveries from large volumes of water. On the other hand, polar and water-soluble compounds have less favorable partition ratios, resulting in relatively low recoveries.

Often, the addition of additives to the aqueous phase is effective in changing the partition ratio, thus increasing low recoveries. This practice is well known in LLE in the form of sodium chloride addition, or "salting out." Another familiar example is pH adjustment to convert ionic analytes to the corresponding neutral species. Salting out or buffering can be equally effective in LSE and is one approach to increasing LSE recoveries of difficult compounds.

Other methods of increasing low recoveries in LLE are to use larger volumes of extracting solvents, different extracting solvents, or extractions of the same water sample with several portions of organic solvent. Approximate LSE analogs of these techniques are respectively a higher mass of sorbent, a sorbent with more selectivity for the analytes, and multiple sorbent beds. An alternative to a higher mass of sorbent is a smaller volume of sample, which also increases the sorbent/sample ratio.

This paper/presentation will explore the use of experimental solid phase extraction disks which are similar to the Empore^{TM} disks used in Method 525, but containing polystyrene/divinylbenzene (SDVB) in place of the C18 silica. The premise of this work is that the SDVB disks offer both a higher mass of sorbent (in terms of organic content) and perhaps more selectivity for aromatic compounds than C18. These features are expected to result in a disk which will offer significantly higher recoveries for polar compounds, such as

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phenolics, from water samples. The analytes used for this work are a series of phenols ranging from relatively hydrophilic to hydrophobic.

EXPERIMENTAL

The experimental portion of this work consisted of two parts: scouting to determine the efficiency of several sorbents at extracting phenolics from water, and more thorough triplicate extraction studies of the most efficient sorbents identified by scouting. The scouting was done by spiking several phenolic compounds into 100 ml of reagent water and passing the water through experimental 47 mm x 0.5 mm SPE disks containing a variety of sorbents, using a standard 47 mm filtration apparatus. The use of the disks has been well documented elsewhere and won't be detailed here (1,2). The disks were then eluted using acetonitrile or acetonitrile followed by ethyl acetate, depending on how tightly the analytes were sorbed to the disk. The final determination was done with HPLC, using a reverse phase system with UV detection. The compounds were: phenol, o-cresol, 2-nitrophenol, 4,6-dinitro-o-cresol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, and 2,4,6-trichlorophenol at concentrations in the water ranging from 0.5 ppm to 20 ppm, depending on the extinction coefficient. The effect of salt addition and pH adjustment was also briefly studied during this phase.

Recovery data were determined by spiking the 11 phenols shown in Table II into 100, 200, 300, and 500 ml of water and passing the water through 47 mm disks, as in the scouting studies. Samples were processed using a vacuum of about 25 inches Hg, generated with an aspirator. Sample flow times ranged from 0.5 minutes for 100 ml through the SDVB disk to 7 minutes for 500 ml through the C18 disk. The 500 ml sample took 2.5 minutes to pass through the SDVB disk, which would correspond to 5 min/L. Each spike was done in triplicate. The approximate concentration of each phenol in the water was 200 ug/L. Since the 11 phenols weren't well resolved by the HPLC, the phenols were tested in two mixtures, one with five and one with six of the compounds. Elution was done with 2 x 2 ml aliquots of tetrahydrofuran (THF), followed by 2 x 2 ml aliquots of methanol. These aliquots were then combined and made to 10 ml with methanol for HPLC analysis. Again, C18 reverse phase HPLC was used with 270 nm detection and a water:methanol gradient.

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Each of the mobile phases contained 0.1 percent acetic acid to suppress ionization of the phenols and improve peak shape. Three types of disks were used - C18 and cyclohexyl (CH) bonded silica, and SDVB.

In both phases of the study, calibration was single point, the standard being at the concentration expected from a 100 percent recovery. Except for the standard 47 mm C18 and CH disks, which are commercially available (Varian Sample Prep Systems, Harbor City, CA), the Empore[TM] disks were experimental, each being prepared at 3M from the specific sorbent particles mentioned. Except for the SDVB particles used in the scouting phase, which were in the 50-100 um size range, all of the particles were 5-15 um. All disks were 47 mm x 0.5 mm with particle loadings of 75-90 percent by weight.

RESULTS AND DISCUSSION

The intent of the scouting work was to quickly test several sorbents for their ability to extract the probe phenolics from 100 ml of water, then use the more promising phases for further study. Standard C18 disks were used as a control, since these disks are beginning to find wide use in environmental laboratories. CH bonded silica was also incorporated into scouting and the subsequent recovery studies, since CH has gained a reputation of being effective for phenol extractions. Besides the C18 bonded silica and CH bonded silica, two proprietary bonded silicas were tried, plus a cyano bonded silica and the SDVB. The phases showing the best recoveries were C18, CH, and SDVB. Although CH is often mentioned as an effective phase for the SPE of phenolics from water, the results failed to show a clear advantage over C18. These results are shown in Table I. The compounds that presented problems with the extraction were the more polar, water soluble compounds, while the hydrophobic phenols were easily extracted from 100 ml samples by most of the sorbents tried.

As an extension of this work, 25% NaCl was added to the water and the pH was lowered to 2 with HCl. These modifications of the sample, done before extraction, were successful in raising the recoveries of several analytes, also shown in Table I. Sample

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modification steps, which added little time or cost to the analysis, make it possible to use standard C18 disks for the quantitative extraction of many phenolics of environmental interest. The only test compound showing a low recovery was phenol, which has a water solubility of almost 10 g/100 ml in water.

In the scouting work, the SDVB resin was clearly the most effective for quantitative extractions of the test compounds from 100 ml of water, even without modification of the sample. Because of the strong interaction between some of the analytes and the resin, acetonitrile elution alone wasn't strong enough, as evidenced by generally low recoveries (not shown) of even the hyrophobic phenols. To overcome this problem, the usual acetonitrile elution was followed by 2 x 1 ml ethyl acetate elutions, which were added to the acetonitrile. There are undoubtedly a number of alternative elution solvents which would have been equally effective.

Once the scouting work had identified SDVB as an effective sorbent for phenolic compound extractions, a more rigorous recovery study was undertaken to confirm the scouting results and progressively increase sample volumes to define the limits of this technique. C18 and CH disks were again included for comparison. The SDVB disks used for these results contained sorbent particles approximately 10 um in size. For this study, the analyte list was modified to contain the traditional priority pollutant phenols, at approximately 200 ug/L each. The reagent water used was unmodified in terms of pH or salt content.

Recovery results are shown in Tables II, III, and IV, at several sample volumes, for C18, CH, and SDVB disks, respectively. Generally, the results contain no surprises. In order of effectiveness for phenol extractions from water, SDVB>>C18>CH, which also parallels the organic content of each sorbent particle. As expected, increasing the volume of the samples decreased the recoveries of marginally recovered compounds. There are a few anomalous results, e.g. the 2,4-dinitrophenol results on the SDVB disk at 300 ml. This may be a reflection of compounds with pK_a's near the pH of the matrix, where a slight change in pH would result in a substantial change in the percentage of the ionic form of those compounds.

Dropping the pH of the samples to 2 would overcome this effect and may increase some of the low recoveries.

While resin sorbents have occasionally been reported in the literature for phenolic extractions, including one of the pioneering publications in SPE, heroic efforts are often needed to clean up these resins before use (3). Although our work was conducted well above method detection limits, we saw no evidence of interferences from the SDVB, which would be expected to contain UV chromophores. The only cleanup step used for these disks was the initial wash step with a few ml of the eluting solvents (1). Given the small particle diameter and short distances needed for contaminants to diffuse into the wash solvent, the initial wash step plus the methanol conditioning step may be sufficient to remove any contaminants. An independent researcher, using these disks prior to LC/MS, also noticed no interferences (4).

Conclusions

This work demonstrates the utility of experimental SDVB, SPE disks as a technique for isolating phenolics from water. Even at 500 ml, quantitative recoveries were seen for all but a few phenols with extraction times corresponding to about 5 min/L. With pH adjustment and salting out, the low recoveries may have been improved. Using 10 um SDVB particles in the disks, no interference problems were encountered, in contrast to literature reports of extensive soxhlet extractions needed for the much larger SDVB particles used in previous research.

References

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TABLE I. Scouting Results for Selected Phenols

	Sorbent				
	C18	CH	SDVB*	C18**	CH**
Phenol	4	5	90	23	14
o-Cresol	20	9	120	94	99
2-Nitrophenol	35	23	108	90	69
2-Methyl-4,6-Dinitrophenol	14	19	96	94	94
2,4-Dichlorophenol	106	102	107	92	88
2,4,5-Trichlorophenol	108	109	95	92	87
2,4,6-Trichlorophenol	110	111	96	92	89

*   eluted with acetonitrile followed by ethyl acetate

`* pH = 2, 25% NaCl

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TABLE II. Results Using C18 Disks - % Recovery (RSD, n=3)

Volume (ml)

	100	200	300	500
Phenol	12.8 (9.5)	7.8 (4.1)	4.5 (6.7)	2.8 (7.3)
2-Nitrophenol	63.9 (3.2)	41.2 (3.2)	25.0 (5.9)	15.4 (5.2)
4-Nitrophenol	29.9 (6.1)	19.1 (6.2)	11.3 (3.8)	6.8 (5.8)
2-Chlorophenol	50.6 (3.9)	30.3 (4.3)	18.2 (5.0)	10.7 (5.2)
2,4-Dinitrophenol	5.9 (17.3)	4.2 (15.2)	8.8 (1.6)	1.6 (5.3)
2,4-Dichlorophenol	67.4 (5.1)	82.9 (10.9)	63.8 (1.1)	47.5 (4.8)
2,4-Dimethylphenol	99.2 (3.0)	89.5 (4.7)	61.8 (7.2)	37.1 (6.7)
4-Chloro-3-Methylphenol	93.0 (7.6)	104.9 (3.9)	89.7 (7.4)	60.5 (7.9)
2,4,6-Trichlorophenol	92.7 (2.5)	111.3 (1.7)	99.7 (2.7)	97.0 (1.4)
2-Methyl-4,6-Dinitrophenol	31.0 (6.6)	31.4 (3.0)	18.6 (4.0)	11.7 (4.3)
Pentachlorophenol	95.1 (2.0)	98.8 (3.8)	102.9 (1.5)	98.2 (1.8)

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TABLE III. Results Using CH Disks - % Recovery (RSD, n=3)

	Volume (ml)			
	100	200	300	500
Phenol	12.2 (8.3)	6.9 (14.9)	2.9 (16.0)	2.0 (16.6)
2-Nitrophenol	41.1 (2.5)	20.2 (6.1)	15.0 (10.5)	8.9 (8.2)
4-Nitrophenol	28.8 (1.4)	16.5 (5.7)	7.9 (7.6)	5.2 (6.1)
2-Chlorophenol	41.6 (3.2)	21.4 (4.6)	15.2 (8.2)	8.9 (6.9)
2,4-Dinitrophenol	2.7 (15.5)	1.9 (8.7)	3.6 (6.5)	0.8 (19.7)
2,4-Dichlorophenol	64.9 (12.9)	59.2 (10.1)	53.4 (6.9)	34.4 (12.6)
2,4-Dimethylphenol	91.6 (0.8)	70.9 (14.4)	33.6 (10.0)	21.6 (18.4)
4-Chloro-3-Methylphenol	89.9 (6.0)	96.5 (9.3)	55.9 (9.3)	35.7 (20.5)
2,4,6-Trichlorophenol	92.4 (4.9)	109.5 (3.1)	79.4 (11.2)	86.7 (9.3)
2-Methyl-4,6-Dinitrophenol	19.8 (18.8)	14.2 (6.6)	9.8 (9.1)	6.3 (11.0)
Pentachlorophenol	99.9 (2.4)	93.5 (2.2)	105.0 (2.0)	98.7 (1.1)

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TABLE IV. Results Using SDVB Disks - % Recovery (RSD, n=3)

	Volume (ml)			
	100	200	300	500
Phenol	50.6 (12.4)	26.8 (10.0)	16.7 (20.9)	9.2 (13.6)
2-Nitrophenol	90.8 (3.6)	101.6 (0.8)	95.9 (2.0)	93.0 (2.7)
4-Nitrophenol	88.2 (10.3)	84.3 (6.1)	53.7 (13.4)	33.1 (12.9)
2-Chlorophenol	89.7 (3.6)	107.7 (0.9)	91.8 (3.4)	71.6 (5.9)
2,4-Dinitrophenol	43.7 (28.2)	54.1 (15.8)	105.1 (12.3)	22.2 (11.6)
2,4-Dichlorophenol	91.3 (6.3)	102.4 (1.2)	94.1 (3.7)	91.8 (0.6)
2,4-Dimethylphenol	98.5 (4.7)	108.6 (3.1)	93.6 (8.4)	95.9 (1.3)
4-Chloro-3-Methylphenol	91.3 (12.3)	111.4 (3.3)	97.3 (14.0)	100.3 (2.9)
2,4,6-Trichlorophenol	90.9 (5.5)	115.7 (3.0)	100.5 (16.3)	97.8 (1.6)
2-Methyl-4,6-Dinitrophenol	64.0 (7.6)	96.9 (4.9)	100.0 (14.4)	85.1 (1.5)
Pentachlorophenol	95.3 (4.6)	100.2 (3.2)	105.0 (0.9)	98.2 (0.1)

48 Comparison of Alternative Methods for Analysis of Volatile Organic Contaminants

by

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The U.S. Environmental Protection Agency (EPA) has published methods for the quantitative analysis of volatile organic contaminants (VOCs) in a variety of environmental sample matrices such as ground water, industrial effluents, drinking water, sludge, soil, and so forth. These methods are largely based upon a "purge-and-trap" methodology in which the volatile constituents are purged from the sample, collected on an adsorbent trap directly connected to a gas chromatograph, and then thermally desorbed onto the GC column for separation and quantitative analysis. These methods vary somewhat in the type of GC column and detectors specified, but the purge-and-trap technique for collecting the organic constituents and introducing them to the GC is essentially the same in all methods. While the purge-and-trap technique offers the advantage of sub parts-per-million sensitivities for many compounds with specific GC detectors, it suffers from several significant disadvantages, including lack of a universally applicable trap adsorbent material, high sample-to-sample carryover, introduction of large quantities of water to the GC and detectors, poor compatibility with capillary columns, and limitations to automating the overall technique.

This study describes an investigation of two alternatives to the common implementation of the EPA purge-and-trap procedures: (1) automated static headspace analysis and (2) what might be termed "off-line" purge-and-trap. Static headspace analysis involves equilibrating a sample with a fixed gas volume in a closed vessel and subsequently introducing an aliquot of this gas directly into the GC. The entire process can be automated using equipment available from a variety of manufacturers. Off-line purge-and-trap involves purging samples using separate adsorbent traps for each sample independent of the GC system. The traps are then thermally desorbed into the GC using automated equipment. Analyses of a series of VOCs have been performed using these two alternative techniques, along with the traditional purge-and-trap approach. Samples analyzed include both water and soil matrices.

In the figures presented below, we show that off-line purge-and-trap methodology compares very favorably with the chromatographic and reproducibility data generated by an on-line methods. However, the carryover is reduced by a factor of 10 with the off-line method because of the use of multiple traps.

On-line purge and trap   Off-line purge and trap
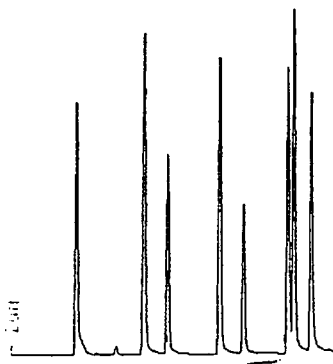
5 ml of sample containing 10 ug/L of benzene, trichloroethane, toluene, tetrachloroethylene, ethylenebenzene, p-xylene, and o-xylene
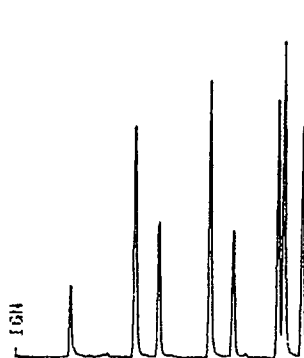
0.53 mm x 50 m DB-624 column, PID detector
4 min @ 50°C, 8°/min to 190 °, 4 min hold
250 mg Tenax trap
4 min desorb @ 180°

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Comparison of Sample Reproducibility and Sample Carryover.

Compound	%RSD Reproducibility		% Carryover	
	On-line	Off-Line	On-Line	Off-line
benzene	2.42	2.24	0.10	0.01
trichloroethylene	5.29	1.41	0.16	0.01
toluene	1.10	2.61	0.22	0.04
tetrachloroethylene	4.59	1.37	0.28	0.02
ethylenebenzene	2.49	0.94	0.34	0.03
p-xylene	3.39	1.72	0.36	0.03
o-xylene	1,80	3.40	0.43	0.04

Data has also been gathered on automated headspace analysis of these compounds in water and in soil.

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49   EVALUATION OF SAMPLE PREPARATION METHODS FOR SOLID MATRICES

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ABSTRACT

Four sample preparation methods: Soxhlet extraction (Method 3540), Soxtec extraction (Method 3541), sonication extraction (Method 3550), and supercritical fluid extraction (SFE) with carbon dioxide (Method 3560) have been evaluated. Thirty target compounds representing organochlorine pesticides, nitroaromatic compounds, haloethers, and chlorinated hydrocarbons were spiked on wet and dry clay, topsoil, sand, and sand mixed with organic compost and were extracted by Soxhlet, Soxtec, and sonication techniques using hexane-acetone (1:1) and methylene chloride-acetone (1:1) and by SFE with carbon dioxide. Data are also presented for 43 base/neutral/acidic compounds spiked on sand or clay and extracted by SFE with carbon dioxide and by Soxtec extraction with hexane-acetone (1:1), and for three standard reference materials extracted by Soxtec and SFE with carbon dioxide.

INTRODUCTION

There are currently two extraction methods listed in SW-846 (1) for the extraction of solid matrices: Method 3540 (Soxhlet extraction) and Method 3550 (sonication extraction). Method 3540 is generally applicable, and a large number of samples can be extracted side by side with limited manpower requirements. However, Soxhlet extractions usually take between 8 and 26 hours, require relatively large amounts of solvents, and involve extract cleanup and concentration. Sonication extractions require much shorter extraction times, but they are labor-intensive, use large amounts of solvent, and require extract cleanup and concentration.

Two new techniques that have become available recently are Soxtec extraction (Method 3541) and supercritical fluid extraction (SFE) (Method 3560). Soxtec extraction is a modified Soxhlet extraction: the thimble with the sample is first immersed in hot solvent, then, after a boiling period of usually up to 1 hour, is raised physically and extracted a la Soxhlet for another hour. The very limited results reported so far by others indicate that Soxtec extraction is at least as exhaustive as Soxhlet extraction (2), but the extraction time is reduced to about 2 hours, less solvent is needed, and the solvent is evaporated and

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condensed without requiring extract transfer. SFE uses a supercritical fluid as extraction solvent in a special extraction system that is operated at pressures and temperatures higher than the critical pressure and critical temperature of the particular fluid. The most commonly used fluid is carbon dioxide; others that are being used, or have been investigated, include nitrous oxide, sulfur hexafluoride, Freon-13, ammonia, xenon, and several hydrocarbons. Carbon dioxide is so popular because of its low critical temperature (31.3°C) and pressure (72.9 atm) and because it is non-toxic, non-flammable, relatively non-reactive and inexpensive, and its use does not result in a waste disposal problem. It is a rather non-polar solvent, similar to hexane or benzene, but both solvent strength and selectivity can be improved by the addition of small amounts of modifiers such as acetone, methanol, or toluene.

The objective of this study was to evaluate the applicability of Soxtec extraction to samples of interest to the EPA and to generate performance data for these four extraction methods for solids. We focused on 30 analytes covering the following groups of compounds environmentally significant to EPA: organochlorine pesticides, chlorinated hydrocarbons, nitroaromatics, and haloethers. To a limited extent, we also generated data for 43 base/neutral/acidic compounds currently on the Hazardous Substances List. The matrices evaluated included sand, clay, topsoil, sand mixed with organic compost, and standard reference materials certified for a limited number of organic compounds (mostly polynuclear aromatic hydrocarbons).

EXPERIMENTAL

Apparatus

- Soxhlet extractor -- 40 mm ID with 500-mL round bottom flask, condenser and heating mantle

- Sonication system -- Horn-type sonicator equipped with titanium tip (Heat Systems Ultrasonics Inc., Farmingdale, New York, Model W-375)

- Soxtec HT-6 extraction system with controlled heated oil bath (Tecator, Inc., Herndon, Virginia)

- Kuderna-Danish apparatus with 10-mL concentrator tube, 500-mL evaporation flask, three-ball macro Snyder column

- Supercritical fluid extractor -- Suprex Model SE-50 including a 4-port and a 12-port valve configured with electronic actuators for automated operation. The system was set up either with two or four extraction vessels for parallel extractions. The 3-mL extraction vessels (1 cm ID x 4 cm length) were obtained from Suprex Corporation (Pittsburgh, Pennsylvania), the 2-mL extraction vessels (0.9 cm ID x 3 cm length) from Alltech Associates (Deerfield, Illinois). Supercritical pressures were maintained inside the extraction vessels by using 60 cm of uncoated fused-silica tubing (50 µm ID x 375 µm OD) from J&W Scientific (Folsom, California) as restrictor. Collection of the extracted material was performed by inserting the

outlet restrictor into a 15-mm x 60-mm glass vial (Supelco Inc., Bellefonte, Pennsylvania) containing 5 mL hexane.

- Gas chromatograph -- A Varian 6000 equipped with two constant-current/pulsed-frequency electron capture detectors and two megabore fused-silica open-tubular columns (30-m x 0.53-mm ID x 0.83-μm film thickness DB-5 column and 30-m x 0.53-mm ID x 1.0-μm film thickness DB-1701 column), connected to a press-fit Y-shaped glass splitter (J&W Scientific Inc., Folsom, California) was used to analyze for the 30 target analytes. The columns were temperature-programmed from 100°C (2-min hold) to 275°C (6-min hold) at 5°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

- Gas chromatograph/mass spectrometer -- A Finnigan 4510B (Finnigan MAT, San Jose, California) interfaced with a data system for data acquisition and processing and equipped with a 30-m x 0.32-mm ID DB-5 fused-silica open-tubular column (1-μm film thickness) was used for all PAH and base/neutral/acidic compound analyses. The column was temperature-programmed from 40°C (4-min hold) to 300°C (6-min hold) at 8°C/min; injector temperature 270°C; interface temperature 270°C.

Materials

- Standards -- Analytical reference standards of the organochlorine pesticides, chlorinated hydrocarbons, nitroaromatics, haloethers, PAHs and base/neutral/acidic compounds were obtained from the U. S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository (Research Triangle Park, North Carolina), Aldrich Chemical (Milwaukee, Wisconsin), Ultrascientific Inc. (Hope, Rhode Island), and Chem Service (West Chester, Pennsylvania). All compounds, except the PAHs and the base/neutral/acidic compounds, were obtained as neat materials. Their purities were stated to be greater than 98 percent. Stock solutions of each test compound were prepared in pesticide-grade hexane at 1 mg/L. Working calibration standards were prepared by serial dilution of a composite stock solution prepared from the individual stock solutions. The PAHs and the base/neutral/acidic compounds were obtained as composite mixtures in methylene chloride or methylene chloride/toluene.

- SFC-grade carbon dioxide (Scott Specialty Gases, Plumsteadville, Pennsylvania)

- Hexane, acetone, methylene chloride -- nanograde or pesticide-grade

- Sample matrices: sand, clay, topsoil, sand mixed with 10 percent organic compost, marine sediments HS-3 and HS-4 (National Research Council of Canada, Halifax, Nova Scotia, Canada), PAH-contaminated soil SRS 103-100 (Fisher Scientific, Pittsburgh, Pennsylvania). The sand and the standard reference materials were dry. The clay, topsoil, and the sand/compost matrices contained 10.6, 2.6, and 4.2 percent moisture.

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Procedures

Spiked samples (10 g each) of sand, sand with 10 percent organic compost, clay, and topsoil were extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) following the procedures given in Methods 3540 and 3550. Spiking of the samples (that were extracted by SFE, Soxhlet, and Soxtec) with the 30 target compounds or the base/neutral/acidic compounds was performed as follows: the sample was weighed out in an aluminum cup and a concentrated stock solution (100 to 1000 μL) containing the target compounds in hexane or methylene chloride and methylene chloride/toluene was added to the sample with a syringe while making sure that the solution did not contact the aluminum cup. Mixing was performed with the tip of a disposable pipette. After the solvent had evaporated completely (approximately 15 min), the spiked sample was transferred to the extraction vessel. Spiking of samples that were extracted by sonication was performed directly into the amber bottle used for extraction.

Soxtec extractions were performed with 10-g samples and 50 mL solvent using an immersion time of 45 or 60 min and an extraction time of 45 or 60 min as indicated in the tables.

SFEs were performed as specified in the Results Section. All SFEs were carried out using the Suprex SE-50 system.

RESULTS AND DISCUSSION

Table 1 presents the average recoveries of the 30 target compounds spiked on sand with 10 percent organic compost and on the clay matrix and extracted by sonication and Soxhlet extraction with hexane-acetone (1:1). The results from the Soxtec extraction are presented in Table 2 and the SFE data in Table 3.

The following conclusions can be drawn from these data:

- The repeatability of the sonication extraction with hexane-acetone (1:1) is much better than that of Soxhlet extraction. The percent RSDs for the 30 target compounds for sonication ranged from 2.3 to 3.9 percent (except for one value at 14.7 percent) for the sand/compost matrix and 0.2 to 6.5 percent for the clay matrix. The percent RSDs for the recoveries from the Soxhlet extraction ranged form 3.9 to 86.9 percent for the clay matrix, with most of the values above 20 percent.

- The repeatability of the Soxtec technique is significantly better than that of the Soxhlet technique. Only the more volatile compounds such as nitrobenzene, benzotrichloride, 4-chloro-2-nitrotoluene, and the dichloronitrobenzenes exhibited RSD values above 10 percent when the extraction was performed with either hexane-acetone or methylene chloride-acetone. The percent RSDs for the other compounds were below 10 percent. The average recoveries using the Soxtec technique were significantly higher than those obtained by Soxhlet or sonication, and similar or slightly higher than the SFE recoveries, for both the hexane-acetone and the methylene chloride-acetone solvent combinations.

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- SFE recoveries were comparable to those obtained by sonication (except for the clay matrix where SFE recoveries were significantly higher than the recoveries via sonication) and Soxhlet techniques, but the RSDs for the SFE values were quite high. The data reported in Table 3 were obtained with our four-vessel setup; therefore,the RSD values for the SFE data are actually those from the combined results from four extractions carried out simultaneously. Work is in progress in our laboratory to investigate the vessel-to-vessel variability.

The data for the base/neutral/acidic compounds are presented in Table 4 and 5 for the SFE and Soxtec extraction, respectively. The recoveries by SFE and Soxtec extraction are comparable (except for the very low SFE recoveries for compounds 4, 5, 7, 12, probably because of their volatilities and for benzoic acid and 4-nitrophenol, probably because of their low solubilities in supercritical carbon dioxide) and the percent RSDs follow the same pattern as discussed above for the group of 30 compounds.

In the case of the three standard reference materials, we noticed significant differences in recoveries obtained by Soxtec and by SFE. For the SRS 103-100 standard reference soil (Table 6), the SFE naphthalene and acenaphthylene recoveries were only about 50 to 60 percent of those measured in the Soxtec extracts. This could be explained by the high volatilities of the two compounds. However, the recoveries of the higher-molecular-weight PAHs benzofluoranthenes and benzo(a)pyrene were 53 and 32 percent by SFE versus 118 and 80 percent by Soxtec. Additional extractions were performed with supercritical carbon dioxide modified with 10 percent hexane, 1 percent toluene, or 15 percent propylene carbonate to improve the extractabilities of the higher-molecular-weight PAHs. Only propylene carbonate showed increased extractabilities for the compounds cited above. For the HS-3 and HS-4 (Table 7), SFE recoveries were approximately around 20 percent when the extraction was performed with carbon dioxide. Addition of modifiers increased the recoveries somewhat. Furthermore, presence of elemental sulfur in these marine sediments created restrictor plugging problems on four commercial extractors evaluated by us as part of another study.

In conclusion, sonication and Soxtec extraction of environmental samples with hexane-acetone (1:1) give comparable results in terms of method precision and accuracy and are fast. However, they both require large amounts of solvents, and the extracts need to be subjected to gel permeation chromatography or some type of column chromatography (e.g., alumina, silica) especially if an electron capture detector will be used for analysis. SFE, on the other hand appears to be much faster and more selective. However, the technique is matrix-dependent, and although we have shown that many compounds of interest to EPA can be extracted from spiked sand, more developmental work is required before SFE can be used routinely with environmental matrices.

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TABLE 1. AVERAGE PERCENT RECOVERIES AND PERCENT RSDs FOR 30 TARGET COMPOUNDS EXTRACTED FROM SPIKED SAND/COMPOST AND CLAY SAMPLES BY SONICATION AND SOXHLET EXTRACTION WITH HEXANE-ACETONE (1:1)

Compound no.	Compound name	Sonication[a] Sand/compost with 20 percent moisture Average recovery	Percent RSD	Sonication[a] Clay with 20 percent moisture Average recovery	Percent RSD	Soxhlet[b] Sand/compost with 20 percent moisture Rep. 1	Rep. 2	Soxhlet[b] Clay with 20 percent moisture Average recovery	Percent RSD
1	1,3-Dichlorobenzene	0	—	0	—	0	0	0	—
2	1,2-Dichlorobenzene	0	—	2	—	0	0	0	—
3	Nitrobenzene	0	—	0	—	0	0	0	—
4	Benzal chloride	63.3	14.7	0	—	30.7	30.7	9.8	86.9
5	Benzotrichloride	0	—	0	—	29.6	29.2	34.0	44.4
6	4-Chloro-2-nitrotoluene	93.3	3.5	34.1	6.5	46.0	44.3	0	—
7	Hexachlorocyclopentadiene	0	—	0	—	—	—	0	—
8	2,4-Dichloronitrobenzene	92.3	2.9	37.0	2.0	40.4	43.8	32.2	57.8
9	3,4-Dichloronitrobenzene	0	—	34.0	5.2	34.4	40.2	24.8	44.0
10	Pentachlorobenzene	82.4	2.7	30.1	7.1	55.0	52.5	53.2	16.6
11	2,3,4,5-Tetrachloronitrobenzene	84.8	3.4	35.5	2.5	32.0	42.8	27.1	38.4
12	Benefin	99.6	2.6	35.4	5.8	49.3	60.7	47.8	11.5
13	alpha-BHC	90.0	2.3	45.0	3.4	67.5	78.8	57.4	47.5
14	Hexachlorobenzene	88.3	2.9	34.4	5.5	58.8	69.7	55.4	24.5
15	delta-BHC	88.6	3.1	47.6	0.2	78.1	84.8	65.0	27.1
16	Heptachlor	90.9	2.8	40.7	3.7	65.4	76.7	59.6	34.1
17	Aldrin	84.6	2.6	42.1	4.3	72.1	79.4	69.8	8.8
18	Isopropalin	95.0	3.7	38.0	4.8	61.1	79.4	64.2	20.8
19	Heptachlor epoxide	90.5	3.7	46.1	1.5	77.7	83.1	72.0	20.8
20	trans-Chlordane	89.9	3.0	44.7	1.4	75.4	82.4	75.6	12.5
21	Endosulfan I	91.6	3.4	45.3	1.0	73.6	81.0	76.4	5.5
22	Dieldrin	91.8	3.7	48.9	1.0	79.4	82.0	74.4	20.0
23	2,5-Dichlorophenyl-4'-nitrophenyl ether	86.2	3.0	44.7	3.2	51.8	75.5	65.9	26.9
24	Endrin	95.3	3.6	44.9	1.1	86.0	88.5	81.0	3.9
25	Endosulfan II	86.7	3.7	47.4	0.3	74.6	80.9	78.5	6.7
26	2,4,6-Trichlorophenyl-4'-nitrophenyl ether	47.3	3.1	23.5	3.1	NSc	NS	NS	NS
27	p,p'-DDT	84.2	3.0	44.7	1.8	69.4	82.2	73.6	38.5
28	2,3,6-Trichlorophenyl-4'-nitrophenyl ether	82.7	3.1	47.1	3.1	35.6	71.1	64.4	34.4
29	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	79.5	3.4	44.1	4.6	46.2	67.6	62.5	29.2
30	Mirex	84.2	3.9	51.3	3.0	74.7	79.8	75.5	15.0

[a] Number of determinations was three. Spiking level was 500 ng/g, except compounds 23, 28, and 29 at 1500 ng/g, compound 26 at 3000 ng/g, compound 3 at 2000 ng/g, and compounds 1 and 2 at 5000 ng/g.

[b] Number of determinations was three except for sand/compost matrix where only two determinations were performed. Spiking level was the same as for the sonication experiments. Extraction time was 16 hours.

[c] NS - not spiked.

TABLE 2. AVERAGE PERCENT RECOVERIES AND PERCENT RSDs FOR THE 30 TARGET COMPOUNDS FROM SPIKED CLAY SAMPLES BY SOXTEC EXTRACTION WITH HEXANE-ACETONE (1:1) AND METHYLENE CHLORIDE-ACETONE (1:1)[a]

Compound no.	Compound name	Hexane-acetone		Methylene chloride-acetone	
		Average recovery	Percent RSD	Average recovery	Percent RSD
1	1,3-Dichlorobenzene	0	--	0	--
2	1,2-Dichlorobenzene	0	--	b	--
3	Nitrobenzene	77.1	18	0	--
4	Benzal chloride	38.3	7.8	0	--
5	Benzotrichloride	33.4	17	32.5	41
6	4-Chloro-2-nitrotoluene	92.8	17	41.6	27
7	Hexachlorocyclopentadiene	46.0	21	0	--
8	2,4-Dichloronitrobenzene	115	8.0	39.9	18
9	3,4-Dichloronitrobenzene	78.3	8.3	54.3	16
10	Pentachlorobenzene	48.6	12	58.7	8.9
11	2,3,4,5-Tetrachloronitrobenzene	122	4.6	89.8	2.3
12	Benefin	82.0	3.7	84.8	3.4
13	alpha-BHC	94.9	5.5	91.8	6.3
14	Hexachlorobenzene	81.7	7.1	85.6	1.8
15	delta-BHC	104	9.7	103	5.7
16	Heptachlor	87.1	5.4	89.4	3.0
17	Aldrin	78.2	5.7	70.7	3.3
18	Isopropalin	97.5	6.9	95.2	8.8
19	Heptachlor epoxide	92.4	0.6	91.0	4.2
20	trans-Chlordane	85.8	2.2	95.8	4.2
21	Endosulfan I	90.5	2.0	92.8	4.3
22	Dieldrin	68.8	2.6	73.4	8.1
23	2,5-Dichlorophenyl-4'-nitrophenylether	99.7	2.0	106	5.3
24	Endrin	112	4.4	119	4.6
25	Endosulfan II	90.3	10	89.5	6.1
26	2,4,6-Trichlorophenyl-4'-nitrophenylether	127	5.0	70.7	8.8
27	p,p'-DDT	61.4	6.5	41.1	16
28	2,3,6-Trichlorophenyl-4'-nitrophenylether	97.2	2.0	96.9	5.3
29	2,3,4-Trichlorophenyl-4'-nitrophenylether	91.6	1.3	94.3	5.3
30	Mirex	84.0	5.1	106	7.4

[a] The operating conditions for Soxtec apparatus were as follows: immersion time - 60 min; extraction time - 60 min; the sample size was 10 g clay; the spiking level was 50 ng/g, except compounds 23, 28, and 29 at 150 ng/g, compound 26 at 300 ng/g, compound 3 at 200 ng/g, and compounds 1 and 2 at 500 ng/g. The number of determinations was four. The moisture content of the matrix was not altered.

[b] Not able to determine because of interference.

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TABLE 3. AVERAGE PERCENT RECOVERIES AND PERCENT RSDs FOR 30 TARGET COMPOUNDS EXTRACTED FROM VARIOUS SPIKED MATRICES WITH SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Sand Average recovery	Sand Percent RSD	Clay Average recovery	Clay Percent RSD	Topsoil Average recovery	Topsoil Percent RSD	Sand with 10 percent organic compost Average recovery	Sand with 10 percent organic compost Percent RSD
1	1,3-Dichlorobenzene	0	—	0	—	0	—	93.6	29.2
2	1,2-Dichlorobenzene	0	—	0	—	0	—	79.5	24.3
3	Nitrobenzene	0	—	0	—	53.6	32.9	76.6	22.7
4	Benzal chloride	0	—	0	—	30.1	36.3	81.6	24.6
5	Benzotrichloride	0	—	0	—	0	—	80.3	27.1
6	4-Chloro-2-nitrotoluene	56.9	25.9	57.8	28.9	68.3	24.4	86.4	24.5
7	Hexachlorocyclopentadiene	16.9	11.8	15.1	60.1	47.4	33.1	81.8	23.6
8	2,4-Dichloronitrobenzene	57.8	16.1	62.3	27.9	68.9	24.2	73.4	22.9
9	3,4-Dichloronitrobenzene	68.7	30.1	62.9	25.6	69.9	23.4	76.0	18.9
10	Pentachlorobenzene	60.9	16.8	50.9	21.8	68.3	20.1	84.0	24.0
11	2,3,4,5-Tetrachloronitrobenzene	75.3	15.1	65.8	26.3	74.2	19.1	73.9	20.5
12	Benefin	70.4	9.5	65.9	27.8	76.0	18.7	73.9	21.9
13	alpha-BHC	72.5	13.6	66.1	31.3	75.3	18.7	75.3	22.7
14	Hexachlorobenzene	60.6	10.2	56.7	28.1	73.5	18.2	74.1	21.9
15	delta-BHC	68.7	2.8	73.8	25.8	81.3	14.7	81.7	21.7
16	Heptachlor	82.9	12.5	63.4	28.6	74.9	17.6	87.7	20.9
17	Aldrin	76.9	19.2	62.0	37.8	75.3	19.3	77.5	19.5
18	Isopropalin	112	11.8	70.8	26.0	76.9	16.8	81.1	17.9
19	Heptachlor epoxide	79.6	11.6	70.7	27.1	79.4	18.7	81.9	19.6
20	trans-Chlordane	71.0	4.3	71.1	28.2	80.4	17.3	80.4	21.3
21	Endosulfan I	76.7	32.2	68.9	24.3	79.2	15.7	78.3	16.2
22	Dieldrin	82.9	29.5	114	21.1	84.5	15.8	82.3	19.6
23	2,5-Dichlorophenyl-4'-nitrophenyl ether	66.9	2.5	74.3	25.2	79.3	16.0	80.6	19.7
24	Endrin	68.5	27.8	76.4	24.7	79.7	15.8	83.9	18.8
25	Endosulfan II	62.8	26.2	76.7	26.5	76.9	13.8	82.8	22.8
26	2,4,6-Trichlorophenyl-4'-nitrophenyl ether	81.6	9.9	76.6	23.3	78.9	14.9	88.3	15.4
27	p,p'-DDT	71.1	15.6	86.9	19.7	82.6	15.6	84.7	12.7
28	2,3,6-Trichlorophenyl-4'-nitrophenyl ether	71.3	3.5	72.9	22.5	79.1	18.2	79.1	17.9
29	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	56.7	22.6	68.7	27.3	68.9	18.6	75.7	19.1
30	Mirex	81.1	30.3	67.3	27.6	79.0	16.4	78.2	20.2

[a]The number of samples extracted in parallel for each matrix was four. The experiments were performed with supercritical carbon dioxide at 300 atm/70°C/60 min dynamic. The sample size was 2 g. The spiking level was 25 ng/g, except compounds 23, 28, and 29 at 75 ng/g, compound 26 at 150 ng/g, compound 3 at 100 ng/g, and compounds 1 and 2 at 250 ng/g. The moisture content of the matrix was not altered.

TABLE 4. AVERAGE PERCENT RECOVERIES AND PERCENT RSDs FOR BASE/NEUTRAL/ACIDIC COMPOUNDS EXTRACTED FROM SPIKED SAND WITH SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound name	Spike level (ng/g)	Average recovery	Percent RSD
1	Phenol	300	50.9	26.3
2	Bis(2-chloroethyl)ether	150	23.6	75.0
3	2-Chlorophenol	· 300	25.9	64.6
4	1,3-Dichlorobenzene	150	4.2	160
5	1,4-Dichlorobenzene	150	4.7	156
6	Benzyl alcohol	150	54.4	13.5
7	1,2-Dichlorobenzene	150	8.2	119
8	2-Methylphenol	300	54.4	25.1
9	Bis(2-chloroisopropyl)ether	150	27.1	69.1
10	4-Methylphenol	300	64.5	15.5
11	N-nitroso-di-n-propylamine	150	58.9	17.9
12	Hexachloroethane	150	5.4	151
13	Nitrobenzene	150	41.9	38.7
14	Isophorone	150	60.4	12.1
15	2-Nitrophenol	300	50.2	31.8
16	2,4-Dimethylphenol	300	65.5	16.4
17	Benzoic acid	300	7.3	24.6
18	Bis(2-chloroethoxy)methane	150	61.6	23.1
19	2,4-Dichlorophenol	300	63.6	16.6
20	1,2,4-Trichlorobenzene	150	32.6	51.7
21	Hexachlorobutadiene	150	25.0	66.4
22	4-Chloro-3-methylphenol	300	71.8	10.1
23	2-Methylnaphthalene	150	62.2	19.4
24	Hexachlorocylopentadiene	150	46.6	33.8
25	2,4,6-Trichlorophenol	300	71.5	9.4
26	2,4,5-Trichlorophenol	300	80.2	7.3
27	2-Chloronaphthalene	150	69.5	14.4
28	Dimethylphthalate	150	59.2	15.5
29	2,4-Dinitrophenol	300	37.2	19.7
30	4-Nitrophenol	300	10.0	27.4
31	Dibenzofuran	150	78.0	6.9
32	2,4-Dinitrotoluene	150	71.0	7.3
33	2,6-Dinitrotoluene	150	78.6	7.3
34	Diethyl phthalate	150	66.7	13.5
35	4-Chlorophenyl-phenylether	150	79.9	10.6
36	4,6-Dinitro-2-methylphenol	300	53.9	16.7
37	4-Bromophenyl-phenylether	150	77.5	11.0
38	Hexachlorobenzene	150	78.2	7.7
39	Pentachlorophenol	300	65.2	12.4
40	Di-n-butylphthalate	150	73.0	12.0
41	Butylbenzylphthalate	150	54.5	19.8
42	Bis(2-ethylhexyl)phthalate	150	71.9	14.0
43	Di-n-octylphthalate	150	58.0	16.1
44	Terphenyl-d_{14}	20.0[b]	92.1	2.2

[a] The number of samples extracted in parallel was four. The experiments were performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic. The sample size was 3 g dry sand.
[b] Spiked at 20 ng/μL in the collection vial.

TABLE 5. AVERAGE PERCENT RECOVERIES AND PERCENT RSDs FOR BASE/NEUTRAL/ACIDIC COMPOUNDS EXTRACTED FROM SPIKED CLAY BY SOXTEC EXTRACTION WITH HEXANE-ACETONE (1:1)

Compound no.	Compound name	Concentration (ng/μL)			Average recovery (percent)	Percent RSD
		Clay 1	Clay 2	Clay 3		
1	Phenol	14.4	15.1	13.5	47.8	5.6
2	Bis(2-chloroethyl)ether	6.5	8.2	8.2	25.4	13
3	2-Chlorophenol	12.3	13.4	12.7	42.7	4.3
4	1,3-Dichlorobenzene	ND	ND	ND	0	—
5	1,4-Dichlorobenzene	ND	ND	ND	0	—
6	Benzyl alcohol	16.9	17.9	15.5	55.9	7.2
7	1,2-Dichlorobenzene	ND	ND	ND	0	—
8	2-Methylphenol	5.3	5.6	4.9	17.6	6.6
9	Bis(2-chloroisopropyl)ether	3.8	4.6	5.1	15.0	14.6
10	4-Methylphenol	7.2	7.4	6.5	23.4	6.7
11	N-nitroso-di-n-propylamine	12.6	13.1	11.6	41.4	6.2
12	Hexachloroethane	ND	ND	ND	0	—
13	Nitrobenzene	7.8	8.5	9.1	28.2	7.7
14	Isophorone	16.7	17.6	16.2	56.1	4.2
15	2-Nitrophenol	10.0	11.1	11.3	36.0	6.5
16	2,4-Dimethylphenol	14.7	16.0	14.4	50.1	5.7
17	Benzoic acid	12.5	12.9	11.1	40.6	7.7
18	Bis(2-chloroethoxy)methane	13.0	17.5	13.0	44.1	3.0
19	2,4-Dichlorophenol	16.5	17.5	16.0	55.6	4.6
20	1,2,4-Trichlorobenzene	4.4	5.3	6.6	18.1	31
21	Hexachlorobutadiene	ND	ND	ND	0	—
22	4-Chloro-3-methylphenol	20.0	20.2	18.4	65.1	5.1
23	2-Methylnaphthalene	12.7	14.7	14.9	47.0	8.6
24	Hexachlorocylopentadiene	4.5	6.4	6.5	19.3	19
25	2,4,6-Trichlorophenol	20.8	22.5	19.9	70.2	6.3
26	2,4,5-Trichlorophenol	7.9	8.3	7.9	26.8	2.9
27	2-Chloronaphthalene	17.2	19.4	18.5	61.2	6.0
28	Dimethyl phthalate	22.2	23.6	21.3	74.6	5.2
29	2,4-Dinitrophenol	28.1	29.7	24.9	91.9	8.9
30	4-Nitrophenol	20.8	20.3	24.9	62.9	16
31	Dibenzofuran	23.9	26.3	23.7	82.1	5.9
32	2,4-Dinitrotoluene	25.1	26.7	24.0	84.2	5.4
33	2,6-Dinitrotoluene	20.8	21.5	19.2	68.3	5.8
34	Diethyl phthalate	22.9	23.4	21.1	74.9	5.4
35	4-Chlorophenyl-phenylether	19.7	20.9	19.9	67.2	3.2
36	4,6-Dinitro-2-methylphenol	20.1	19.4	17.6	63.4	6.8
37	4-Bromophenyl-phenylether	18.7	19.3	18.2	62.4	3.0
38	Hexachlorobenzene	21.4	22.7	21.2	72.6	3.7
39	Pentachlorophenol	19.7	19.2	17.5	62.7	6.1
40	Di-n-butyl phthalate	33.2	23.0	14.3	78.3	40
41	Butylbenzyl phthalate	20.4	20.6	18.7	66.3	5.2
42	Bis(2-ethylhexyl)phthalate	23.6	24.0	21.9	77.2	4.8
43	Di-n-octyl phthalate	23.8	26.2	24.8	83.1	4.8

[a]Soxtec samples included additional 21 compounds not listed here. The operating conditions for the Soxtec apparatus were as follows: immersion time - 45 min; extraction time - 45 min; the sample size was 10 g clay; the spiking level was 6 μg/g. The moisture content of the matrix was not altered.

TABLE 6. **PERCENT RECOVERIES OF COMPOUNDS EXTRACTED FROM THE SRS 103-100 STANDARD REFERENCE MATERIAL BY SOXTEC EXTRACTION (HEXANE-ACETONE 1:1) AND BY SFE WITH SUPERCRITICAL CARBON DIOXIDE**

Compound name	Certified value (mg/kg)		Soxtec[a] percent recovery	SFE[b] percent recovery
Naphthalene	32.4	± 8.2	127	63.8
2-Methylnaphthalene	62.1	± 11.5	127	82.6
Acenaphthylene	19.1	± 4.4	110	64.6
Acenaphthene	632	± 105	108	98.2
Dibenzofuran	307	± 49	123	92.9
Fluorene	492	± 78	92.7	80.4
Phenanthrene	1618	± 348	81.3	124
Anthracene	422	± 49	131	78.4
Fluoranthene	1280	± 220	81.3	92.3
Pyrene	1033	± 289	69.1	78.2
Benzo(a)anthracene	252	± 38	95.2	67.6
Chrysene	297	± 26	91.6	68.4
Benzo(k+b)fluoranthene	152	± 22	118	53.3
Benzo(a)pyrene	97.2	± 17.1	80.2	32.2
Pentachlorophenol	965	± 374	111	141

[a] Single determination. The operating conditions for the Soxtec apparatus were as follows: immersion time - 45 min; extraction time - 45 min; the sample size was 10 g.

[b] The values given represent the average recoveries for three replicate samples extracted sequentially. The sample size was 2.5 g. The extraction was performed with carbon dioxide at 300 atm and 70°C for 60 min; 10 percent moisture was added to each sample prior to extraction.

TABLE 7. PERCENT RECOVERIES OF COMPOUNDS EXTRACTED FROM THE HS-3 AND HS-4 MARINE SEDIMENTS BY SOXTEC EXTRACTION (HEXANE-ACETONE 1:1) AND BY SFE WITH SUPERCRITICAL CARBON DIOXIDE

Compound name	Certified value (mg/kg)	HS-3 percent recovery		Certified value (mg/kg)	HS-4 percent recovery	
		Soxtec[a]	SFE[b]		Soxtec[a]	SFE[b]
Naphthalene	9.0 ± 0.7	47.8	11.1	0.15	--	--
Acenaphthylene	0.3 ± 0.1	167	--	0.15	--	--
Acenaphthene	4.5 ± 1.5	129	18.9	0.15	--	--
Fluorene	13.6 ± 3.1	53.7	15.1	0.15	--	--
Phenanthrene	85 ±20	44.9	26.1	0.68	85.3	26.5
Anthracene	13.4 ± 0.5	75.4	12.3	0.14 ±0.07	129	--
Fluoranthene	60 ± 9	51.3	28.7	1.25 ±0.10	88.0	21.6
Pyrene	39 ± 9	43.1	27.7	0.94 ±0.12	95.7	18.1
Benzo(a)anthracene	14.6 ± 2.0	56.2	28.1	0.53 ±0.05	71.7	--
Chrysene	14.1 ± 2.0	57.4	30.5	0.65 ±0.08	76.9	--
Benzo(a)pyrene	7.4 ± 3.6	48.6	9.5	0.65 ±0.08	58.5	--
Benzo(b)fluoranthene	7.7 ± 1.2	71.4	22.1	0.70 ±0.15	71.4	--
Benzo(k)fluroanthene	2.8 ± 2.0	175	85.7	0.36 ±0.05	133	--
Benzo(ghi)perylene	5.0 ± 2.0	56.0	--	0.58 ±0.22	--	--
Dibenzo(ah)anthracene	1.3 ± 0.5	92.3	--	0.12 ±0.05	--	--
Indeno(1,2,3-cd)pyrene	5.4 ± 1.3	51.9	--	0.51 ±0.15	--	--

[a] Single determinations. The operating conditions for the Soxtec apparatus were as follows: immersion time - 45 min; extraction time - 45 min; the sample size was 10 g.

[b] The HS-3 sample (2 g) was extracted at 350 atm and 60°C for 20 min (single determination). The HS-4 sample (four 1.5-g samples extracted in parallel, the extracts were then combined) was extracted at 350 atm and 70°C for 30 min.

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50 ANALYSIS FOR SELECTED APPENDIX IX COMPOUNDS IN ENVIRONMENTAL MATRICES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/PARTICLE BEAM MASS SPECTROMETRY

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ABSTRACT

A method is described for the analysis of selected Appendix IX analytes in environmental matrices, using high performance liquid chromatography-mass spectrometry (LC/MS) employing a particle beam interface. The method is targeted at compounds that are not easily extracted and/or analyzed by the current methodologies. The five selected compounds are chromatographed on an octadecylsilane (C-18) reverse phase column, using methanol and ammonium acetate in water. A commercial particle beam interface is used in conjunction with a quadrupole mass spectrometer for detection and quantitation of the analytes. One internal standard and two surrogate standards have been included. Multipoint calibration curves indicate that concentration versus response data fit a second order polynomial model. This second order equation can then be used for quantitation of subsequent check standards and samples.

Sample preparation methods are described to extract these compounds from water and soil samples. For controlled matrices, the average recovery of the analytes from water samples is 73% and 84% for soils.

INTRODUCTION

In 1987, the Environmental Protection Agency (EPA) promulgated regulations which required owners and operators of hazardous waste treatment, storage and disposal facilities to analyze their ground water for a list of 232 constituents listed in Appendix IX of 40 CFR, Part 264 (52 Federal Register 25942). The Appendix IX list consists of metal, anions, and a wide variety of organic compounds, including nitrosamines, phenols, polynuclear aromatic hydrocarbons, volatile organics, pesticides, herbicides and chlorinated dioxins.

Since promulgation of this regulation, commercial laboratories have struggled to develop analytical protocols to address this extensive list. In particular, a number of polar compounds which are not amenable to conventional methodologies have presented challenges to the laboratory community. A review of the public docket to the Appendix IX rule making, funded research by EPA, presentations at analytical methods caucuses and SW-846, indicate that these exotic compounds still pose a challenge for routine analysis (1). Although several laboratories have evaluated conventional HPLC as an analytical tool, this approach has not been widely accepted, due to detection limit and identification reliability concerns, especially in contaminated matrices (2).

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Enseco's approach for Appendix IX analyses has been described elsewhere (3). The current approach provides reliable data for all Appendix IX compounds except for five polar compounds. These compounds are: p-phenylenediamine, dimethoate, 4-nitroquinoline-n-oxide, famphur and hexachlorophene. Although it is possible to incorporate dimethoate and famphur into method 8140, method 8270 was the recommended method for these compounds. Our recovery studies using method 8270 have consistently indicated that these compounds are not measurable using method 8270 with conventional sample preparation techniques (4). Because of this, we have developed the following LC/MS technique, combined with modified 8270-like sample preparation methods to provide reliable data for these compounds in environmental matrices.

EXPERIMENTAL

Reagents and Chemicals

All analytes were obtained at 98% purity or higher from Aldrich, Cambridge Isotope Laboratories and MSD Isotopes. Standards at working concentrations were verified using USEPA certified check standards, where available. Labeled compounds were verified against their native counterparts. All reagents used were HPLC grade or equivalent. All standards stocks and working concentrations are made in acetonitrile (p-phenylenediamine degrades in methanol). The compounds of interest are listed below and their structures shown in Figure 1.

CAS Number	Target Compound
106-50-3	p-Phenylenediamine
60-51-5	Dimethoate
56-57-5	4-Nitroquinoline-n-oxide
52-85-7	Famphur
70-30-4	Hexachlorophene

Internal Standard: Caffeine-13-C3

Surrogate Standards: p-Phenylenediamine-d4
                      Malathion-d10

The deuterated phenylenediamine (PDA) was chosen as a surrogate as the native PDA has been the most difficult compound to extract, and can be quite reactive. Labeled malathion was included due to its similarity to dimethoate and famphur.

Instrumental Conditions

The HPLC instrumentation consisted of a Hewlett Packard 1090L liquid chromatograph with a ternary pumping system and a filter photometric detector. The UV detector was useful for off-line method development and as a diagnostic tool. The LC was equipped with a variable volume injector (2 uL was the nominal injection volume) and an autosampler. The column used was an Ultracarb ODS(30) 2x250mm manufactured by Phenomenex. The mobile phase consisted of water (modified with 0.01M ammonium acetate) and methanol used in the following gradient at a flow rate of 0.20 mL/min.

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Figure 1

CAS Number = 106503
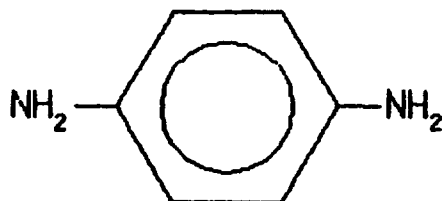
CAS Number = 56575
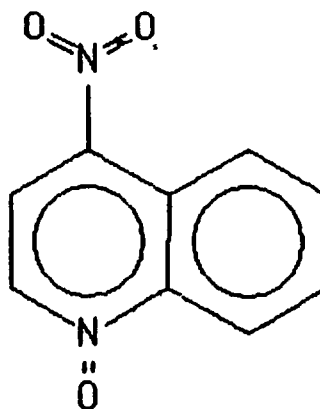
CAS Number = 60515
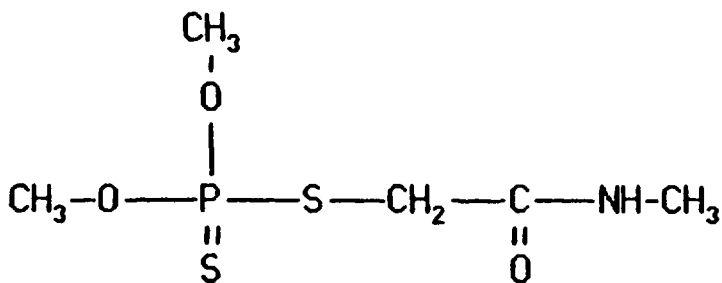
(tautomer)

CAS Number = 52857

CAS Number = 70304

II-55
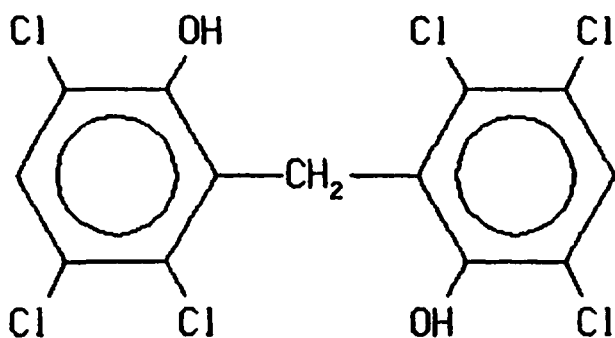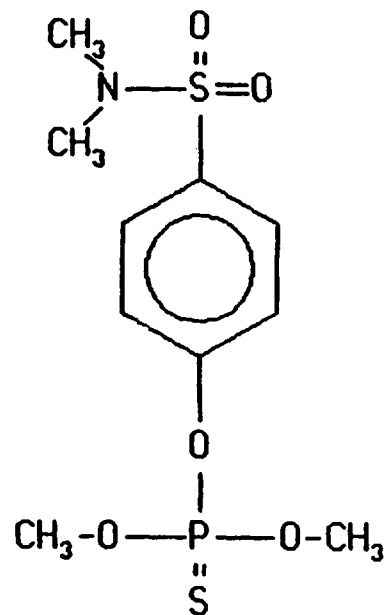
Water*	Methanol	Minutes
50%	50%	0
0%	100%	9

* with 0.01M ammomium acetate

The particle beam interface used was a Hewlett Packard model 59980A. Typical helium pressures were from 35 to 45 psi, desolvation chamber temperatures from 45-55 degrees and nebulizer position was determined experimentally based on flow injections of caffeine. The interface was connected (via the standard transfer line) to a Hewlett Packard model 5988A mass spectrometer operated in the electron impact ionization mode at 70 eV and 300 uA emission current. The ion source was operated at 250 to 300 degrees and the scan range 62 to 450 amu at sufficient speed to allow for at least 10 scans per chromatographic peak. The electron multiplier was operated at between 2100 and 2300 volts.

As a starting point an autotune routine using perfluorotributylamine (PFTBA) can be used for mass spectrometer tuning. It was often useful to then maximize the tune on m/z 219 to provide good mid-mass sensitivity. The instrument was tuned using the following guidelines for PFTBA.

m/z	abundance
69	100%
131	25-75%
219	25-75%
502	>0.5%

These abundances will allow reasonable correlation with NIST or other EI MS libraries. Mass peak width and axis calibrations are performed as needed.

The particle beam interface is optimized using manufacturer guidelines. This performance is verified on a daily basis following tuning but prior to the injection of calibration standard(s). Several flow injections (column bypassed) of 20 ng (2uL injections of a 10 ng/uL solution) of caffeine are performed at 50:50 methanol:water with 0.01M ammonium acetate. Data is acquired in the SIM mode monitoring m/z 194. The peak areas are integrated and evaluated for sensitivity and precision. It was typical to expect approximately 500,000 area counts with a precision of approximately 5%, injection to injection. This step establishes that the system is functioning properly before doing any chromatography.

Calibration and Quantitation

There has been a great deal of discussion regarding quantitation in the area of particle beam LC/MS (5,6,7). We have found that the relationship between concentration and response is not linear in the traditional sense (e.g. GC/MS and the use of average response factors in environmental analyses). Instead, this relationship is best described using a second order polynomial expression. Although this has not historically been the approach for environmental analysis, data has recently been shown that the

accuracy of an existing method (based on linear calibration) can be improved by utilizing a second order calibration (8). Once established, quantitation can be performed using the second order equation, rather than an average response factor.

The initial or multipoint calibration consists of a minimum of five points covering one order of magnitude for each analyte and surrogate. Plots of concentration versus response (using extracted ion areas) are generated following analysis and data processing of the points. Given a reasonable fit (r=0.95 or better), the data system is updated with the second degree equations and the points requantitated against the curve. The percent difference between actual and theoretical concentration is calculated to determine the quality of the calibration curve for each analyte.

The continuing calibrations consist of a midpoint level standard of all analytes and surrogates, to be performed after the nebulizer performance verification, but before sample analysis. Again, concentration values are calculated by the data system using the second order equations determined in the initial calibration. The percent difference between these concentrations and the theoretical values are calculated for each compound to determine if samples can be analyzed. Other continuing calibrations (at differing concentration levels) will be analyzed every five samples and percent differences checked as before.

Background Subtraction

Due to the constant presence of background spectra, characteristic of the interface, a background subtraction procedure was used to make low level spectra identification easier. First, a copy of the original data file is made and archived so that an unaltered version will always be available. Next, spectra for ten scans (+/- 5 scans at 1 minute into the run) is averaged and the resulting spectra is subtracted from each scan in the data file. (This spectra is also archived on the data system). One minute was chosen because this is before the void volume of the column has eluted as was found to be representative of the background ions present. A report is generated showing the total ion chromatogram (TIC) before subtraction, the spectra used for subtraction and the TIC after subtraction.

Sample Preparation

The preparation of water samples consisted of extraction with methylene chloride by continuous liquid-liquid extractor and Kuderna-Danish (K-D) evaporative concentration. For the controlled matrix experiments, 1 liter of de-ionized, carbon filtered water was spiked with the target compounds and surrogates. The pH was measured, and buffered at pH 7 with a potassium dihydrogen phosphate/sodium hydroxide buffer. This is added because pH control is critical to the extraction of phenylenediamine. Additionally, sodium chloride (35 g) is added to the water to facilitate the extraction of dimethoate. Methylene chloride was then added and the extraction run for 18 hours, as in method 3520, SW-846. Following this, the extract was concentrated to approximately 5 mL in a K-D. The concentration was continued to about 1mL under a stream of nitrogen and then exchanged to acetonitrile. The extract was then evaporated to a final volume of 0.5 mL.

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The sample preparation method for soils uses a 30 gram extraction using 1:1 methanol:methylene chloride by sonication (as in method 3550), and concentration by Kuderna-Danish (K-D). For the controlled matrix experiments, ottowa sand was spiked with the target compounds and surrogates. A 100mL aliquot of 1:1 methanol:methylene chloride was added and the samples sonicated for 3 minutes at an output setting of 10 and a duty cycle of 50%. The extract was decanted and two more 100mL sonications were performed. The methanol/methylene chloride extract was then filtered and concentrated to approximately 5 mL in a K-D. The concentration was continued under a stream of nitrogen and simultaneously exchanged to acetonitrile. The extract was then evaporated to a final volume of 0.5mL.

RESULTS AND DISCUSSION

Several authors have discussed that mobile phase modifiers such as ammonium acetate can enhance the MS response of some compounds when using the particle beam interface (9,10). Although we have also confirmed this effect, ammonium acetate was also used for chromatographic reasons. It was found that without this modifier, p-phenylenediamine and hexachlorophene showed very poor peak shape. Two possible explanations are that the ammonium acetate is acting as either an ion pairing agent, or simply deactivating silanol sites on the stationary phase. New columns must be conditioned for several hours with the gradient described before acceptable chromatography can be achieved. Once this is done, however, all compounds show good peak shape and separation, as shown in the total ion chromatogram in Figure 2.

The numbers labeling the peaks in figures 2 and 3, as well as the numbers labeling spectra in figure 4 all correspond to the following definitions:

Compound

1 - p-Phenylenediamine and p-phenylenediamine-d4
2 - Dimethoate
3 - 4-Nitroquinoline-n-oxide
4 - Famphur
5 - Malathion-d10
6 - Hexachlorophene

It is interesting to note that in the MS total ion chromatogram, hexachlorophene exhibits significantly more peak tailing than in the UV chromatogram shown in Figure 3. This is likely due to memory effects in the ion source itself. This effect becomes more pronounced at lower source temperatures (200-250 degrees) and diminishes as source temperature increases (250-300 degrees). Since a 300 degree source temperature had no negative affect on other compounds response, much of the work was done at this temperature.

All of the spectra obtained for these analytes show good correlation with NIST spectra with one exception. 4-Nitroquinoline-n-oxide shows a base m/z of 190 (the molecular ion) in the reference spectra, but this was not obtained experimentally. The base mass we obtained was m/z 144 and a small (10% relative abundance) peak at m/z 190. The difference of 46 is

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Figure 2

File >PB894 62.0-450.0 amu. 2UL-AP9 STD.5/9-100 ;50/50 MeOH/H2O+.01M NH
TIC

File >01179 1.0 amu. TIC

UV = 254 nm
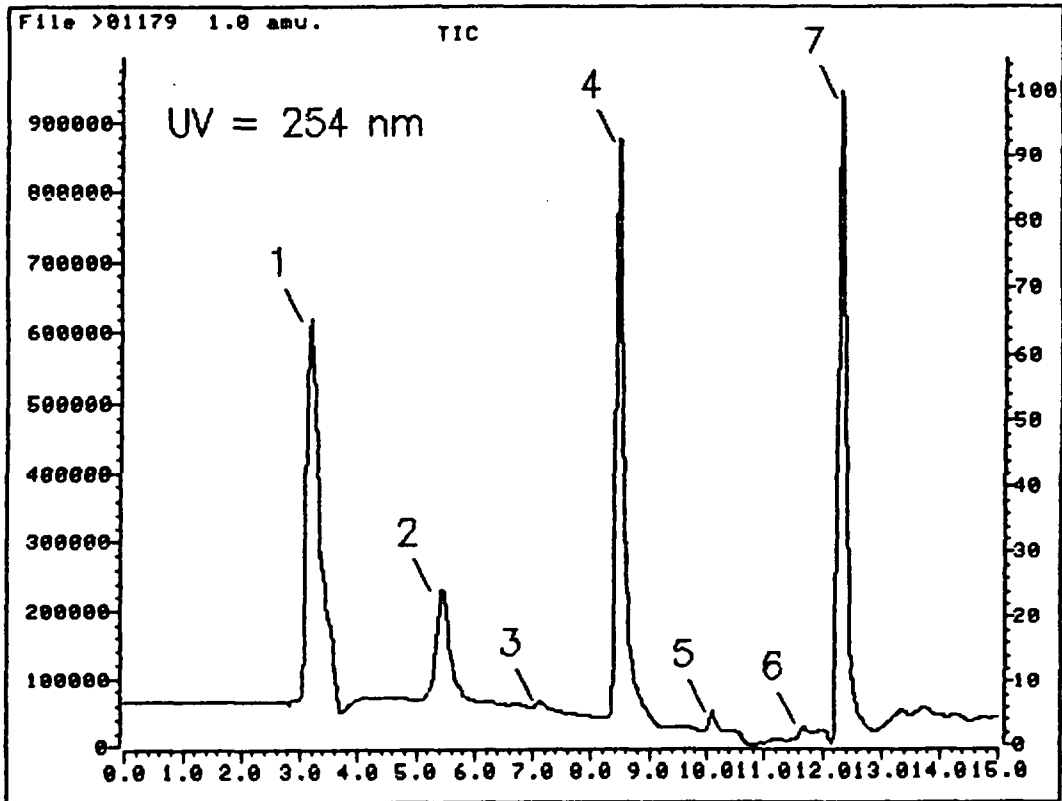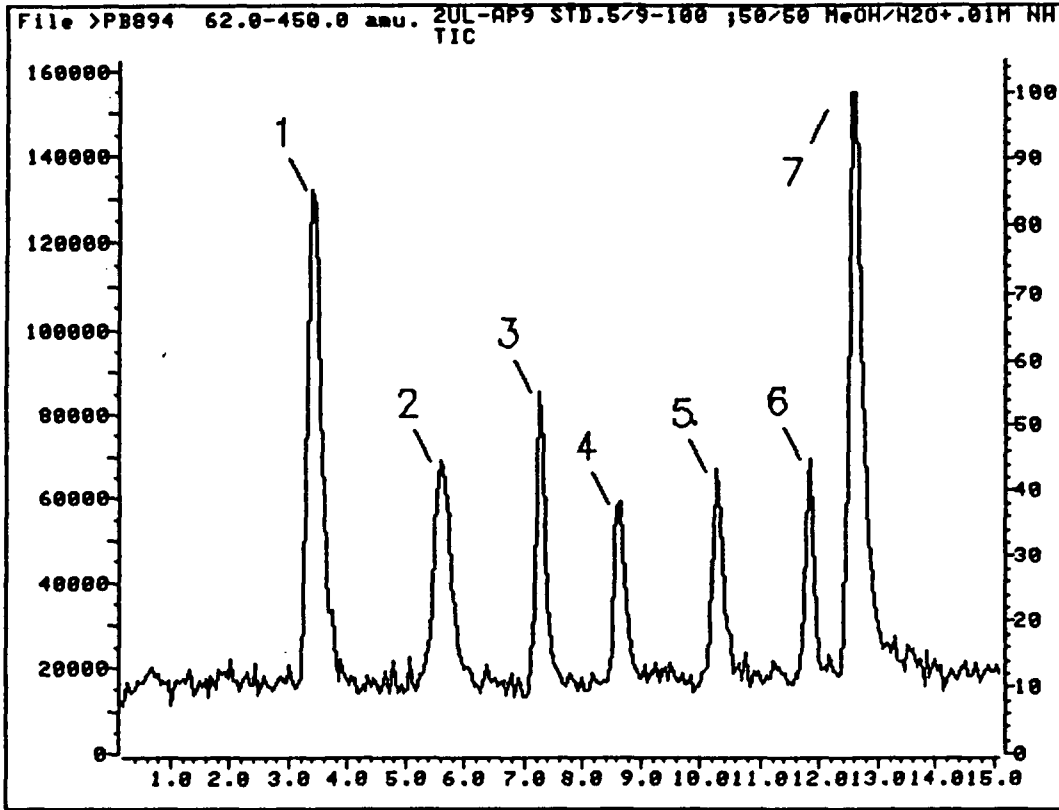
Figure 3

Figure 4
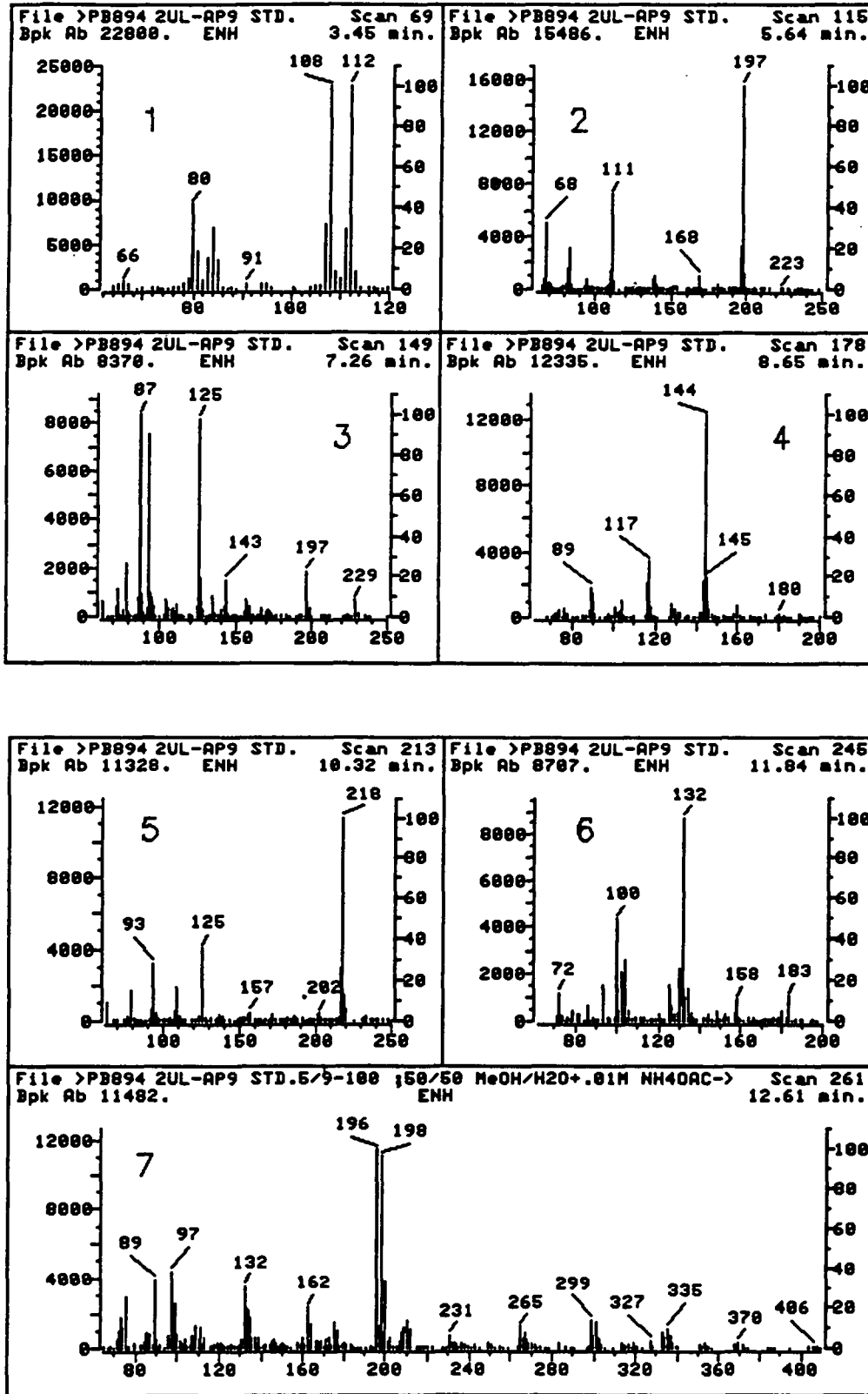
accounted for by the loss of the nitro group, caused by decomposition in the ion source. The relative abundance of m/z 190 increases(with a decrease in m/z 144) at lower source temperatures (225 or less). Given the reduction in overall response of all compounds at lower temperatures (and the increased memory effect), source temperatures of 250 to 300 degrees were best for this analysis. Spectra obtained from a midpoint standard are shown in Figure 4.

Calibration and Quantitation

Several calibration curves have been run for the analytes and surrogates using from five to ten points, covering nearly one order of magnitude. The concentration versus response plots indicate that the relationships are best described by second order polynomial equations. An example of a 5 point calibration for 4-nitroquinoline-n-oxide is shown in Figure 5. The correlation of these curves is usually 0.99 or better. Once the data system is updated with this information, the curve can be requantitated against itself and percent differences calculated. The data for four different calibrations is shown in Table 1.

Figure 5
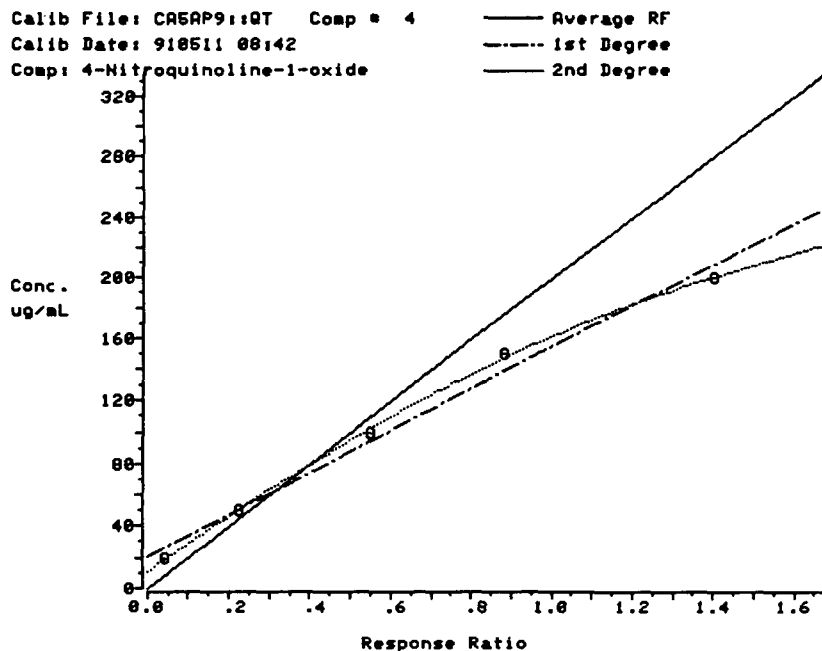
Compound # 4 Calib File: CA5AP9::QT

Compound: 4-Nitroquinoline-1-oxide
    Istd: 13-C3-Caffeine

File: >PB895 >PB896 >PB894 >PB897 >PB898
Conc: 20.00 50.00 100.00 150.00 200.00
  Rf: .22431 .44609 .54931 .58918 .70075

    Average of 5 Rfs: .50193   (35.86 % Rsd)   Rx: .0000000 Ry: .0000000
   1st Degree Equation: y = .2089807 + 1.339279(x)
  1st Degree Corr Coef: .9936900
   2nd Degree Equation: y = .1066935 + 1.872203(x) + -.368519(x^2)
  2nd Degree Corr Coef: .9996580

  In the above equations:

$$y = \frac{Conc\ Std}{Conc\ Istd} \qquad x = \frac{Area\ Std}{Area\ Istd}$$

  Istd Conc for all calibration points is: 100.00

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Table 1

INITIAL CALIBRATION:

Percent Difference Data

	Curve "A" *		Curve "B" *	
Compound	Ave. %Diff.	S.D.	Ave. %Diff	S.D.
p-Phenylenediamine	19	12	11	5.3
Dimethoate	5.9	6.8	5.2	3.4
4-Nitroquinoline-n-oxide	16	4.8	4.1	3.4
Famphur	4.7	4.3	4.1	3.4
Hexachlorophene	22	8.5	3.8	3.2

	Curve "C" #		Curve "D" #	
Compound	Ave. %Diff.	S.D.	Ave. %Diff.	S.D.
p-Phenylenediamine-d4	n/a	n/a	3.1	2.6
p-Phenylenediamine	2.7	2.2	6.1	3.8
Diemthoate	2.7	2.5	8.6	12
4-Nitroquinoline-n-oxide	0.72	0.93	1.3	1.5
Famphur	1.8	1.8	1.9	1.9
Malathion-d10	n/a	n/a	4.8	5.8
Hexachlorophene	1.0	0.89	1.5	1.1

* For curves "A" and "B", the concentration range covered is as follows: p-phenylenediamine; dimethoate and 4-nitroquinoline-n-oxide ranged from 40 to 180 ug/mL in 20 ug/mL increments; famphur covered 20 to 90 ug/mL in 10 ug/mL increments; and hexachlorophene ranged from 200 to 900 ug/mL in 100 ug/mL steps.

For curves "C" and "D", the concentration range covered in five points is as follows; p-phenylenediamine, p-phenylenediamine-d4 ("D" only) and 4-nitroquinoline-n-oxide ranged from 25 to 200 ug/mL; dimethoate and malathion-d10 ("D" only) ranged from 50 to 400 ug/mL; famphur ranged from 12.5 to 100 ug/mL; and hexachlorophene ranged from 125 to 1000 ug/mL.

Based on the data in Table 1, the points fit the second order calibrations very well. However, one has to look at how well the continuing calibrations over time, compare with the curves to know if this response remains predictable. Table 2 summarizes the percent differences obtained for 16 standards run over a two week period after the analysis of curve "A". Concentrations were calculated by the data system using the second degree equations and then percent differences were calculated comparing these concentrations to true values. The data shows that all percent differences were less than 30% until the 13th day after the initial calibration, indicating good stability of the initial calibration. Based on this data, one would have likely decided to establish a new initial calibration on the 13th day.

Table 2

CONTINUING CALIBRATION:

Percent Difference Data

Day and Standard Level

Cmpd.	2-M	2-L	2-H	3-M	3-M	6-M	6-L	6-H	6-M
PDA	0.2	0.6	6.3	5.8	3.6	11	6.4	12	14
DMT	22	1.6	8.6	14	18	12	5.0	4.6	15
NQO	3.6	26	6.4	13	9.5	15	7.1	19	9.9
FMR	12	4.6	0.4	16	20	7.0	3.0	3.8	11
HXN	12	3.2	1.7	8.4	6.5	20	10	1.6	16

Cmpd.	7-M	8-M	9-M	9-M	13-M	13-M	14-M	avg.%diff	S.D.
PDA	13	13	11	23	28	19	0.9	10	8.0
DMT	1.4	4.1	19	4.4	0.8	25	4.4	10	7.9
NQO	5.7	13	23	19	37	39	28	17	11
FMR	2.8	11	11	3.3	9.9	5.7	3.9	7.8	5.4
HXN	3.9	5.2	25	2.3	13	45	9.0	11	11

Notes:

The initial multipoint calibration (curve "A") was run on Day 1.

L = Low standard, usually half the concentration of the midpoint.
M = Midpoint standard, the middle of the calibration range.
H = High standard, usually 1.5-2 time the level of the midpoint.

Sample Extraction Results

Seven 1L replicates of carbon filtered, deionized water were spiked at the levels shown below. The average percent recovery and standard deviation are also shown.

Compound	ug/L Conc.Spiked	Avg.% Rec.	S.D.
p-Phenylenediamine-d4	50	59	16
p-Phenylenediamine	50	59	15
Dimethoate	100	86	5.8
4-Nitroquinoline-n-oxide	50	74	6.2
Famphur	25	81	6.8
Malathion-d10	100	87	9.3
Hexachlorophene	250	63	7.9

Similarly, seven controlled soils (Ottowa Sand) were spiked at the levels shown below and the results expressed as average percent recovery and corresponding standard deviations.

Compound	ug/kg Conc.Spiked	Avg.% Rec.	S.D.
p-Phenylenediamine-d4	1670	64	23
p-Phenylenediamine	1670	65	21
Dimethoate	3330	90	9.0
4-Nitroquinoline-n-oxide	1670	77	12
Famphur	833	97	12
Malathion-d10	3330	97	14
Hexachlorophene	8330	96	10

The levels at which the waters and soils were spiked, falls at the mid point in terms of instrument calibrations and final extract concentration. Because of this, the actual method detection limits will likely be 2 to 4 times lower than the spiking level shown above.

SUMMARY

A method using particle beam LC/MS has been developed for the analysis of some intractable Appendix IX compounds. Together, with previously established methods, it will be possible to measure the entire Appendix IX list. Calibration and subsequent quantitation is performed by taking advantage of the second order behavior that appears to be characteristic of the particle beam interface for these compounds. The data demonstrates that this approach provides a reliable method of initial calibration. Furthermore, the analytical stability of the curves over several days has been demonstrated.

It is noteworthy that quantitation by UV detection was not practical given the poor UV response of two compounds and one surrogate. Additionally, the labeled PDA could not have been used as a recovery surrogate with UV as the quantitation method. Lastly, when "real" environmental samples with various contaminants are analyzed, the interferences associated with UV detection could make quantitation difficult.

ACKNOWLEDGEMENTS

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Additionally, Hewlett Packard is to be acknowledged for their outstanding level of technical assistance and support.

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51 THE IMPLEMENTATION OF HPLC/POST-COLUMN TECHNIQUES FOR RUGGED CARBAMATE AND GLYPHOSATE ANALYSIS

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ABSTRACT

This paper provides an overview of the fundamental concepts of post-column derivatization techniques used in EPA Methods 531.1 (carbamates) and Method 547 (glyphosate). Problem areas for their practical implementation are described. Specific solutions leading to a more reliable analysis are discussed.

INTRODUCTION

Carbamates are broad spectrum pesticides which exhibit strong cholinergic effects on insects. Their low soil persistence and phytotoxicity, make them a favorite for food crop applications. The recent discovery of aldicarb (Temik^{TM}) in the ground waters of agricultural regions has prompted the U.S. Environmental Agency (U. S. EPA) and other agencies to regulate pesticide use and require routine monitoring of drinking water and raw source water. The recommended HPLC analytical method (EPA method 531.1 for drinking water and method 8318 for solid wastes) is based on a 2-stage post-column reaction followed by fluorescence detection. Carbamates are hydrolyzed at elevated temperatures by sodium hydroxide to provide methylamine, which subsequently reacts with o-phthalaldehyde (OPA) and 2-mercaptoethnaol (MCE) at a high pH to produce a highly fluorescent isoindole. This technique has excellent sensitivity and selectivity to allow direct injection of drinking water samples without sample enrichment or cleanup.

Glyphosate (N-(phosphono-methyl)-glycine) or Roundup^{TM}) is a nonselective herbicide commonly used in post-harvest application. Maximum residue tolerance limits for glyphosate and its metabolite aminomethylphosponic acid (AMPA) in various food crops vary widely from 0.1 to 15 mg/kg. Glyphosate is a trivalent negative anion under neutral pHs (pK$_j$ = 2.3) , though it can be analyzed by cation exchange chromatography under acidic pHs. Analysis of glyphosate according to EPA method 547 utilizes the same HPLC post-column equipment used in carbamate analysis.

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Hypochlorite is used as the first post-column reagent to oxidize glyphosate into glycine which is subsequently reacted with OPA to form a fluorophore.

IMPROVED HPLC/POST-COLUMN TECHNIQUE

The practical implementation of several improvements to enhance method performance and ruggedness is discussed. For carbamate analysis, which utilizes a 0.05 N sodium hydroxide hydrolysis reagent, the prevention of backflow of this reagent into the silica-based analytical column is critical (1). For glyphosate analysis, the replacement of the calcium hypochlorite oxidant with sodium hypochlorite eliminates reactor blockage problems (due to the formation of calcium phosphate from the reaction of calcium ions with phosphate ions of the mobile phase). Also, the regeneration of the cation exchange column after each analysis with 5mM potassium hydroxide is necessary to maintain retention time reproducibility.

For both carbamate and glyphosate assays, the incorporation of several post-column pressure monitoring points and pressure relief valves in the system significantly enhances system reliability by aiding problem diagnostics and preventing rupture of the heated fluorocarbon reaction coil. The use of guard columns is mandatory to prolong analytical column lifetime. Additional sample cleanup (i.e., filtration and solid-phase extraction) are required for some water samples and vegetable extracts. The substitution of volatile 2-mercaptoethanol in the ortho-phthalaldehyde (OPA) reagent with the nonvolatile N,N-dimethyl-2-mercaptoethylamine hydrochloride (ThioFluor^{TM}) reduces odor problems in the laboratory. The use of borate salts which contain high levels of insoluble matter, should be avoided in preparing the OPA buffer. Boric acid, available in very pure form, should be used instead and adjusted to pH 10 with sodium hydroxide. The teflon tubing in the OPA reagent line should be replaced by Saran tubing which prevents oxygen permeation (causes OPA degradation). The proper operating sequence for system start-up and shutdown is also important to prevent possible reagent precipitation or system damage (2).

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DETERMINATION OF LOW-LEVEL EXPLOSIVE RESIDUES IN WATER BY HPLC: SOLID-PHASE EXTRACTION VS. SALTING-OUT SOLVENT EXTRACTION

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ABSTRACT

The December 1990 SW846 draft protocol for the determination of low concentrations (1-50 µg/L) of nitroaromatic and nitramine compounds in ground and surface water by high pressure liquid chromatography (HPLC) (Method 8330) proposes the use of a salting-out solvent extraction technique using sodium chloride (NaCl) and acetonitrile (ACN), followed by a Kuderna-Danish extract concentration. This sample preparation procedure was developed and validated by the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) for 8 selected analytes - RDX, 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3-dinitrobenzene (1,3-DNB), 2,4,6-trinitrotoluene (2,4,6-TNT), 4-amino-2,6-dinitrotoluene (4-Am-2,6-DNT), 2-amino-4,6-dinitrotoluene (2-Am4,6-DNT), 2,6-dinitrotoluene (2,6-DNT), and 2,4-dinitrotoluene (2,4-DNT). The adoption of this procedure in Draft Method 8330, which includes six additional analytes - HMX, nitrobenzene (NB), tetryl, and the 2,3,4-isomers of nitrotoluene (2-NT, 3-NT, 4-NT)- should be assumed to be applicable only to the eight analytes validated by CRREL, because its applicability to the six additional analytes is not supported with experimental data. A discussion of this salting-out solvent procedure and the results of laboratory analyses applying it to the determination of all fourteen target analytes are presented.

An alternative sample preparation procedure for the determination in water of low concentrations of all fourteen nitroaromatic and nitramine compounds listed in Draft Method 8330 is proposed. This procedure, which has been routinely used to determine explosive residues in water samples for the Army, uses Porapak R solid sorbent for the extraction of explosive residues from water samples. A discussion of this solid-phase procedure and the results of laboratory analyses are presented.

Broad scope applicabilty, ease of use, and cost effectiveness are three factors which should be considered when adopting an analytical method or procedure for inclusion in SW-846. In proposing the salting-out extraction procedure in Draft Method 8330 for the determination of low concentration explosive residues in water samples, these factors seem to have been neglected. For comparison, the solid-phase extraction procedure, which does successfully test itself against these three factors, is presented.

INTRODUCTION

Nitroaromatic and nitramine compounds are some the most widely used munitions components. They have been and continue to be produced in large quantities and are therefore, along with certain of their degradation products and production impurites, subject to environmental regulation. The primary concern has been the contamination

of ground and surface waters near ballistic test ranges and munitions processing and storage facilities. In recent years, the EPA has issued health advisories on several of these compounds in drinking water (2,6-DNT 2,4-DNT, TNT, RDX). The result has been the need for an analytical method that can routinely acheive detection limits of 1 µg/L and less for the majority of the compounds of interest.

Gas chromatographic (GC) methods have been used effectively to detect nitrated munitions components with excellent sensitivity and selectivity, especially when employing the electon capture detector. However, these methods have been applicable to only a limited number of target analytes, for various reasons: partial or complete degradation of thermally labile species; loss due to volatilization of some species during extract concentration; the difficulty in selecting a single organic extraction solvent.

The use of HPLC with UV detection has become the preferred method for the analysis of wide range of munitions compounds. In order to achieve detection limits less than 1 µg/L in water samples, sample concentration prior to HPLC analysis is required. SW846 Draft Method 8330 has proposed a salting-out solvent extraction procedure using NaCl and ACN. It is the intent of this paper to suggest that a solid sorbent extraction procedure using the hydrophilic resin Porapak R warrants strong consideration as the preferred extraction procedure for incorporation into Method 8330. Tests employing both procedures are described below, and the results are presented for comparison and discussion.

EXPERIMENTAL

Analytical standards were prepared from Standard Analytical Reference Materials (SARMs) obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), except for the three nitrotoluenes and the surrogate 3,4-DNT which were obtained from Aldrich Chemical Co., and the two amino-dinitrotoluenes which were obtained from the Naval Surface Weapons Center (NSWC). For each of the two extraction procedures, ten 500-mL samples were prepared at ten concentration levels on four consecutive days - a total of 40 samples per procedure were analyzed. The laboratory samples were prepared in ASTM Type II/HPLC grade water. Target analytes were spiked at the levels indicated in Table 1. Concentration level x represents the target limit of detection. In addition, each of the laboratory samples was spiked with a surrogate compound, 3,4-dinitrotoluene, at approximately 5 µg/L. Calibration standards were prepared in 30% ACN/70% H_2O so that the UV responses of each of the target analytes would bracket the predicted responses of the target analytes in the final extracts of the spiked laboratory samples.

Salting-Out Solvent Extraction Procedure

A 400-mL aliquot of water sample was placed into a 500-mL separatory funnel and shaken vigorously with 130 g of NaCl until the NaCl was completely dissolved. 100 mL of acetonitrile (ACN) was added to the separatory funnel and the contents were shaken for 5 min. The phases were then allowed to separate for 30 min. The lower water layer was then drained off and discarded. The upper layer (~23 mL) was collected in a 25-mL Kuderna-Danish (K-D) receiver. The separatory funnel was rinsed with 5 mL of ACN and the rinsate was added to the extract in the receiver. (If the ACN extract is turbid, it

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should be transferred to a 40-mL centrifuge tube with teflon-lined screw cap and centrifuged at 4000 rpm for 5 min. The ACN layer is then removed with a pasteur pipette to the 25 mL K-D receiver.) The receiver was then fitted with a a micro (40 mL) K-D flask and modified two-ball micro snyder column. The ACN extract was reduced to less than 1.0 mL and brought to the 1-mL mark with ACN. The extract was then diluted to a final volume of 4 mL with ASTM Type II/HPLC water and filtered through a 0.45 μM Teflon filter. The first 0.5 mL was discarded. The remaining filtrate was then ready for HPLC analysis. The salting-out solvent extracture procedure is summarized in Table 2.

Solid-Phase Extraction Procedure

An empty 6-mL Baker Disposable Extraction Column with a 20-μM frit at the bottom was packed with 0.5 g of cleaned 80-100 mesh Porapak R. Another frit was placed at the top of the sorbent bed to assist packing and help prevent channeling. The column was first conditioned with 15 mL of ACN followed by 30 mL of ASTM Type II/HPLC water. A 500-mL aliquot of water sample was passed through the column at 10 mL/min. utilizing a Visiprep Solid-Phase Extraction Vacuum Manifold (Supelco).

Figure 1 plots the results of an experiment to determine the optimum sample flow rate through the extraction system. Five representative target analytes were spiked at 40-50 ug/L into 500 mL of ASTM Type II/HPLC water. Duplicate samples were extracted at five different flow rates ranging from 2 to 50 mL/min.

This system allows 12 samples to be processed simultaneously in about 50 min. The sorbent column was then eluted with 3 mL of ACN at ≤ 3 mL/min. into a graduated centrifuge tube. The ACN eluent was concentrated to 2 mL under a gentle stream of nitrogen. The eluent was diluted to a final volume of 6 mL with ASTM Type II/HPLC water prior to HPLC analysis. Table 2 summarizes the solid-phase extraction procedure.

HPLC Analysis

A Shimadzu model LC-6A high-pressure liquid chromatograph (HPLC) equipped with a Shimadzu SPD-6A autosampler and a Kratos 757 variable wavelength ultraviolet absorbance (UV) detector set at 250 nanometers was used for analysis of the ACN/H2O extracts. The samples were eluted from a 25 cm x 4.6 mm I.D. Phenomenex ODS (5-μM particle size) reverse-phase column. Analyses were performed isocratically with a 55 % methanol/45 % H2O (V/V) mobile phase at a 0.8 mL/min. flow rate. Analytical runs lasted 30 min., the last target compound eluting at about 25 min. Refer to Figure 3, 4, and 5 for calibration standard and spike sample chromatograms. The injection volume was 500 μL. The instrument operating conditions are summarized in Table 2. Data was collected and quantitated using a Nelson 2700 Turbochrom data system.

Calculations

The percent recovery for each target analyte in the spiked water samples was calculated by comparison of the calculated concentrations to the target concentrations. The calculated concentrations were obtained from the initial calibration quadratic regression

equations. Calibration standards were analyzed at a minimum of five concentration levels with responses that bracketed the responses of the samples. The lower limits of detection for each procedure were determined by the Certified Reporting Limit (CRL) test used by USATHAMA (1990) rather than by the Method Detection Limit (MDL) test outlined by EPA (Federal Register 1984). For an excellent comparison of the two tests, see Reference 2.

RESULTS AND DISCUSSION

The accuracy and precision data for both sample preparation procedures are presented in Table 3. Percent recovery outliers were eliminated from the calculation of the mean percent recovery of each target analyte. Figure 2 graphs a comparison of the mean percent recoveries for each procedure. Table 4 lists the CRLs for each procedure.

For both procedures, the mean percent recoveries exceeded 70% for all analytes. However, the overall accuracy of the solid-phase procedure was significantly greater than that of the salting-out solvent procedure. The average percent recovery of the solid-phase procedure (94.3) exceeded that of the salting-out solvent procedure (84.6) by nearly10%. The overall precision of both procedures were very similar, although the average standard deviation of the solid-phase procedure (10.3) was nearly one percent point lower than that of the salting-out solvent procedure (11.2). As a result of these differences in accuracy and precision, for all analytes except 2,4,6-TNT, the calculated CRLs were significantly lower for the solid-phase procedure.

From a comparison of the test results, it is clear that the solid-phase procedure, when applied to laboratory water samples spiked with the 14 nitroaromatic and nitramine munitions compounds listed in SW846 Draft Method 8330, performs better than the salting-out solvent procedure proposed in the method. But this is not surprising, considering the complexity and labor intensive nature of the salting-out procedure. It required 16 hours using the salting-out procedure to prepare a batch of 20 samples for HPLC analysis. It required only 6 hours using the solid-phase procedure. Further, it was quite surprising that the test results for the salting-out procedure were as good as they were. This would not be predicted for a procedure that applies considerable amounts of heat to a group of target analytes containing species that are either very thermally labile, such as tetryl, or quite volatile, such as the nitrobenzenes.

In light of the above, it is strongly recommended that the solid-phase sample preparation procedure using Porapak R be given consideration for adoption in SW846 Method 8330 as the sample preparation procedure for determination of low concentrations of nitroaromatic and nitramine compounds in water.

SUMMARY

For the determination of low concentrations of fourteen nitroaromatic and nitramine compounds in water, SW846 Draft Method 8330 (Revision 1, December 1990) proposes a salting-out solvent extraction procedure using sodium chloride and acetonitrile. An alternative procedure, which employs the solid sorbent Porapak R for the extraction process, is presented. Both extraction procedures are tested on spiked water samples. The sample extracts are analyzed by HPLC with UV detection. The

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analytical results from both extraction procedures are presented for comparison. The advantages for inclusion of the solid-phase extraction procedure into SW846 Method 8330 are discussed.

ACKNOWLEDGEMENTS

We thank P. Dumas, D. Dabney, and S. McMillen for their laboratory assistance.

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Table 1   TARGET ANALYTE CONCENTRATIONS (μg/L)

	0X	.5X	X	2X	5X	10X	20X	50X	100X	200X
HMX	0	0.302	0.604	1.21	3.02	6.04	12.1	30.2	60.4	121
RDX	0	0.292	0.584	1.17	2.92	5.84	11.7	29.2	58.4	117
1,3,5-TNB	0	0.148	0.296	0.592	1.48	2.96	5.92	14.8	29.6	59.2
1,3-DNB	0	0.138	0.275	0.55	1.38	2.75	5.5	13.8	27.5	55
Tetryl	0	1.08	2.15	4.3	10.8	21.5	43	108	215	430
NB	0	0.645	1.29	2.58	6.45	12.9	25.8	64.5	129	258
2,4,6-TNT	0	0.28	0.56	1.12	2.8	5.6	11.2	28	56	112
4-Am-2,6-DNT	0	0.052	0.104	0.208	0.52	1.04	2.08	5.2	10.4	20.8
2-Am-2,4-DNT	0	0.055	0.11	0.22	0.55	1.1	2.2	5.5	11	22
2,6-DNT	0	0.061	0.122	0.244	0.61	1.22	2.44	6.1	12.2	24.4
2,4-DNT	0	0.053	0.106	0.212	0.53	1.06	2.12	5.3	10.6	21.2
2-NT	0	0.307	0.613	1.23	3.07	6.13	12.3	30.7	61.3	123
4-NT	0	0.301	0.602	1.2	3.01	6.02	12	30.1	60.2	120
3-NT	0	0.292	0.584	1.17	2.92	5.84	11.7	29.2	58.4	117

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Table 2 SUMMARY OF EXTRACTION PROCEDURES AND CHROMATOGRAPHIC CONDITIONS

SALTING-OUT SOLVENT EXTRACTION
• 400 mL water sample in a 500 mL separatory funnel. • Add and dissolve 130 g of NaCl. • Add 100 mL ACN and shake for 5 min. • Let phases separate for 30 min. • Discard lower water layer; recover ACN; (~23 mL) in a 40 mL vial. • Rinse separatory funnel with 5 mL ACN; recover in the 40 mL vial. • If ACN extract is turbid, centrifuge at 4000 rpm for 5 min. • Remove ACN layer with a pasteur pipette to a K-D evaporator. • Reduce to < 1.0 mL and bring to 1.0 mL with ACN. • Dilute with 3.0 mL reagent water to 4.0 mL final volume. • Filter through 0.45 μM Teflon filter; discard first 0.5 mL. • Analyze by RP-HPLC/UV.
SOLID-PHASE EXTRACTION
• 6 mL Disposable Extraction Column packed with 0.5 g of cleaned 80-100mesh Porapak R. • Precondition column first with 15 mL ACN and then with 30 mL ASTM Type II/HPLC water. • Measure 500 mL of water sample and pass through column at 10mL/min. • Elute column with 3 mL ACN at ≤ 3 mL/min. into a graduated centrifuge tube. • Concentrate eluent to 2 mL under a gentle stream of nitrogen. • Dilute to 6 mL final volume with ASTM Type II/HPLC water. • Analyze by RP-HPLC/UV.
CHROMATOGRAPHIC CONDITIONS
• Column: Phenomenex ODS reverse phase HPLC column, 25-cm x 4.6-mm, 5-μM. • Mobile Phase: Isocratic, 55% methanol/45% water (V/V). • Flow Rate: 0.8 mL/min. • Injection Volume: 500 μL. • UV Detector: 250 nm.

Table 3   PRECISION   AND   ACCURACY   DATA

Salting-Out Solvent Extraction	MEAN %REC	STD DEV	RANGE	N
HMX	91.8	5.5	84.2 - 106	36
RDX	86.7	6.2	67.2 - 98.6	36
1,3,5-TNB	70.8	18.6	44.3 - 98.3	36
1,3-DNB	83.9	8.6	64.5 - 103	36
TETRYL	80.1	14.5	46.5 - 103	36
NB	81.5	9.1	67.8 - 109	34
3,4-DNT (SUR)	91.6	12.5	70.0 - 121	21
2,4,6-TNT	89.4	14.1	64.5 - 123	35
4-AM-2,6-DNT	126	19.1	101 - 167	19
2-AM-4,6-DNT	78.4	11.2	54.9 - 102	35
2,6-DNT	83.6	12.8	58.6 - 117	36
2,4-DNT	76.7	9.9	56.4 - 99.2	35
2-NT	76.6	7.3	63.4 - 103	34
4-NT	75.1	7.1	63.2 - 95.7	34
3-NT	77.3	11.1	62.6 - 96.2	35
Solid-Phase Extraction				
HMX	97.8	4.1	87.9 - 106	36
RDX	95.5	6.6	81.3 - 109	36
1,3,5-TNB	84.7	16	54.5 - 105	35
1,3-DNB	97.1	6.5	78.8 - 112	36
TETRYL	91.1	11.6	73.6 - 120	36
NB	92.7	7	77.4 - 108	36
3,4-DNT (SUR)	102	8.3	69.4 - 125	40
2,4,6-TNT	96.8	12.6	75.4 - 123	35
4-AM-2,6-DNT	123	18.3	96.8 - 164	35
2-AM-4,6-DNT	92.2	12.4	68.2 - 117	35
2,6-DNT	90.3	11	64.4 - 108	35
2,4-DNT	85.2	9.1	66.2 - 101	36
2-NT	91.9	8	67.7 - 106	34
4-NT	84.1	10	63.6 - 96.3	36
3-NT	90.8	12.6	69.4 - 129	32

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Table 4   CERTIFIED   REPORTING   LIMITS   (UG/L)

	SOLID-PHASE	SALTING-OUT SOLVENT
HMX	0.3	0.45
RDX	0.29	0.64
1,3,5-TNB	0.45	0.75
1,3-DNB	0.15	0.38
TETRYL	2.49	4.07
NITROBENZENE	0.65	4.4
2,4,6-TNT	0.64	0.57
4-AM-2,6-DNT	1.57	3.98
2-AM-4,6-DNT	0.16	0.86
2,6-DNT	0.074	0.123
2,4-DNT	0.064	0.088
2-NT	0.41	2.11
4-NT	0.62	2.07
3-NT	1.4	2.03

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Figure 1   PERCENT RECOVERY vs FLOW RATE

Figure 2   PERCENT RECOVERY COMPARISON

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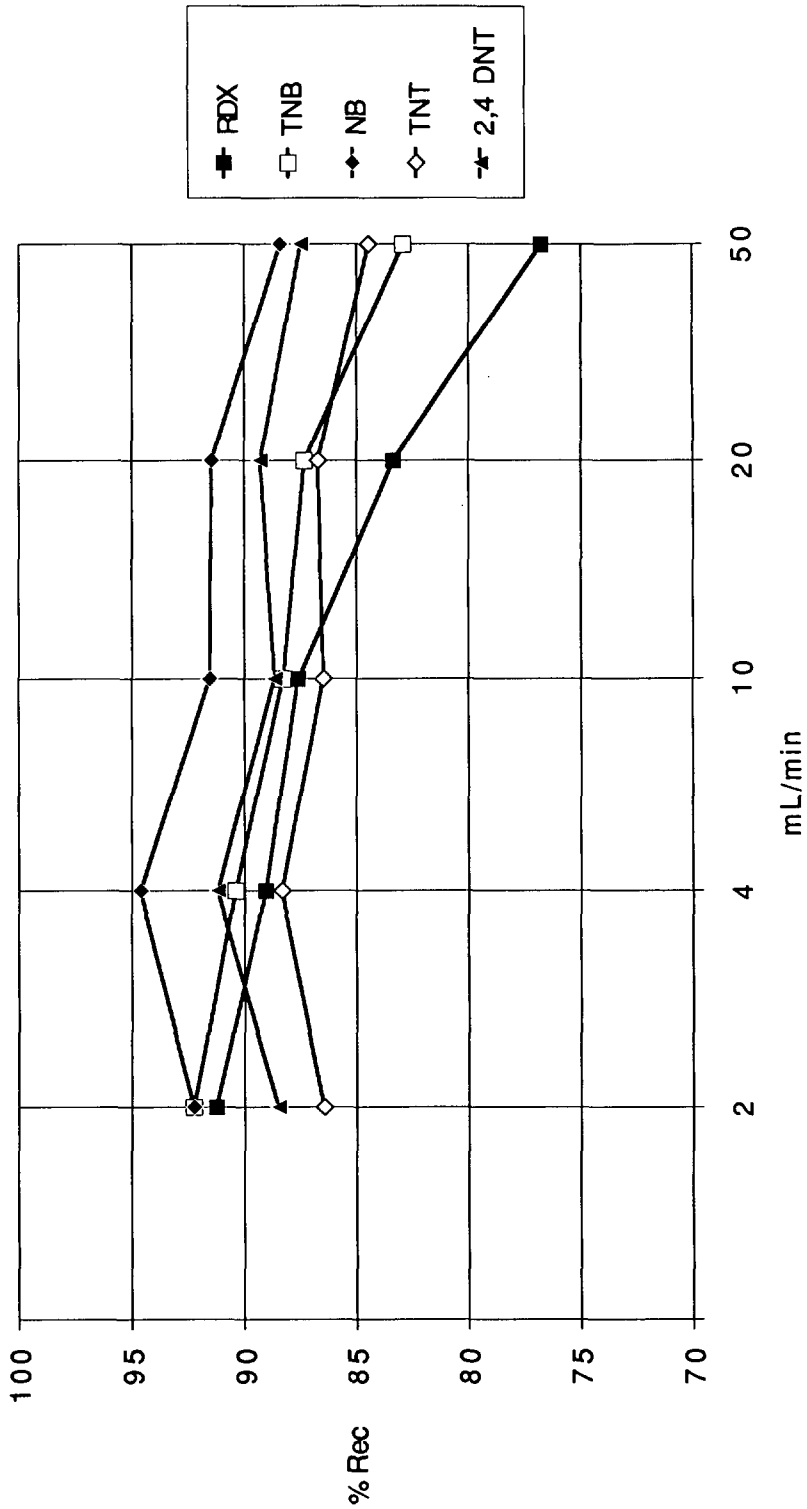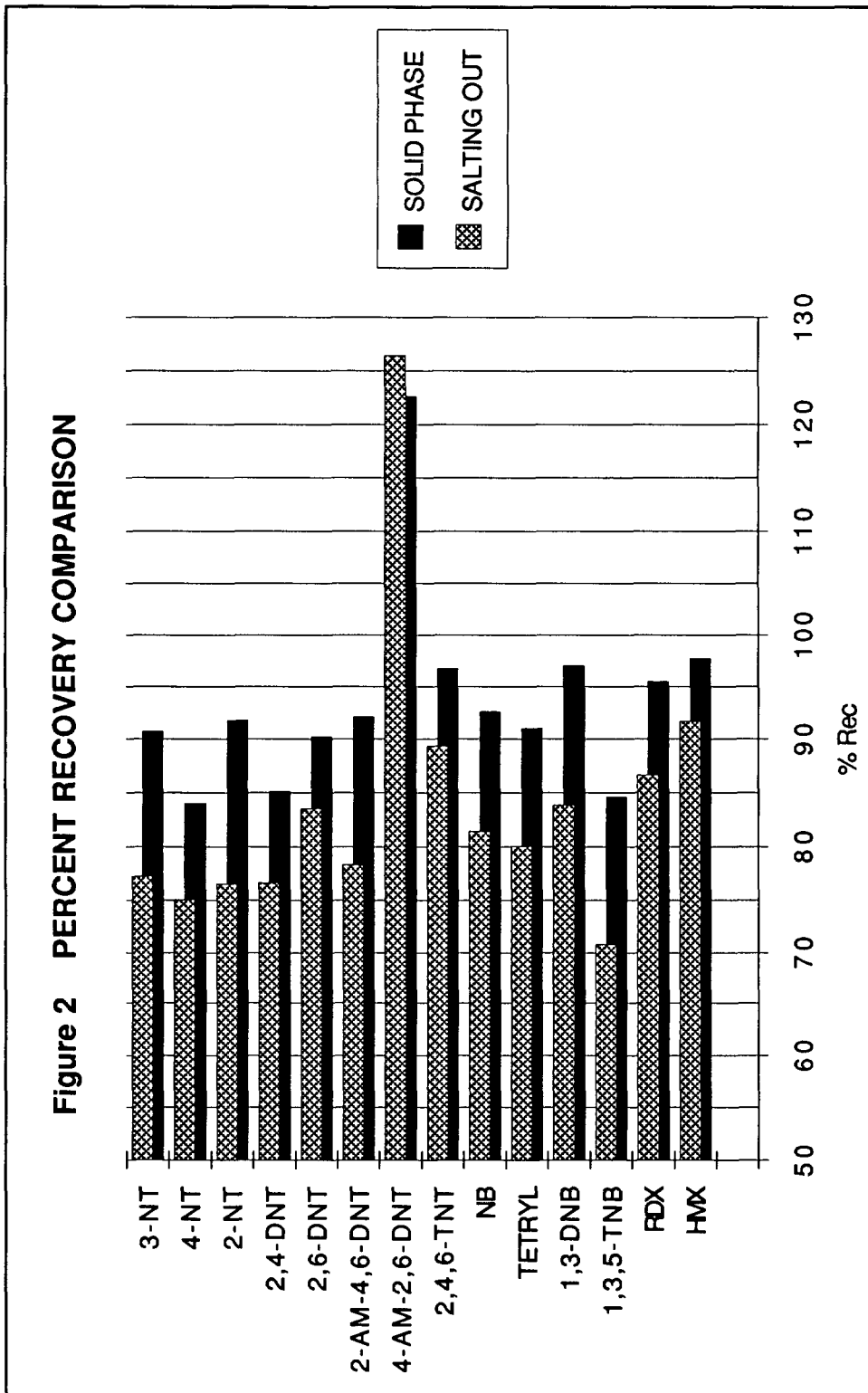
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Scale Factor: 0   Plot Offset: 0 mV   Plot Scale: 100 mV

Compound	ng/mL
HMX	720
RDX	1008
1,3,5-TNB	484
1,3-DNB	648
TETRYL	680
NB	3500
3,4-DNT	1001
2,4,6-TNT	652
4-Am-2,6-DNT	500
2-Am-4,6-DNT	483
2,6-DNT	1675
2,4-DNT	1236
2-NT	2440
4-NT	2372
3-NT	2324
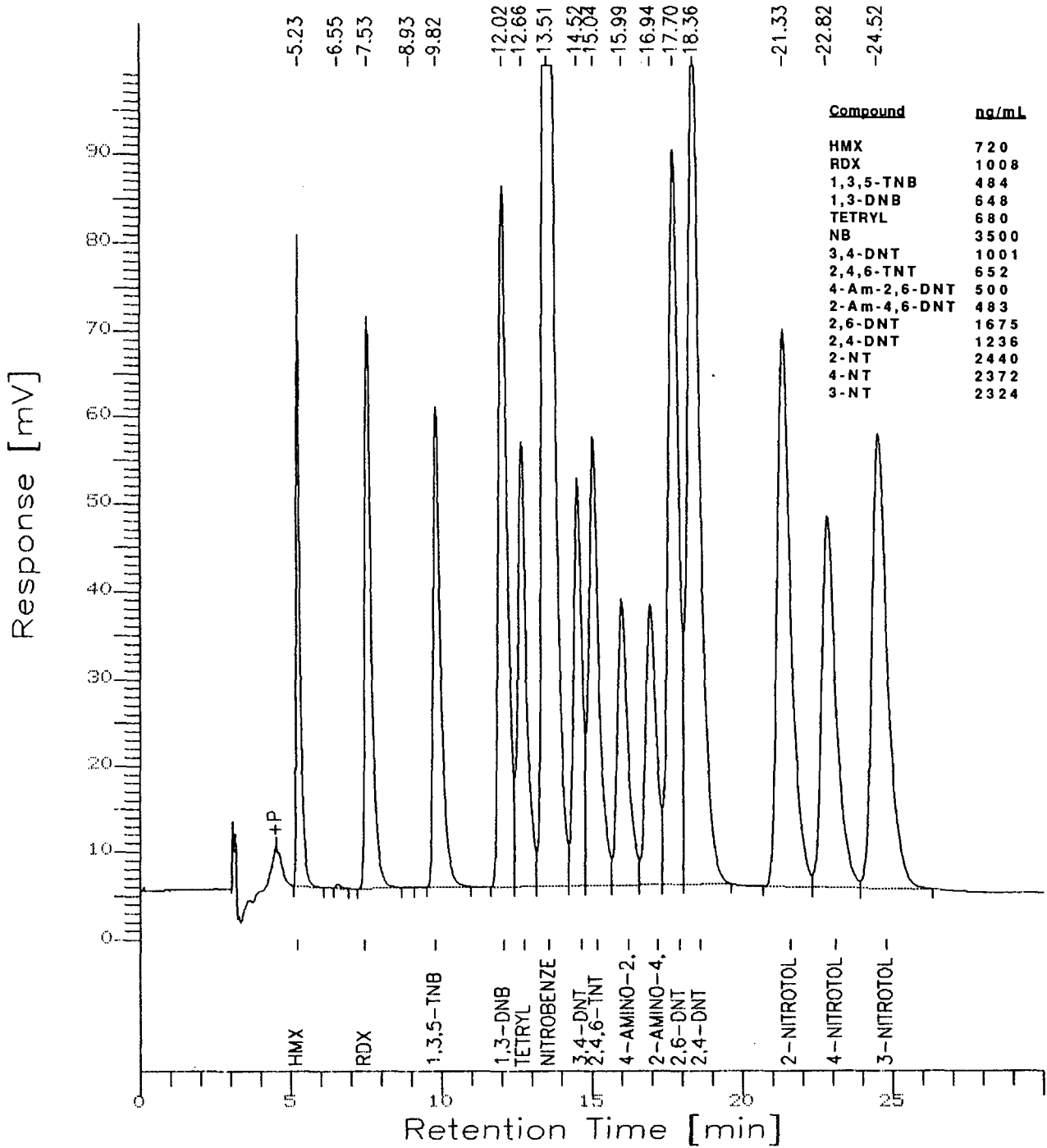
Figure 3   CHROMATOGRAM OF CALIBRATION STANDARD

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Chromatogram

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Scale Factor: 0   Plot Offset: 0 mV   Plot Scale: 50 mV

Compound	µg/L
HMX	3.02
RDX	2.92
1,3,5-TNB	1.48
1,3-DNB	1.38
TETRYL	10.8
NB	6.45
3,4-DNT	4.94
2,4,6-TNT	2.80
4-Am-2,6-DNT	0.52
2-Am-4,6-DNT	0.55
2,6-DNT	0.61
2,4-DNT	0.53
2-NT	3.07
4-NT	3.01
3-NT	2.92
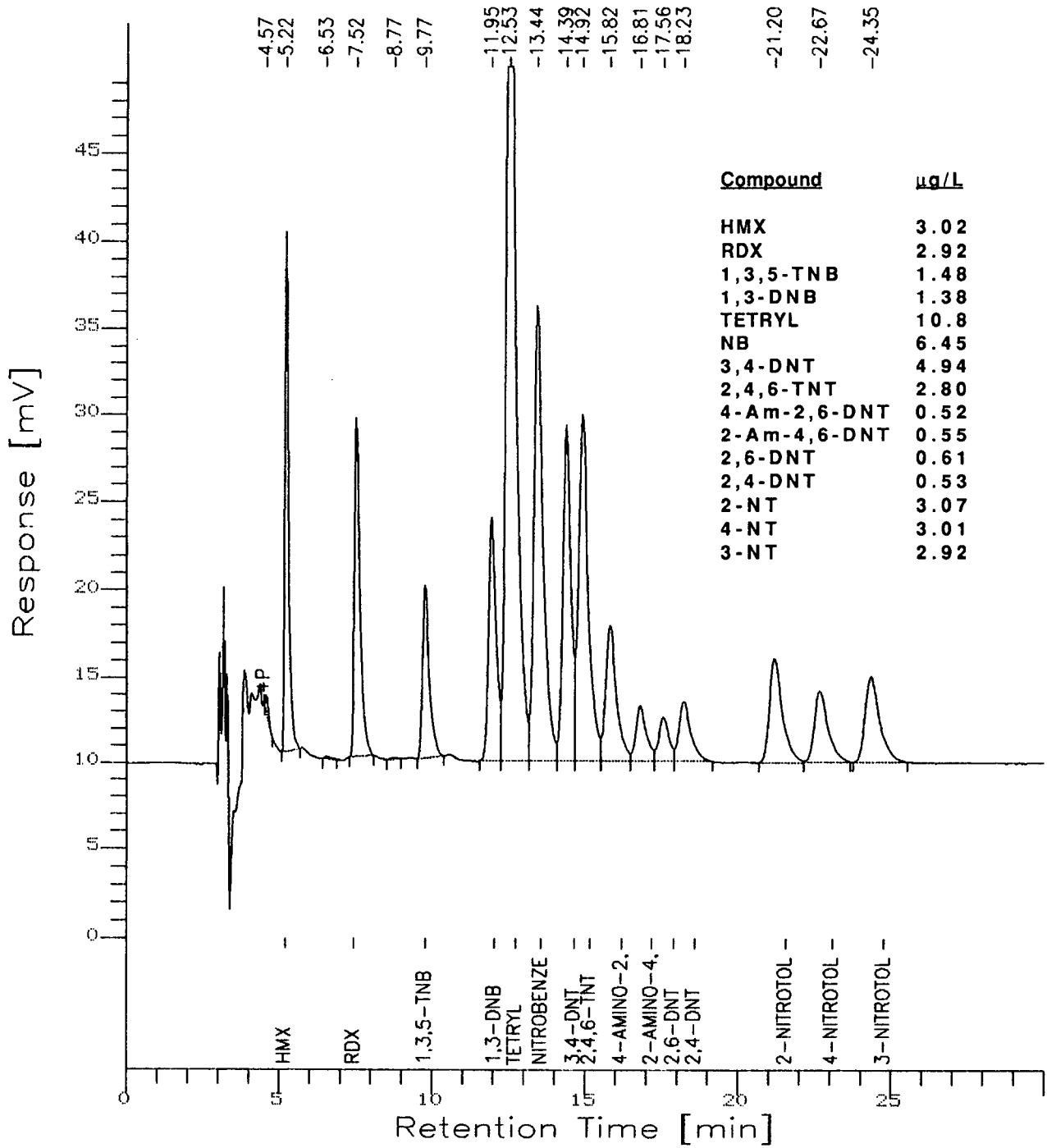
Figure 4   CHROMATOGRAM OF SALTING-OUT EXTRACTION SAMPLE

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Chromatogram

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Start Time : 0.00 min   End Time : 30.00 min   Low Point : -0.00 mV   High Point : 50.00 mV
Scale Factor: 0   Plot Offset: 0 mV   Plot Scale: 50 mV

Compound	µg/L
HMX	3.02
RDX	2.92
1,3,5-TNB	1.48
1,3-DNB	1.38
TETRYL	10.8
NB	6.45
3,4-DNT	4.94
2,4,6-TNT	2.80
4-Am-2,6-DNT	0.52
2-Am-4,6-DNT	0.55
2,6-DNT	0.61
2,4-DNT	0.53
2-NT	3.07
4-NT	3.01
3-NT	2.92
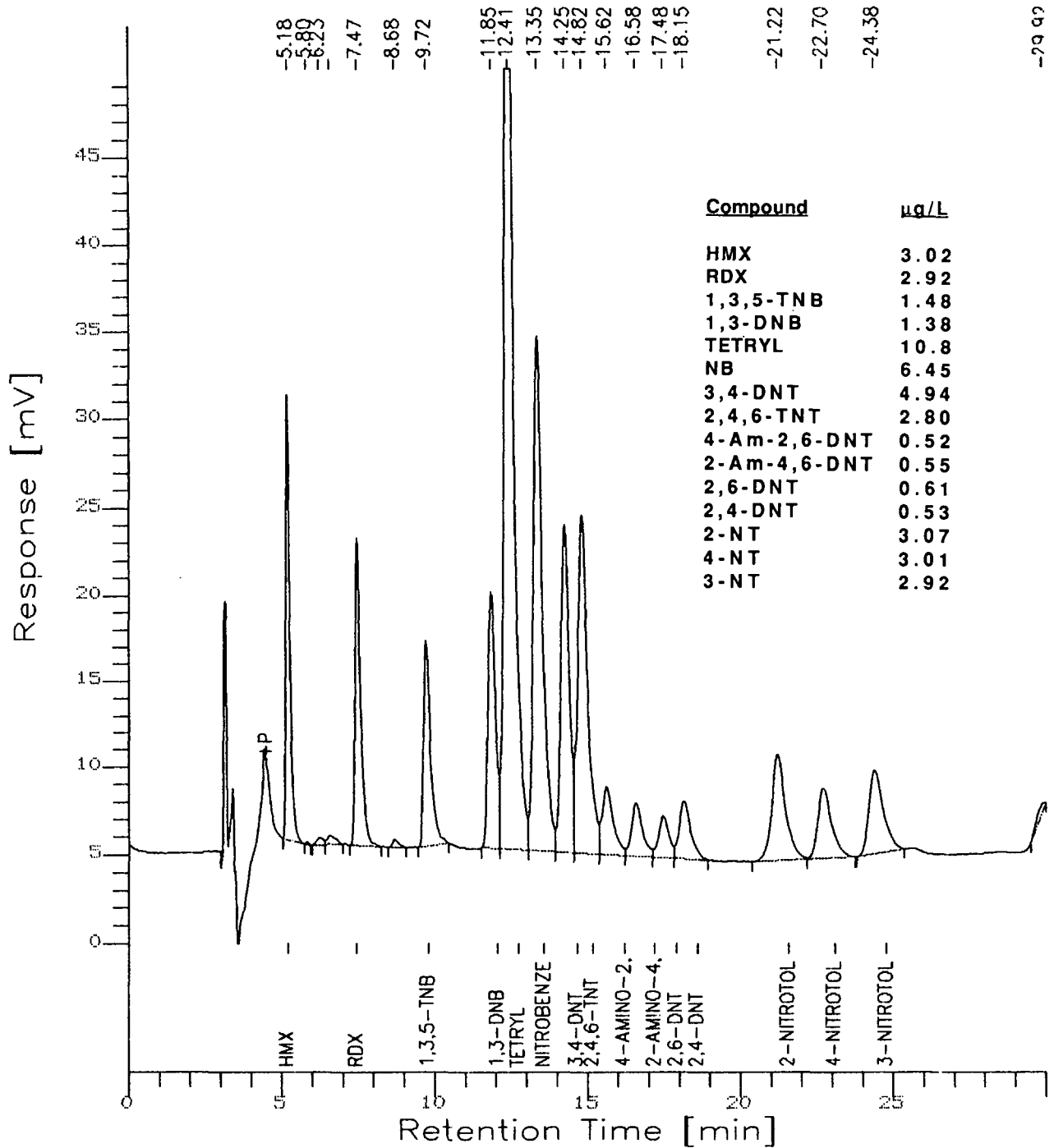
Figure 5   CHROMATOGRAM OF SOLID-PHASE EXTRACTION SAMPLE

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53   REDUCTION OF AZO DYES TO AROMATIC AMINES FOR ENVIRONMENTAL MONITORING

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Azo dyes are of great environmental concern due to their potential to form carcinogenic aromatic amines under reducing conditions. As a result, it is necessary to evaluate both the intact molecule and its potential reductive cleavage products to adequately assess the potential risk of a dye stuff to the health of man and the environment. With over 100 million pounds of azo dyes produced annually, the development of a method that effects the reductive cleavage products _in vitro_ and permits their characterization would aid in determining modern complex and structurally unknown dyes and their genotoxicity.

A logical approach would involve the evaluation of procedures for the reductive cleavage of azo dyes followed by mass spectroscopic (MS) analysis of their products. To best determine the approach in achieving this goal, the reduction of representative samples from several of the major azo dye classes (e.g. disperse and solvent dyes), was accomplished using chemical means. Two chemical procedures were evaluated for the reduction of azo dyes. The first reduction agent, $SnCl_2$, is especially important in the reductive cleavage of azo linkages in the presence of other easily reduced groups such as a nitro group. The second method involved sodium dithionate, $Na_2S_2O_4$, which has been used to effect the reductive cleavage of water soluble azo dyes for decolorizing purposes and for Salmonella bacterial assays for mutagenicity.

Initial screening of the various reduction products from each procedure was accomplished using thin layer chromatography (TLC). Confirmation of the postulated reduction products involved a combination of particle beam and thermospray LC/MS and GC/MS. Standards of the proposed reduction products and

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aromatic amines of the products tentatively identified, when available, were employed to confirm identities. It was observed that the chemical reduction methods resulted in nearly 100% reduction of the azo bond to form the characteristic amines for the 16 dye standards evaluated. Overall the $SnCl_2$ method was a more powerful reducing agent yielding a greater number of products. In addition to the reduction of the azo bond, dyes containing acetate groups exhibited both acid and base catalyzed hydrolysis of the ester groups to form the respective alcohols. The presence of electron withdrawing halogen groups on the aromatic ring appear to make the nitro groups more susceptible to reduction. Also small yields of N-dealkylation products were observed for $SnCl_2$ reduction of some dyes.

Current efforts are evaluating the use of chemical reductions for determining aromatic amine content of wastewater, sludge and sediment contaminated with azo dyes. Reduction conditions using $SnCl_2$ or $Na_2S_2O_4$ needed to be modified to insure complete reduction of azo dyes in wastewater and sludge. Variables, including the presence of sediment in a sample, temperature, reaction time and amount of reductant, influence the yield of the aromatic amines. The analysis of the reduced azo dye samples provided an estimate of total dye (amine) content, but identity of specific azo dye could not be determined. Most mono and diamino reduction products could be analyzed by GC/MS. More polar reduction products containing three amine groups or multiple function groups (e.g. SO_3, OH, NO_2) were best analyzed by LC/MS.

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54   HAZARDOUS WASTE COMPONENT IDENTIFICATION USING AUTOMATED COMBINED GC/FTIR/MS

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INTRODUCTION

Our modern industrial civilization contains many items which have the potential to produce hazardous waste in their production or use. In general, plastics, paints, petroleum, petrochemicals, leather, textiles, pesticides, and medicines can generate volatile solvents, reaction residues, oils, and non-volatile heavy metals, dyes, pigments, salts, acids, and caustics. To properly dispose of these hazardous wastes is a complex problem. The first step in this process is determining what is there, i.e., chemical analysis of the waste sample. The scheme for identification and quantitation of certain specific toxic compounds is quite well delineated in the U.S. Environmental Protection Agency methodology. However, tentatively identified compounds (T.I.C.s) and other hazardous components that are non-target compounds in the E.P.A. methods are not accurately determined by those methods. These contaminants need to be identified before proper disposal of hazardous waste can occur or a waste site can be remediated.

Qualitative analysis of organic pollutants currently relies heavily on the mass spectrometer, both in its GC/MS and LC/MS forms. The mass spectrometer produces powerful structural information based on molecular fragmentation, often including molecular weight data. It is weak in the areas of aromatic substitution, isomer differentiation, ring junctions, alcohol identification, and functional group classification. Fortunately, the infrared spectrometer is strong in these areas. The E.P.A. has recognized this and has developed Method 8410 for the GC/FT-IR analysis of semivolatile organics (1). Combining GC/MS and GC/FT-IR provides a higher confidence result than either one alone (2). Combining the two into one doubly hyphenated system with powerful automated computing capability provides the analyst with an efficient system for analyzing hazardous waste. An example of that is shown in this paper, utilizing a sample from an actual hazardous waste drum.

HARDWARE

The gas chromatograph, an HP 5890A, was set up using the common, most routinely used column for environmental

screening, a 25 meter 5% phenyl methyl silicone (HP-5) under standard analytical operating parameters. The column effluent was split at the end of the column at a 10 to 1 ratio with the bulk of the flow going to the HP 5965B IRD and the lesser amount to the HP 5970B MSD. The details of this parallel flow configuration are described elsewhere (3).

SOFTWARE

One of the characteristics of environmental samples in general and hazardous waste samples in particular is that they contain many components. The sample used in this paper contains many dozens of compounds, the specific number analyzed for is determined only by the instruments' sensitivities and operational parameters. Figure 1 is the Total Ion Chromatogram (TIC) from the MSD and the Total Response Chromatogram (TRC) from the IRD. Easily well over 100 components are detectable in each chromatogram, but for illustration, the integration threshold was set to allow only about 50 to be analyzed. Those peaks are shown in the integrated chromatograms of Figure 2.

In order to aid the chemist in characterizing multicomponent, complex chromatograms, the standard software of the HP 5965B includes the Macro Program 'Qualrpt'. This automated software routine performs a qualitative analysis, i.e., library searchs on previously integrated chromatograms. This Qualrpt macro works on the integrated Total Response Chromatogram (TRC) from the IRD and/or the Total Ion Chromatogram (TIC) from the MSD. The Qualrpt output for individual IRD and MSD data consists of a tabulation of the GC peaks found (times , areas, etc.), a chromatogram, and library search results. When the data from the IRD and MSD are combined in Data Editor, the Qualrpt macro produces a tabulation of the peaks found, a combined chromatogram, and combined list of library search results for each peak. The combined search list is merged by common CAS Registry numbers into three categories. Class 1 contains those entries which are on both lists. When comparing IRD and MSD library searches, these entries, (or more often, this entry) have a high probability of correctly identifying unknowns. Class 2 contains those entries which are only on one hit list because they exist in only one of the two libraries searched. Class 3 consists of those entries which are in both libraries but nonetheless showed up in only one of the two hit lists. Isomers, because of their nearly identical spectra often appear only on the MSD hit list while homologous series because of their spectral similarities only appear on the IRD hit list. If the IR spectrum of a specific unknown compound is not in the library, typically the near misses are of the same chemical

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class. This is a very powerful feature of infrared spectroscopy which is favorably exploited in the IRD Qualrpt software.

Once the appropriate libraries are selected, in this case the 49000 entry NIST/NBS library of mass spectra and the 3000 entry EPA Vapor Phase Infrared library, Qualrpt can be initiated. Several examples have been selected from the Qualrpt combined search results for discussion.

RESULTS

The sample was from a waste drum presumed to contain paint and perhaps other hazardous solvent materials. 50 peaks were integrated in the TRC and the TIC. The chromatograms are not totally identical. There are some differences, air and water peaks in the TRC, and a few more small components in the TIC. There were 41 common peaks found and 23 Class 1 hits. Some peaks were found in the TIC only and some in the TRC only. Differing detector response factors account for this fact. Carbon dioxide (from air), water (from the sample and/or air), and the solvent methylene chloride are early components found by the IRD. In addition, acetone and methanol were found and elute before the solvent methylene chloride.

A typical example of a Class 1 hit is shown in Figure 3. The PBM mass spectrometry search and the IRD search both indicate that the compound is ethyl acetate. Note that the highest quality hits are in Class 1. All of the lesser quality IRD matches are acetates. Infrared spectroscopy is very good at functional group/compound class differentiation. IR and MS confirm each other in this case for a very high confidence result.

Figure 4 shows an example where the top quality PBM hit is not confirmed by the IRD. In this case the top IRD hit is ethyl benzene and the top MSD hit is meta xylene. As can be seen from the Class 3 listing, all three xylenes are in the EPA IR library but their spectra are so different they don't appear on the hit list while the spectrally similar ethyl, propyl, and butyl benzenes do. Clearly the infrared information confirms that ethyl benzene is the correct assignment.

Figure 5 is an example where the top IR hit is not confirmed by PBM. Here the top quality IR hit is butyl benzene and the top MSD hit is propyl benzene. The likely molecular ion at m/z 120 is very important information pointing toward the assignment of propyl benzene. Note that all the listed IR hits are alkyl benzenes.

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Since the NIST/NBS MS library is more than sixteen times larger the than EPA IR library it is obvious many MS hits cannot be confirmed by IR. Most of the time in this case of Class 2 hits, however, the chemical class and isomeric configuration is confirmed. Figure 6 is an example of this situation where the spectra of the ethyl methyl benzenes are not in the EPA Library but the closest IR hits are mostly all 1,4-disubstituted benzenes. This indicates that the best qualitative assignment is 1-ethyl-4-methyl benzene, not the 1,2- or 1,3- isomers.

Table 1 is a condensation of the Qualrpt combined search results. It can be seen there are 56 total peaks reported, 41 common ones, and 23 Class 1 hits. The compound assignments when no Class 1 hit was found is the most likely based on further examination of the spectra. In some cases the molecular ion was of some use. Clearly use of the largest MS and IR libraries available would improve the searching and is the subject of future work.

CONCLUSION

The combined technique of GC/FT-IR/MS using the HP 5890A, HP 5965B, and HP 5970B with the Qualrpt automated spectral output and combined library searching has been shown to be very useful in the rapid high confidence qualitative analysis of hazardous waste components.

REFERENCES

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CONDITIONS

Gas Chromatograph Column: 25 m x 0.32 mm id HP-5 (5% phenylmethyl silicone), 0.52 micrometer film Carrier Gas: Helium at 10 psi, 2.0 mL/min Oven: 40 C (1.0 min) to 240 C at 4 C/min Injection Port: 250 C Sample Injection: 2 microliters split 10:1

IRD Parameters Light Pipe: 250 C Transfer Lines: 260 C Sweep Gas: Nitrogen, 15 psi inlet, 5 psi outlet Scan Parameters: 8 cm-1 resolution, 2 co-adds, 3 scans/second stored Detector: Wide band (550 to 4000 cm-1) MCT

MSD Parameters Mass Range: 10 to 310 daltons Scan Parameters: 2 A/D samples, 1.4 scans/second stored Transfer Line: 280 C
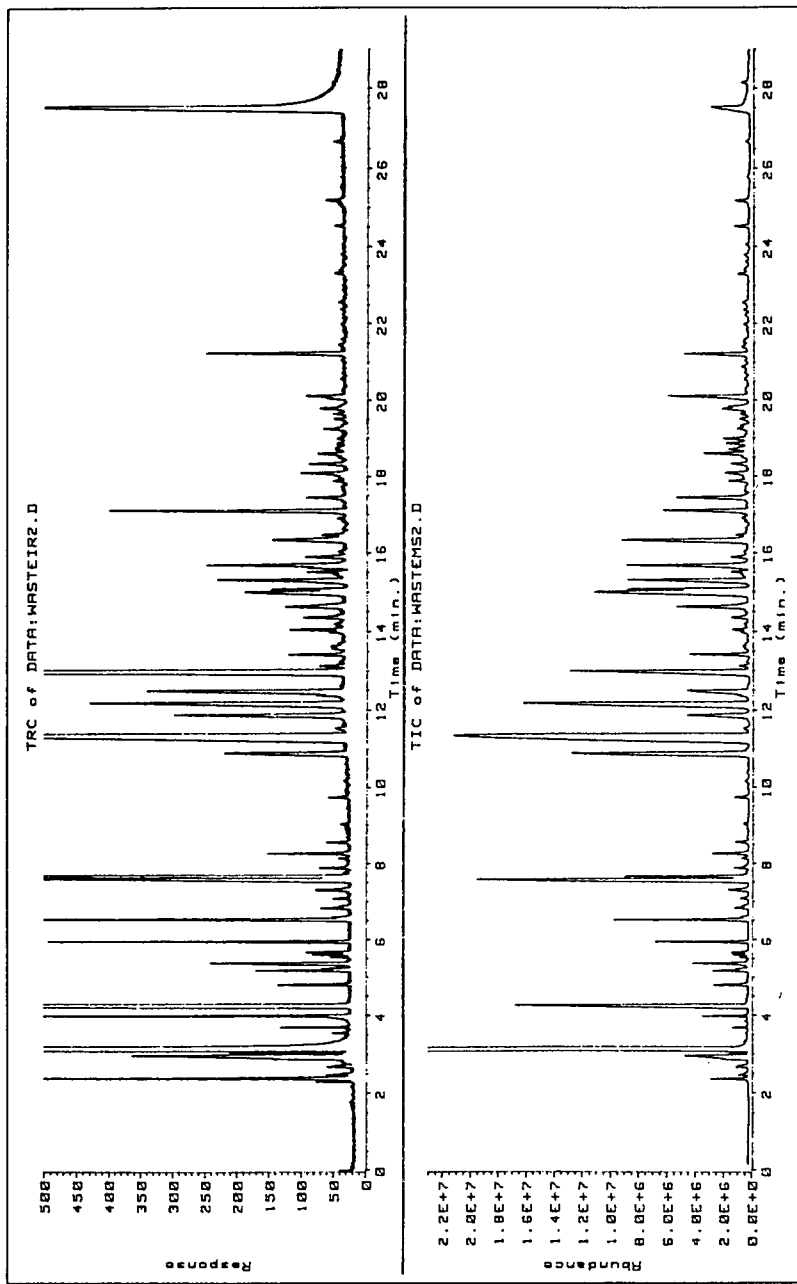
Figure 1. Total Response Chromatogram (TRC) from IRD and Total Ion Chromatogram (TIC) from MSD of hazardous waste sample
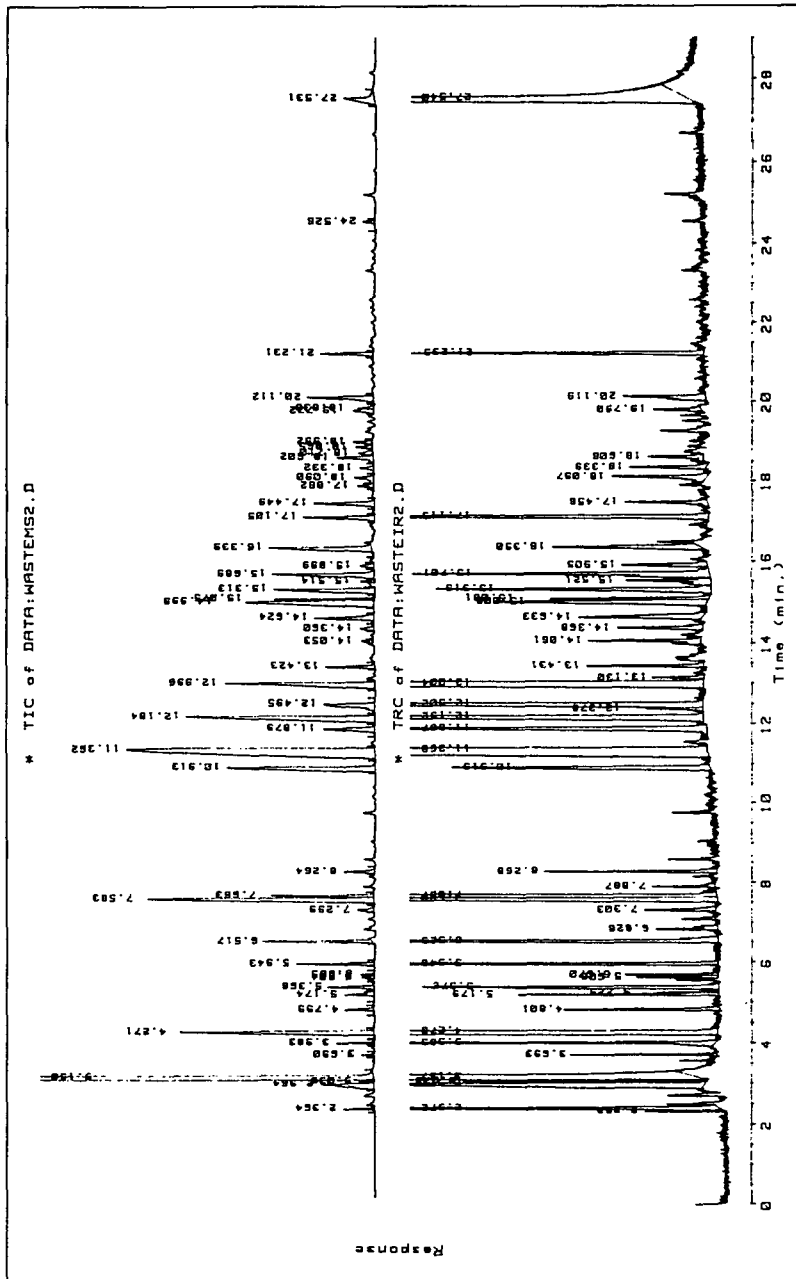
Figure 2. Total Response Chromatogram (TRC) from IRD and Total Ion Chromatogram (TIC) from MSD of hazardous waste sample showing integration of peaks used in this brief

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Figure 3. Qualrpt output of peak 7, Class 1 result indicating ethyl acetate

Figure 4. Qualrpt output of peak 23, Class 1 result indicating ethyl benzene

Figure 5. Qualrpt output of peak 34, Class 1 result indicating propyl benzene

Peak 36 of 56,   --- Both MS and IR found

(1205:1208 - ... Avg 15.058:15.096 min. from DATA:WASTEMS2.D

Abundance

2.5E+6
2.0E+6
1.5E+6
1.0E+6
5.0E+5
0.0E+0

15 27   39 65   77 91   120   139   165   203 207

50   100   150   200

Mass/Charge

(2666:2674 - ... ASP 15.051:15.096 min. from DATA:WASTEIR2.D

Absorbance (mAU)

5.0
4.0
3.0
2.0
1.0

4000 3500 3000 2500 2000 1500 1000

Frequency (cm-1)

COMPARISON OF RESULTS FROM
PBM Search of Library file: DATA:NBS49K.L
Avg 15.058:15.096 min. from DATA:WASTEMS2.D

AND

IR Search of Library file: DATA:EPA_REVA.L
ASP 15.051:15.096 min. from DATA:WASTEIR2.D

Class 1 (on both lists)

•••• NO COMMON COMPOUNDS FOUND IN SEPARATE REPORTS ••••

Class 2 (in only one library)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
1.	000622-96-8	91	---	120	C9H12	Benzene, 1-ethyl-4-methyl-
2.	000108-67-8	83	---	120	C9H12	Benzene, 1,3,5-trimethyl-
3.	003141-02-4	56	---	120	C9H12	1,3-Cyclopentadiene, 5-(1-methyl
4.	005814-85-7	53	---	196	C15H16	Benzene, 1,1'-(1-methyl-1,2-etha
5.	061142-17-4	50	---	174	C13H18	Benzene, (1,2,2-trimethyl-3-bute
6.	029634-38-6	43	---	267	C14H1403S	Phenol, o-[(.alpha.-methylbenzyl
7.	007214-61-1	37	---	151	C8H9NO2	Benzene, (1-nitroethyl)-
8.	041898-89-9	25	---	120	C9H12	2,3-Heptadien-5-yne, 2,4-dimethy
9.	001484-50-0	12	---	274	C14H11BrO	Ethanone, 2-bromo-1,2-diphenyl-
10.	004132-77-8	---	937	148	C11H16	BENZENE, 1,2-DIMETHYL-4-ISOPROPY

Class 3 (in both libraries, but on only one list)

	CAS Number	PBM Qual	IR Qual	MWt	Formula	Name
11.	000620-14-4	91	---	120	C9H12	Benzene, 1-ethyl-3-methyl-
12.	000611-14-3	91	---	120	C9H12	Benzene, 1-ethyl-2-methyl-
13.	000526-73-8	80	---	120	C9H12	Benzene, 1,2,3-trimethyl-
14.	000098-82-8	80	---	120	C9H12	Benzene, (1-methylethyl)-
15.	000095-63-6	47	---	120	C9H12	Benzene, 1,2,4-trimethyl-
16.	000098-86-2	25	---	120	C8H8O	Ethanone, 1-phenyl-
17.	000105-05-5	---	950	134	C10H14	BENZENE, P-DIETHYL
18.	000099-87-6	---	949	134	C10H14	BENZENE, 1-ISOPROPYL-4-METHYL
19.	001632-16-2	---	935	117	C8H16	1-HEXENE, 2-ETHYL
20.	000098-51-1	---	934	148	C11H16	TOLUENE, P-TERT-BUTYL

Figure 6. Qualrpt output of peak 36, Class 2 and 3 results indicating 1-ethyl-4-methyl benzene

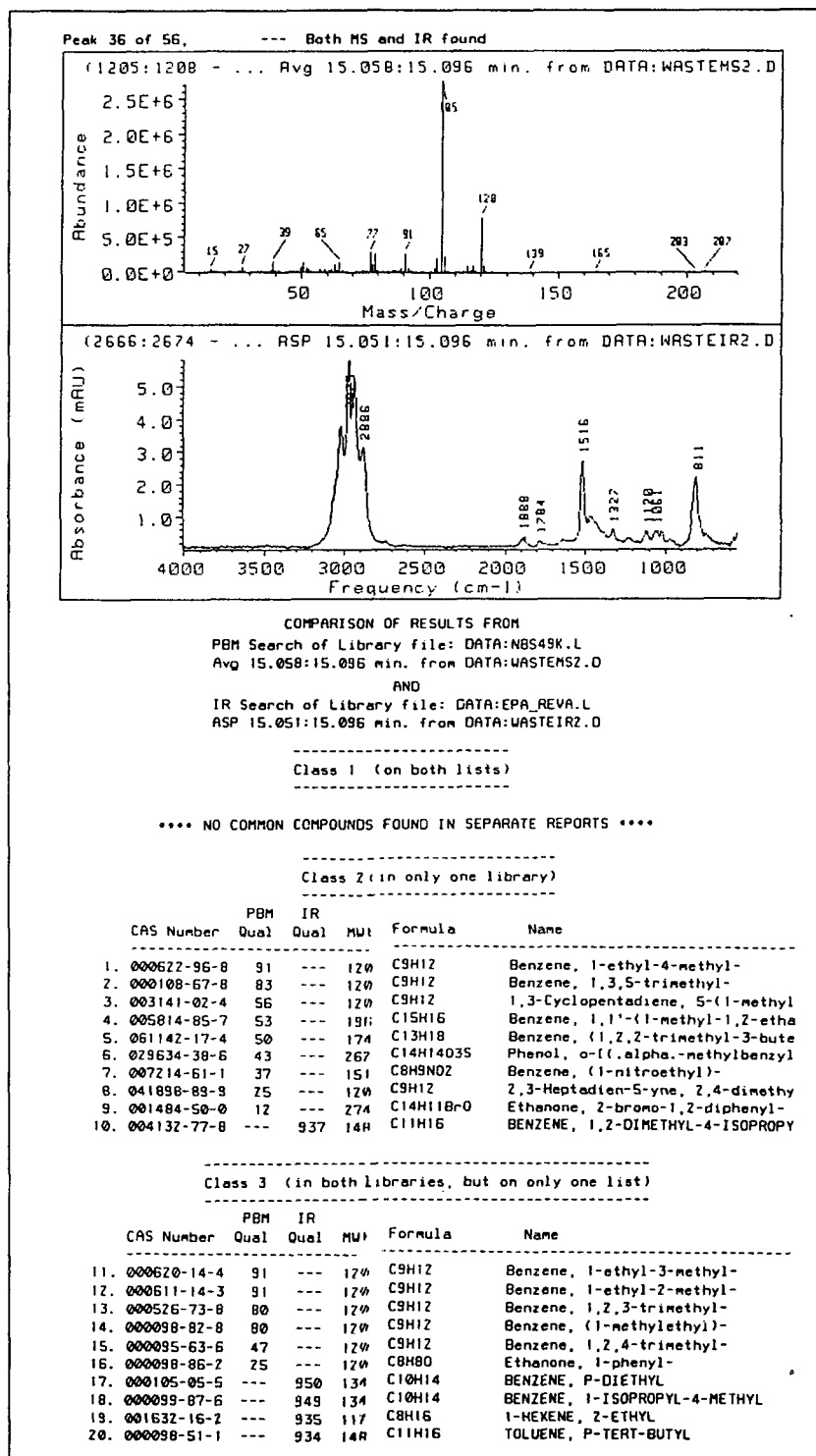| Peak #	Retention Time, TIC	PBM Quality	Retention Time, TRC	IRD Quality	Class 1 Hit	Identification, Most likely if not Class 1
1	–	–	2.293	–	–	Carbon dioxide (air)
2	2.364	–	2.372	843	–	Water
3	2.964	72	2.971	978	+	2-Propanol
4	3.033	–	3.038	940	–	Acetone
5	3.150	–	3.157	915	–	Methylene chloride
6	3.690	59	3.693	921	+	2-Butanone
7	3.983	64	3.989	979	+	Acetic acid, ethyl ester
8	4.271	49	4.278	984	+	1-Propanol, 2-methyl
9	4.799	45	4.801	930	–	2-Isopropoxy ethanol
10	5.174	47	5.179	965	–	Branched paraffin
11	–	–	5.229	923	–	2,3-Dimethyl pentane
12	5.368	64	5.372	958	–	Branched paraffin
13	5.604	47	5.608	917	–	Olefin or cycloparaffin
14	5.665	95	5.670	939	–	1,2-Dimethyl cyclopentane
15	5.943	91	5.948	984	+	Heptane
16	6.517	95	6.523	971	–	Methyl cyclohexane
17	–	–	6.828	938	–	Ethyl cyclopentane
18	7.299	53	7.303	920	–	1-Methoxy butane
19	7.583	91	7.588	981	+	Toluene
20	7.663	83	7.667	977	–	iso Butyl acetate
21	–	–	7.887	906	–	2-Methyl Heptane
22	8.264	64	8.268	922	–	2,2-Diethoxy propane
23	10.913	64	10.919	966	+	Ethyl Benzene
24	11.362	91	11.369	953	+	Meta xylene
25	11.879	43	11.887	952	–	alcohol
26	12.184	91	12.192	976	+	Ortho xylene
27	–	–	12.378	948	–	1,4-Dimethyl cyclohexane
28	12.495	59	12.502	972	+	2-Butoxy ethanol
29	12.996	74	13.004	969	+	Isobutyl butyrate
30	–	–	13.130	945	–	1,2-Dimethyl cyclohexane
31	13.423	87	13.431	967	+	Cumene
32	14.053	90	14.061	970	+	Propyl cyclohexane
33	14.360	90	14.368	951	–	3-Methyl nonane
34	14.624	80	14.633	941	+	Propyl benzene
35	14.999	91	15.006	972	+	1-Ethyl-3-methyl benzene
36	15.075	91	15.081	950	–	1-Ethyl-4-methyl benzene
37	15.313	91	15.319	901	+	1,2,4-Trimethyl benzene
38	15.514	72	15.521	950	–	4-Methyl nonane
39	15.689	70	15.701	926	+	1-Ethyl-2-methyl benzene
40	15.899	45	15.905	950	–	3-Methyl nonane
41	16.339	91	16.350	967	+	1,2,4-Trimethyl benzene
42	17.105	96	17.113	982	–	Decane
43	17.449	80	17.456	949	+	1,2,3-Trimethyl benzene
44	17.882	59	–	–	–	1-Ethenyl-2-methyl benzene
45	18.090	86	18.097	951	–	4-Methyl decane
46	18.332	81	18.339	947	+	Isobutyl cyclohexane
47	18.602	91	18.606	939	+	1,3-Diethyl benzene
48	18.710	38	–	–	–	Diethyl benzene
49	18.865	90	–	–	–	1,3,8-P-Menthatriene
50	18.992	94	–	–	–	1-Ethyl-2,4-dimethylbenzene
51	19.772	93	19.790	920	–	2-Ethyl-1,4-dimethylbenzene
52	19.838	94	–	–	–	1-Methyl-3-isopropylbenzene
53	20.112	83	20.119	929	+	1,2,4,5-tetramethylbenzene
54	21.231	94	21.239	983	–	Undecane
55	24.526	43	–	–	–	1,3-Dioxolane-2-methanol
56	27.531	91	27.540	989	+	Phthalic anhydride

Table 1. Summary of compounds found in hazardous waste sample

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Environmental Applications of Multispectral Analysis
by
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Beginning in the early '70s, extensive application of gas chromatography/mass spectrometry (GC/MS) for identification of organics in water led to its now being the accepted method for positive identification of target analytes. GC/MS with automated spectra matching against a reference collection of mass spectra is known to be excellent for specific substantiation of target compounds, but its current success rate for tentative identification of unknowns is poor. In particular, it fails to detect and/or identify compounds whose mass spectra are not in the spectral libraries.

In order to improve the identifications of non-target compounds, we have applied other existing techniques to environmental sample extracts. This Multispectral Analysis approach uses high resolution mass spectrometry (HRMS) to determine elemental compositions of ions, Fourier transform infrared (FTIR) spectroscopy to recognize sub-molecular structures, and chemical ionization (CI) mass spectrometry to establish molecular weights of the unknowns. The spectral information is then melded together to postulate the structures of the unknown compounds. Results on application of this technique to unidentified compounds in environmental samples have been excellent. Upon re-examination of samples from a survey conducted by the EPA Office of Water, we identified two series of aldehydes as well as a variety of organo-phosphates whose spectra were not included in the reference collection of mass spectra. In the course of the work, the approach was also applied to correct a misidentification made by routine spectra matching.

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56   SAMPLE PREPARATION USING SUPERCRITICAL FLUID EXTRACTION METHODOLOGY

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ABSTRACT

Although extraction of analytical samples with supercritical fluids (SFs) has received much attention during the last 10 or 20 years, applications of supercritical fluid extraction (SFE) techniques to the extraction of compounds regulated by the Environmental Protection Agency (EPA) from matrices of concern to the EPA have been rather limited. In late 1988, we started a project to develop SFE methods for samples of interest to the EPA. Based on our results, which are summarized in this paper, we developed a draft protocol for SFE of environmental samples that has undergone a limited multi-laboratory evaluation. Furthermore, an EPA work group for SFE development has been formed, with participants from EPA, other Government agencies, industry (especially the SFE equipment manufacturers) and academia, and evaluation of commercially available SFE instrumentation is continuing. The results to date demonstrate that SFE is a viable alternative to conventional methods for the extraction of organic pollutants from solid samples. However, our results also demonstrate that the many factors affecting SFE efficiency make it difficult to optimize the method, and that more developmental work has to be done before SFE becomes an easy-to-use, off-the-shelf method.

INTRODUCTION

The Environmental Protection Agency (EPA) is interested in new and improved analytical methods which are faster, better and cheaper than present methods, and which, at the same time, are safe and environment-friendly (by minimizing the generation of waste). Such methods, when not developed specifically for the analysis of environmental samples, must be adapted to EPA needs with respect to matrices, analytes or analyte groups, sample sizes, data quality objectives (precision and accuracy requirements), etc. The methods should be generic, as far as analytes and matrices are concerned, and they should not be restricted to any particular brand of instrumentation or equipment.

Sample extraction techniques should, to the extent possible, yield quantitative recoveries of the target analytes from the matrices, be selective so that extraction of interferants is minimized, not generate large volumes of waste solvents, require little sample and extract handling to minimize analyte losses and contamination, and be fast and inexpensive. The two methods that are at present included in the SW-846 methods manual[1], Soxhlet extraction (Method 3540) and sonication extraction (Method 3550), only partially fulfill these extraction goals. A third extraction method, Soxtec extraction (which is basically a modification of Soxhlet extraction), comes somewhat closer to reaching these goals. These three methods have recently been evaluated for their relative merits[2].

For a number of years now, supercritical fluid extraction (SFE) has been publicized as a new and promising technique for the extraction of organic compounds from solid matrices. Some of the claimed advantages of SFE over conventional extraction methods include much shorter extraction times and close to quantitative recoveries. No toxic and expensive solvents are required which results in reduced materials and waste disposal costs, and in reduced environmental pollution. No solvent removal is required, and no glassware cleaning. SFE conditions can be optimized by varying pressure and temperature and by using modified supercritical fluids (SFs), and extractions can be performed at relatively low temperatures, if desired. Overall, the use of SFE techniques in place of conventional methods could result in substantial cost and labor savings.

In principle, SFE is similar to other solvent extraction techniques, except that the solvent is in its supercritical (SC) state. SFs have some unique properties that put them between liquid and gases. Their viscosities are much lower than those of liquids and their surface tension is zero, that means, they can penetrate into the pores of solids much more easily than liquids. Their densities are close to those of liquids which means their capacities for carrying dissolved materials are similar to those of liquids.

The most commonly used SF is CO_2; others that are being used, or have been investigated, include nitrous oxide, sulfur hexafluoride, Freon-13, ammonia, xenon and several hydrocarbons. SF CO_2 is so popular because of its low critical temperature (31.3°C) and pressure (72.9 atm), and because it is non-toxic, non-flammable, relatively non-reactive and inexpensive, and its use does not result in a waste disposal problem. It is a rather non-polar solvent, similar to hexane or benzene, but both solvent strength and selectivity can be improved by the addition of small amounts of modifiers, such as acetone, methanol, or toluene.

Application of SFE to the extraction of compounds regulated by the EPA from solid analytical samples has been limited. Brady et al.[3] extracted PCBs, DDT and toxaphene from spiked soil samples with SC CO_2. Schantz and Chesler[4] extracted urban particulate matter and sediments

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with SC CO_2 and found that recoveries of PCBs and PAHs were approximately equivalent to those obtained via Soxhlet extraction. Smith and coworkers[5,6] used SC CO_2 and SC isobutane to extract various condensed aromatic and heterocyclic compounds from urban dust and from XAD-2 Spherocarb. Hawthorne et al.[7-10] used SC CO_2 and SC nitrous oxide to extract PAHs from samples of urban dust, fly ash and river sediment. Other authors reported extraction of triazine herbicides with SC CO_2 from spiked sediment samples[11], PCDDs and PCDFs from fly ash samples with SC nitrous oxide[12], and PCDDs from sediment samples[13]. Additional applications of SFE techniques to environmental sample extractions have been reported at recent scientific meetings and symposia[14-17].

SUMMARY OF EXPERIMENTAL RESULTS

We started with our experimental studies in late 1988 with a Suprex Model SE-50 extraction system using either a single-extraction vessel arrangement, or a two- or four-vessel arrangement where two or four extractions were performed simultaneously. In the multi-vessel experiments we were mainly interested in establishing the equivalency of the results obtained from the parallel extractions. All experimental work was performed at the Mid-Pacific Environmental Laboratory (formally Acurex Corp.). The bulk of the results is summarized below (for details see ref. 18):

Single-Vessel Extractions

°   Seventeen organochlorine pesticides (OCPs) were spiked on sand at 500 and 2,500 ppb and extracted with SC CO_2 for 30 min at 150 atm and 50°C. The mean recoveries were almost quantitative for most of the compounds. A combination of static and dynamic extraction, as well as variations of P and T, gave similar results.

°   Forty-one OCPs were spiked on sand and extracted with SC CO_2 modified with 10% methanol. The recoveries from the triplicate samples were 79% or higher for 38 of the 41 compounds.

°   OCPs were spiked at two levels on soil containing 10% moisture and extracted with SC CO_2 using a combination of static and dynamic steps at various p and T settings. The mean recoveries were 80 to 90% (but only about 50% for endrin aldehyde). The moisture (which can be regarded as a modifier) obviously did not drastically change the extraction efficiencies under these conditions.

°   Aroclors 1232 and 1260 were spiked at 5000 ppb on Florisil and extracted for 40 min with SC CO_2 at various conditions for p and T. The recoveries were quantitative at relatively low temperatures and high pressures.

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° Fourteen phenols were spiked on sand at 3.6 to 18 ppm and extracted with SC CO_2. The recoveries ranged from 53 to 129%, except for 2,4-dinitrophenol with only 27% recovery.

° Twenty-five organophosphorus pesticides (OPPs) were spiked on sand at 2.5 µg/g and extracted with SC CO_2 or SC CO_2 modified with 10% methanol. The recoveries were significantly higher when methanol-modified CO_2 was used (20 recoveries $\geq$ 80%, compared to only 8 recoveries $\geq$ 80% for SC CO_2 alone); however, in both cases, several OPPs were not recovered at all.

° Sixteen polynuclear aromatic hydrocarbons (PAHs) were spiked on coal, coal fly ash, sand and urban dust. Mean recoveries after extraction with SC CO_2 at 150 atm/50°C/60 min were almost quantitative for samples of the coal and coal fly ash but only 57% for the urban dust samples. Mean recoveries from the spiked sand samples under two sets of conditions improved with added modifier (200 µL acetone, added to the sample) from 74 to 81% in one case and from 58 to 89% in the other case.

° Soil samples (SRS 103-100, Fisher Scientific), certified for 13 PAHs, dibenzofuran and pentachlorophenol, were extracted with SC CO_2 at 300 atm/70°C/60 min. Ten percent water was added to each sample prior to extraction. All recoveries were >60%, except for benzo(b and k)fluoranthene (53%) and benzo(a)pyrene (32%).

° Sand was spiked with 43 neutral/acidic compounds and extracted with SC CO_2, with and without modifier (200 µL acetone) added to the sample. Some 20 recoveries were lower when the modifier was used, and only 14 recoveries increased.

Two-Vessel Extractions

° Sand was spiked with 36 nitroaromatic compounds and extracted with SC CO_2 under two sets of experimental conditions. The agreement between the duplicate extractions performed in parallel was excellent (generally within 10%). The more volatile nitroaromatics gave good recoveries at lower (200 atm) but not at higher (300 atm) pressures.

° 19 haloethers spiked on sand and extracted with SC CO_2 gave mean recoveries of 73 to 99% for all but two compounds. The agreement between the duplicate extractions performed in parallel was within 15% for most of the compounds.

Four-Vessel Extractions

° Sand was spiked with 19 haloethers and extracted with SC CO_2 at 250 atm/60°C/60 min. Of the 19 compounds, 15 were recovered at >75%, and the other four all at above 45%. The agreement between the

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parallel extractions, expressed as % RSD, ranged from 1.2 to 35.6%, with 12 values being below 10%.

° Of 42 OCPs, spiked on sand and extracted with SC CO_2, 35 gave recoveries >50% whereas two (chlorobenzilate and endosulfan sulfate) were not recovered at all. Twenty-six of the RSDs were <10%, and the others were between 10 and 23%, except for 1,2-dibromo-3-chloropropane (30.8%).

The only limitations we have experienced with the four-vessel arrangement was in the duration of the extraction. When working with 2-mL extraction vessels and using 50-μm restrictors, the 250-mL syringe pump allows a maximum extraction time of 60 min.

DISCUSSION

As can be seen from the above summary of our experimental results, the extraction efficiencies we achieved with a variety of samples are in general good to reasonable, especially since in most cases we had not tried to optimize our extraction conditions. Some of our recoveries were much lower than those reported by others. However, one has to realize that at least in some of the cases reported in the literature the extraction conditions had been optimized in a trial-and-error approach. In addition, such experiments were often conducted with homemade equipment, focused mostly on PAHs, and used small sample sizes (as small as a few milligrams). In order to develop a SFE method that can successfully be applied to samples of interest to the EPA, we have to use commercially available equipment, consider a wide variety of sample matrices and groups of pollutants, and use sample sizes large enough (1 to 10 g, preferably at least 5 g) for the inevitable inhomogeneities of most real environmental and hazardous waste samples.

There is a lack of standard reference materials that include the matrices and pollutants of environmental concern. The materials that are available are either spiked matrices (soils, etc.), or they are certified for only a very limited number of compounds, e.g., PAHs. It is therefore difficult, even currently impossible, to determine absolute extraction efficiencies for most analytes because in most cases removal of a spike from a sample matrix is much easier than removal of "incorporated" or "native" compounds. This, however, is a problem that hampers the evaluation of all extraction methods, not just SFE, and one is usually confined to comparing relative extraction efficiencies.

Temperature and pressure changes affect the density and viscosity of a SF and therefore its solubilizing ability. However, it is little understood what happens on the surfaces of the solid matrices during the extraction process, and what the desorption, solvation and trans-port mechanisms are, and little is known about how to optimize p and T for specific matrices and analyte groups. Just raising the pressure does not seem to be the answer.

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An understanding of the desorption and transport mechanisms of solutes under SC conditions would provide clues whether the use of static or dynamic extraction conditions, or a combination of the two, would be advantageous; whether rapid pressure fluctuations would improve extraction rates and, maybe, extraction efficiencies and selectivities; and whether application of ultrasound could enhance extraction efficiency and rate, as has been suggested[6,19].

CURRENT ACTIVITIES

Summarized below are the SFE activities in which EPA is at present involved.

EPA SFE Methods Development Group

In January 1990, an SFE Methods Development Group was formed. The overall goal of this group is to assist and advise in the development of SFE to make it a viable, attractive and affordable alternative to conventional extraction methods. This effort includes

° development of a general, standardized SFE method, or set of methods, for a variety of analytes and matrices,

° generating performance data for the method(s) through intra- and interlaboratory evaluation studies, and

° improving and, to the extent practical, standardizing hardware.

The SFE Methods Development Group members come from EPA (OSWER, ORD, and Regional laboratory personnel), instrument manufacturers, academia, and other interested contractor laboratories. Semi-annual meetings provide a forum for candid discussions of results and problems, of new approaches and of specific applications.

Protocol Development and Evaluation

Based on our results we developed a draft protocol in the SW-846 format "Extraction Procedure Using Supercritical Fluids." Our goal was to write a generic protocol that is applicable to as many different SFE systems as possible. It is written for solid matrices like soils and sediments; the target analytes include organochlorine pesticides, polychlorinated biphenyls, polynuclear aromatic hydrocarbons, phenols, phthalate esters, and organophosphorus pesticides. The protocol addresses interferences, apparatus and materials, sample preparation (including extraction), and quality assurance. An updated protocol version was recently evaluated by 10 laboratories for its feasibility[21]. The analytical data generated by the different laboratories varied substantially, however, it was confirmed that the protocol could be followed without problems by all operators involved, independent of

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the particular SFE system used, and this has been the main purpose of the evaluation study.

Instrument Evaluation

Most of the commercially available SFE systems have been evaluated at the Mid-Pacific Environmental Laboratory under contract to the EPA. The generous help from the instrument manufacturing companies is acknowledged and greatly appreciated. The main goal was to assure that our protocol was compatible with all instruments. In general, all instruments performed adequately, although, as can be expected, none of the instruments was without some problems, and feedback was provided to the manufacturers as to problem areas and perceived weaknesses of their instruments. However, it must be understood that evaluation of an instrument does not constitute endorsement by the EPA.

Extraction and Optimization Studies

Work is continuing in EPA laboratories and laboratories under contract to the EPA on different matrices (e.g., fly ash, bottom ash, clay-type soil, soil high in organics, river and marine sediments, etc.) and on method optimization. Currently, a method for the extraction of oil/ grease and total petroleum hydrocarbons from soil is being developed. The current EPA methods specify extraction with Freon , however, Bicking et al.[21] and others have shown that these materials can be extracted with CO_2 under SC conditions. Our own results confirmed this, and a draft protocol for the determination of oil/grease and total petroleum hydrocarbons has been prepared. Another method of current concern is the extraction of phenoxyacid herbicides and other acidic compounds for soil. Miller et al.[22] have shown that acidic compounds can be derivatized by adding trimethyl phenyl ammonium hydroxide in methanol to the material in the extraction vessel, followed by static and then dynamic SFE. Finally, we are looking at the effect of ultrasound application during SFE which, as discussed earlier, seems to increase extraction rate and possibly extraction efficiency.

CONCLUSION

Supercritical fluid extraction is an attractive method for the extraction of organic contaminants from matrices of concern to the EPA. The most-used extraction medium, carbon dioxide, is non-toxic and non-polluting, and creates no waste-disposal problems. Potential advantages of the method include reduced material and manpower needs, speed, high efficiencies, selectivity (in combination with modifiers), and high versatility, especially in combination with advanced analytical techniques. However, more developmental work has to be done before SFE becomes an easy-to-use, off-the-shelf method.

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57 THE RESEARCH STATUS OF SUPERCRITICAL FLUID EXTRACTION FOR THE ANALYSIS OF PCBs IN INCINERATOR ASH

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ABSTRACT

The extraction time of PCBs from incinerator ash can be reduced to less than one hour using supercritical fluid extraction with carbon dioxide.

SW-846 Method 8080 is currently the only EPA approved method for the extraction of PCBs in solid matrices. The sample is first extracted in a Soxhlet apparatus for 16 hours with hexane/acetone. The solvent volume is then reduced using a Kuderna-Danish apparatus, prior to GC-ECD analysis. The time intensive extraction step is the current limiting factor in reducing the turnaround time of the analysis.

Supercritical fluids combine the mass transport properties of a gas with the solvation properties of a liquids. This research applied supercritical fluid technology to a specific combustion matrix, incinerator ash, both to reduce the turnaround time of the method and to minimize solvent usage. The conditions required for extraction, including sample preparation, extraction temperature, extraction time, modifier type etc. were determined in a systematic manner to maximize the extraction speed and PCB recovery. The effect of the adsorptive properties of the matrix on the analyte were also investigated.

The application of supercritical fluid extraction technology for PCB extraction will enable laboratories to provide same day analytical service, while reducing laboratory costs.

PURPOSE OF WORK

The purpose of this work was to apply supercritical fluid technology to develop a method for the extraction of PCBs from incinerator ash. The technical approach used to define method parameters was the systematic evaluation of each element while holding all remaining variables constant. In this type of study it is extremely important to differentiate between Comparative and Absolute extraction. In the comparative situation there is a fixed goal based on data generated by an accepted method. In the absolute case there is confirmation via several alternative techniques that the extraction is indeed complete. The authors have chosen a comparative study because of matrix considerations and analyte concentrations.

MATRIX OVERVIEW

Incinerator ash is defined as a combustion matrix. It is a by-product of the incineration process containing a variety of newly formed active organic and inorganic adsorption sites. The adsorptive strengths of the sites can vary as well as their distribution throughout the ash particle. Although the ash is primarily a glassy product containing a small amount of carbon polymer, it does have some pore structure. An ash particle is illustrated schematically in Figure 1.

The irregularly shaped polyhedron represents the basic ash particle contaminated with PCBs. The light and dark dots represent weakly and strongly adsorbed PCBs. The material on the surface is fairly easy to remove, its "removability" depends on the strength of the adsorptive site compared to that of the extractant. The material within the pore not only must be desorbed, but must diffuse to the pore mouth prior to being swept into the flowing CO_2. This makes the removal of these materials diffusion limited. Any material occluded within the vitreous ash will never be removed unless the ash is physically degraded to expose the PCB to the extractant.

SUPERCRITICAL FLUID OVERVIEW

The molecules of a liquid are bonded by electrostatic forces, which are a function of the molecule's polarity. The heat of vaporization represents the energy required to break these associative bonds as the liquid becomes a vapor. When a liquid in equilibrium with its vapor, is sealed in a tube and heated, the pressure of the closed system rises and the liquid's heat of vaporization, and corresponding intermolecular associative forces decrease. When the associative forces reach zero, the liquid and gas phases become one. This temperature and the corresponding pressure, which are unique for each liquid, are known at the critical constants.

This non-associated supercritical phase (fluid) has unique physio-chemical properties. Its viscosity and diffusion constant approximate those of a gas, making it an ideal material to permeate small pores. Its density and solvency approach those of a liquid, enabling it to dissolve a broad range of organic compounds. The technique is not thermally driven, thus it is also possible to extract thermally labile and non-volatile materials.

The solvency of the mobile phase is a function of its density. Increasing the density generally increases the solubility of larger molecular weight species. Carbon dioxide is the most frequently used material because of its low critical temperature, inertness and safety.

INSTRUMENT DESCRIPTION

The supercritical fluid extraction instrumentation was purchased from the Lee Scientific Co., and consists of the following components.

Pump - A pump to supply pressurized liquid CO_2 to the extraction cell, that has the ability to deliver at least 20 mL of liquid CO_2 at an operating pressure of up to 400 atmospheres, (6150 PSI).

Oven - An oven capable of maintaining a temperature of 100 degrees C.

Extraction Cell - consisting of a 10 cm, 4.6 mm ID HPLC column, 2 micron frits, and hardware to seal the end of the column.

Restrictors - Fused silica capillary producing a carbon dioxide flow rate of 1.8 mL/min of liquid, or 900 mL/min gas through the cell, usually about 60 cm long, 50 micron ID.

Liquid Carbon Dioxide - Supercritical fluid grade, in a tank that must contain a dip tube to deliver liquid product (Scott Specialty Gases).

Figure 2a shows a schematic of the apparatus used for the study. The components occupy about 6 ft^2 of bench and floor space, including space for a single gas cylinder.

EXPERIMENTAL PROCEDURE

Sample Selection

The authors felt that the best technical approach was to select a hazardous waste incinerator ash sample containing native, as opposed to spiked, PCBs. Typical incinerator ash PCB concentrations approximated 3 ppm, about 15 times lower than the regulatory level.

The initial work for this study was performed on this type of ash. Reproducibility difficulties, arising from sample size and GC detection limits constraints, required that a sample of higher concentration be obtained. This, due to the nature of the typical incinerator ash, dictated that the sample be spiked. A 250 gram sample of incinerator ash was then spiked to a level of 50 ppm with Aroclor 1260, by the technique of solvent evaporation in a rotary evaporator.

Sample Preparation and Analysis

A gallon of incinerator ash was crushed in a reciprocating jaw crusher. All of the ash was sifted through a 9.5mm screen to remove non-extractable items, such as large metallic shards etc. Particles greater than 1.0mm were hand ground in a mortar and pestle until they passed through the 16 mesh screen. The ash sample was homogenized by passing it through a riffler three times. The moisture content was determined to be 3.14% by oven drying at 110C. The PCB was determined to be 3.4ppm of Aroclor 1260, using SW-846 Method 8080.

Preparation of Spiked Sample

Preparation of 250g of ash, spiked to a concentration of 50ppm, was accomplished by slurrying 30 gram portions of incinerator ash with acetone and spiking the slurry with 1.5mL of 1000ppm Aroclor 1260 spiking solution. After mixing for a few minutes, the solvent was driven off slowly in a rotoevaporator over the period of approximately 45 min. This spiking method was repeated several times to create enough ash for experimental purposes. The spiked ash was homogenized by combining all fractions into a single container and riffling three times. The PCB was determined to be 54.4ppm of Aroclor 1260, using SW-846 Method 8080.

Extraction Procedure and PCB Analysis

The cell was assembled as shown in Figure 2b. The extraction cell was completely filled with ash to eliminate dead space. The carbon dioxide was turned on slowly and brought up to pressure within one to two minutes. The collection fluid was five mL of hexane in a ten mL graduated cylinder. Additional hexane was added to the graduated cylinder at the completion of the extraction to compensate for evaporative losses. All PCB analysis were performed using SW-846 Method 8080, GC-ECD (a capillary column technique), along with a compliment of QA including calibration standards, spikes and duplicate spikes.

Effect of Time on PCB Extraction

In order to determine the effect of time on the extractability of PCBs from the ash, weighed ash samples were extracted with unmodified CO_2 for varying time periods ranging from 5 to 60 minutes. These data are presented in Figure 3 and show that the extraction curve reaches a plateau in about 45 minutes. The following extraction conditions were used:

$$CO_2 \text{ flow} = 1.8 \text{ mL/min}$$
$$\text{Temperature} = 100 \text{ }^{\circ}C$$
$$\text{Pressure} = 400 \text{ atm}$$

Effect of Temperature on PCB Extraction

In order to determine the effect of temperature, and thus density, on the extractability of PCBs from the ash, weighed ash samples were extracted with unmodified CO_2 for varying time periods and at the following temperatures:

Temperature $^{\circ}C$	Phase	Density g/mL
35	Liquid	.98
100	SCF	.76
200	SCF	.50
300	SCF	.36

These data are presented in Figure 4 and show that the maximum amount of PCB is extracted at a temperature of $100^{\circ}C$. This indicates that density is more important than the increase in diffusion coefficient for removing PCBs from the incinerator matrix. Liquid CO_2 doesn't work as well as the corresponding supercritical fluid because of the decreased transport properties of carbon dioxide in the liquid state.

Effect of Particle Size PCB Extraction

In order to determine the effect of particle size on the extraction of PCBs from ash, weighed ash samples of two different mesh sizes were extracted with unmodified CO_2 for varying time periods ranging from 5 to 60 minutes. The data are presented below and show that more PCBs are extracted from the sample when it is ground to a mesh size of 60 or more.

Mesh Size	Amount Extracted ppm
10 -20	3.2
40 -60	4.2

The following extraction conditions were used.

CO_2 flow	= 1.8 mL/min
Temperature	= 100 $^{\circ}$C
Pressure	= 400 atm
Time	= 40 min

Static-Dynamic Extraction using a Pre-Modifier

Based on information presented at the NIST conference by Mary McNally [1], liquid methanol was introduced directly into the cell in an attempt to improve the extraction efficiency. After sealing the cell containing methanol, the cell was allowed to equilibrate for five minutes and then the CO_2 pressure was brought up to 400 atmospheres and held in the static mode for ten minutes. The run then proceeded as described earlier. Samples were extracted using methanol, acetone and toluene with only small improvements being noted.

Dynamic Extraction using Modified CO_2

Based on the slight increase of PCB extracted using the different premodifiers, work was initiated with modifiers directly added to the CO_2. This work and that of Larry Taylor [2] at VPI, influenced the choice of 5% toluene as the modifier of choice for CO_2.

Extractive Reproducibility
Comparison of Soxhlet and SFE Extraction

Replicate SFE runs using toluene modified CO_2 extractions and Soxhlet extraction were made using the same sample. The results are compared in Figure 5. These data show recoveries, PCB by Soxhlet extraction, of 100% from the spiked ash with relative standard deviation (RSD) of only 5%. The SCF extractions show 81% PCB recovery, with a RSD of 12%. This brings the SCF extraction for PCBs in incinerator ash into the equivalency range of Soxhlet technology.

Research Overview and Direction

Although the extraction recovery data has increased over the time period of the research, more work needs to be done, in the areas of improved PCB recoveries, and analytical precision. The use of toluene as a modifier improves PCB recoveries, but considering the superior extractive properties of supercritical fluid CO_2, one would expect the recoveries of the two techniques to be more equivalent. Altering the toluene modifier content or experimenting with different modifiers are two possible approaches.

Analytical precision data generated in earlier experiment, for both extraction techniques is the reverse of that presented in Figure 5. This suggests that there is a additional degree of freedom that has not yet been addressed. Before an SCF method can be finalized comparable precision data must be generated, to demonstrate the absence of any additional variables.

The work clearly shows that SCF is a viable technique for the extraction of PCBs from incinerator ash. These problems may be overcome and the application of SCF for PCB extraction from incinerator ash will soon become a reality.

CONCLUSIONS

1 - PCBs can be extracted from incinerator ash using supercritical fluid carbon dioxide modified with toluene.

2 - The extraction time is reduced to 50 minutes from 18 hours and uses only 5 mL of collection solvent.

3 - SFE is clearly a viable equivalent technique for PCB extraction to minimize solvent use in the laboratory.

4 - Additional work needs to focus on improved recoveries and analytical precision.

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FIGURE 1

PCB's IN INCINERATOR ASH
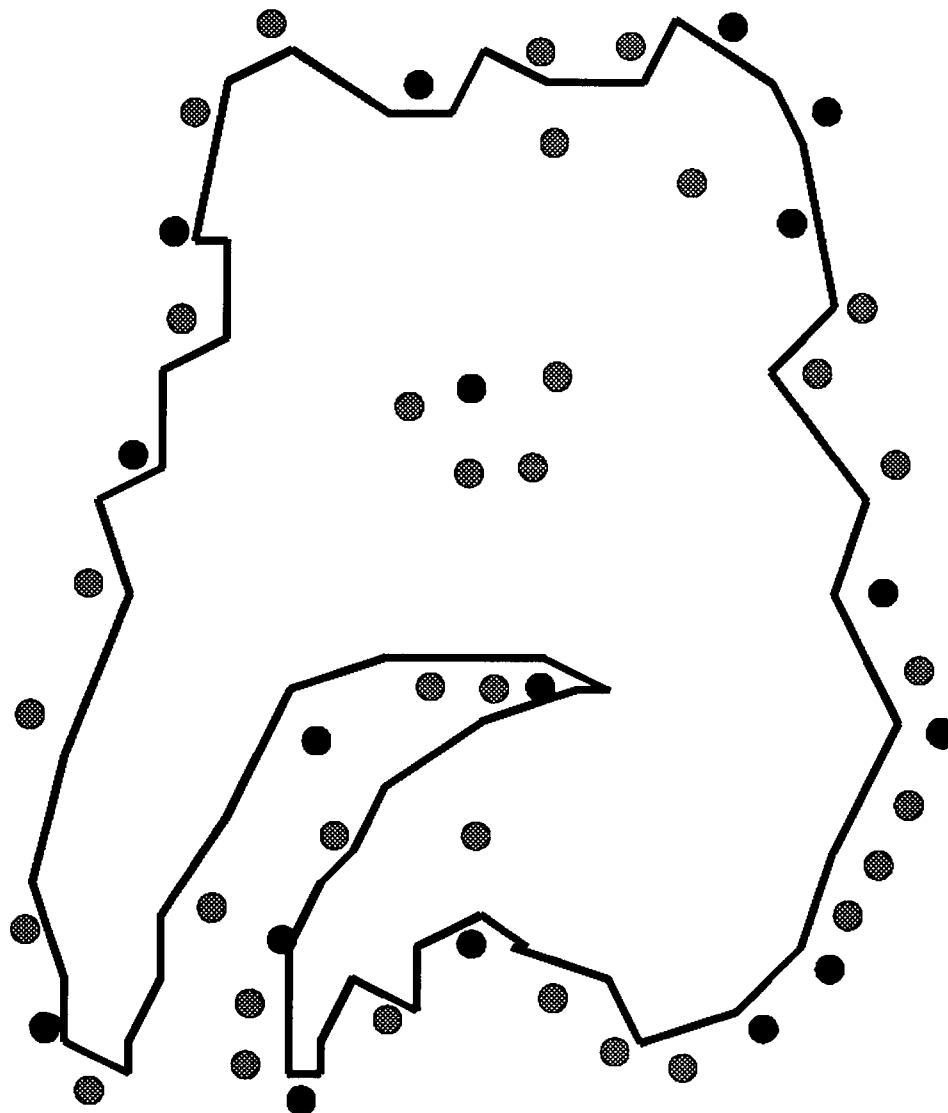
FIGURE 2A

INSTRUMENT SCHEMATIC
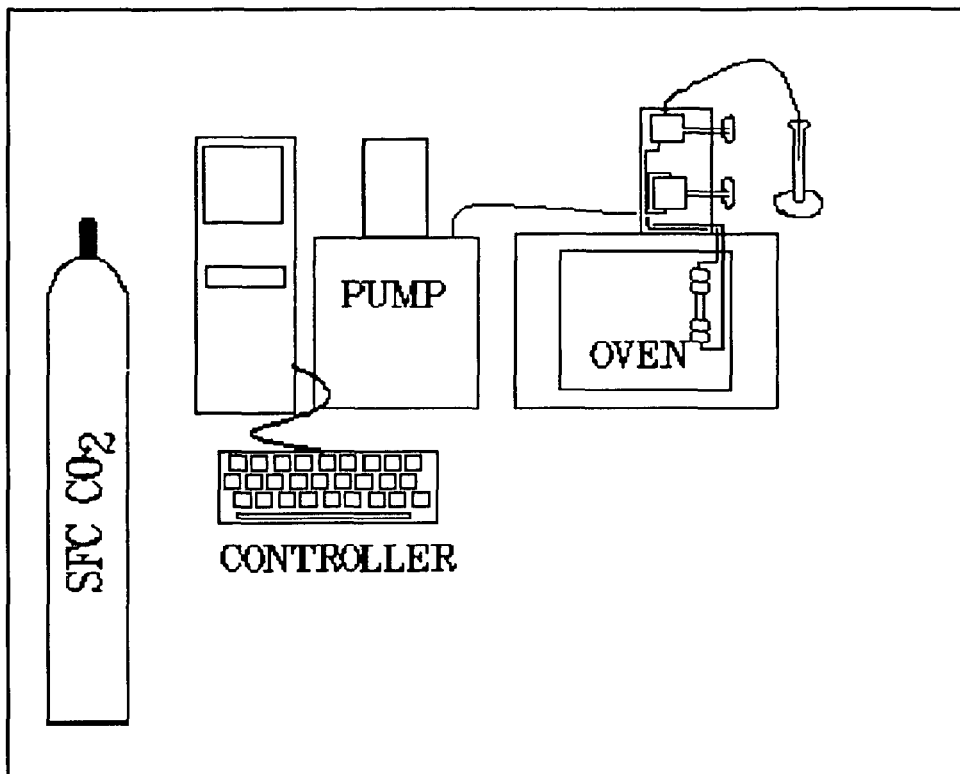
FIGURE 2B
CELL SCHEMATIC
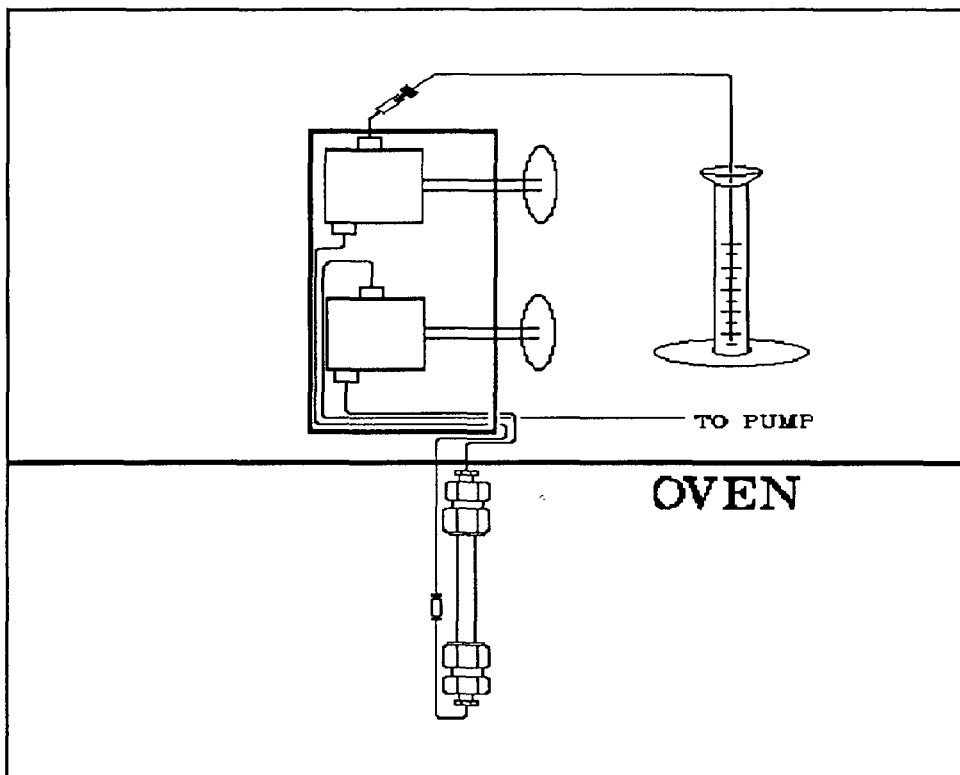
FIGURE 3

SFE OF PCB'S
EFFECT OF TIME ON PCB EXTRACTION

PPM EXTRACTED

TIME MINUTES

—+— 100 deg C (10-20)
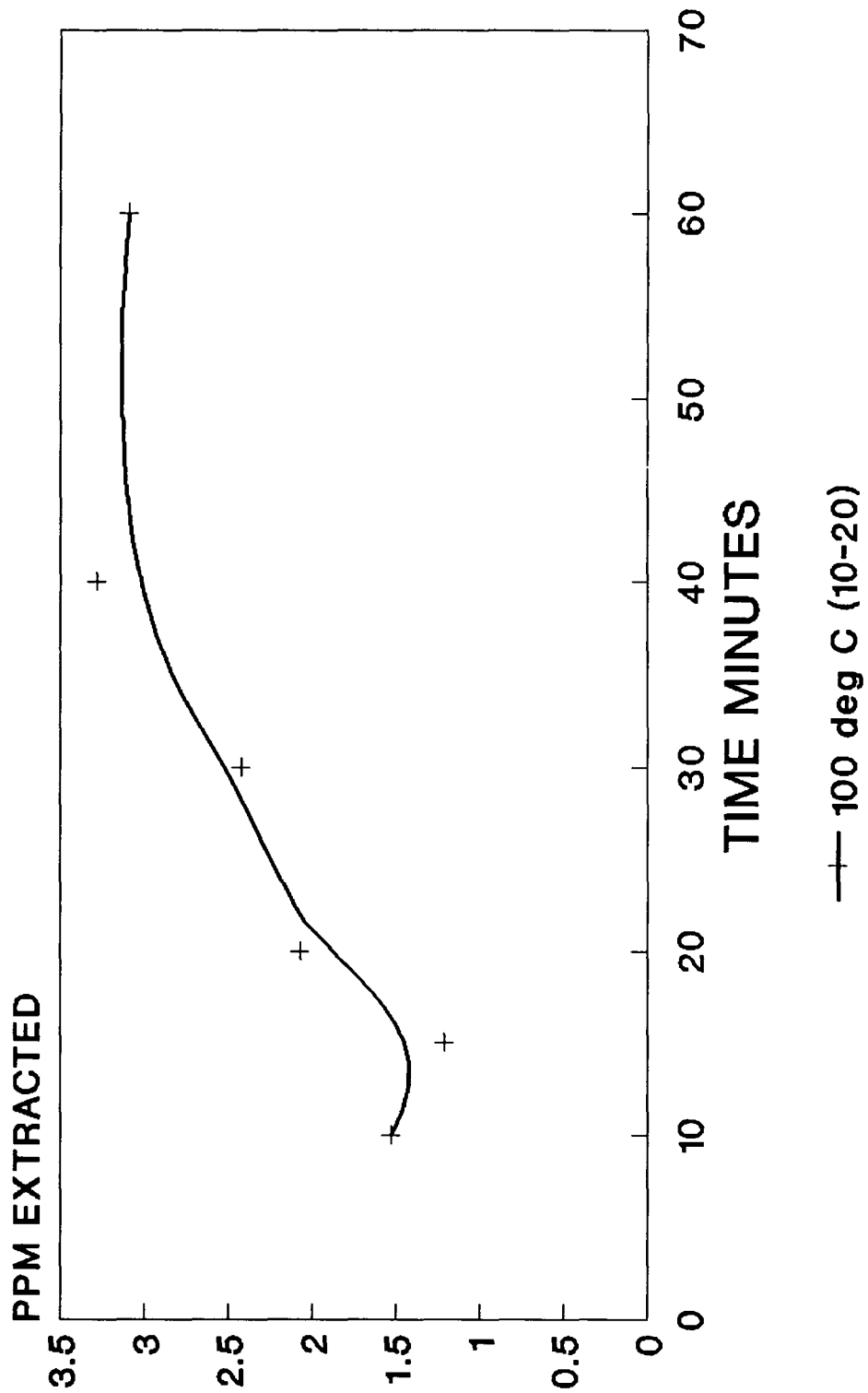
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FIGURE 4

SFE OF PCB'S
EXTRACTION TEMPERATURE SELECTION

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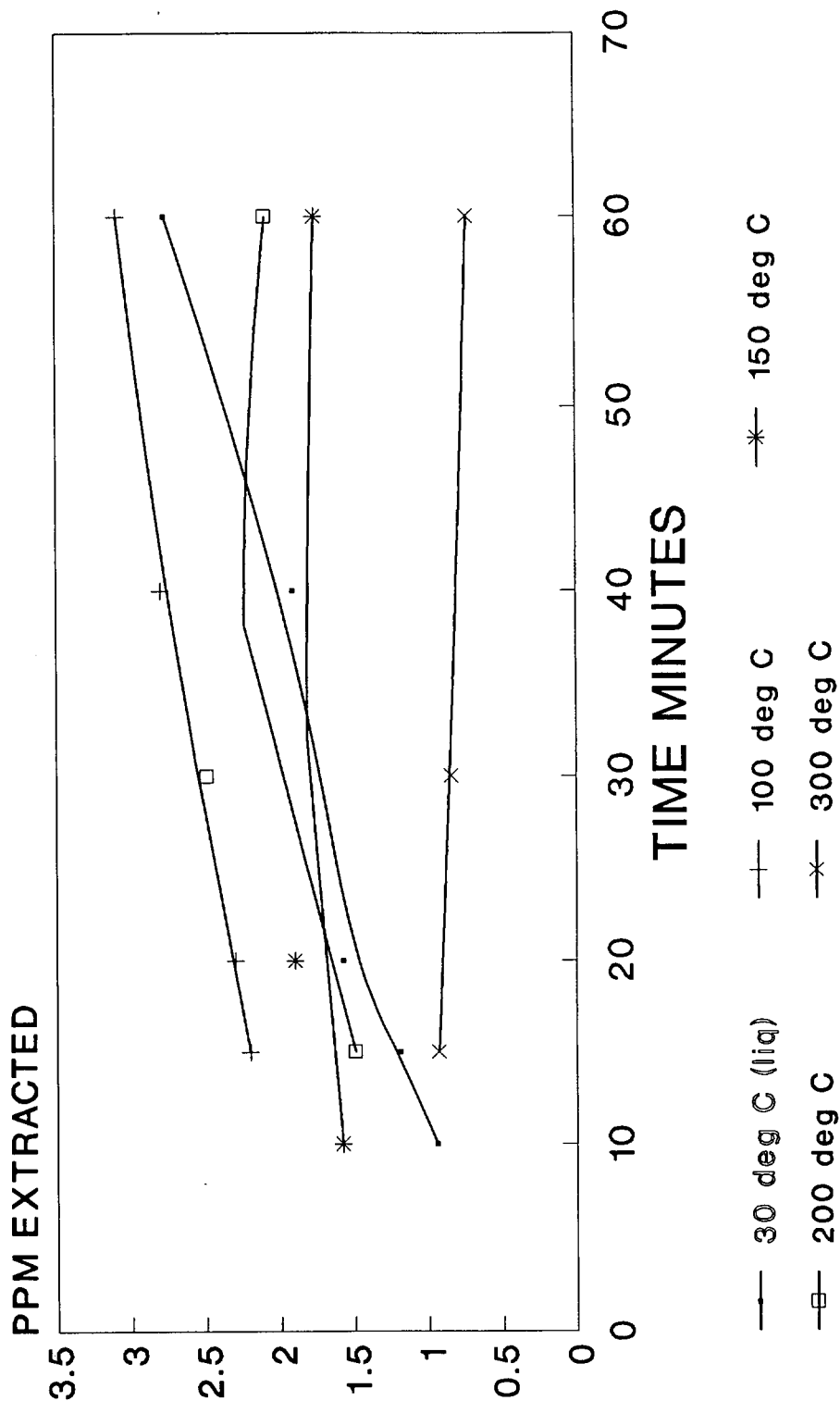
FIGURE 5

Dynamic Extraction using Modifier

MEAN 45ppm

MEAN 54ppm

SFE TOLUENE MODIFIER

SOXHLET

SPIKE

CONC PCB (ppm)
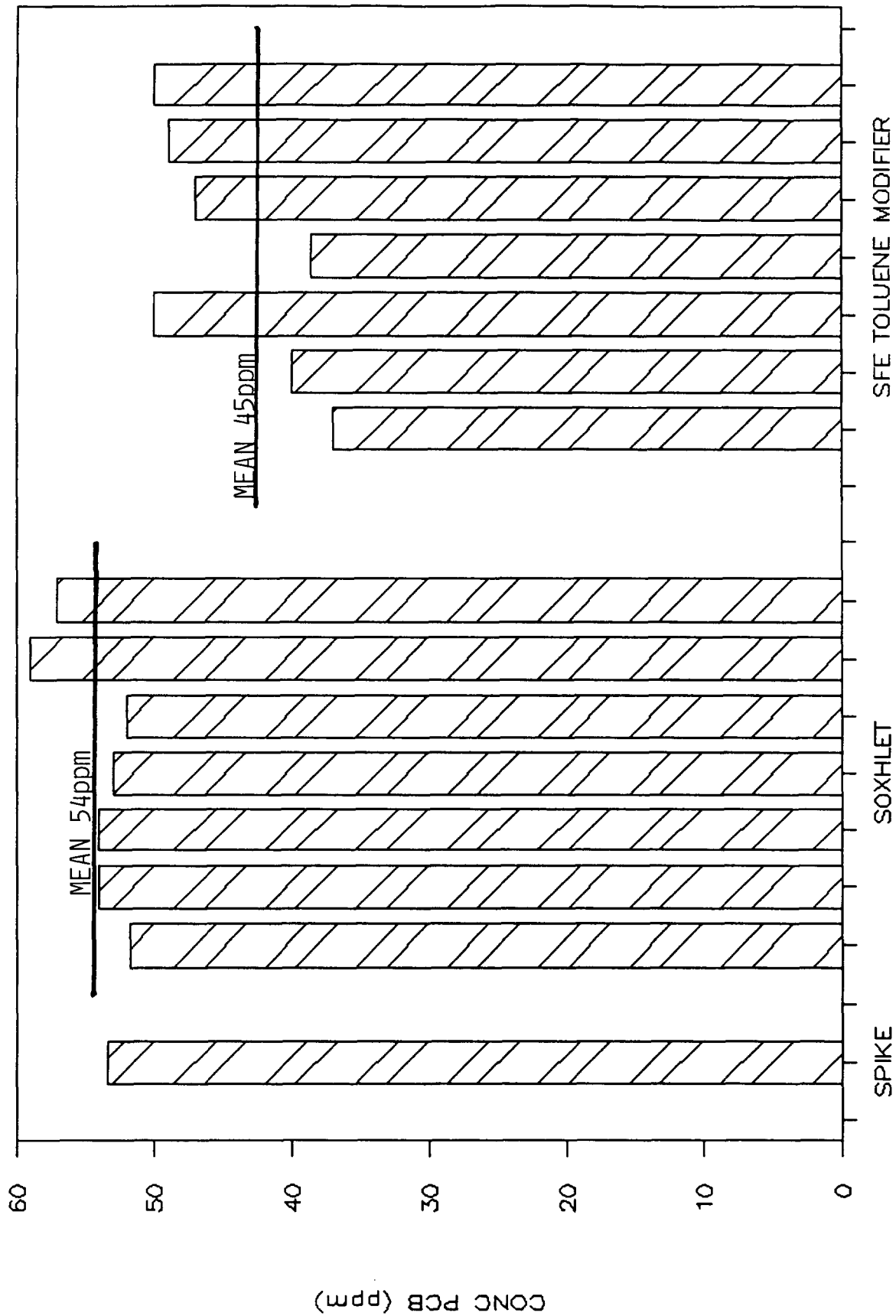
58 SUPERCRITICAL FLUID EXTRACTION (SFE) OF TOTAL PETROLEUM HYDROCARBONS (TPHs) WITH ANALYSIS BY INFRARED SPECTROSCOPY

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ABSTRACT

Infrared spectroscopy is an attractive analysis procedure for the screening of petroleum hydrocarbons in solid matrices because of its low cost and rapid sample throughput. Coupled with off-line supercritical fluid extraction (SFE), this method provides a rapid monitoring procedure with an order of magnitude reduction in the amount of solvent used compared to the present Soxhlet method. This method uses supercritical carbon dioxide as the extraction solvent to remove the target components from a solid sample and deposit them into a collection vial containing 5 mL of solvent. Freon-113® has been replaced in this application by Fluorinert® FC-77 as the collection solvent. An extraction time of 25 minutes at 400 atmospheres and an oven temperature of 60°C provides a rapid, effective means of extracting petroleum hydrocarbons from sand and Kaolin matrices.

INTRODUCTION

The methodologies for sample preparation have not kept pace with the developments in sample analysis. The method that Franz Ritter von Soxhlet developed at the turn of the century has changed very little. It is still the predominant method for the preparation of solid samples. The need for an alternative sample preparation method is critical in the analysis of petroleum hydrocarbons.

According to EPA estimates there are three to five million underground storage tanks in the United States (1). Approximately 100,000 of these tanks are believed to be leaking. In addition, as many as 300,000 more tanks are predicted to begin leaking in the next five years (1). At present, semivolatile petroleum hydrocarbons are extracted by Soxhlet, sonication, or Soxtec® using an organic solvent followed by gas chromatographic or infrared analysis.

Freon-113® is used when the analysis is performed by infrared spectroscopy. It is a known ozone depleter (2), making it unacceptable as a laboratory solvent. According to M.P. McCormick of Langley Center's Aerosol Research Branch, polar stratospheric clouds provide a surface on which chlorofluorocarbons (CFCs) can react to free the chlorine to react with ozone (2). In accordance to the Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) and the Clean Air Act Amendments of 1990 (CAA), CFCs will be phased out by the year 2000.

This paper presents a method in which supercritical fluid extraction (SFE) is used in the preparation of solid samples containing trace concentrations of petroleum hydrocarbons. A fluorocarbon is used as the collection solvent followed by infrared spectroscopic analysis.

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Fluorocarbons contain no chlorine and should not be confused with CFCs. There has been no evidence of the cleavage of carbon-fluorine bonds, nor has there been a link between fluorine and the depletion of stratospheric ozone (3). The benefits of SFE are well documented in several informative reviews (4,5,6). The use of the fluorocarbon Fluorinert® FC-77 as the collection solvent in this method eliminates the use of Freon-113® and compliments SFE's ability to provide an effective alternative to the present TPH extraction methods.

INSTRUMENTAL, EQUIPMENT and SUPPLIES

Supercritical Fluid Extractor
  Suprex, SFE/50
  5 mL extraction vessel
  600 mm fused silica restricter, 32 micron ID
Infrared Spectrograph
  Perkin-Elmer, 710 Infrared Spectrophotometer
  10 mm, 3 mL quartz cell
Hardware
  16 x 60 mm glass vial
  16 x 100 mm glass culture tube
  500 mL round bottom flask
  Modified Neilson-Kryger distillation apparatus
  Heating mantel, Glas-Col 115 volts, 270 watts TM106
  Temperature controller, Glas-Col 115 volts, 1500 watts, PL-312 Minitrol
  Glass beads, 5 mm OD
  Glass Pasteur pipets
  Filter paper ashless 41,Whatman
  Glass wool-silane treated, Supelco
Reagents and Standards
  Freon-113®, EM Science
  Fluorinert® FC-72, 3M
  Fluorinert,® FC-77, 3M
  Isooctane, Mallinckrodt
  Xylenes, Mallinckrodt
  Hexadecane, EM Science
  Kaolin, Baker Analyzed
  Diesel fuel, retail Fuel outlet
  Sand, washed and dried, Mallinckrodt
  CO_2, SFC grade with 1500 PSIA Helium headspace with dip tube, Scott Specialty Gases
  Hexafluorobenzene, Aldrich*
  Octafluorotoluene, Aldrich*
  Bromopentafluorobenzene, Aldrich*

* These compounds were only used in the initial collection solvent search.

RESULTS and DISSCUSSION

The development for this method was conducted in two areas the search for a suitable collection solvent and the optimization of supercritical fluid extraction parameters. The approaches and representative results are discussed below.

Collection solvent

The search for an appropriate collection solvent was broken down into four stages. In the first stage, the catalogs of seven chemical vendors were examined for potential solvents. This search resulted in sixty-six possible collection solvents.

In the second stage, vendors were contacted for additional product information regarding the potential collection solvents as to their hydrocarbon solubility, IR spectra, and material safety data. This information was used to eliminate all but six solvents. Small amounts of these solvents were obtained for further testing.

The third stage was to confirm conclusions drawn from the information provided by the vendors. All solvents were tested for hydrocarbon contamination by measuring the C-H stretch region of the infrared spectrum (2900-3100 cm^{-1}). Even with background correction, the concentration of hydrocarbon contamination of the possible collection solvents was prohibitively high for all solvents except the Fluorinerts® FC-77 and FC-72. The 3M Fluorinerts® FC-77 and FC-72 provided an acceptable baseline over the spectral region of interest with background correction.

A 10,000 mg/L diesel fuel standard was prepared in 25 mL Freon-113® for solubility comparison studies with solutions of FC-77 and FC-72 that were saturated with diesel fuel. Using Freon-113® as a solubility reference, it was estimated that the solubility limit of diesel fuel in FC-77 and FC-72 is approximately 5000 mg/L. The low molecular weight fraction of the diesel fuel appeared to be preferentially more soluble than the higher molecular weight components when compared to the Freon-113® standard.

The same three standard solutions used in the hydrocarbon solubility studies were used as a mock collection solvent. This was to test the ability of the FC-77 and FC-72 to retain hydrocarbons when CO_2 was bubbled through them. These standard solutions were purged for 10 minutes with a calculated liquid CO_2 flow rate of 2.5 ml/min. Freon-113® retained 74% of the diesel fuel. FC-77 and FC-72 retained 46% and 35% respectively of the diesel fuel. When FC-77 was purged with a liquid CO_2 flow rate of 0.7 ml/min the retention rate improved to 85%.

In stage four, FC-77 was chosen as the collection solvent over FC-72 because of its slightly higher retention of hydrocarbons. A sand sample spiked with 100 mg/kg diesel fuel was extracted off-line using 0.5 mL/min supercritical CO_2. The absorbance was measured by comparing the extract to FC-77. When FC-77 was used as the collection solvent, a negative absorbance was obtained in the 3050 cm^{-1} region of the infrared spectrum (the reference IR cell contained a higher concentration of a component than the sample cell containing the extract). A volatile component of the solvent had apparently been purged out by the CO_2 during the extraction. A 3M technical representative indicated that this volatile component could be contamination resulting from a methanol wash used in the production process of the Fluorinert® solvent.

A 100 mL volume FC-77 was distilled for thirty minutes. The absorbance of the distilled FC-77 was measured relative to FC-77 that had not been distilled. After distillation, a large negative peak was obtained that extended over the 2900 to 3100 cm^{-1} region of the

spectrum. It was concluded from this result that the volatile component contamination and a portion of the hydrocarbon background contamination were distilled out of the solvent. Distilled FC-77 was used as the collection solvent in an off-line extraction using CO_2 at 0.500 mL/min of sand and Kaolin blank samples When the absorbance of the extract was measured using distilled FC-77 for background correction, a flat baseline was obtained without an interfering negative peak. Sand samples spiked with 1000 mg/kg diesel fuel were extracted using the distilled FC-77. The spiked concentration recovery was 85%. It is concluded from this data, that FC-77 can be used as the collection solvent for this method.

Optimization of Extraction Parameters

The goal of this stage of the method development was to optimize the extraction parameters (Tables 1&3) so that this method could be used with as broad a spectrum of environmental matrices and hydrocarbon mixtures as possible. Due to the lack of standard reference materials (SRMs) with known "native" TPH concentrations, spiked samples were used in the development of this method. Using the recovery of spiked analytes to prove quantitive extraction of "native" analytes is an uncertain comparison method. There is no way of determining how spiked compounds compare to native pollutants in their interactions or absorptive qualities that result from long term association with a matrix. This work attempted to approximate matrix absorptive interactions by tumbling at a rate of 30 revolutions per minute diesel spiked Kaolin samples (porcelain clay) for approximately 24 hours. Kaolin is a highly absorptive, fine particle matrix with a high surface area. By tumbling a spiked Kaolin sample these characteristic qualities would enhance the absorbance of the spiked compounds. It was speculated that tumbling agitation over an extended period of time would be a more realistic approximation of a "real world" environmental sample than a sample that has been spiked and immediately extracted. Both spiking techniques were used to investigate the ability of SFE to yield quantitative recovery of petroleum hydrocarbons. Representative results from each approach are discussed below.

Spiked samples (immediate extraction)

The initial evaluation of extraction parameters was conducted with the aid of statistical experimental design software (Design-Ease®). Two Plackett-Burman designs were used to screen the effects of the major extraction parameters (see Tables 1&3) using Freon-113® as the collection solvent. A Plackett-Burman experimental design is a special class of fractional factorial design. This design was used to screen variables for further study by isolating strong main effects. Interactions between variables were not considered.

Sand was the matrix throughout the first Plackett-Burman experimental design. All samples were spiked with a 100 mg/kg TPH mixture consisting of 33% isooctane, 24% xylenes, and 42% hexadecane, by weight. As Table 2 shows, TPH recoveries were high throughout most of the range of conditions. This demonstrates the ease with which hydrocarbons can be extracted when matrix interactions are minimal.

In the second Plackett-Burman in which Kaolin and sand were the variables, the matrix was indicated as a main effect (see Table 4). When Kaolin was the matrix a mechanical problem was discovered during the extraction . Due to the small partical size of this matrix, periodic blockage of the extraction vessel frits resulted in fluctuation of the CO_2 flow rate.

This fluctuation resulted in unacceptably low precision with replicate extractions (53%-120%). A steady vigorous CO_2 flow rate was obtained when a paper cartridge containing the Kaolin was extracted. A paper cartridge was made out of folded filter paper into which the Kaolin was directly weighed. The paper was folded and rolled so that the cartridge could fit into the extraction chamber. Samples of 2 g of Kaolin in paper cartridges were spiked to a 1000 mg/kg concentration of diesel fuel and extracted immediately with approximately 0.7 mL/min CO_2 (400 atm, 60°C, 10 min. static, 15 min. dynamic) using FC-77 as the collection solvent. Recoveries of 80%-85% were obtained. A higher pressure was needed in these extractions to improve the extraction effeciency of the higher molecular weight components of diesel fuel.

Table 1. Plackett-Burman #1*

Factors	Positive Version of Factor	Negative Version of Factor	units
Mass of sample	5	1	Grams
Pressure	360	150	Atmospheres
Oven temperature.	60	35	Degree-C
Type of extraction	Dynamic (Dyn)	Static	
Equilibrium time	10	5	Minutes
Extraction time	20	10	Minutes
Orientation of extraction cell	Vertical (Vert)	Horizontal (Horz)	

* All samples were spiked to a 100 mg/kg concentration of the TPH mixture. Samples were extracted using a 5 mL extraction vessel and a 600 mm length of 32 micron ID fused silica restricter. Initial equilibrium time was a static step prior to the dynamic extraction period.

Table 2. Plackett-Burman #1 Results

	run order	1	2	3	4	5	6	7	8
	Standard Order	8	3	5	7	1	4	6	2
Factors	Units								
Mass of sample	grams	1	1	1	5	5	5	5	1
Pressure	Atmospheres	150	150	360	360	360	150	150	360
Oven temperature	Degree-C	35	60	35	35	60	35	60	60
Type of extraction		Static	Dyn	Static	Dyn	Static	Dyn	Static	Dyn
Equilibrium time	Minutes	5	10	10	5	10	10	5	5
Extraction time	Minutes	10	10	20	10	10	20	20	20
Orientation of extraction cell		Horiz	Vert	Vert	Vert	Horiz	Horiz	Vert	Horiz
Recoveries	Percent	66.5	66.6	137	76	84.9	84.8	97.6	80.4

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Table 3.   Plackett-Burman #2*

Factors	Positive Version of Factor	Negative Version of Factor	Units
Pressure	360	150	Atmospheres
Oven temperature	60	35	Degrees-C
Equilibrium time	5	10	Minutes
Extraction time	20	10	Minutes
Mass of sample	1	3	Grams
Type of extraction	Dynamic (Dyn)	Static	
Matrix of sample	Kaolin	Sand	
Orientation of extraction cell	Vertical (Vert)	Horizontal (Horz)	

* All samples were spiked to a 100 mg/kg concentration of the TPH mixture. Samples were extracted using a 5 mL extraction vessel and a 600 mm length of 32 micron ID fused silica restricter. Initial Equilibrium time was a static step prior to the extraction period.

Spiked, Tumbled Samples (delayed extractions)

Thirty grams of Kaolin was spiked with 3 mL of 5000 mg/L diesel standard to give a 500 mg/kg concentration. This sample was tumbled at a rate of 30 revolutions per minute for approximately 24 hours. Two gram aliquots of this sample were extracted off-line using approximately 0.7 mL/min supercritical CO_2 (400 atm, 60°C) using FC-77 as the collection solvent. The initial static step was 10 minutes followed by a dynamic step of 15 minutes. Using these extraction conditions the best recoveries achieved were 62%. Pressure was increased to 420 atm. and the temperature of the oven was decreased to 40°C to achieve a greater supercritical fluid density. The liquid CO_2 flow rate was increased to approximately 0.8 mL/min. The recoveries did not change appreciably. Maintaining the same pressure the extraction oven temperature was increased to 100° C. This also did not significantly change the recoveries of the diesel fuel. It was thought that possibly water could displace the spiked hydrocarbons from the Kaolin and allow them to be swept out by the supercritical CO_2 and into the collection solvent (7). Water was added to the extraction chamber prior to an extraction in three different cases in 200 uL, 300 uL and 1 mL volumes. Recoveries decreased as the volume of water increased.

Method validation is in progress and the data is not available at this time. Validation will consist of detection limit studies, performance comparision with Soxlet, sonication, and Soxtec® extractions and precision studies involving several soil matrices.

Summary

Quantitative extraction and analysis of petroleum hydrocarbons was demonstrated by immediate extraction of spiked samples. Because of the limitations that are inherent to spiked samples in estimating recoveries of native components spiked samples were tumbled for 24 hours. This was to allow greater mixing and enable the matrix to absorb the spiked compounds. Some general comments can made from the development of this method:

1) Fluorinert® FC-77 provides an adequate solubility limit for this application and with pre-extraction distillation has an acceptably low hydrocarbon background contamination level.

2) Though the approximate limit of hydrocarbon solubility in FC-77 is 5000 mg/L, lower molecular weight hydrocarbons are more soluble than higher molecular weight hydrocarbons. This should be taken into consideration when extracting higher molecular weight hydrocarbon mixtures such as motor or crude oil.

3) When the matrix interaction with the analytes of interest is minimal, as in the case of sand and immediatly extracted spiked samples, recoveries can be quantitatively high. When the matrix interaction with analytes are increased, as with the tumbled spiked samples, extraction of petroleum hydrocarbons is less efficient and might be improved by using higher pressures than those explored in this study.

ACKNOWLEDGEMENTS

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Table #4. Plackett-Burman #2 Results*

run order		1	2	3	4	5	6	7	8	9	10	11	12
Standard Order		9	1	6	2	4	7	3	11	12	5	8	10
Factors	**Units**												
Pressure	Atmosphere	360	360	150	150	150	360	360	360	150	150	360	150
Oven temperature	Degree-C	60	60	35	60	60	35	35	35	35	35	60	60
Equilibrium time	Minute	10	5	5	10	5	5	10	10	5	10	5	10
Extraction time	Minute	10	20	20	10	20	10	20	20	10	10	10	20
Mass of sample	Gram	1	3	1	3	3	3	1	3	1	3	1	1
Type of extraction		Static	Dyn	Dyn	Dyn	Static	Static	Dyn	Static	Static	Dyn	Dyn	Static
Type of matrix		Sand	Kaolin	Sand	Sand	Sand	Sand	Sand	Kaolin	Kaolin	Kaolin	Kaolin	Kaolin
Orientation of extraction cell		Horiz	Horiz	Horiz	Horiz	Vert	Vert	Vert	Horiz	Horiz	Vert	Vert	Vert
Recoveries	Percent	152	40	154	68	86	38	164	37	76	59	102	150

*These recoveries are not background corrected by subtraction of native contaminates from sand or Kaolin. Kaolin has been found to have a hydrocarbon contamination of up to 40 mg/kg by other extraction methods (7).

59 APPLICATION OF SUPERCRITICAL FLUID EXTRACTION OF DIOXINS/FURANS FROM SOIL AND PUF

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The supercritical fluid extraction of dioxins/furans from soil and polyurethane foam plug (PUF) is always interesting in the environmental application.

In this study, dioxins/furans spiked on soils or PUFs will be evaluated. The soils or PUFs will be extracted with Suprex supercritical fluid extractor using carbon dioxide. The final extract will be analyzed by a GC/MS.

The extract can also be directly transferred from the supercritical fluid extractor to a GC/MS for the purpose of reaching lower detection limits.

For both cases, five concentrations of target compounds will be evaluated to determine the detection limit and linearity of the entire system.

60 THE APPLICATION OF SUPERCRITICAL FLUID CHROMATORAPHY TO THE ANALYSIS OF HERBICIDES AND PESTICIDES IN TCLP EXTRACTS

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ABSTRACT

Supercritical fluid chromatography with electron capture detection was used to consolidate two hazardous waste methods for pesticides and herbicides, in TCLP extracts, into a single cost effective protocol.

Herbicide and pesticide analysis of TCLP extracts of hazardous waste is currently performed using SW-846 Methods 8150 and 8080 respectively. Both methods utilize different sample preparation techniques. Method 8150 incorporates ether extraction, caustic hydrolysis and diazomethane esterification, while a selection of different preparatory methods can be utilized for Method 8080. The overall methodology required for the analysis produces a turnaround time of up to two days, for a group of 6 to 8 samples.

A single SFC-ECD analytical method, with a consolidated sample preparation procedure, can be applied to the analysis of both the herbicides and pesticides in TCLP extracts. The technology is rugged enough to handle the compound type distribution of both the analytes and the typical interferences found in hazardous waste samples. Chromatograms, response factors, and the SFC mass spectroscopic data used to confirm the identity of the peaks will be presented. The application of SCF-ECD technology to the consolidation of these methods clearly reduces the costs and sample turnaround times.

INTRODUCTION

Pesticides and herbicides are analytes of major concern to regulatory agencies. The analysis of the pesticides Lindane, Heptachlor, Chlordane, Endrin, Methoxychlor, and Toxaphene, coupled with the chlorophenoxy herbicides 2,4-D and Silvex, are now required for TCLP extracts. Two different methods are used for these analytes: SW-846 Method 8080 for the pesticides and Method 8150 for the herbicides. The sample preparation procedures for both methods are significantly different, labor intensive, and hazardous. Both methods require multiple separatory funnel extractions using ethyl ether or methylene chloride. Increasingly health, safety and environmental concerns are being raised from the usage and disposal of these and other hazardous solvents. Also of prime concern is the usage of diazomethane as a methylating agent for the chlorophenoxy acid herbicides. The Merck Index, Edition 10 lists diazomethane as a very toxic, insidious poison, that may explode upon heating or contact with rough glass surfaces.

PURPOSE

The purpose of this work is to develop a single streamlined method utilizing SFC-ECD, which can determine both pesticides and herbicides in TCLP extracts. The simplification of the extraction, hydrolysis and derivatization steps will increase analyst safety, reduce hazardous solvent usage, and significantly reduce the analytical costs and sample turnaround time.

SCF THEORY

The molecules of a liquid are bonded by electrostatic forces. The energy required to break these associative bonds, as the liquid becomes a vapor, is known as the heat of vaporization. When a liquid, in equilibrium with its vapor, is sealed in a tube and heated, the pressure of the closed system rises and the liquid's density and heat of vaporization decrease. When the associative forces reach zero, the liquid and gas phases become one. This temperature and the corresponding pressure are unique for each liquid and termed the critical constants, which for CO_2 are $31^{\circ}C$ and 73 atm., respectively.

A supercritical phase has the solvency of a liquid. It can dissolve, and thus partition the analyte(s) between the mobile and stationary phase. It has the low viscosity and high diffusion coefficient of a gas, resulting in low column pressure drops and rapid mobile/liquid phase equilibration. The chromatographic efficiencies approach those of GC. The technique is not thermally driven thus it is also possible to analyze thermally labile and non-volatile materials. A supercritical fluid, therefore combines the best qualities of a gas and liquid in a single process. Carbon dioxide is the most popular material used for extraction because of its low critical temperature, inertness, safety and ease of purification.

The solvency of the mobile phase can vary and is a function of its density. Density programming has the same effect on an SFC separation as temperature and solvent composition have on GC and LC. When utilizing density programming to improve a separation, the system controller must vary the pressure to linearize the density.

INSTRUMENT DESCRIPTION

The supercritical fluid instrumentation used for this work was purchased from the Lee Scientific Company, the mass spectrometer from the Finnigan Company, and the electron capture detector from the Hewlett Packard Company. Two instruments were used for the study and were configured as follows:

Instrument #1 SFC-MS

Lee Scientific Model 600 SFC pump, oven and controller interfaced to a Finnigan INCOS-50 Mass Spectrometer via a heated transfer line. Transfer line manufactured by Lee Scientific.

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Restrictor - Fifty micron fused silica frit restrictors producing a carbon dioxide linear velocity of 0.6 cm/sec at 75°C and 75 atm were used for all SFC-MS work. Restrictors were purchased from Lee Scientific.

Instrument #2 SFC-ECD

Supercritical Fluid Chromatograph - Lee Scientific Model 600 SFC pump and controller interfaced to a Hewlett Packard 5890 GC equipped with an ECD detector.

Restrictor - Fifty micron fused silica frit restrictors producing a carbon dioxide linear velocity of 1.8 cm/sec at 75°C and 75 atm were used for all SFC-ECD work.

Liquid Carbon Dioxide - Supercritical grade. The tank must contain a dip tube to deliver liquid product (Scott Specialty Gases).

EXPERIMENTAL PROCEDURE AND DATA REVIEW

EQUIVALENCY SUPPORT DATA

Analyte Recovery from The Empore
Solid Phase Disk

In order to evaluate the performance of the method, initial studies were done using blank TCLP extraction fluid, and extracts from a variety of sample matrices. Recovery data was generated for the pesticides, herbicide acids, and their respective methyl esters. The Empore disk extraction, hydrolysis, and esterification efficiencies were determined. Recovery data is presented in Figure 1. The analyte recovery range of 59% to 117% shows that the Empore Solid Phase disk is an acceptable means of analyte concentration.

Included in the study were sample types such as: filter press cake, oil dry + gas, hydrocarbon contaminated soil, dimethyl disulfide spill debris, terminal plant sludge, grease, spent carbon filter media, and others.

Analyte Chromatography and Mass
Spectrometric Verification

In order to determine that no analyte alteration, reaction or modification occurred during the supercritical fluid chromatographic procedure, the chromatograph was linked to a mass spectrometer for spectral confirmation. The column selected for this work was a Phenyl-5, 10 meter, 50 micron ID, having a 0.25 micron film thickness. A Finnigan INCOS-50 was used for the confirming spectrometer. Figures 2 and 3 show the SFC-MS total ion chromatogram and library matched spectra produced by the run. The NIST library searches for all of the analytes produced library match factors of 800+. The data show that no analyte alteration, reaction or degradation occurred in the system.

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EQUIVALENCY METHOD DATA

CWM Combined Herbicide - Pesticide Sample Preparation

The first part of the method involves the two part streamlined sample preparation procedure. Both procedures are compared with the corresponding SW-846 methods in Figures 4 and 5.

1 - One hundred mL of TCLP extract, including the surrogate, is made alkaline using a KOH solution. The extract is stirred at $70^{\circ}C$ for one hour. The extract is reacidified to a pH of 2 and passed through an Empore solid phase extraction disk, which removes the herbicide acids. The acids are eluted from the disk with methanol. Methane sulfonic acid is added to the extract and the extract solution is heated for one hour to esterify the acids and reduce the solution volume.

2 - A second 250 mL volume of TCLP extract, including surrogates, is neutralized with KOH and passed through a second Empore solid phase extraction disk. The pesticides are eluted using acetone. The extract solution volume is reduced using nitrogen blowdown.

The two extract solutions are combined, Aldrin is added as an internal standard and the analysis is performed on the combined extract.

SFC-ECD Chromatography

An SFC-ECD chromatogram of the herbicide methyl esters and pesticides is shown in Figure 6. All of the peaks are sharp, baseline resolved and of approximate equal intensity.

Initial studies were performed using a mass spectrometer but to simplify the method even further, final studies were done using the ECD detector. All work was done under isothermal, density programmed chromatographic conditions. They are as follows:

Oven temperature $100^{\circ}C$ isothermal
Initial density   0.13 (equivalent to 74 atm)
Hold   2 minutes
Ramp at .006 to   0.42 (equivalent to 178 atm)
Ramp at 0.2 to   0.75(equivalent to 390 atm)
Final Hold Time   7 minutes

Response factor, relative retention time and method detection limits are listed in Figure 7.

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EPA Equivalency Study Data Generation

To begin formal EPA Equivalency spike recovery studies have been done on a wide variety of sample types. To this date six samples have been completed in duplicate. The six sample types include incinerator ash, wastewater treatment sludge, plating filter cake, soil contaminated with 1,1,1-TCE, grease/oil debris, and copper reclamation tailings.

Recovery data from these six sample types is listed in Figure 8. The data quality is high and meets formal EPA Equivalency requirements.

CONCLUSIONS

1 -   A single SCF method requiring less than 5 hours has been developed for the analysis of both herbicides and pesticides in TCLP extracts, at detection levels well within the regulatory range.

2 -   The data generated shows that it meets the EPA's formal Equivalency criteria.

3 -   The use of ether and methylene chloride is eliminated. No explosive derivatization agents are used, and general solvent use is reduced by a factor of 5.

4 -   The analyte recovery and SFC-MS support data show that there is no chemical reactivity between the analytes and the supercritical phase.

FIGURE 1

EQUIVALENCY SUPPORT DATA

% RECOVERIES

	Extract 1	Extract 2	Extract 3	Extract 4	Extract 5	Extract 6	Extract 7	Extract 8	Extract 9	Extract 10	AVERAGE
LINDANE	91	92	92	91	94	92	94	92	92	91	92
HEPTACHLOR	55	56	59	49	58	60	65	63	60	62	59
g-CHLORDANE	76	80	105	88	73	75	76	77	75	71	80
a-CHLORDANE	82	84	108	92	78	80	81	80	78	77	84
ENDRIN	99	98	110	100	103	93	102	90	99	98	99
METHOXYCHLOR	85	88	114	96	93	87	106	93	96	89	95
TOXAPHENE	81	77	148	126	123	140	139	102	115		117
2,4-D	98	100	85	118	91	88	95	106	90	99	97
SILVEX	55	56	93	68	51	61	79	84	95	99	74
TCMX(SURR)	54	57	61	47	50	79	57	51	48	48	55
DBC(SURR)	101	102	124	133	98	95	99	95	96	92	103
2,4,5-T(SURR)	87	81	87	110	88	107	121				97
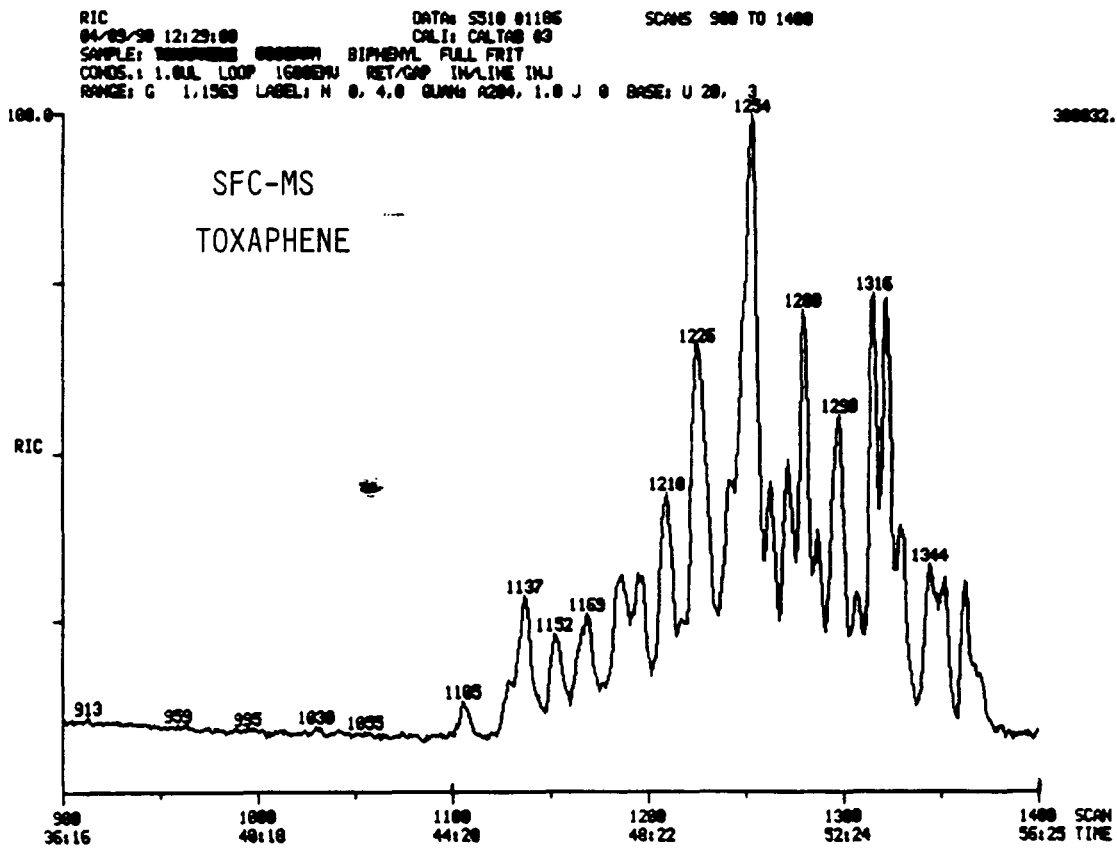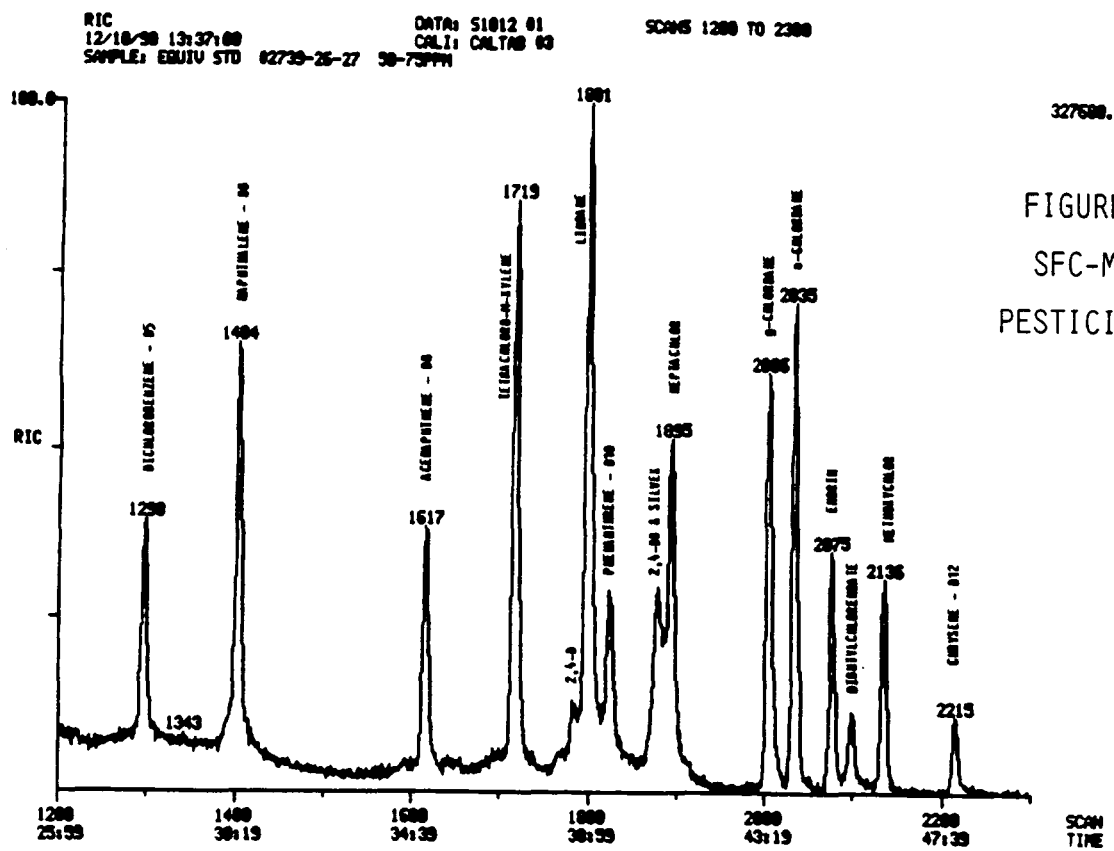
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FIGURE 2
SFC-MS
PESTICIDES

SFC-MS
TOXAPHENE

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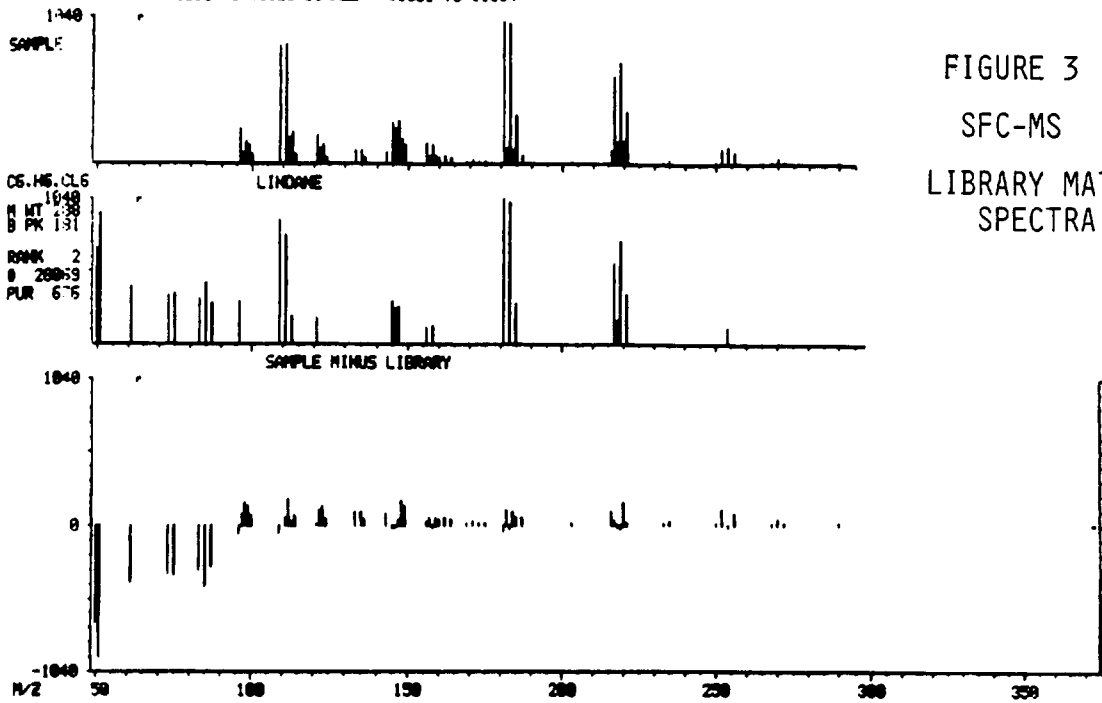
FIGURE 3

SFC-MS

LIBRARY MATCH
SPECTRA

II-133
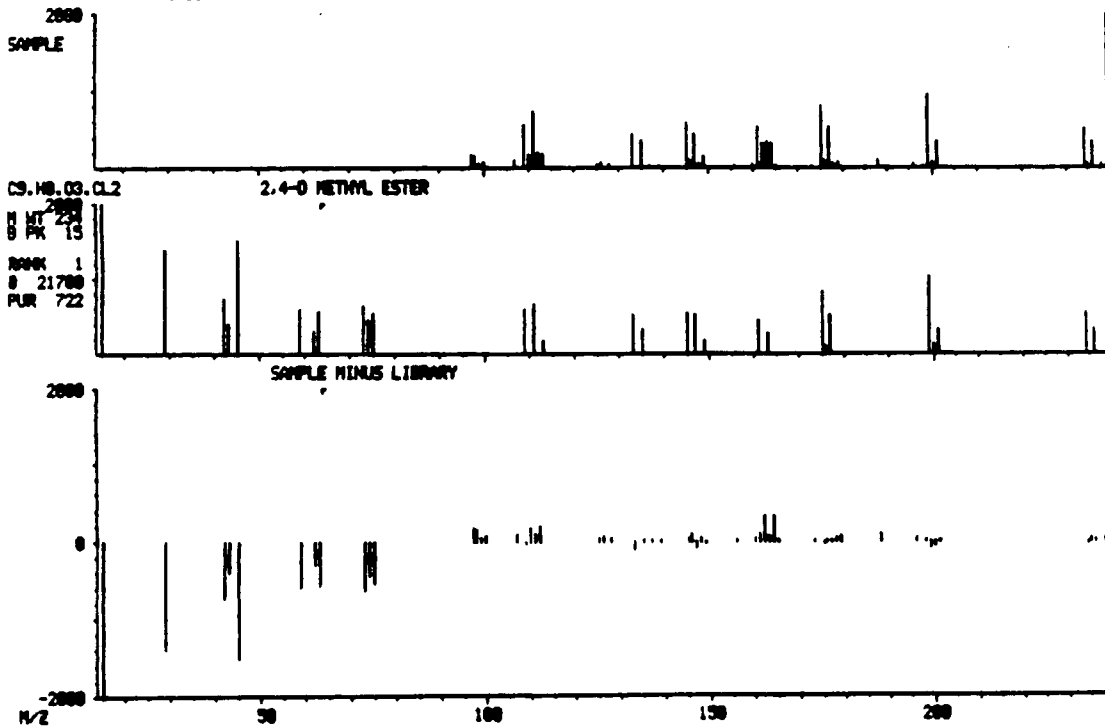
FIGURE 4

FLOWCHART COMPARISON BETWEEN
EPA METHOD 8150 and CWM HERBICIDE METHOD
FOR TCLP EXTRACTS

<u>EPA METHOD 8150</u>   <u>CWM METHOD</u>

1) ETHER EXTRACT AT pH=2   NONE REQUIRED
      1 time at 150 mL
      2 times at 50 mL

2) HYDROLYSIS   TCLP EXTRACT HYDROLYSIS
      2 mL of 37% KOH   2 mL 37% KOH

3) ETHER EXTRACT AT pH=11   NONE REQUIRED
      2 times at 20 mL

4) ETHER EXTRACT AT pH=2   NONE REQUIRED
      1 time at 20 mL
      2 times at 10 mL
      2 mL of (1:3)H_2SO_4

                                      EMPORE EXTRACT AT pH=2
                                         21 mL of METHANOL
                                         2 mL of (1:1)H_2SO_4

                                      EMPORE ANALYTE ELUTION
                                         15 mL of METHANOL

5) EXTRACT TRANSFER TO K-D   NONE REQUIRED
      1 time at 30 mL

6) INITIAL K-D

7) MICRO K-D

8) DIAZOMETHANE ESTERIFY   MSA ESTERIFICATION
                                         100 1L of MSA

9) GC-ECD ANALYSES   SFC-ECD ANALYSES
                                      COMBINED EXTRACT
                                      (See Figure 6)

FIGURE 5

FLOWCHART COMPARISON BETWEEN
EPA METHOD 8080 and CWM PESTICIDE METHOD
FOR TCLP EXTRACTS

<u>EPA METHOD 8080</u>	<u>CWM METHOD</u>
1) SEPARATORY FUNNEL EXTRACT 3 times at 60 mL MeCl$_2$ NEUTRAL pH	EMPORE DISK EXTRACT 20 mL ACETONE NEUTRAL pH
2) K-D TO 5 mL	ANALYTE ELUTION 15 mL ACETONE
3) NITROGEN BLOWDOWN	NITROGEN BLOWDOWN
4) SOLVENT EXCHANGE 9 mL HEXANE	NONE REQUIRED
5) GC-ECD ANALYSES	SFC-ECD ANALYSES COMBINED EXTRACT

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AN A:029E4820.BNC
RUN # 168   MAY 13, 1991   10:19:24
START

FIGURE 6
SFC-ECD
CHROMATOGRAPHY

10.492

11.381   11.142

29.185 2,4-D Methyl Ester

30.957 Tetra-Chloro-M-Xylene (Surr)

31.923 Silvex Methyl Ester

33.015 2,4,5-T Methyl Ester (Surr)

34.093

34.778 Lindane

38.394 Heptachlor

39.722

40.849 Aldrin (internal Std)

42.898 Gamma-Chlordane

43.899 Alpha-Chlorda

44.720

45.572 Endrin

46.806

48.084 Dibutylchlorendate (Surr)

48.818 Methoxychlor

TIMETABLE STOP

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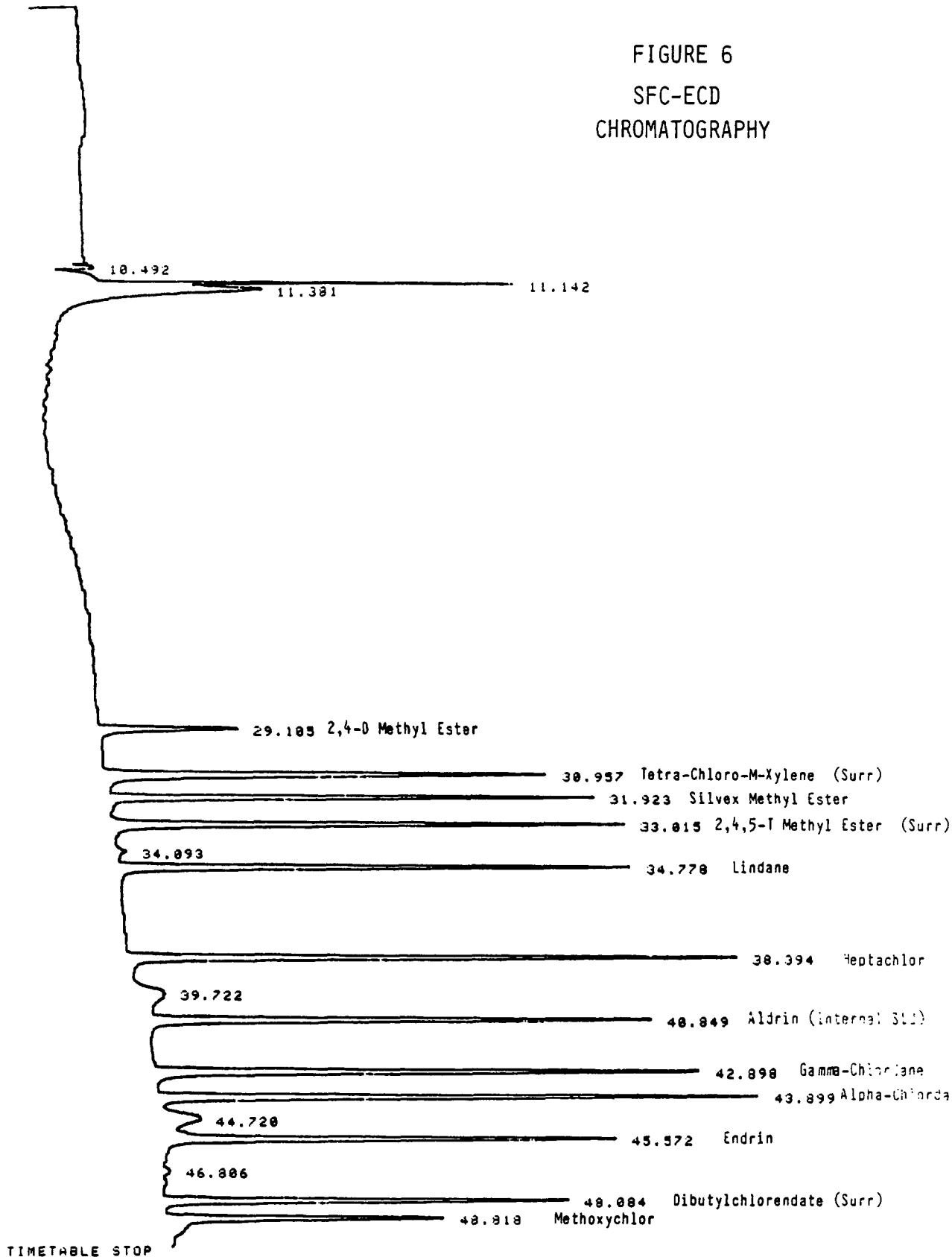
FIGURE 7

RESPONSE FACTORS , RELATIVE RETENTION TIMES
AND METHOD DETECTION LIMITS(NG/ML)

TARGET COMPOUNDS

	RF	**RRT**	**MDL**
2,4-D Methyl Ester	.267	.712	10
Silvex Methyl Ester	.949	.781	10
Lindane	.981	.851	0.5
Heptachlor	1.20	.939	0.2
g-Chlordane	1.13	1.05	0.2
a-Chlordane	1.24	1.07	0.2
Endrin	.992	1.11	1.0
Methoxychlor	.525	1.19	0.6
Toxaphene(4 Peaks)	.140	1.13	75
		1.25	
		1.26	
		1.31	

SURROGATES

2,4,5-T Methyl Ester	.885	.808	NA
Tetra-chloro-m-xylene	1.06	.758	NA
Dibutylchlorendate	.866	1.17	NA

INTERNAL STANDARD 0.5 PPM ALDRIN

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FIGURE 8
TCLP EXTRACT SPIKE RECOVERY DATA
DUPLICATE RESULTS

	Wastewater Treatment Sludge		Soil Cont. with 1,1,1-TCE		Plating Filter Cake		Incinerator Ash		Grease/Oil Debris		Copper Reclaimation Tailings		AVERAGE
LINDANE	94	99	106	98	94	94	99	97	76	71	80	90	92
HEPTACHLOR	86	93	88	68	76	79	75	84	76	98	77	84	82
g-CHLORDANE	92	94	96	78	89	88	86	92	86	82	80	84	87
a-CHLORDANE	92	95	100	84	90	88	90	95	90	91	78	78	89
ENDRIN	111	106	108	92	100	98	98	98	88	89	78	86	96
METHOXYCHLOR	108	108	121	110	110	110	104	104	102	100	92	100	105
TOXAPHENE	121	126	118	90	59	104	108	102	78	128	84	99	101
2,4-D	93	96	48	82	94	84	97	84	76	83	94	83	84
SILVEX	86	81	92	66	85	88	86	94	81	93	84	86	85
TCMX(SURR)	75	87	86	68	59	70	76	78	82	84	76	88	77
DBC(SURR)	101	102	110	100	100	100	104	102	94	90	88	94	98
2,4,5-T(SURR)	83	96	38	75	90	93	95	94	81	88	90	91	84

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PROBLEM SOLVING IN THE ORGANIC EXTRACTIONS LABORATORY: HERBICIDES

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ABSTRACT

In the commercial laboratory, it is often difficult to set aside time and resources to improve and optimize execution of acceptable methods without a dedicated "special projects" group. At IEA, Inc. - New Jersey, method development for sample preparation is carried out by the Organic Extractions Group as a whole, from experimental design through data interpretation, within the normal flow of production laboratory work. This problem-solving process, with supporting data, including matrix spike and surrogate recoveries of real samples, is illustrated for the extraction of herbicides.

INTRODUCTION

The "routine" extraction of samples for herbicide analysis by SW846 methods has presented difficulties for the laboratory. Problems including the use of the reagents diazomethane and ethyl ether in a production environment, the inconsistency of spike and surrogate recoveries, and the elaborate sample manipulations required, result in a procedure that is time-consuming and frustrating. IEA, Inc. - NJ has optimized an existing trial USEPA method[1] which addresses the compounds 2,4-D, Silvex, and 2,4,5-T. We present here results of this optimized IEA method for water and leachate samples and show evidence that it is adaptable to a variety of matrices.

METHOD DEVELOPMENT

Preliminary trials using the above mentioned USEPA method as written yielded poor surrogate and spike recoveries. However, we were interested in pursuing optimization of this method because of the many advantages it offered. A general meeting of the entire extractions staff, QA, and laboratory management was called to organize a systematic approach for method optimization. Data from extractions using the trial USEPA method were discussed and all agreed upon the next course of action, which was a limited experiment to be conducted along with normal extraction batches. The group reconvened the next

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week to discuss the results of the experiment. This process evolved into an on-going program of weekly meetings followed by limited experiments, which resulted in method definition and refinement.

EXTRACTION OF HERBICIDES FROM AQUEOUS SAMPLES

Poor performance (shown in Table 1.0) of the trial USEPA method forced critical examination of the variables displayed in Table 2.0.

TABLE 1.0

TYPICAL SURROGATE AND SPIKE RECOVERIES USING USEPA TRIAL METHOD[1]				
SAMPLE	2,4-DB SURR.	2,4-D	SILVEX	2,4,5-T
LEACHATE 1	59			
LEACHATE 2	73			
LEACHATE 3	78	60	66	49
LEACHATE 4	97	52	54	45
LEACHATE 5	100	36	59	91
LEACHATE 6	30			
LEACHATE 7	54			

TABLE 2.0

VARIABLES INVESTIGATED FOR OPTIMIZATION OF HERBICIDE EXTRACTION

   1.0   Acid-Washing of <u>all</u> glassware and materials
   2.0   pH (2, 3, <2)
   3.0   Use of microsnyders
   4.0   Concentration of extract to dryness prior to esterification
   5.0   Use of Na_2SO_4 column cleanup
   6.0   Presence of acetic acid in TCLP leachates
   7.0   Use of BCl_3 versus BF_3
   8.0   Temperature for esterification
   9.0   Methylene Chloride volume versus sample volume
  10.0   Alkaline hydrolysis required?

We found that acid-washing of all equipment was most crucial to the success of the extraction, and that aqueous samples should be taken to pH 1. Neither use of microsnyders nor concentration to dryness improved recoveries. Also, we found Sodium Sulfate column clean-up to be unnecessary. Since leachates performed better than "plain" aqueous samples, we investigated the addition of acetic acid to the water samples, but the recoveries were unaffected. Best recovery occurred when esterification was carried out with BF_3 at $60°$ C. We are still optimizing sample and solvent volumes, and investigating the necessity of the alkaline hydrolysis. The IEA method is summarized in Table 3.0:

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TABLE 3.0

METHOD FOR HERBICIDE EXTRACTION OF WATER SAMPLES
1.0 Acid wash all glassware and materials
2.0 Adjust pH of sample to < 2.0
3.0 Extract 500 ml sample three times with 60/40/40 ml methylene chloride
4.0 Concentrate extract to 4.0 ml
5.0 Solvent exchange with hexane
6.0 Concentrate extract to 1.0 ml
7.0 Esterify with BF_3 at 60^0 C for 10 minutes
8.0 Dilute to 5.0 ml with hexane
9.0 Add 10 ml 7% Na_2SO_4, vortex
10.0 Collect 1.0 ml hexane extract for analysis

We tested this IEA method for extraction of the most recent USEPA WS series proficiency samples; the results are shown in Table 4.0.

TABLE 4.0

PROFICIENCY RESULTS: WS027			
ANALYTE	**REPORTED**	**TRUE**	**ACCEPTANCE LIMITS**
2,4-D	45.9	46.3	15.1 - 59.1
SILVEX	17.9	18.1	7.47 - 24.4

The majority of aqueous herbicide analyses requested are for TCLP leachates; surrogate recovery results for leachate blanks and samples are presented in Figures 1.0 and 2.0; spike and surrogate recovery data are presented in Table 5.0. Results of similar analyses of a series of spiked reagent blanks are shown in Table 6.0. Note that leached samples consistently performed better than water samples.

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TABLE 5.0

FREE ACID SURROGATE AND SPIKE RECOVERIES TCLP LEACHATES				
SAMPLE	2,4-DB	2,4-D	SILVEX	2,4,5-T
LEACH BLANK	100			
LEACH BLANK SPIKE	104	83	85	66
LEACHATE X3	106			
LEACHATE X3 MS	109	95	94	78
LEACHATE BLANK	95			
LEACH BLANK SPIKE	97	83	83	67
LEACHATE WP1	98			
LEACHATE WP1 MS	93	82	77	66
LEACH BLANK	116			
LEACH BLANK SPIKE	101	88	89	76
LEACHATE WP9	114			
LEACHATE WP9 MS	120	105	110	89
LEACH BLANK	75			
LEACH BLANK SPIKE	89	65	71	59
LEACHATE D3	78			
LEACHATE D3 MS	85	64	75	57
LEACHATE D4	94			
LEACHATE D4 MS	104	72	74	61
LEACH BLANK	85			
LEACH BLANK SPIKE	79	81	66	55
LEACHATE 191	80			
LEACHATE 191 MS	77	75	69	54
LEACHATE 380	70			
LEACHATE 380 MS	70	72	58	53

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TABLE 6.0

FREE ACID SURROGATE AND SPIKE RECOVERIES REPLICATE BLANK ANALYSIS				
SAMPLE	2,4-DB	2,4-D	SILVEX	2,4,5-T
BLANK	99			
BLANK SPIKE 1	104	61	83	49
BLANK SPIKE 2	79	44	58	29
BLANK SPIKE 3	108	67	82	51
BLANK SPIKE 4	112	53	75	38
BLANK SPIKE 5	104	60	80	42
BLANK SPIKE 6	114	68	91	53

Although there were incidents of low spike and surrogate recoveries, the results were generally good. Lower recoveries were consistent throughout a complete batch, indicating that an isolated extraction procedure, not the method, had performed poorly. The compound 2,4,5-T was the poorest performer throughout the aqueous studies, with the lowest recoveries noted in spiked reagent blanks.

EXTRACTION OF HERBICIDES IN ESTER FORM

We suspected that herbicides in various ester forms would not be converted efficiently to the methyl ester, since the alkaline hydrolysis step was omitted[4]. An extraction of reagent water spiked with the propylene glycol butyl ether ester of Silvex (Silvex PGBE) was carried out without performing an alkaline hydrolysis step. The results of this preliminary investigation are presented in Table 7.0 with an example chromatogram shown in Figure 3.0.

II-144

TABLE 7.0

PERCENT RECOVERIES OF ESTERS OF HERBICIDES (BLANK SPIKES)		
SAMPLE	**2,4-DB** **(SURR.)**	**SILVEX**
BLANK	109	
BUTYL ESTER, SILVEX		26
BUTYL ESTER, SILVEX DUP		24

The recovery of Silvex PGBE as a methyl ester was marginal, but we feel that additional development work will result in improved recoveries. Further experiments are in progress to determine the conversion efficiency of a greater variety of esters.

EXTRACTION OF HERBICIDES FROM ORGANIC MATRICES

IEA, Inc. - NJ is frequently called upon to perform the TCLP on organic matrices, but we had been unable to carry out herbicide analysis on this matrix type. We tried an approach similar to a BNA partition [3]. First, the sample is washed with a basic aqueous solution to separate all acids into the water layer. The water fraction is then acidified and extracted with methylene chloride. The methylene chloride extract is then subjected to the IEA herbicide procedure. The results presented in Table 8.0 indicate that analysis of herbicides in organic matrices is meaningful. This capability is important to clients because it permits complete sample characterization; inability to test the herbicide fraction allows potential classification of a sample as a hazard.

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TABLE 8.0

PERCENT RECOVERY OF HERBICIDES IN AN ORGANIC MATRIX				
SAMPLE	2,4-DB	2,4-D	SILVEX	2,4,5-T
BLANK	96			
BLANK SPIKE	82	64	59	52
SAMPLE 1	69	61	48	51
SAMPLE 2	96	88	54	57
SAMPLE 3	82	52	47	44

In this example:

Sample 1 -   One gram of motor oil was diluted to 10 ml with methylene chloride, spike was added during dilution.

Sample 2 -   One gram of motor oil was diluted to 25 ml with methylene chloride, spike was added during dilution.

Sample 3 -   One gram of motor oil was diluted to 25 ml with methylene chloride, spike was added directly to motor oil, prior to dilution.

EXTRACTION OF HERBICIDES FROM SOIL/SEDIMENT MATRICES

Most of our non-TCLP requests for herbicide analysis are for soils; therefore we wanted to extend the IEA herbicide procedure to soil analysis. Data from preliminary trials of the IEA method are shown in Table 9.0. Note that the soil sample showed better spike recovery than a blank sand matrix. Further development is in progress.

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TABLE 9.0

FREE ACID SURROGATE AND SPIKE RECOVERIES SOILS				
SAMPLE	**2,4-DB**	**2,4-D**	**SILVEX**	**2,4,5-T**
BLANK (SAND)	37			
BLANK SPIKE	56	52	60	93
SOIL D1	49			
SOIL D2	82			
SOIL U1	73			
SOIL U1 MS	75	98	115	91
SOIL U1 MSD	81	94	113	86
SOIL U2	77			
SOIL BK	66			
SOIL R1	98			
SOIL R2	79			

CONCLUSIONS

Because the demand for herbicide analysis fluctuates and the scope of requested analytes is limited, a method that can be performed without a period of fine-tuning required to achieve acceptable recovery is needed. The IEA method described here has the advantages of simplicity, use of routine reagents, and improved reproducible analyte recoveries. Production is doubled. Along with the development of the extraction procedure, there were many intangible benefits to working on the problem as a group. However, the ultimate success will be in the achievement of full method approval.

SUMMARY

The concept of using regular group problem-solving sessions has resulted in development of a simple, effective methylene chloride extraction for the determination of herbicides. Generally acceptable spike and surrogate recoveries of commonly requested herbicide analytes in aqueous, leachate, soil, and organic matrices were achieved. This method is easily implemented and results in increased capacity.

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FIGURE 1.0

2,4—DB Surrogate Recovery

Leach Blank/Leach Blank Spike
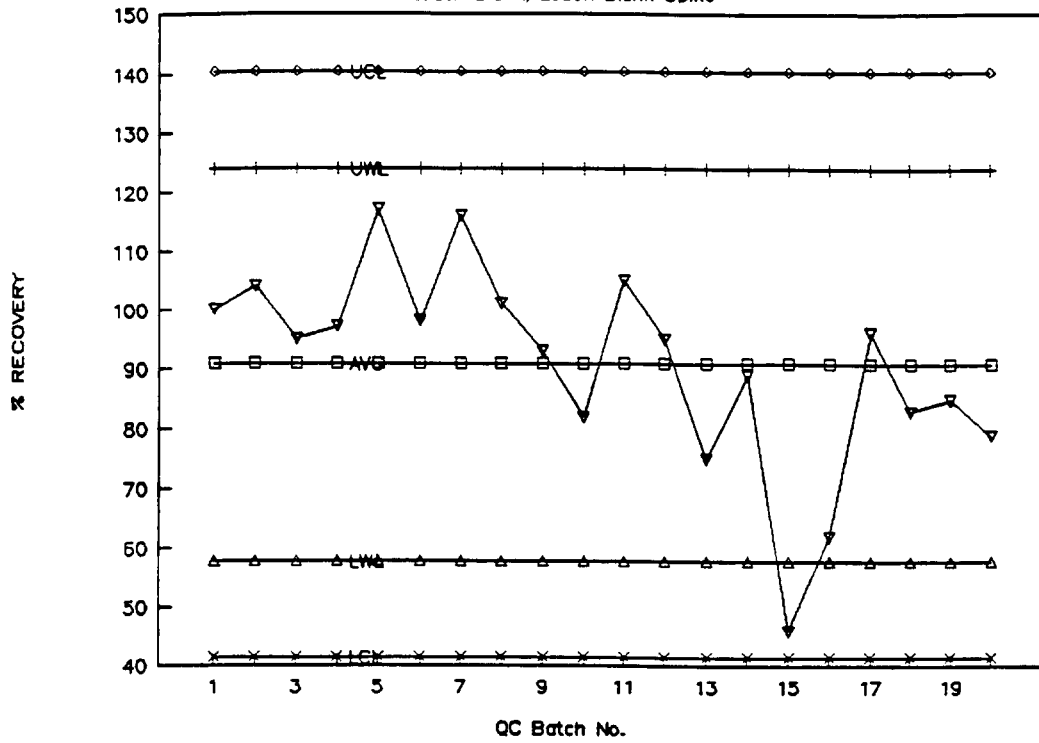
FIGURE 2.0

2,4—DB Surrogate Recovery

Sample/Sample Spike

II-149
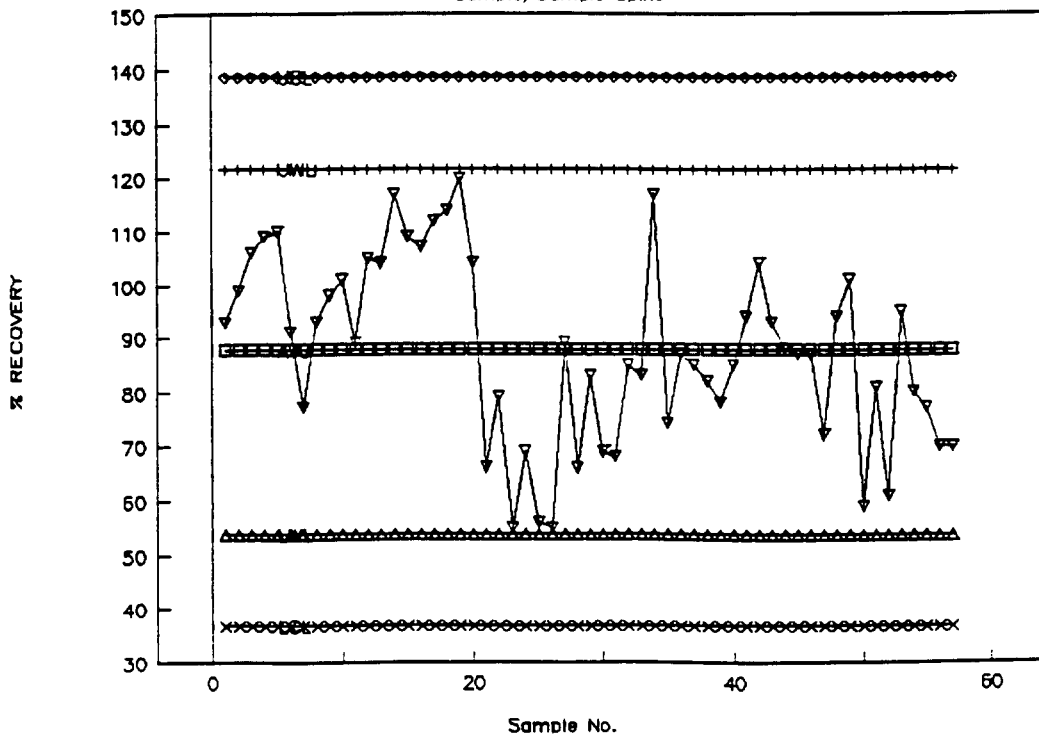
FIGURE 3

SILVEX
BUTYL ESTER

4.601

3.831

3.478

2.921

2.308
2.160
2.022

1.629

1.385

1.176
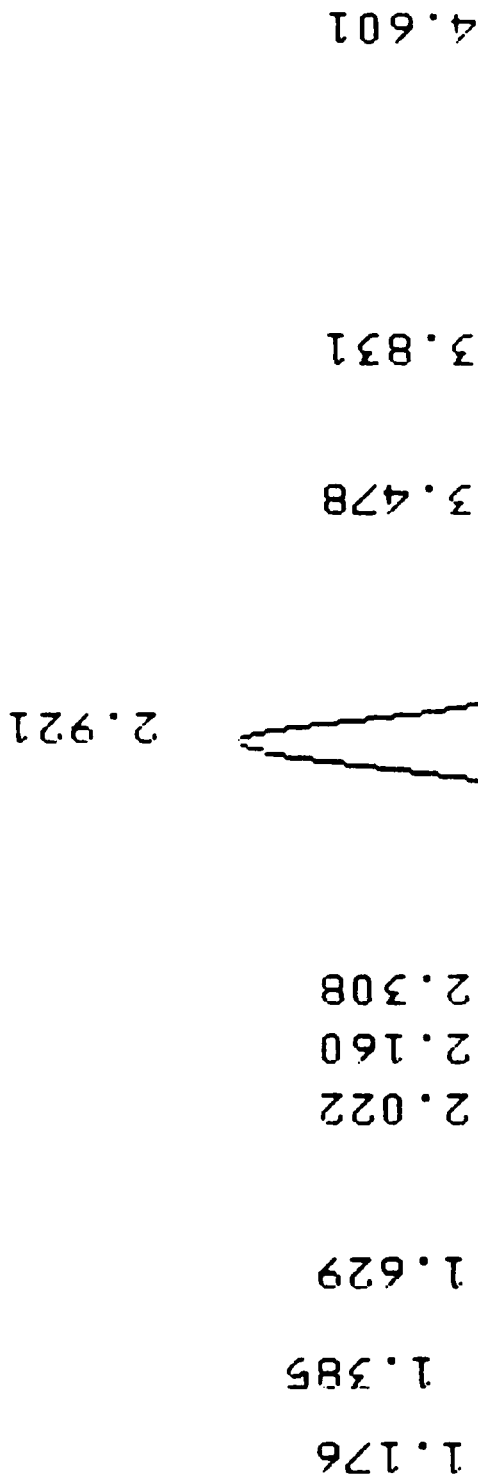
FIGURE 4

HERBICIDES

ORGANIC MATRIX

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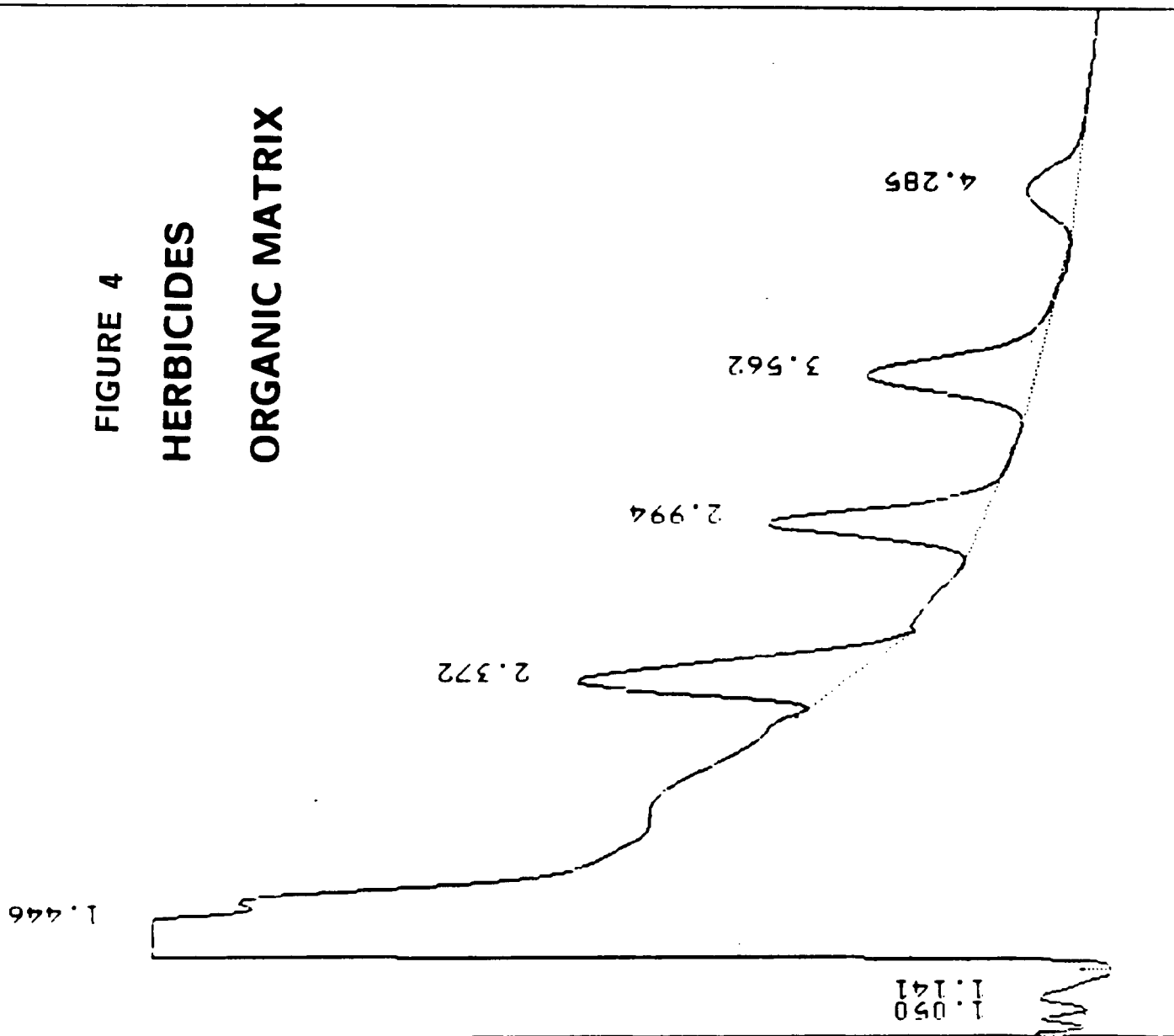
62 Infrared Microsampling for the Qualitative Analysis of Organics Extracted from Soil Samples

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Infrared spectroscopy provides a unique "fingerprint" that can often be used to identify the structure of unknown compounds.   Often spectral library searches are used to make this type of identification. The primary difficulty in determining the identity of unknowns in this manner is usually spectral contamination caused by the absorbances of components other than the target compound.   It is possible to separate many organic compounds using thin layer chromatography (TLC) techniques.   The relative elution distance can then be related to separations of standard mixtures and the structure of unknown compounds elucidated.   Many times, however, it is impossible to absolutely identify components in this manner.

Recently we have investigated the use of TLC separations combined with infrared microspectroscopy for the identification of organic compounds extracted from soil samples.   The soil extract is separated using standard TLC procedures and the resulting "spots" are analyzed both directly on the plates and after extraction with appropriate solvents.   The results of these experiments will be described and compared with GC/FT-IR measurements obtained on the soil extracts.

63 A PERFORMANCE COMPARISON STUDY OF DIFFERENT TYPES OF DEVICES FOR SOLID PHASE EXTRACTION

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ABSTRACT

Solid Phase Extraction (SPE) is rapidly becoming an alternative to separatory funnel extraction and continuous liquid-liquid extraction for the isolation of organic compounds from environmental samples. SPE can provide analytical data in a timely manner for decision-making during site inspections, remediations, and emergency removal activities. It is especially useful if there is knowledge regarding potential matrix interference at the site. SPE utilizes a compact manifold that can process multiple samples simultaneously. Solvent usage is minimized and the sample preparation can be performed rapidly. The extraction can be accomplished by using glass cartridges, plastic cartridges, or extraction disks. Characteristics of these extraction devices, including recovery, capacity, interferences, and contamination for polycyclic aromatic hydrocarbons, phenols, pesticides, and Aroclors have been compared and will be discussed. The performance results presented are data generated as part of the Superfund Contract Laboratory Program Quick Turnaround Method development and validation process.

64   STANDARD REFERENCE SPECTRA for MS/MS QUALITY ASSURANCE, PERFORMANCE EVALUATION, and PROFICIENCY TESTING: X[rf]Q TANDEM MASS SPECTROMETERS

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ABSTRACT

The collisionally-activated dissociation (CAD) of the acetone cation (m/z 58) can be used for quality assurance, performance evaluation, and proficiency testing of CAD measurements in tandem mass spectrometry (MS/MS) instruments which use rf-only multipole collision cells. The absolute branching ratios (product distributions) of the CAD fragment ions, when measured as a function of the center-of-mass collision energy E_{cm}, can provide an objective basis for quality assurance whenever MS/MS methods are used (viz., to validate how well the target thickness, ion containment efficiency, and collision energy are being controlled in various instruments).

INTRODUCTION

Tandem mass spectrometry (MS/MS) instruments which use rf-only multipole collision cells are complex ion-optical devices.[1-9] Such MS/MS instruments are denoted hereinafter by the generic symbol X[rf]Q, where Q denotes a quadrupole mass filter, [rf] denotes an rf-only multipole collision cell used for collisionally-activated dissociation (CAD), and X can be either a Q or a sector analyzer (denoted by EB or BE). There are several types of X[rf]Q MS/MS instruments (e.g., QqQ, BEqQ, QoQ, QhQ, etc.; here q, h, and o denote, respectively, rf-only collision cells which use quadrupole, hexapole, and octopole rod assemblies). There are currently more than 400 X[rf]Q instruments worldwide, representing a capital investment of more than \$200M.

In this note we discuss an objective basis for quality assurance of CAD measurements in "dynamically-correct"[8] X[rf]Q instruments. The practical tuning criteria and guidelines herein can be used routinely (e.g., on a daily basis) to check instrument and/or operator performance once it has been certified (cf. section 4a of ref. 10) that

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dynamically-correct[8] product distributions can be measured in any particular instrument.

Technical Background:

To study ion-neutral reaction mechanisms in X[rf]Q instruments, it is crucial that one measure dynamically-correct[8] product distributions which are instrument independent. Otherwise one may measure a distorted representation of the reaction dynamics, which consequently can lead to incorrect conclusions about the pertinent reaction mechanisms. The dynamical prerequisites for obtaining dynamically-correct[8] product distributions (branching ratios) within X[rf]Q instruments have been detailed elsewhere.[8]

It follows, therefore, that to develop an instrument-independent database (or library) for MS/MS measurements within X[rf]Q instruments one must obtain substantially the same representation for any reaction [e.g., CAD] occurring within any such instrument (i.e., no discrimination effects; see Appendix of reference 9).[8,10]

A measurement protocol[10] was developed at the National Institute of Standards and Technology (NIST; formerly National Bureau of Standards) to provide a basis for precise and accurate ($\pm 10\%$) instrument-independent, dynamically-correct measurements within XqQ instruments. The precepts of the NIST protocol should also be applicable to other types of X[rf]Q tandem mass spectrometers which have strong focusing properties (e.g., QhQ, QoQ, etc.), so long as the collision energy range is the same as for XqQ instruments.

The NIST protocol[10] was validated by the recent NIST-EPA International Round Robin[11] which indicated that at least 50% of the QqQ instruments which have been sold and are currently in the field can provide an instrument-independent, dynamically-correct representation of any ion-neutral reaction mechanism when this kinetics-based measurement protocol is used. Hence, the NIST protocol can be used to develop an instrument-independent database of CAD spectra for dynamically-correct X[rf]Q tandem mass spectrometers[12,13] (and/or to study the kinetics and mechanism of ion-neutral reactions). The NIST protocol is to be incorporated into EPA's SW-846 Test Methods for Evaluating Solid Waste as an 8000 series tuning procedure for dynamically-correct X[rf]Q instruments.

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DISCUSSION

After one has proven that a given X[rf]Q instrument is capable of measuring dynamically-correct product distributions (cf. section 4a of ref. 10), it becomes imperative that standardized operating conditions be maintained to ensure precision and accuracy of the CAD measurements,[10] especially each time CAD spectra are to be taken for inclusion in a NIST standardized database.

Maintaining Standardized Operating Conditions:

The CAD of the acetone cation is especially well suited for the requisite **quality assurance, performance evaluation, and proficiency testing** applications because:

(a)   it provides a relatively simple test case (if one cannot generate instrument-independent CAD spectra for the acetone cation, then it may not be possible to develop an instrument-independent database under any conditions), and

(b)   there is a wealth of information about the unimolecular and collisionally-activated dissociation of the acetone cation.[14-37]

and, most importantly, because of the following unique characteristics:

(c)   there are distinct differences in the energy dependences of the branching ratios obtained under single-collision {SC} vs. multiple-collision {MC} conditions[9]. Therefore, one can readily determine whether or not the target thickness is within the single-collision regime. Comparison of the {SC} and {MC} data in Tables 1 and 2 of ref. 9 indicated that the control of the target thickness becomes extremely critical if one hopes to measure instrument-independent product distributions (i.e., CAD spectra).

(d)   the production of 15^+ is a significant decomposition channel.[37] This allows one to gauge how well the reaction-induced mass discrimination[8,10] due to CAD is controlled in various X[rf]Q instruments [i.e., how well one can compensate for differences in ion containment efficiencies, especially for low-mass

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daughter ions (here $m_{daughter}/m_{parent}$ = 15/58= 0.25)].
If one cannot measure dynamically-correct branching
ratios vs. E_{cm} for 15^+, then one obtains an incorrect
representation of the low-energy CAD mechanism for
$Me_2CO^{+\bullet}$.

(e)   the energy dependence of the branching ratio for
      production of 15^+ goes through a sharp maximum.[37]   This
      allows one to gauge how well the collision energy is
      controlled in various instruments.

It is proposed, therefore, that the standard spectra for the
CAD of the acetone cation[37] be used by the MS/MS community
to periodically recheck the performance of dynamically-
correct X[rf]Q instruments (viz., how well the key MS/MS
parameters such as target thickness, ion containment
efficiency, and collision energy are being controlled in a
X[rf]Q instrument).   These standard CAD spectra can also be
used to test the proficiency of X[rf]Q operators of varying
skill levels, thus providing an objective basis for quality
assurance whenever one uses MS/MS methods such as the EPA's
SW-846 method.

Reference Spectra for the CAD of the Acetone Cation:

Table 1 shows the absolute branching ratios (from ref. 37)
for the CAD of $Me_2CO^{+\bullet}$ [generated by 70 eV electron
ionization (EI)[10] of acetone].   They were measured with the
NIST protocol in NIST's dynamically-correct QqQ
instrument[38] under single-collision conditions (Ar target)
at the center-of-mass collision energies (E_{cm}) indicated.
The E_{cm} of Table 1 were selected iteratively to optimize the
information about competitive reaction channels (including
the absolute maximum branching ratio for Me^+ production at
E_{cm} = 32.6 eV).   The reader is referred to the EXPERIMENTAL
section of ref. 9 for a summary of the iterative measurement
procedure.

The CAD of $Me_2CO^{+\bullet}$ (58^+) produces the fragment ions
indicated in Table 1 (e.g., 14^+, 15^+, etc.) and a
complementary neutral fragment (not shown).   No other
product ions were observed.   The absolute total cross
sections were 24 to 35 Å^2 for E_{cm} = 1-60 eV.   The major
fragment ions are the acetyl cation (m/z 43; branching
ratios of 0.96-0.60 for E_{cm} = 1-60 eV) and the methyl cation
(m/z 15; branching ratios of 0.02-0.26 for E_{cm} = 1-60 eV).

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The ketene cation (m/z 42; branching ratios of 0.02-0.06 for E_{cm}= 1-60 eV) is a minor CAD fragment.

MS/MS Quality Assurance:

One's ability to reproduce the dynamically-correct branching ratios shown in Table 1 for the CAD of the acetone cation[37] should indicate that one's X[rf]Q instrument is functioning properly, and is ready to measure standardized CAD spectra. This provides an objective basis for quality assurance of CAD measurements in "dynamically-correct"[8] X[rf]Q instruments.

Branching Ratios and Target Thickness:

One should be able to replicate the values in Table 1 to within the maximum uncertainty indicated by the bracketed values in Table 1 for branching ratios >0.01. This would ensure that the Ar target thickness is within the single-collision regime.

Collision Energy:

It was shown in ref. 37 that the complementary energy dependences for production of $MeCO^+$ and Me^+ are due to a competition between three fast, primary (direct) reactions, each of which opens sequentially at its respective threshold energy [viz., (1), (2), and (3)].[37]

$$Me_2CO^+ \cdot \longrightarrow MeCO^+ + Me \cdot \ (X \ ^2A"_2) \qquad \Delta H= 0.82 \ eV \qquad (1)$$

$$\longrightarrow Me^+ + Me \cdot + CO \qquad \Delta H= 4.24 \ eV \qquad (2)$$

$$\longrightarrow MeCO^+ + Me \cdot \ (B,1 \ ^2A'_1) \qquad \Delta H= 6.55 \ eV \qquad (3)$$
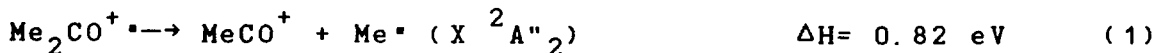
That is, the maximum in the branching ratio vs. E_{cm} curve for Me^+ production at E_{cm} = 32.6 eV corresponds to the opening of reaction (3) when the collisionally-activated $Me_2CO^+ \cdot$ has acquired an internal excitation E_{int} ≃ 6.55 eV. This E_{int} is corroborated by the increased production of 42^+ for E_{cm}>32.6 eV, which was attributed (in ref. 37) to the opening of a new direct reaction channel [(5) or (6)] for production of $H_2C=C=O^+$.

$$Me_2CO^+ \cdot \longrightarrow H_2C=C=O^+ + CH_4 \qquad \Delta H= 0.89 \ eV \qquad (4)$$

$$\longrightarrow H_2C=C=O^+ + H + Me \cdot \qquad \Delta H= 5.43 \ eV \qquad (5)$$

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$$\rightarrow H_2C=C=O^+ + CH_2 + H_2 \qquad\qquad \Delta H = 5.69 \text{ eV} \qquad (6)$$

Hence, $E_{cm} = 32.6$ eV corresponds to $E_{int} \approx 5.43-6.55$ eV [for reactions (3), (5), (6)]. That is, an uncertainty in E_{int} of ca. 1 eV (=6.55-5.43) corresponds to an uncertainty in E_{cm} of ca. 5-6 eV at $E_{cm} = 32.6$ eV.

SUMMARY

The absolute branching ratios (product distributions) for the CAD of the acetone cation (measured as a function of E_{cm}) provide an objective basis for quality assurance, performance evaluation, and proficiency testing of CAD measurements in dynamically-correct tandem mass spectrometers which use rf-only multipole collision cells. That is, by replicating NIST's standard reference spectra, an operator can determine that the key MS/MS parameters (e.g., the target thickness, ion containment efficiency, and collision energy) are under control, and that one's X[rf]Q instrument is functioning properly and is ready to measure standardized CAD spectra .

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The term "dynamically correct" was coined (see Appendix of reference 9)[8,10] to indicate those branching ratios measured in X[rf]Q instruments which correspond to the distribution of reaction products which, in principle, would be observed at the scattering center of an idealized crossed molecular beam machine (if one were able to integrate over all angles the ion intensities of each reaction product channel). This correspondence is attributed to the strong focusing properties of rf-only multipoles which provide high ion-containment efficiencies for ions scattered through a broad range of angles.[66] Hence, dynamically-correct branching ratios are those which have been appropriately corrected for discrimination effects, and, therefore, provide an

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instrument-independent representation of the primary
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In this paper[37] we describe the kinetics and mechanism of the CAD of the acetone cation which indicates that there is a correspondence between the distribution of internal energies accessed by the photoionization of acetone [viz., the PEPICO data of ref. 29 and 31] and the energy deposition function accessed by collisional activation of acetone cations formed by 70 eV EI [viz., our CAD data]. That is, the low-energy CAD of the acetone cation involves electronic transitions (rather than vibrational excitation),[34,35] and dissociation occurs primarily from the same electronic states in both the CAD and PEPICO experiments.[37]

The concordance of our findings[37] with those of PEPICO[29,31] and molecular beam experiments[33-35] indicates again[11] that the NIST kinetics-based protocol developed in this laboratory makes it possible for one to measure dynamically-correct product distributions which have been appropriately corrected for discrimination effects. That is, one can obtain an undistorted (instrument-independent) representation of ion-neutral interactions (e.g., CAD). This is essential for the development of a standardized, instrument-independent MS/MS database for X[rf]Q instruments. The data in Table 1 constitute some of the first elements of such a database.

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Table 1. Branching Ratios[1] vs. E_{cm} for the CAD of 58^+ from Acetone

<u>Parent Ion</u>: $C_3H_6O^+$ (m/z 58)   <u>Source Compound</u>: 2-Propanone (>99.7%)

<u>Ionization Mode</u>: 70 eV electrons   <u>Target Gas</u>: Ar (single collision)

E_{cm} (eV)	σ (Å^2)	Branching Ratios for the CAD of 58^+					
		(14^+)	(15^+)	(26^+)	(27^+)	(28^+)	(29^+)
1.2	24 [10]	0.0000	0.0153 [8]	0.0000	0.0000	0.0000	0.0000
4.1	31 [15]	0.0000	0.0151 [10]	0.0000	0.0000	0.0000	0.0000
10.6	32 [15]	0.0000	0.1581 [3]	0.0005 [50]	0.0046 [20]	0.0033 [15]	0.0054 [15]
32.6	34 [25]	0.0128 [25]	0.2561 [75]	0.0054 [10]	0.0578 [30]	0.0062 [7]	0.0308 [15]
44.9	35 [10]	0.0000	0.0444 [10]	0.0059 [100]	0.0882 [15]	0.0059 [100]	0.0738 [20]
61.2	34 [20]	0.0000	0.0278 [10]	0.0000	0.0195 [20]	0.0000	0.0124 [35]

E_{cm} (eV)	Branching Ratios for the CAD of 58^+					
	(31^+)	(39^+)	(40^+)	(41^+)	(42^+)	(43^+)
1.2	0.0000	0.0000	0.0000	0.0000	0.0195 [20]	0.965 [4]
4.1	0.0000	0.0000	0.0000	0.0000	0.0241 [20]	0.961 [4]
10.6	0.0008 [35]	0.0000	0.0000	0.0000	0.0177 [25]	0.810 [5]
32.6	0.0020 [60]	0.0029 [50]	0.0014 [50]	0.0047 [30]	0.0218 [15]	0.598 [2]
44.9	0.0059 [100]	0.0036 [35]	0.0012 [100]	0.0084 [30]	0.0323 [20]	0.730 [3]
61.2	0.0000	0.0120 [20]	0.0084 [30]	0.0169 [20]	0.0580 [15]	0.845 [5]

[1] The CAD of 58^+ produces only the fragment ions indicated (e.g., 14^+, 15^+, etc.) and a complementary neutral fragment (not shown). Numbers in square brackets represent maximum possible uncertainty in the cross section σ and in the branching ratios, expressed as a percentage of each σ and of each branching ratio. Hence, at E_{cm}=44.9 eV, the branching ratio for $58^+ \rightarrow 43^+$ is 0.730 (±0.02 max), while that for $58^+ \rightarrow 31^+$ is 0.0059 (±0.0059 max).

65 IMPROVED TECHNIQUES FOR FORMALDEHYDE ANALYSIS BY HPLC USING AUTOMATED SAMPLE PREPARATION AND DIODE ARRAY DETECTION

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ABSTRACT

Formaldehyde, one of the more widely produced intermediates in the U.S. chemical industry, is formed by combustion and biological processes, making its presence in the environment ubiquitous. Because formaldehyde is a probable carcinogen, reliable analytical methods for identifying trace levels of this analyte must be found. In this study, we examined some of the difficulties involved in a common HPLC method, exemplified by draft EPA Method 8315 and California Air Resources Board (CARB) 430, and considered approaches for reducing systematic error. Using spectral confirmation, we also investigated the frequency at which interferences or false positives occur.

The common method relies on pre-column derivatization of the aldehydes with 2,4-dinitrophenylhydrazine (DNPH) followed by reversed-phase HPLC analysis. As others have noted, this method of determining formaldehyde at trace levels presents a major problem: contamination, which results in elevated blank levels and increased detection limits. Causes of contamination include solvents and solid-phase extraction columns as well as the exposure of reagents and samples to ambient air. Introduction of contamination counteracts the advantages of concentrating the sample through extended preparation procedures, such as liquid/liquid and solid-phase extraction. Because concentration is not needed to meet detection limits on the order of 20-50 ppb, which are satisfactory for most regulatory purposes, we have investigated the application of automated pre-column derivation using the Hewlett-Packard 1090 Series II HPLC system. The paper presents details of this procedure.

The application of the diode array UV-visible detector to this analysis provides many advantages over fixed-wavelength analysis. Shifts in retention time during the course of analyzing batches of real-world samples are quite common, and lead to misidentification in the case of single-wavelength, single-column detection. With spectral information available from the diode array detector, false positives can be virtually eliminated. The paper provides examples of chemical interferents and misidentifications observed in environmental analysis.

INTRODUCTION

Formaldehyde analysis of environmental samples is becoming more common in the analytical lab. The detection of this compund plus other carbonyls is important due to the health hazards and possible role they play in environmental reaction pathways. These compounds are formed by incomplete combustion and atmospheric photoxidation of hydrocarbons. Formaldehyde is a very common ingredient in cosmetics, building materials, as well as a key chemical for chemical synthesis. The fact that formaldehyde is universally present leads to positive detection by any analytical procedure. The blank levels that are observed can vary dramatically when an extensive sample preparation procedure is used. This paper will discuss the application of two slightly different approved procedures, EPA 8315 and CARB 430, plus compare these methods to an on-line HPLC sample preparation procedure that controls the sample contamination problem.

EPA Method 8315 involves the analysis of aqueous and solid samples by DNPH derivatization followed by HPLC detection. This research did not investigate the application of 8315 to solid samples. Aqueous samples are mixed with a derivatizing solution of DNPH in ethanol plus acetic acid. The pH for this reaction is adjusted to around 5 and derivatization is allowed to proceed for at least a half hour. This solution is then extracted by either liquid/liquid or solid phase extraction. The liquid/liquid procedure partitions the DNPH hydrazone product into methylene chloride. The SPE process uses a C18 column to separate the derivatized product. In both preparations the final extract must be exchanged for one that is suitable for HPLC analysis, acetonitrile (ACN) or

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methanol. The reader is referred to the actual methods for more details on this preparation.

CARB 430 is the California approved air sampling method for airborne formaldehyde. It involves the use of DNPH impinger solution that is composed of approximately 2N hydrochloric acid (HCL). This acidic solution traps and derivatizes immediatley all carbonyl species that bubble through. The sample solution is then extracted with 70/30 vol/vol % hexane/methylene chloride. The extract is again exchanged to a suitable HPLC solvent. Therefore, the final extracts that are obtained by these two methods are identical and all HPLC conditions are the same.

Both approved methods and many journal publications mention the high blank levels obtained by these sample preparation procedures. CARB 430 outlines a very detailed purification procedure involving multiple recrystallizations of DNPH followed by storage in a nitrogen purged dessicator. All impinger solution must be checked for contamination prior to use with 48 hours as the maximum time between preparation and use. 8315 also mentions that blank levels are a major problem but the only precaution mentioned is to use the highest quality reagents. In both methods it is suggested that the blank level is subtracted from all sample data. 8315 mentions this blank subtraction procedure only in the context of the establishing of the method detection limit. The work reported here has centered around trying to clean up this blank problem and therefore not do blank subtraction when reporting data.

EXPERIMENTAL

Reagents and standards.
All organic solvents were of HPLC UV spectral grade. Many vendors were consulted during solvent selection and no guarantee of low (<50 ppb) formaldehyde levels could be confirmed. The results obtained here indicate that the purity of the DNPH and water is more critical then that of the organic solvents. DNPH was purchased from ChemService (West Chester, PA) and recrystallized twice in pure ACN according to the CARB 430 method. Impinger solution was prepared from 90 ml of concentrated HCL (Baker Analyzed) to which .250 grams of pure DNPH is added. After the

crystals have dissolved organic free water is added to produce 500 ml of solution. The water used throughout this work was distilled then passed through a Barnstead Nanopure II system, heated to near boiling and purged for a hour with helium, and finally charcoal filtered. This impinger solution was used directly as the on-line (autoprep) derivatization solution in the Hewlett Packard HPLC.

Formaldehyde for calibration and quality control solutions was obtained also from ChemService as a 70% aqueous solution. Known concentrations (1000 ppm) of a aqueous stock were prepared according to method 8315. This procedure uses a pH titration procedure to establish the concentration of formaldehyde in the stock. CARB 430 recommends the production of pure formaldehyde hydrazone crystals for calibration. Our experience with this procedure has never produced quantitative information that compares favorably with 8315. Even though the melting point observed for the product appeared to be acceptable these crystals always produce standards that gave very low responses. All calibration standards were prepared exactly like as a analytical sample for all three methods. The autoprep technique involved the production of spiked water at 4 or 5 calibration concentrations which were placed on the instrument and derivatized on-line.

Instrumentation.
The HPLC instrumentation consists of a Hewlett Packard 1090 series II with a diode array detector. Computer control is provided with a HP ChemStation with a Pascal based operating system. This instrument is a binary gradient low pressure mixing system. The mobile phase consists of 0.01 molar phosphoric acid (channel A) and pure ACN (channel B). The selection of a weak acidic mobile phase provides two benefits. First it assures that the DNPH reaction proceeds to completion plus it stops the columns from becoming clogged. Without a acidic mobile phase the reverse phase columns used in our lab have stopped functioning after as few as 30 samples. With the introduction of a phosphoric acid mobile phase the current column has completed over 300 analytical runs. Due to the nature of the samples we analyze (high organic contamination), inexpensive C18 columns are purchased from Alltech (Deerfield, IL). The column used for this work is a Econosphere C18 with 5 micron particle packing (150mm x 4.6mm). The gradient

conditions are shown in Table 1 The spectroscopy parameters are also presented.

The procedure for on-line derivatization is presented in Table 2. The first step (line 1) prompts the autosampler to draw up into the sample loop 2.5 micro liters (ul) of DNPH impinger (vial #1) solution. Next 10 ul of sample is drawn up followed by a syringe rinse in solvent (ACN). Another plug of DNPH is then drawn up to sandwich the sample Line 5 is the mixing step which moves the sample plus reagent back and forth through the heated reaction furnace which is at 50C. After mixing a final 10 ul of solvent is drawn in order to optimize the position of the sample in the reaction furnace. The autosampler then waits two minutes before performing the analytical injection.

RESULTS AND SUMMARY

Method development on the autoprep derivatization technique involved experimenting with different reagent combinations. The starting point used the reagents suggested by EPA 8315. Thus, the derivatizing solution was a combination of 5M acetic acid plus saturated DNPH/ethanol. This combination did not give satisfactory results. The blank values observed were very high (at least 100 ppb). Also, the sensitivity was not comparable to standards prepared by Method 8315. This lack of sensitivity was most likely due to the use of a weak acid for derivatization. It had been observed previously in our lab that this reaction was not complete in a few minutes. In order for the autoprep technique to be time effective different reagents had to be selected. The application of a strong acid such as HCL or sulfuric was suggested to us by a fellow researcher. Because we always are preparing clean HCL impinger solution for Method CARB 430 this was the easiest reagent to use. It was proposed that the injection of 5 ul's of this acid solution could be tolerated by the HPLC.

Over the course of approximately 3 months a calibration comparison between the autoprep procedure and the approved sample preparation procedures was performed. The results of this study is graphically displayed in Figure 1. Each calibration curve has a least squares fit equation and line associated with it. The

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equation in the top of the each plot is associated with the top line on the right hand border. The linearity (correlation coefficient R^2) of these calibration curves are all > 0.990 with only one of the autoprep coefficients being < 0.995.

There is no criterion for linearity in EPA Method 8315. CARB 430 mentions that linearity through the origin may be assumed if an R^2 of 0.999 is obtained. As this data indicates an R^2 of 0.999 does not guarantee that the calibration curve passes through the origin. In fact, in our experience these calibration curves rarely include the origin. If one tries to force the orgin as a data point then the R^2 goes down. The fact that these calibration curves behave in this manner is not surprising. One must remember that contamination by formaldehyde can occur during any stage of the standard preparation. It is this random contamination that leads to the spread in these calibration plots. By comparing the autoprep data to that obtained by the two approved methods it is seen that all three techniques are fairly comparable.

One point that is not obvious from the calibration data is the comparison of blank levels obtained by each technique. In the cases of 8315 and CARB 430, the blank response is frequently as high as the lowest calibration standard (100 ppb). The blanks obtained on clean water by autoprep show substantially less response. Assigning an absolute quantifiable number to the autoprep blank is difficult, because preparation of calibration standards at these low (<100 ppb) levels is nearly impossible. Basically, the peak areas obtained for the autoprep blanks are 4 to 5 times less than those obtained through normal sample preparations. This lack of low level quantification information also makes it difficult to establish a method detection limit (MDL) for the autoprep technique. The approved methods however both use blank subtraction to establish their MDL's. If one looks at the absolute instrumental response from the HP1090 it can be estimated that a detection limit of around 5-10 ppb should be obtainable.

Figure 2 depicts the chromatgraphic response of a high level formaldehyde standard. The peak shape for the formaldehyde derivative is obviously not symmetrical. However, with the

spectral power of the diode array it can be demonstrated that this peak is pure. On a brand new column the standards do initially appear symmetrical. But after a few real world samples the peak shapes deteriorate. This deterioration is not due to column overload because even low level standards are asymmetrical. In order to check the performance of the used columns a pesticide mixture was run under the same mobile phase. The gradient program was slightly different. As can be seen in Figure 2B the chromatography of this mix displays better peak shape. From the point of view of a production laboratory a new column for formaldehyde analysis cannot be justified.

The analytical results for a number of different types of water samples are presented in Table 3. In every case the normal 8315 preparation of these samples produced higher results than the autoprep technique. Not only did the normal preparation produce contaminated sample extracts this preparation requires a lot of labor. The normal preparation involves liquid/liquid separatory extractions in triplicate followed by concentration and solvent exchange. Reagent consumption for the normal preparation is hundreds of milliliters compared to ul by autoprep. The only manipulation done for the autoprep procedure is to load a autosampler vial with sample and place it on the HPLC.

Another advantage of the autoprep technique is due to the fact that the HPLC injects the sample directly rather then a concentrated extract. The solvent extraction processes of 8315 and CARB 430 extract all the organic components in the sample and these then can cause many types of chromatographic problems. Not only does it appear that the extraction process contaminates the samples but chromatographic interferences can be promoted by the concentration procedure. The HPLC chromatograms generated by autoprep are less likely to produce complicated peak shapes, retention time shifts, or UV/Vis spectral complications. An example of the type of problems observed for a sample that has been prepared according to Method 8315 is shown in Figure 3. The top portion of this figure shows the chromatogram and the bottom portion contains selected UV/Vis spectral scans. It is fairly obvious from the chromatogram that the formaldehyde derivative (retention time = 7.0) peak is not a single component. If one is

performing this test with a single beam UV/Visible instrument no further insight into this coelution is possible.

Because the diode array system gathers and stores complete spectral scans during each peak the presence of an interfering species can be confirmed. Three spectral responses are shown for 1- the first peak max at 6.7 min., 2 - the peak max at 6.9 min., and 3- the tailing edge at 7.3 min.. Spectra 1's response is indicative of pure formaldehyde derivative which quickly becomes convolved with a coeluting species spectra shown in spectra 2. Even though the interfering species peak maximum is at a different wavelength (250 nm) than that used for formaldehyde (360 nm) the absorbance is strong and probably adds to the total peak area. The three spectra shown in the figure are all scaled to the same axis. Nothing about absolute intensity is displayed. It was observed that the absorbance from the interfering species was approximately three times as strong as that seen for formaldehyde. The presence of this interfering species remains throughout the remainder of the chromatographic peak. Spectra 3 still displays the low wavelength absorption due to its presence. Because of the diode array information these analytical results could be reported to the client as elevated due to this interferent.

8315 Calibration

$y = 0.28190 \ X +113.87$
$R^2 = 0.995$

$y = 0.23850 \ X + 33.865$
$R^2 = 0.999$

Peak Area

Concentration (ppb)

CARB 430 Calibration

$y = 0.31547 \ X + 30.224$
$R^2 = 0.999$

$y = 0.2483 \ X +67.438$
$R^2 = 0.997$

Peak Area

Concentration (ppb)

Impinger Autoprep Calibration

$y = 0.25544 \ X - 21.179$
$R^2 = 0.991$

$y = 0.20985 \ X + 88.569$
$R^2 = 0.999$

Peak Area

Concentration (ppb)

Composite Calibration Data

Peak Area

Concentration (ppb)

- auto prep
- auto prep
- carb 430
- carb 430
- 8315
- 8315

Figure 1 - Comparison of Calibration Data
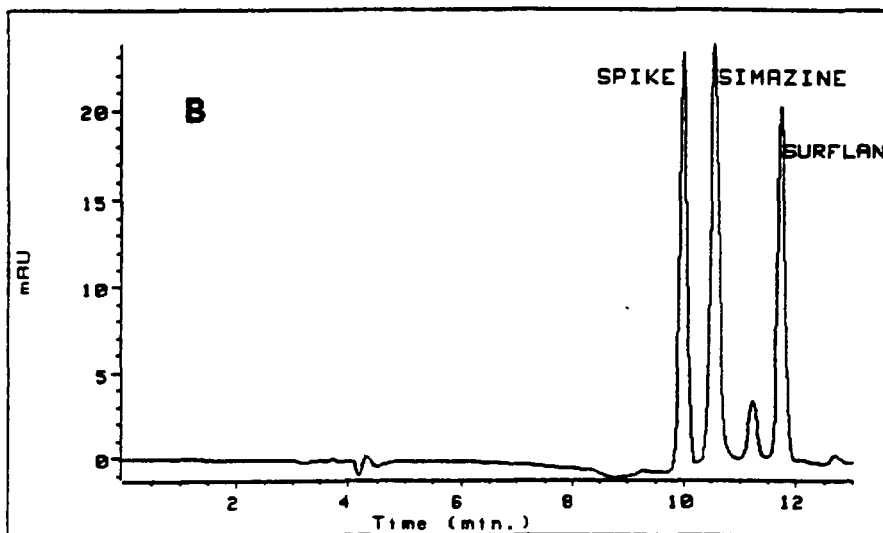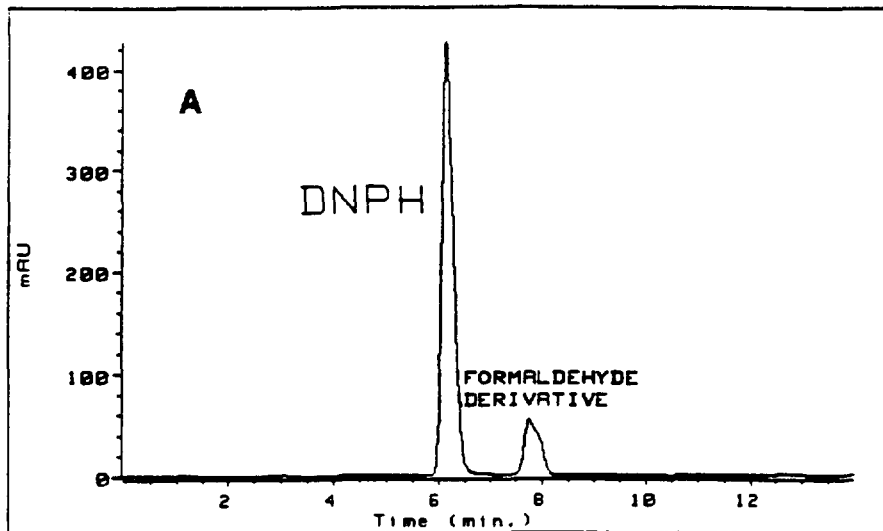
Figure 2 - HPLC Chromatograms
A) 5000 ppb formaldehyde std.
B) Pesticide test mix
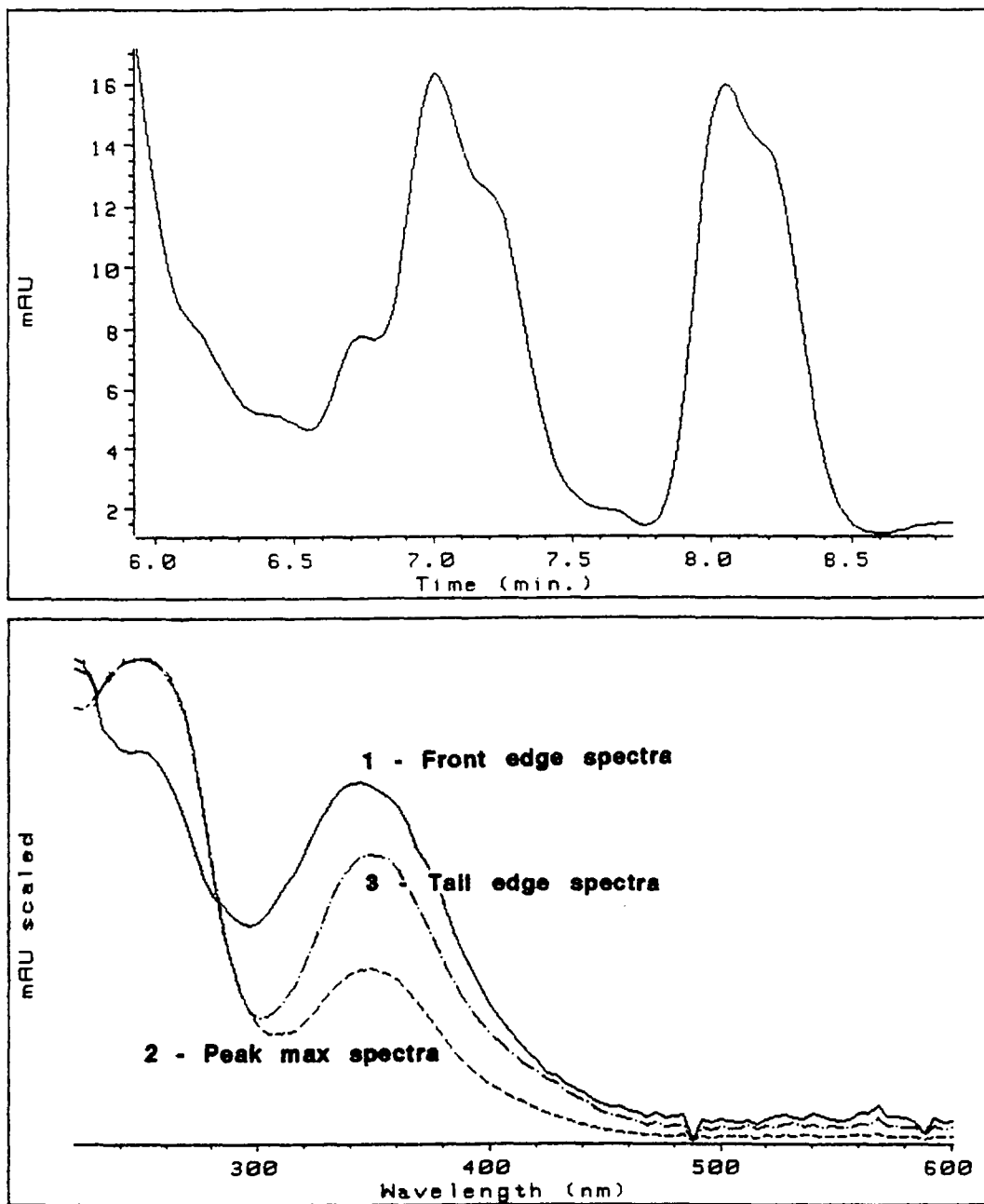
Figure 3 - Example of a Chromatographic/ Spectral Interferent.

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```
L I Q U I D   C H R O M A T O G R A P H                    initial parameters


              Flow :      0.500 ml/min
        Solvent  A :      40.0 %
                 B :      60.0 %


      Max Pressure :        400 bar            Min Pressure :     off

         Stop Time :      14.00 min
         Post Time :       0.00 min

  Injection Volume :      10.0 ul


  L I Q U I D   C H R O M A T O G R A P H

  Time (min)
       1.00     Solvent    A:  40.0 %   B:  60.0 %
       5.00     Solvent    A:  30.0 %   B:  70.0 %
       7.00     Solvent    A:   0.0 %   B: 100.0 %
       8.00     Solvent    A:   0.0 %   B: 100.0 %
      10.00     Solvent    A:  40.0 %   B:  60.0 %
      14.00     Solvent    A:  40.0 %   B:  60.0 %


  D I O D E - A R R A Y   D E T E C T O R             signals & spectra

         SIGNALS       A        B        C
  Sample    (nm)
       Wavelength :    360      340      380
        Bandwidth :     80       80       80
  Reference (nm)
       Wavelength :    560      560      560
        Bandwidth :     40       40       40


  Store Spectrum :   peak controlled    about    896 Records acquired during Run
       Threshold :      0.1 mAU

       Peakwidth :   0.150 min              Sampling Interval      960 ms
       Stop Time :  14.00 min          Spectrum Range from :      220 nm
       Post Time :   0.00 min                           to :      600 nm
  Prerun Balance :       Yes                          step :        4 nm
```

Table 1 - HPLC Chromatography and
Diode Array Parameters

```
I N J E C T O R   P R O G R A M

Slowdown  Draw & Eject :    2
                    Mix :    2
Hold after Draw & Eject :    0  seconds

    Line#      Function
       1       Draw     :   2.5   ul  from : Vial# :    1
       2       Draw     :  10.0   ul  from : Sample
       3       Draw     :   0.0   ul  from : Vial# :    0
       4       Draw     :   2.5   ul  from : Vial# :    1
       5       Mix      :  10.0   ul   cycles :  10
       6       Draw     :  10.0   ul  from : Vial# :    0
       7       Wait     :   2.00  minutes
       8       Inject


       25.0   ul accumulated in Syringe with Line#   5
```

Table 2 - Autoprep Injector Program

TABLE 3 - COMPARISON OF ANALYTICAL RESULTS

(ALL RESULTS ARE PPB)

SAMPLE DESCRIPTION	8315 RESULT	AUTOPREP RESULT
WASTE WATER	104	53
SEWER COMPOSITE #1	226	<25
SEWER COMPOSITE #2	230	<25
GROUND WATER #1	110	<25
" #2	45	"
" #3	62	"
" #4	87	"
" #5	94	"
" #6	95	"
" #7	82	"
" #8	113	"
AQUEOUS SAMPLE	389	<25

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AN INTERLABORATORY COMPARISON STUDY OF SUPERCRITICAL FLUID EXTRACTION FOR ENVIRONMENTAL SAMPLES; Tammy L. Jones, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Las Vegas, Las Vegas, NV 89193, Tom C.H. Chiang, Lockheed Engineering and Sciences Company, Las Vegas, NV 89119

The U.S. Environmental Protection Agency recently conducted a multilaboratory evaluation of a supercritical fluid extraction (SFE) protocol. SFE is a relatively new technique which can be used to extract compounds of environmental interest from solid matrices (soils, sediments, fly ash, etc.) by using supercritical CO_2. Ten laboratories participated in this study that was designed to evaluate the feasibility and applicability of a protocol developed for the extraction of environmentally significant analytes from environmental matrices.

The efficiency of analyte (polynuclear aromatic hydrocarbons and phenols) recoveries, using SFE, from three solid matrices (two standard reference materials and one spiked sand) was studied. The analyses of the resulting extracts from all the laboratories were performed by a single laboratory using gas chromatography/mass spectrometry (GC/MS). The data were evaluated in terms of precision, accuracy, and the intra-laboratory and inter-laboratory variations within this technique. In general the percent recoveries of the analytes from the various laboratories ranged from poor (< 40%) to very good (> 90%). There was a trend noticed that those laboratories who performed satisfactorily on one sample matrix also continued to do so on the other two. NOTICE: Although the research described in this article has been supported by the

U. S. Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency. This document is intended for internal Agency use only. Mention of trade names or commercial products does not constitute endorsement nor recommendation for use.

67 AN ANALYTICAL MANUAL FOR PETROLEUM PRODUCTS IN THE ENVIRONMENT

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Abstract

The New Jersey Department of Environmental Protection (NJDEP) Analytical Chemistry Manual for Petroleum Products in the Environment was drafted to help project managers select appropriate analytical methods. Eight NJDEP programs administer regulations concerning petroleum products. The analytical methodologies for these programs have not been codified within federal or state regulations, and several method variants exist.

Preparatory to drafting the Manual, we conducted an extensive review of the regulatory programs. The methods and standards reviewed include those of federal and state agency departments, as well as those of the American Public Health Association, American Society for Testing and Materials, and American Petroleum Institute. Selected methods and procedures for free product, aqueous matrices and nonaqueous matrices were edited to establish a Department Manual. Methods for volatile petroleum products (e.g., gasoline, jet fuel, kerosene, solvents) and semivolatile petroleum products (e.g. diesel, fuel oils #2-#6) are presented.

The analytical laboratory methods contained in the Manual will become part of the revised NJDEP Regulations Governing Laboratory Certification and Standards of Performance, N.J.A.C. 7:18.

The paper discusses a survey method, two quantitative methods and one fingerprint method. These methods are representative of the fifteen methods in the first edition of the Department Manual. A gas chromatography-photoionization-flame ionization detector (GC-PID-FID) survey method is presented for volatile petroleum products. A quantitative GC-PID-FID method is discussed for volatile petroleum products. Gas chromatography-mass spectroscopy is discussed for the identification and quantification of specific semivolatile compounds in petroleum contaminated soil. The identification of specific petroleum products in contaminated water and soil or free product is accomplished by GC-PID-FID fingerprinting.

Each method contains calibration procedures for petroleum products, and quality control requirements. The manual also contains a users guide for environmental professionals.

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EVALUATION OF LIQUID/SOLID EXTRACTION FOR THE ANALYSIS OF ORGANOCHLORINE PESTICIDES AND PCB'S IN TYPICAL GROUND AND SURFACE WATER MATRICES

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ABSTRACT

Method 608/8080 is used for the analysis of organochlorine pesticides and PCB's in water and wastewater. The main features of the method are liquid/liquid extraction (LLE) with methylene chloride, removal of the methylene chloride to concentrate the analytes, a solvent exchange into hexane, and gas chromatographic analysis with electron capture detection. Because several of the 500 series drinking water methods are being updated with the inclusion of liquid/solid extraction (LSE), a similar modification was evaluated for Method 608. The LLE steps were replaced with a solid-phase disk (47mm C18) extraction, elution of analytes with ethyl acetate, and direct GC analysis of this eluate.

The LSE evaluation study was performed with reagent water and composites of typical ground and surface waters, including groundwater composites with very high particulate content. The single organochlorine pesticides and the multicomponent mixtures were all spiked at two concentration levels, a "validation" level and an "MDL" level. Elution efficiency was determined for all sample types.

The recovery efficiencies, %RSD's, and method detection limits obtained demonstrate that LSE is at least equivalent to LLE for the Method 608/8080 analytes, and, in most cases, an improvement. The LSE disk modification was successfully applied to all water matrices typically encountered in our laboratory. Disk LSE provides a clear advantage in terms of time and cost per analysis and solvent use and disposal.

INTRODUCTION

The use of LSE instead of LLE for the isolation and concentration of organic components in environmental water samples is becoming more extensive because of the time and cost benefits it provides. LSE is less labor-intensive, uses substantially less glassware, and significantly reduces the volume of hazardous and costly solvents required. The solid phase used most frequently is octadecane (C18) chemically bonded to porous silica particles. It is commonly packed into disposable plastic cartridges, producing LC mini-columns. SPE using these cartridges is an alternative sample preparation procedure cited in the Drinking Water Methods 506, 525.1, and 550.1. Method 525.1 addresses many of the same

analytes covered by Method 608/8080 (1).

Recently 3M introduced membrane disks, Empore™, as an LSE medium (2). Instead of being packed in a cartridge, the C18-bonded silica particles are enmeshed in PTFE fibrils. The large diameter, thin disks (47mm x 0.5mm) provide a large cross-sectional area with low back pressure. The primary advantage of the disk technology is the speed of extraction possible with equivalent extraction efficiency. Efficiency is achieved with a smaller particle size, a uniform, high density packing, and an effective low linear velocity through the disk at high sample flow rates. The 47mm diameter disks fit standard glass filtration assemblies, allowing the extraction to be carried out in an all glass/PTFE environment. One of the principal disadvantages of the LSE cartridges is the amount of trace contaminants contributed by plastic housings. Disk LSE is designated as an approved technique for Methods 506/8061, 513, 525.1, and 550.1.

The organochlorine pesticides and PCB's determined by Method 608/8080 present good candidates for LSE. They are extracted at a neutral pH, are insoluble in water (large capacity factor, k', for C18/water reversed-phase conditions, soluble in organic solvents (easily eluted), and are relatively non-volatile. In addition, the 608/8080 Method is very susceptible to interferences from trace level contamination because of the high sensitivity of the electron capture detector. A procedure that significantly reduces both the amount of glassware that must be kept scrupulously clean and the volume of solvent concentrated for the final extract will also significantly reduce contamination interferences.

The evaluation of Empore™ disks for LSE of the Method 608/8080 analytes was performed using reagent water, composites of "average" ground and surface waters, and composites of groundwater samples with a very high total suspended solids (TSS) content. The technique was to be challenged with all the types of water samples normally encountered. The single organochlorine pesticides and the multicomponent mixtures were all spiked at two concentration levels, a "validation" level and an "MDL" level. Elution efficiency was determined for all analytes in all sample types.

EXPERIMENTAL

Materials. Empore™ Extraction Disks, C18, 47mm (Varian Sample Preparation Products, Harbor City, CA, Cat. #1214-5004). Whatman Multigrade GMF 150 graded density glass microfibre filters, 37mm (Cat. #1841-047, Clifton, NJ).

Apparatus. Glass filtration apparatus, 47mm, 300mL funnel, 1000mL flask Nuclepore Cat. #410502 (Pleasanton, CA). Millipore (Bedford, MA) vacuum/pressure pump (Cat. #XX55 000 00). A tee with a pinch clamp is placed in the line between the filtration assembly and the pump to allow fine control of the vacuum for the preconditioning and eluting steps.

<u>Procedure</u>. The filtration unit is assembled with the Empore™ disk. The funnel and disk are washed with 10mL of ethyl acetate (the elution solvent), then with 10mL of methanol (preconditioning wetting agent), and finally with two 10mL rinses of reagent water. The 1L water sample, to which surrogate standard and 0.5% methanol wetting agent have been added, is then passed through the disk at full vacuum (25" Hg, 85 kPa). A thin layer of liquid is maintained on the disk from the methanol conditioning step until the entire sample has been extracted. The disk is subsequently eluted with two 5mL portions of ethyl acetate; the first portion is also used to rinse the sample bottle. During the elution step, the ethyl acetate is allowed to equilibrate on the disk for a few minutes. The eluate is collected in a 10mL Kuderna-Danish (KD) concentrator tube. Internal standard is added to the extract and it is made up to volume. Na_2SO_4 is added to dry the sample.

Liquid-liquid extraction analyses were performed using continuous liquid-liquid extractors for an 18-hour period.

<u>GC Analysis</u>. Samples were analyzed on a Hewlett-Packard Model 5890A GC with electron capture detection, using a Hewlett-Packard Model 7673A autosampler and Fisons/VG Multichrom Data System, Version 1.8. The column was a J&W Scientific (Folsom, CA) DB608, 30m x 0.53mm i.d., 0.83μm film thickness (Part No. 125-1730). Helium was the carrier gas at μ=45cm/sec, with argon-5%methane make-up at 65mL/min. The injection port was at 200°C, and the detector at 300°C. The temperature program was: isothermal at 140°C for 0.5 min, 140°-275° @ 6°C/min, hold 15 min. The injection was 2 μL splitless.

RESULTS AND DISCUSSION

Table I summarizes the results obtained for Empore™ LSE extraction of the 608/8080 analytes from reagent water at a "validation" concentration levels. For all experiments, the amount of analyte spiked into the sample water was also spiked into 10mL K-D concentrator tubes containing ethyl acetate, the "spike check" sample. The sample extracts and the triplicate spike check samples were treated identically for analysis. The mean of the spike check samples was the basis for the recovery efficiency calculation.

To test the completeness of elution with the two 5mL volumes of ethyl acetate, a second set of 5mL washes was passed through the disk, after the first elution, and collected in a second 10mL concentrator tube. Elution efficiency was calculated as the fraction of analyte concentration in the first eluant compared to the total analyte concentration in both eluants. Elution efficiency tests were run for representative Aroclors, not the entire set.

Table I data show excellent recovery and elution efficiencies. The mean %Recovery for all analytes was 91.5%, and the mean elution efficiency was 0.991. The lower recovery value for Aldrin is a function of its higher

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volatility.   The same effect is seen in the lower recovery for the surrogate standard, which is more volatile than the rest of the analytes. The precision of the method is also excellent.   The mean %RSD for all the analytes was 3.0%.

Method validation data for the single organochlorine pesticides using LLE are presented in Table II for comparison. The mean accuracy of the method is 88.2%; the mean precision is 2.7 %RSD.   Aldrin is seen to have the lowest recovery by LLE also.

Results for the disk extraction of the 608/8080 analytes from an average groundwater composite at validation concentration levels are compiled in Table III.   Representative Aroclors were included in this study, not the entire list. The data indicate that very good accuracy and precision can be expected for disk LSE applied to actual samples. For these groundwater composites, the mean %Recovery was 92.6, the mean precision was 4.4 %RSD, and the mean elution efficiency was 0.993.

Summary Table IV contains the results for the disk LSE of all the analytes from reagent water at MDL concentration levels. The MDL's calculated from the Empore^{TM} data and the current laboratory MDL's for LLE are also listed. Several of the Empore^{TM} MDL's would have to be rerun at a lower level to meet the requirements of 40 CFR, Part 136, Appendix B.   Accuracy (%R) values at these levels are good; the mean %Recovery is 91.9%. Except for a contaminant interfering with endrin aldehyde, the precision data are also good, with the mean at 5.3 %RSD.   Comparison of the MDL values for LSE and LLE shows lower results for LSE in all cases except the endrin aldehyde.   The lower level of contaminants accounts for the lower MDL's by LSE, a factor more evident in the MDL differences for multicomponent analytes (Chlordane, Toxaphene, and the PCB's).

Table V shows analysis results for disk LSE of the analytes from actual groundwater composites at the low MDL concentration levels.   MDL's calculated from these data compare favorably with the MDL's determined in reagent water. Mean accuracy was 81.3% Recovery, and precision was 7.1 %RSD.

A liter of reagent water could be processed through the disk in an average time of 7-8 min. The processing time for the "average" groundwater composites ranged from 8-18 min. In production, several samples could be extracted simultaneously. Many of these experiments were run using a manifold with four extraction stations.

High Particulate Samples

Composites of samples with very high particulate content were prepared to study the procedure modifications that might be necessary to handle these sample types. The composites had TSS contents in the range of 1.8-18 g/L. In contrast, the "average" groundwater composites had TSS contents of 1- 5 mg/L. The high particulate samples took several hours to process through the disk, even after allowing the particulates to settle and

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decanting most of the sample volume.

The problem of excessive filter time was managed with a pre-filter positioned on top of the Empore™ disk. Five different pre-filters of varying pore size were evaluated. The best results were achieved with the Whatman graded density filter. With this prefilter, and decanting most of the sample volume before transferring the bulk of the particulates, the high particulate composites could be extracted in approximately 20-40 min.

The more critical problem presented by high TSS content samples is effective recovery of analytes sorbed on the particulates. It requires efficient elution of the filter cake of particulates that results from sample filtered through the Empore disk and prefilter. Consistent recoveries were obtained by adding 1mL of methanol to the disk and collected particulates with the first 5ml of ethyl acetate eluant, mixing the particulates so that they were well dispersed in the eluant mix, and than allowing some time for equilibration (~3 min). A larger K-D concentrator tube is used to allow for the larger water/methanol layer (1-4mL) in the total collected eluant.

Table VI shows Empore™ LSE results on two of the very high TSS content composite groundwaters. Data for LLE, using continuous liquid-liquid extractors, were also obtained for comparison. Recovery data are consistently good for the LSE analyses. Precision data obtained for LSE and LLE on these high particulate samples are very comparable.

The slightly higher total average recovery values for LSE compared with LLE are the result of poorer recoveries for selected analytes by LLE: Aldrin, Heptachlor, Methoxychlor, and the 4,4'-DDT, -DDE, and -DDD. Various mechanisms may be at work contributing to the loss/degradation of these analytes -- light and temperature conditions during the 18-hour extraction, or particulate surface reaction effects.

Results on elution efficiency tests for four different high particulate groundwater composites are compiled in Table VII. These data indicate that the procedure used adequately eluted the analytes from the collected particulates, prefilter, and Empore disk. More exhaustive elution is not required.

CONCLUSIONS

The experimental data clearly validate the substitution of LSE using Empore™ C18 disks for LLE in the analysis of the organochlorine pesticides and PCB's tested. This study went beyond the required validation and MDL determination in reagent water; the method was validated in the types of water sample matrices typically encountered in an environmental laboratory. LSE is not only equivalent to LLE, it is preferred because of its time and cost benefits, and especially because of its environmental benefits. It represents a substantial reduction in the volume of hazardous solvents required for sample preparation.

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ACKNOWLEDGEMENT

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(2) Hagen, D. F.; Markell, C. G.; Schmitt, G. A.; Blevins, D. D. Analyt. Chim. Acta 1990, 236, 157-164.(1) Method 525.

TABLE I

EMPORE™ EXTRACTION OF ORGANOCHLORINE PESTICIDES AND
PCB's FROM REAGENT WATER AT VALIDATION CONCENTRATION LEVELS

Analyte	SPIKE µg/L	SAMPLE ANALYSIS Mean[a] %R	%RSD	Elution Efficiency[b]
Aldrin	1.27	77	3.9	0.990
a-BHC	1.30	93	3.3	0.995
b-BHC	1.33	93	2.9	0.992
d-BHC	1.24	94	3.3	0.996
g-BHC (Lindane)	1.33	93	3.0	0.995
Chlordane	12.44	94	4.0	0.991
4,4'-DDD	1.33	93	2.7	0.994
4,4'-DDE	1.19	90	3.5	0.993
4,4'-DDT	1.36	92	2.8	0.992
Dieldrin	1.41	92	2.7	0.993
Endosulfan I	1.27	93	3.0	0.991
Endosulfan II	1.22	94	2.5	0.989
Endosulfan sulfate	1.13	93	2.3	0.992
Endrin	1.36	95	3.4	0.991
Endrin aldehyde	1.38	93	3.6	0.987
Endrin ketone	1.34	93	2.3	0.992
Heptachlor	1.60	87	2.4	0.992
Heptachlor epoxide	1.33	93	2.8	0.992
Methoxychlor	4.21	91	3.1	0.992
Toxaphene	6.31	90	6.0	0.995
PCB-1016	5.86	96	3.9	0.988
PCB-1221	11.83	94	1.8	N.A.
PCB-1232	7.95	88	1.5	N.A.
PCB-1242	7.13	87	2.0	N.A.
PCB-1248	5.75	89	3.1	0.990
PCB-1254	2.51	88	3.5	0.986
PCB-1260	2.08	96	2.6	0.996

[a]n=8, R=recovery (accuracy)
[b]A/(A+B) A=analyte concentration in first 10mL eluant
     B=analyte concentration in second 10mL eluant

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TABLE II

LIQUID-LIQUID EXTRACTION OF ORGANOCHLORINE PESTICIDES
FROM REAGENT WATER AT VALIDATION CONCENTRATION LEVELS

Analyte	SPIKE µg/L	SAMPLE ANALYSIS Mean[a] %R	%RSD
Aldrin	1.241	65	3.4
a-BHC	1.236	84	3.8
b-BHC	1.251	91	1.5
d-BHC	1.093	93	3.0
g-BHC (Lindane)	1.246	85	3.6
4,4'-DDD	1.220	88	1.7
4,4'-DDE	1.214	87	1.8
4,4'-DDT	1.177	91	0.9
Dieldrin	1.248	88	2.6
Endosulfan I	1.264	86	2.3
Endosulfan II	1.240	88	1.9
Endosulfan sulfate	1.225	90	2.0
Endrin	1.196	95	2.6
Endrin aldehyde	1.268	80	3.7
Endrin ketone	1.308	85	2.1
Heptachlor	1.011	113	6.8
Heptachlor epoxide	1.263	86	2.8
Methoxychlor	4.000	90	2.1

[a]n=4, R=recovery (accuracy)

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TABLE III

EMPORE™ EXTRACTION OF ORGANOCHLORINE PESTICIDES AND PCB's FROM COMPOSITE AVERAGE GROUNDWATER AT VALIDATION CONCENTRATION LEVELS

Analyte	SPIKE µg/L	SAMPLE ANALYSIS Mean[a] %R	%RSD	Elution Efficiency
Aldrin	0.83	84	6.2	0.991
a-BHC	0.81	96	4.7	0.997
b-BHC	0.87	96	4.4	0.994
d-BHC	0.52	96	4.6	0.997
g-BHC (Lindane)	0.84	96	4.6	0.997
Chlordane	12.36	82	6.0	0.978
4,4'-DDD	0.97	94	4.5	0.995
4,4'-DDE	0.85	90	3.9	0.993
4,4'-DDT	0.99	95	4.3	0.993
Dieldrin	0.96	96	4.6	0.994
Endosulfan I	0.85	95	4.4	0.994
Endosulfan II	0.87	94	4.1	0.993
Endosulfan sulfate	0.82	96	4.2	0.994
Endrin	1.00	100	4.6	0.993
Endrin aldehyde	0.94	90	3.6	0.988
Endrin ketone	0.98	96	4.3	0.995
Heptachlor	0.94	86	5.4	0.993
Heptachlor epoxide	0.88	96	4.5	0.994
Methoxychlor	3.43	95	4.4	0.993
Toxaphene	5.51	93	5.0	0.985
PCB-1016	6.23	86	2.4	0.996
PCB-1260	2.18	88	1.7	0.995

[a]n=8

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TABLE IV

EMPORE™ EXTRACTION OF ORGANOCHLORINE PESTICIDES AND
PCB's FROM REAGENT WATER AT MDL CONCENTRATION LEVELS

Analyte	SPIKE μg/L	SAMPLE ANALYSIS Mean[a] %R	%RSD	MDL[b], μg/L LSE	LLE
Aldrin	0.019	89	7.7	0.004	0.011
a-BHC	0.010	100	5.1	0.001	0.009
b-BHC	0.020	95	4.1	0.002	0.013
d-BHC	0.010	95	6.3	0.002	0.006
g-BHC (Lindane)	0.012	96	4.1	0.002	0.004
Chlordane	0.313	96	3.8	0.035	0.081
4,4'-DDD	0.017	93	4.9	0.003	0.006
4,4'-DDE	0.015	93	3.9	0.002	0.007
4,4'-DDT	0.019	84	6.0	0.004	0.006
Dieldrin	0.019	104	11.0	0.006	0.007
Endosulfan I	0.019	93	4.1	0.002	0.005
Endosulfan II	0.021	102	5.1	0.004	0.006
Endosulfan sulfate	0.020	82	4.0	0.006	0.020
Endrin	0.021	95	3.5	0.003	0.006
Endrin aldehyde	0.026	89	23.5	0.017	0.011
Endrin ketone	0.019	91	3.5	0.002	0.015
Heptachlor	0.024	90	4.1	0.004	0.005
Heptachlor epoxide	0.019	93	3.9	0.002	0.004
Methoxychlor	0.078	89	5.1	0.011	0.036
Toxaphene	0.378	100	3.0	0.034	0.093
PCB-1016	0.583	87	4.6	0.070	0.21
PCB-1221	0.613	84	2.4	0.048	0.37
PCB-1232	0.431	90	4.2	0.049	0.11
PCB-1242	0.246	101	5.7	0.042	0.096
PCB-1248	0.307	78	3.3	0.024	0.11
PCB-1254	0.303	86	2.4	0.019	0.098
PCB-1260	0.130	87	3.8	0.013	0.016

[a]n=8
[b]40CFR, Part 136, Appendix B. The minimum detection limit (MDL) is
defined as the minimum concentration of a substance that can be
measured and reported with 99% confidence that the analyte
concentration is greater than zero.

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TABLE V

EMPORE™ EXTRACTION OF ORGANOCHLORINE PESTICIDES AND
PCB's FROM COMPOSITE AVERAGE GROUNDWATER
AT MDL CONCENTRATION LEVELS

Analyte	SPIKE µg/L	SAMPLE ANALYSIS Mean[a] %R	%RSD	MDL µg/L
Aldrin	0.016	109	8.4	0.004
a-BHC	0.011	82	6.1	0.002
b-BHC	0.024	71	6.5	0.003
d-BHC	0.011	80	7.6	0.002
g-BHC (Lindane)	0.014	76	6.8	0.002
Chlordane	0.317	80	11.2	0.035
4,4'-DDD	0.018	77	5.7	0.002
4,4'-DDE	0.022	59	5.2	0.002
4,4'-DDT	0.017	90	5.6	0.003
Dieldrin	0.018	90	14.0	0.007
Endosulfan I	0.018	89	5.7	0.016
Endosulfan II	0.029	62	10.3	0.006
Endosulfan sulfate	0.022	74	8.1	0.017
Endrin	0.024	76	5.4	0.003
Endrin aldehyde	0.027	82	12.9	0.008
Endrin ketone	0.019	83	6.2	0.016
Heptachlor	0.027	71	6.5	0.004
Heptachlor epoxide	0.019	84	6.0	0.003
Methoxychlor	0.076	85	6.0	0.012
PCB-1016	0.563	91	2.5	0.038
PCB-1260	0.127	95	2.7	0.010

[a]n=8

TABLE VI

COMPARISON OF LIQUID-SOLID AND LIQUID-LIQUID EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM COMPOSITE HIGH PARTICULATE GROUNDWATERS AT VALIDATION CONCENTRATION LEVELS (1ug/L)

Analyte	GROUNDWATER #1: 5/9 EMPORE LSE		GROUNDWATER #1: TSS = 18 g/L 4/25 LLE		GROUNDWATER #2: 5/14 EMPORE LSE		GROUNDWATER #2: TSS = 15 g/L 5/14 LLE	
	Mean %R n=5	%RSD	Mean %R n=3	%RSD	Mean %R n=5	%RSD	Mean %R n=4	%RSD
Aldrin	72	6.5	31	6.9	59	8.8	45	13.6
a-BHC	78	8.5	79	4.2	73	4.9	89	0.4
b-BHC	80	8.0	94	3.3	77	3.6	101	2.7
d-BHC	77	9.3	84	3.6	75	5.6	94	1.1
g-BHC (Lindane)	80	8.3	82	4.1	76	4.7	93	3.1
4,4'-DDD	79	5.6	35	4.4	62	6.1	43	9.8
4,4'-DDE	78	5.8	31	5.7	60	6.8	35	8.3
4,4'-DDT	72	5.4	26	3.6	65	5.7	32	8.6
Dieldrin	81	7.6	54	6.2	73	3.8	67	6.2
Endosulfan I	78	7.5	61	5.4	74	4.2	74	6.4
Endosulfan II	76	7.5	64	5.4	72	4.4	72	6.7
Endosulfan sulfate	81	8.4	75	4.2	77	4.5	84	6.1
Endrin	82	7.1	56	4.8	77	3.4	71	6.0
Endrin aldehyde	66	6.5	77	3.8	77	6.0	89	2.1
Endrin ketone	83	8.7	78	5.5	77	4.3	85	3.9
Heptachlor	72	6.6	38	4.5	61	5.0	37	10.2
Heptatchlor epoxide	81	7.4	64	4.8	75	3.6	74	5.1
Methoxychlor	79	5.6	36	0.7	68	2.2	48	7.7
AVERAGE:	77	7.2	59	4.5	71	4.9	68	6.0

TABLE VII

EMPORE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM
COMPOSITE HIGH PARTICULATE GROUNDWATERS AT
VALIDATION CONCENTRATION LEVELS (1ug/L)
MEAN ELUTION EFFICIENCIES: A/(A+B)

TSS (g/L)	18	15	2.4	1.8	
n =	5	5	6	3	
Analyte	GW #1	GW #2	GW #3	GW #4	Mean
Aldrin	0.925	0.864	0.930	0.959	0.920
a-BHC	0.991	0.977	0.977	0.988	0.983
b-BHC	0.980	0.964	0.956	0.976	0.969
d-BHC	0.987	0.972	0.973	0.986	0.980
g-BHC (Lindane)	0.991	0.976	0.974	0.982	0.981
4,4'-DDD	0.929	0.861	0.933	0.968	0.923
4,4'-DDE	0.926	0.856	0.922	0.962	0.917
4,4'-DDT	0.928	0.873	0.917	0.954	0.918
Dieldrin	0.955	0.923	0.946	0.957	0.945
Endosulfan I	0.954	0.930	0.941	0.967	0.948
Endosulfan II	0.956	0.925	0.942	0.970	0.948
Endosulfan sulfate	0.968	0.937	0.949	0.976	0.957
Endrin	0.956	0.926	0.943	0.969	0.949
Endrin aldehyde	0.973	0.953	0.948	0.965	0.960
Endrin ketone	0.975	0.948	0.958	0.980	0.965
Heptachlor	0.932	0.898	0.925	0.952	0.927
Heptachlor epoxide	0.959	0.935	0.946	0.968	0.952
Methoxychlor	0.923	0.873	0.910	0.954	0.915
AVERAGE:	0.956	0.922	0.944	0.968	0.948

69 IMPROVING THE ANALYSIS OF SEMI-VOLATILE POLLUTANTS

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ABSTRACT

Complex resolution and monitoring requirements established in EPA Method 8270 demand the use of capillary columns that have high inertness, efficiency, and thermal stability. Recent polymer technology has been developed that substantially improves capillary columns used in the analysis of semi-volatile pollutants. Columns produced with this technology exhibit increased response factors for active compounds such as 2,4-Dinitrophenol and 4-Nitrophenol and increased thermal stability, resulting in faster analysis times and lower column bleed. Data and chromatograms will be shown comparing the analysis of semi-volatile pollutants on conventional capillary column and columns made with new technology. Direct comparisons will be shown of response factors, analysis times, and column bleed between the columns.

INTRODUCTION

The complex resolution and monitoring requirements established under RCRA, SARA, and SDWA, demanded improvements in existing analytical methodology. The EPA responded to this need with the development of method 8270, a GC/MS method for the analysis of semi-volatile pollutants. This method utilizes high resolution capillary chromatography. Capillary columns have the required inertness to allow acidic, basic, and neutral compounds to be analyzed simultaneously, the efficiency to separate highly complex mixtures, and the thermal stability to analyze high molecular weight compounds.

With the widespread use of method 8270, it has become evident that not all capillary columns have the necessary inertness for trace analysis of active compounds. Others do not have the efficiency to resolve isomer pairs which cannot be distinguished by their spectra alone. Still other columns do not have the thermal stability essential to analyze high molecular weight compounds and reduce analysis times.

Recent polymer technology has been developed that yields a column with substantially improved inertness, efficiency, and thermal stability for the analysis of semi-volatile pollutants - the XTI-5.

The response of phenols is an excellent indication of capillary column inertness. Figure 1 shows a total ion chromatogram of fifteen phenols and six internal standards on a XTI-5 capillary column. The phenols show excellent peak symmetry and response at 50ng/ul, indicating the inertness of the column.

Figure 1 - Phenols Look Exceptional With GC/MS Analysis on an XTI-5
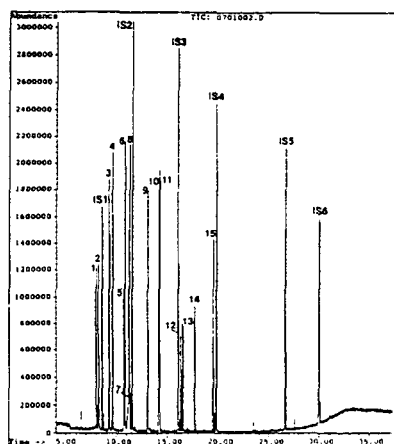
Phenols
1. Phenol
2. 2-chlorophenol
3. 2-methylphenol
4. 4-methylphenol
5. 2-nitrophenol
6. 2,4-dimethylphenol
7. Benzoic acid
8. 2,4-dichlorophenol
9. 4-chloro-3-methylphenol
10. 2,4,6-trichlorophenol
11. 2,4,5-trichlorophenol
12. 2,4-dinitrophenol
13. 4-nitrophenol
14. 4,6-dinitro-2-methylphenol
15. Pentachlorophenol

IS
IS1. 1,4-dichlorobenzene-d4
IS2. Naphthalene-d8
IS3. Acenaphthalene-d10
IS4. Phenanthracene-d10
IS5. Chrysene-d12
IS6. Perylene-d12

30m, 0.25mm ID, 0.25μm XTI-5 (cat.# 12223).
1.0μl splitless injection. 40ng of phenols and IS mix.
Oven temp.:   40°C to 350°C @ 15°C/min.   Hold 15min.
Inj. temp.:   350°C   Det.:   MS (TIC)
Scan rate: 1.5scan/sec. Scan Range: 35-400AMU

Many EPA and CLP methods require minimum response factors and linear calibration curves over a concentration range of 20 to 160ng. Linear response factors are another indication of column inertness and critical for environmental analyses. CLP protocols list nineteen semi-volatile compounds as having minimum Relative Response Factors (RRF) criteria of 0.010. These low response factors are due to these compound's poor linearity and sensitivity. Figure 2 shows calibration curves on the XTI-5 for two erractically performing compounds, 2,4-dinitrophenol and 4-nitrophenol. The calibration curves of these phenols on the XTI-5 is very linear, even over a concentration range of 20 to 160ng.
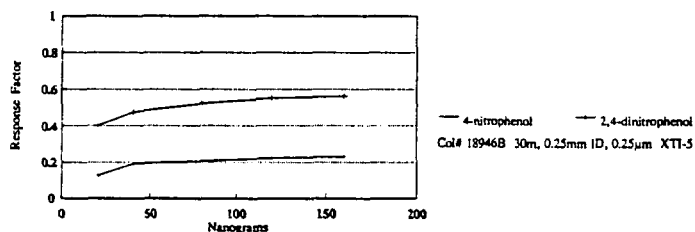
Figure 2 - XTI-5 Calibration Curve

Table 1 shows the response factors and percentage of Relative Standard Deviations (RSD) calculated for 2,4-dinitrophenol, 4-nitrophenol, pentachlorophenol, and benzoic acid. The response factors were calculated by using the internal standard that elutes closest to the compound (ie., d10-phenanthracene for Pentachlorophenol and d10-acenaphthene for 2,4-dinitrophenol). Five data points at concentrations of 20, 40, 80, 120, and 160ng/ul were plotted for the calibration curve. The linear plots of the phenols clearly indicate the highly inert nature of the XTI-5 column. All response factors meet or exceed the minimum criteria and all RSD percentages are well below the maximum deviation criteria of 20.5%.

Table 1 - Response Factors are Linear for XTI-5 Capillary Columns

Compound	Col#	20ng	50ng	80ng	120ng	160ng	mean	std. dev.	%RSD
2,4-dinitrophenol	1	0.402	0.503	0.523	0.553	0.561	0.508	0.057	11.3%
	2	0.419	0.502	0.550	0.494	0.560	0.507	0.050	9.9%
min. CLP RF=.01	3	0.389	0.475	0.496	0.524	0.550	0.503	0.055	11.0%
	4	0.372	0.480	0.498	0.445	0.444	0.447	0.043	9.6%
4-nitrophenol	1	0.188	0.194	0.208	0.225	0.232	0.209	0.017	8.1%
	2	0.158	0.196	0.223	0.206	0.167	0.190	0.024	12.8%
min. CLP RF=.01	3	0.085	0.110	0.122	0.144	0.147	0.122	0.023	18.7%
	4	0.127	0.138	0.157	0.163	0.133	0.144	0.014	9.7%
Pentachlorophenol	1	0.184	0.233	0.253	0.268	0.278	0.243	0.033	13.6%
	2	0.181	0.223	0.242	0.233	0.215	0.219	0.021	9.6%
min. CLP RF=.05	3	0.160	0.182	0.203	0.219	0.236	0.200	0.027	13.4%
	4	0.275	0.243	0.260	0.272	0.267	0.263	0.011	4.3%
Benzoic Acid	1	0.302	0.453	0.466	0.491	0.504	0.443	0.073	16.4%
	2	0.321	0.453	0.494	0.523	0.583	0.475	0.088	18.5%
min. CLP RF=N/A	3	0.314	0.426	0.465	0.520	0.485	0.442	0.071	16.0%
	4	0.359	0.451	0.539	0.433	0.489	0.454	0.060	13.2%

Thermal stability is of extreme importance when analyzing high molecular weight compounds, such as PNA's found in semi-volatile pollutant analyses. Column bleed can present several problems when analyzing environmental samples. The rise in baseline associated with column bleed can lead to inaccurate quantitative results, confuse spectral interpretation and, in extreme cases, cause misidentification. Figure 3 shows total ion chromatograms bleed profiles of the XTI-5, the conventional Rt_x-5, and a competitors, environmental column. MSD test results clearly show the XTI-5 exhibits the lowest bleed.

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Figure 3 - XTI Shows Lowest Bleed of any Column

Oven temp.: 40°C to 350°C @ 15°C/min. Hold 15min.
Inj. temp.: 350°C   Det.: MS (TIC)
Scan rate: 1.5scan/sec. Scan Range: 35-400AMU
MS temp: 270°C
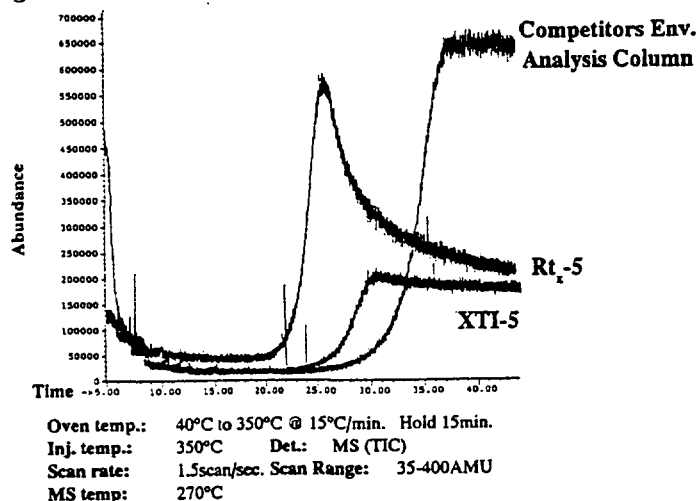
Figure 4 shows the analysis of the semi-volatile compounds monitored in EPA's Contract Lab Program on a 30m, 0.25mm ID, 1.0um XTI-5. Analysis times is complete in 45 minutes and bleed is minimal at 325°C.

Figure 4 - Semi-Volatile Pollutant Analysis on 30m, 0.25mm ID, 1.0um XTI-5
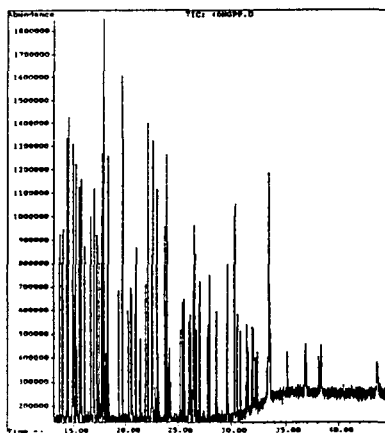
The new XTI-5 capillary column can improve the consistency and reliability of your semi-volatile pollutant data. The technology used to produce these columns yields capillary columns with improved inertness, increased efficiency, and higher thermal stability.

```
File:              A:\0701002.D
Operator:
Date Acquired:     3 Jan 91    5:38 pm
Method File Name: benzphen.M
Sample Name:                   40ng std
Misc Info:                     rtx5 xti 30,.25,.25 40(1)-350 @ 10/min
Bottle Number:     7
```
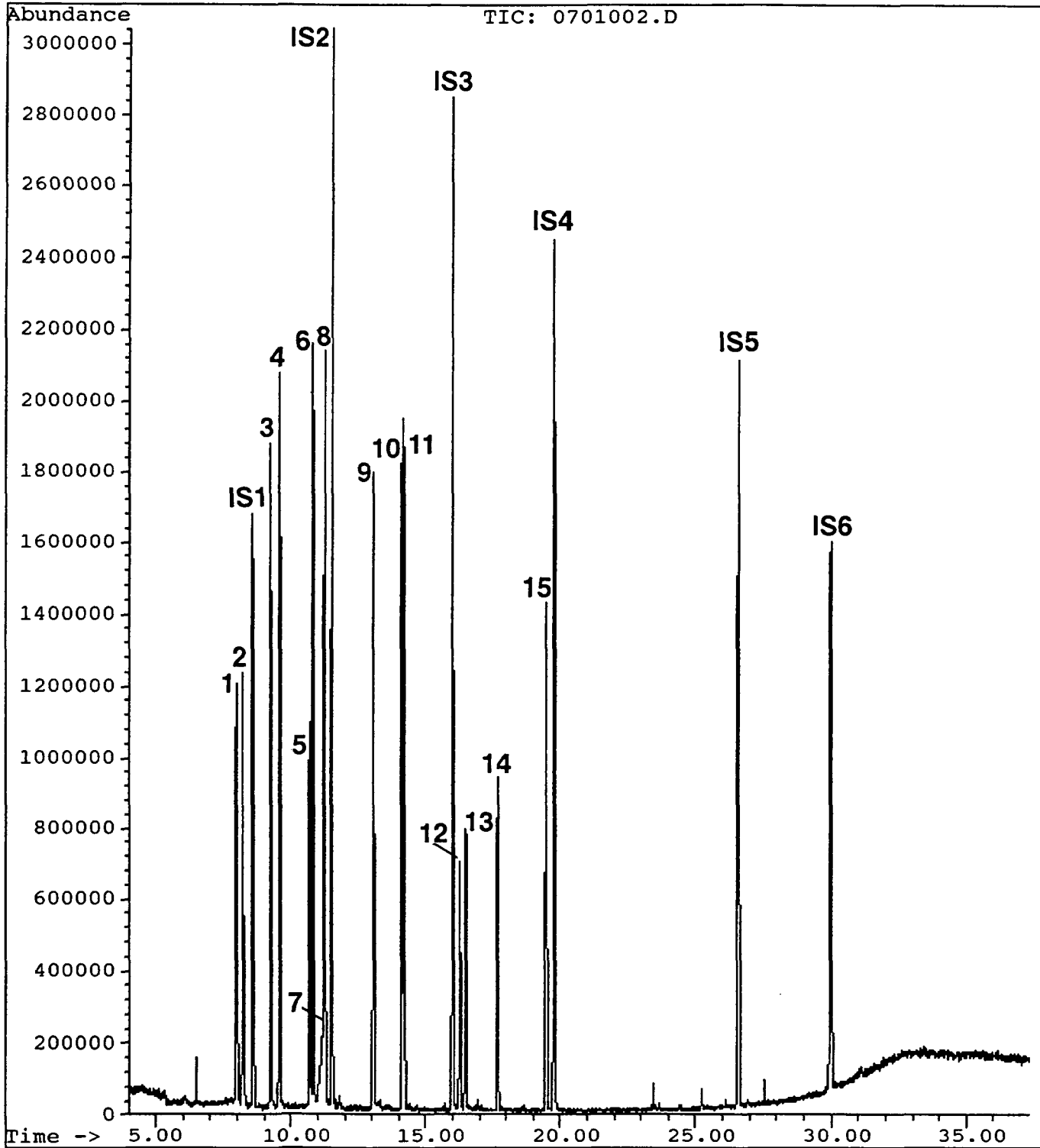
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4-nitrophenol	1	0.188	0.194	0.208	0.225	0.232	0.209	0.017	8.1%
	2	0.158	0.196	0.223	0.206	0.167	0.190	0.024	12.8%
min. CLP RF=.01	3	0.085	0.110	0.122	0.144	0.147	0.122	0.023	18.7%
	4	0.127	0.138	0.157	0.163	0.133	0.144	0.014	9.7%
Pentachlorophenol	1	0.184	0.233	0.253	0.268	0.278	0.243	0.033	13.6%
	2	0.181	0.223	0.242	0.233	0.215	0.219	0.021	9.6%
min. CLP RF=.05	3	0.160	0.182	0.203	0.219	0.236	0.200	0.027	13.4%
	4	0.275	0.243	0.260	0.272	0.267	0.263	0.011	4.3%
Benzoic Acid	1	0.302	0.453	0.466	0.491	0.504	0.443	0.073	16.4%
	2	0.321	0.453	0.494	0.523	0.583	0.475	0.088	18.5%
min. CLP RF=N/A	3	0.314	0.426	0.465	0.520	0.485	0.442	0.071	16.0%
	4	0.359	0.451	0.539	0.433	0.489	0.454	0.060	13.2%

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Figure 3 - XTI Shows Lowest Bleed of any Column

Oven temp.: 40°C to 350°C @ 15°C/min. Hold 15min.
Inj. temp.: 350°C   **Det.:** MS (TIC)
Scan rate: 1.5scan/sec. **Scan Range:** 35-400AMU
MS temp: 270°C

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```
File:              D:\DATA\40NGPP.D
Operator:
Date Acquired:      1 Apr 91   12:39 pm
Method File Name: PP.M
Sample Name:
Misc Info:
Bottle Number:      1
```


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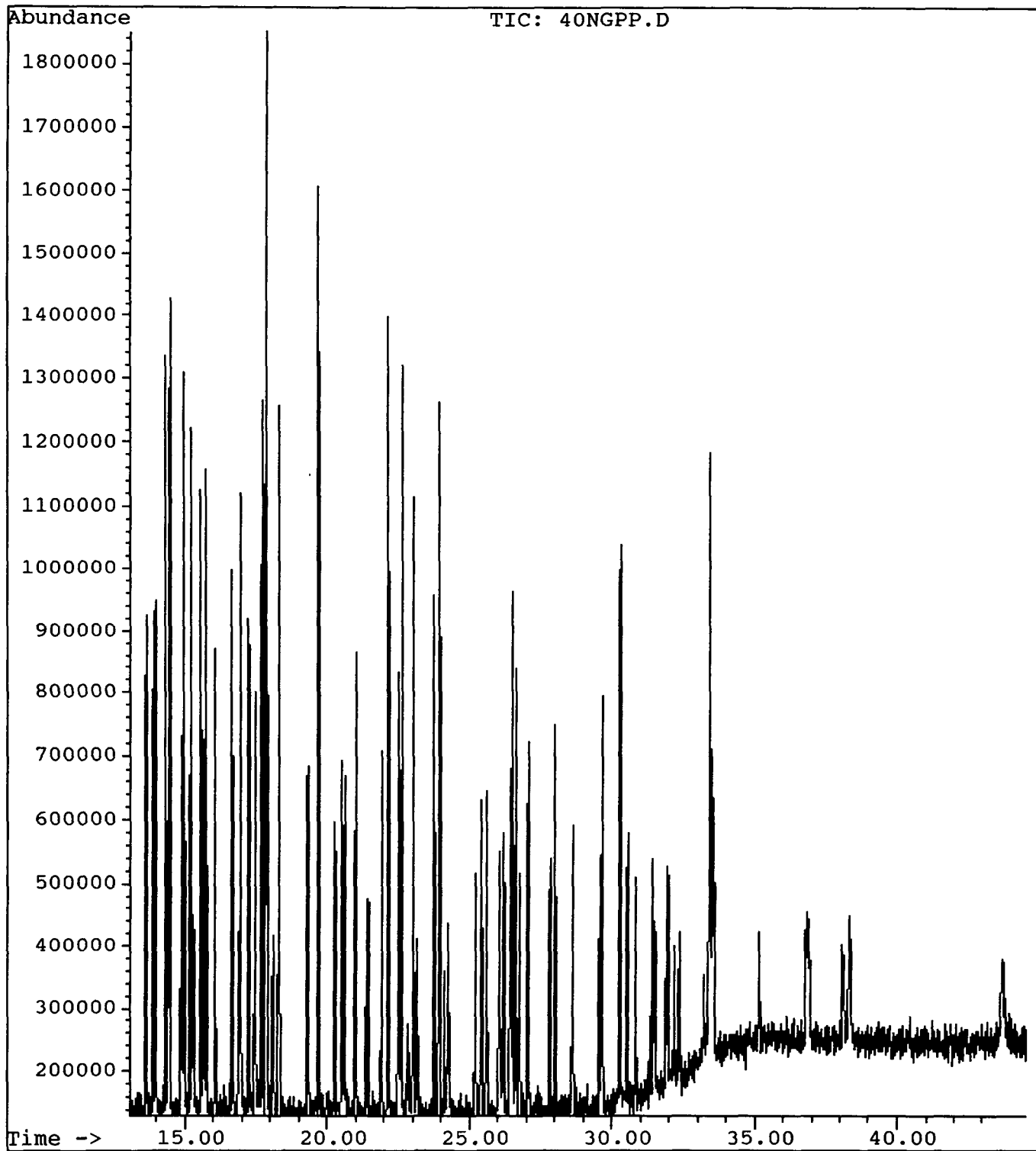
Electrospray Combined with Ion Trap Mass Spectrometry for Environmental Monitoring

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Environmental monitoring of many non-volatile or thermally unstable polar organics relies on the development of sensitive, specific and cost effective LC/MS techniques. Electrospray can meet these goals since it has the capability to generate molecular ions from low pg quantities of most environmentally relevant compounds. The coupling of electrospray with an ion trap mass spectrometer (ITMS) offers the potential to gain structural information through MS/MS without the additional cost of multiple mass analyzers, as well as achieving better sensitivity than conventional quadrupole mass analyzers. This paper reports on the coupling of a commercial electrospray interface to an ITMS. The system was evaluated for its use for environmental monitoring.

The electrospray source was interfaced to a second analyzer mounted in the ITMS vacuum chamber with minimal changes to either commercial unit. The use of a second analyzer in the ITMS minimized switch time between EI and electrospray operations. Ions formed in the electrospray interface were gated into the ITMS analyzer, using the 180 V gating circuit employed for EI operations, with good efficiency and minimal losses from collisional activation. The determination of numerous pesticides, herbicides, dyes, and potential DNA adducts proved that the electrospray ITMS combination could acquire high fg to low pg full scan spectra. These sensitivities were 10-30 times superior to those obtained by electrospray

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on a quadrupole mass analyzer. The electrospray spectra of these compounds usually only consisted of $[M+H]^+$ and/or $[M+Na]^+$ ions and no fragment ions. No thermal decomposition products were detected for the thermally labile compounds analyzed. Occasionally other adduct ions were detected, such as $[M+NH_4]^+$ and $[M+H+triethylamine]^+$ when buffers such as ammonium salts or triethylamine were used in the LC mobile phase. The use of collisional activation decomposition in the ITMS analyzer proved useful in generating MS/MS spectra from the protonated molecular ion or adduct ion for each compound, resulting in fragment ions for identification or confirmation.

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71 Recent Advances In the Use of Supercritical Fluid Extraction for Environmental Applications

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One of the distinct advantages In using supercritical fluid extraction (SFE) is the ability to achieve selective extractions based upon differences in threshold solubilities of different analytes. Different threshold solubilities can be attained by varying extraction pressures and/or temperatures. The addition of modifiers to the supercritical fluid extracting phase has also enhanced the extraction efficiency of specific analytes. Depending on the sample matrix, the enhancement of solubilities could be offset by diffusion enhancement or by the displacement of analytes from the outer or Inner surface of matrix particles. There also Is the possibility of performing chemical reactions, such as acid hydrolysis and functional group derivatization, during the SFE step thereby achieving distinct ctivity enhancements for specific analytes In complex matrices. Further selectivity enhancements can be achieved by utilizing different adsorbents which are added to the extraction vessel with the sample or are packed Into secondary extraction vessels which are placed down stream of the sample extraction vessel. In this work, each of these enhancements will be Investigated and demonstrated using a newly developed directly coupled SFE/GC field portable system with environmental matrices such as soils, marine sediments, drilling muds, sludges, and ashes.

72 USING SUPERCRITICAL FLUID EXTRACTION TO SEPARATE DIESEL FROM SOIL MATRICES

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ABSTRACT
The initial and arguably the most crucial step in most
environmental analytical analyses is the separation of
analytes from the sample matrix. Separating or extracting
organic compounds from soil is currently accomplished by
several methods: heating, purging or by solvent extraction.
Of these, solvent extraction is the principal method used.
Because there is interest in reducing dependance on solvent-
use extraction technologies, we have examined Supercritical
Fluid Extraction (SFE) as a method to separate semi-volatile
organic analytes from soil matrices. Our initial data indicate
that SFE works very well to extract diesel from soil samples
and reduces the amount of solvent required by a factor of ten
compared to UltraSonic Extraction (USE). This paper will
present the results of a direct comparison study of diesel
levels in soil extracts; where each soil sample was submitted
for both USE and SFE extraction and the extracts analyzed by
gas chromatographic methods.

INTRODUCTION
Supercritical fluid extraction of analytes from environmental
sample matrices is generating interest in the analytical
laboratory. The interest stems from reports of initial success
in separating organic analytes from samples.[1-8] In addition to
the technical feasibility, there is a genuine concern among
the environmental lab community to reduce the amount of toxic
and hazardous solvents in the work-place. These two
influencing factors guided our efforts to investigate the use
of SFE. Our efforts have focused upon comparing the extraction
techniques (USE and SFE) directly. We accomplish this by
submitting soil samples to both extraction methods and
comparing the results of the GC-FID quantitation for the
extracts. The soil samples that we investigated were actual
soil samples which had been submitted by clients to BC
Analytical for diesel hydrocarbon analysis.

Diesel hydrocarbons are herein defined as a class of C_{12}-C_{25} hydrocarbons. A GC chromatogram of a common diesel standard is provided in Figure 1. To quantitate the diesel in a sample extract, integration of peak areas over the entire diesel spectrum range was done. In addition to the integration, diesel must be qualitatively identified by a characteristic chromatographic fingerprint. This is necessary to insure that diesel not gasoline or mineral spirits has been quantitated by the integration.

EXPERIMENTAL

Supercritical fluid extractions were all performed using a Dionex Model 703 Extraction System. All of the extraction cells were 5 cm X 9.4 mm I.D.; the end caps contained stainless steel frits (0.5 um pore size). Eight extractions were run simultaneously, the outlet of each cell was connected to a separate temperature controlled restrictor. Collection of the analytes involved a unique dual chamber vial and double-sided Teflon coated septa. Approximately 10 mL of methylene chloride were placed into each vial. The collection system was then electronically cooled to 5°C. Extractions were carried out with 100% CO_2 that contained 1500 psi of helium headspace (Scott Specialty Gases). All extractions were run at 75°C and 300 atmospheres for a total of 15 min. The restrictors were heated to 150°C to eliminate restrictor plugging. The flow rate was on average 250 mL/min as gas.

Three one gram samples of each soil were weighed and placed in separate vials. The sample size was selected for ease of handling and extraction. No effort was taken to optimize the weight of the sample extracted by SFE. Two of the three 1g samples were extracted under the conditions detailed above. The third 1g sample was used to determine the moisture content of the soil.

Each SFE extract (approximately 10 mL) was reduced to less than 5 mL total volume under a flush of high-purity grade nitrogen gas. The extracts were then transferred to 10 mL concentrator tubes via pasture pipets that were packed with anhydrous sodium sulfate. Each extract vial was then rinsed with 1-3 mL of methylene chloride, and the rinsate added to the concentrator tubes. The extracts were then reduced to 1 mL final volume under a flush of nitrogen. The 1 mL extracts were quantitatively transferred to 1.5 mL vials with Teflon lined septa and screw caps. These extracts were stored at 4 °C prior to GC analysis.

Ultrasonic extraction was carried out in accordance with EPA method 3550A. Flow diagrams of the USE and SFE methods are shown in Figures 2 and 3.

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Gas chromatographic identification and quantitation of diesel in the USE and SFE extracts was accomplished with a HP 5890 gas chromatograph using a 30 meter DB5 capillary column. Prior to each daily run, column and septa conditioning was conducted at 300°C for 90 minutes. The oven temperature was brought to 40°C and allowed to stabilize. The instrument was calibrated using 50, 100, 250, 500, and 1000 ppm diesel standard. Data were analyzed with Nelson 2600 software.

RESULTS AND DISCUSSION
This investigation involved analyzing extracts from 42 soil samples. The soil samples were submitted by clients to BC Analytical for analysis of diesel hydrocarbons. Once the study was under way, all of the samples submitted to BCA for diesel analysis were extracted by both USE and SFE methods. Many of the soil samples investigated have less than the reporting detection limit of diesel in the USE extract. Thirty two of the 42 samples were reported as "not detected" for diesel hydrocarbons by ultrasonic extraction and GC-FID quantitation. (See Table 1.) The remaining ten samples had reported quantities of diesel in the 3550A extract ranging between 1-2800 ppm.

Similarly, 32 of the 42 SFE extracts were confirmed not to contain diesel hydrocarbons. Supercritical extracts were reported to contain diesel if duplicate extracts contained diesel. (See Table 1.) In several cases, a duplicate extract was unavailable; the data were then based upon a single replicate.

Both extraction methods yielded ten soil extracts with diesel hydrocarbons identified. Seven of these ten extracts were for the same soils independent of the extraction method. (See Table 2.) For three soils, a diesel quantity was reported using extraction method 3550A and no confirmation was reported in the SFE extracts. Alternatively, three SFE extracts gave reportable levels of diesel when the 3550A extract had no diesel hydrocarbons reported. However, there is generally good agreement between the incidence of soil extracts containing diesel hydrocarbons using these two extraction methods.

During the investigation, the accuracy of the SFE extraction was not measured using surrogates or spiked soils. Therefore the "true" value of analyte in the soil is taken to be the value reported for the 3550A method. Of the seven soil samples for which both extraction methods gave positive results for diesel analysis, only two results were significantly different. Sample 32 was reported to give 700 ppm diesel via method 3550A while the same soil gave only 115 ppm in the SFE

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extract. However, the converse was also observed. For soil 18, the reported quantity of diesel in the 3550A extract was 46 ppm and the SFE extract gave 535 ppm.

Most of the GC-FID chromatograms of the SFE extracts had a characteristic pattern which was not attributed to hydrocarbon in the soil. (See Figure 4.) However this pattern was not observed in the sample blank. This interference was manually subtracted from each chromatogram to allow for quantitation. The source of the contamination is unknown and is currently under investigation. As a result of the contamination, the reporting detection limit (RDL) for the SFE extracts was set at 5 ppm. The problem that one encounters with a 5 ppm RDL is that a hydrocarbon pattern (such as the mineral spirits identified in Figure 4) may be observed but not reliably quantitated because of the high level of interference.

SUMMARY

Supercritical fluid extraction will find wide use in the environmental laboratory because of the ability to extract organic analytes from soil matrices without the use of large volumes of hazardous solvents. However, before this will happen, the utility of SFE techniques on actual field samples must be demonstrated. Our results indicate that SFE works very well to extract diesel hydrocarbons from soil matrices. In fact these results indicate that SFE is as efficient as ultrasonic extraction in removing diesel from sample matrices. Of the 42 samples that were analyzed, SFE gave similar results to those obtained using USE. In addition the differences that were observed were not one sided. In three cases diesel was identified in the ultrasonic extract and was not confirmed in the corresponding SFE extracts. Similarly, there were three sets of SFE extracts where reportable levels of diesel were identified, yet no diesel was found in the USE extracts. In these six instances, the reported quantity of diesel in the soil was less than 31 ppm. The differences observed between these extracts might very well be attributed to non-representative sample sizes, or sample inhomogeneity. During the next phase of the research we plan to investigate the effect of sample size on extraction optimization. In addition, a reduction in the interference observed by the FID detector in the SFE extracts must be eliminated in order to lower the detection limit to levels equivalent to current methods.

Supercritical fluid extraction does significantly reduce the amount of solvent required for the extraction of diesel hydrocarbons from soil samples from approximately 400 mL for EPA method 3550A to approximately 20 mL for the SFE. Because of these initial successes we plan to continue to investigate the use of SFE to separate diesel from soil matrices.

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25 millivolts (full scale)

Figure 1. Capillary gas chromatogram of a 250 ppm diesel hydrocarbon standard

Ultrasonic Extraction (SW-846 Method 3550A)

General Tasks　　　　　　　　　　**Analysis Specific Tasks**

Weigh 30g of sample
into a 400 mL beaker

Add 150 mL of extraction
solvent to beaker

→ Pesticides, PCB . . . Hexane/Acetone
Semivolatile organics, Diesel . . . CH_2Cl_2

Sonicate sample
for 5 minutes

Decant solvent over Na_2SO_4
into evaporator

Add 100 mL of extraction
solvent to beaker

Sonicate for 5 minutes

Repeat twice (3 sonications total)

Rinse beaker with 50 mL
of extraction solvent

Total volume of
solvent required
400 mL

Decant solvent over Na_2SO_4
into evaporator

Distill off solvent

→ Solvent exchange to hexane
for pesticide and PCB analysis

Evaporate remaining solution
to correct final volume

→ 1 mL for diesel analysis
2 mL for semivolatile organics
10 mL for pesticides and PCB

Transfer sample to vial

→ Florisil cleanup . . . Pesticides
Acid cleanup . . . PCB

Figure 2. Flow diagram of ultrasonic extraction

Supercritical Fluid Extraction

General Tasks

Analysis Specific Tasks

Weigh 1g of sample into an extraction thimble

↓

Load cell into extractor

↓

Extract for 15 minutes

↓

Collect analyte in solvent trap → Pesticide, PCB . . .Hexane
Semivolatile organics, Diesel . . . CH_2Cl_2

↓

Transfer solvent with pipet and Na_2SO_4 into concentrator

↓

Rinse vial with 5 mL of solvent

Total volume of solvent required
20 mL

↓

Evaporate remaining solution to correct final volume → 1 mL for diesel analysis
2 mL for semivolatile organics
10 mL for pesticides and PCB

↓

Transfer sample to vial → Florisil cleanup . . .Pesticides
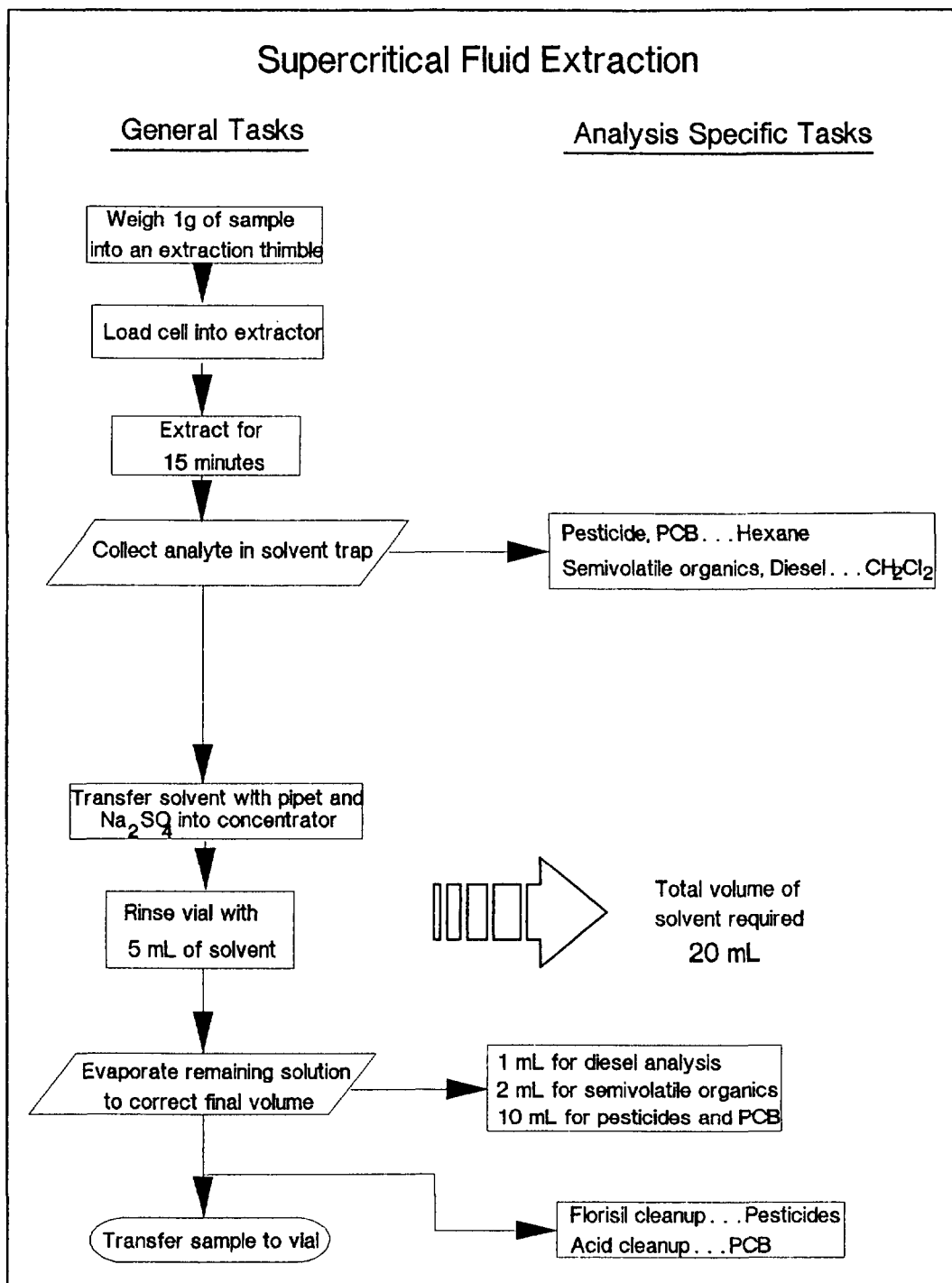Acid cleanup . . . PCB

Figure 3. Flow diagram of Supercritical fluid extraction

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25 millivolts (full scale)

Figure 4. Capillary gas chromatogram of supercritical fluid extract for sample number 31
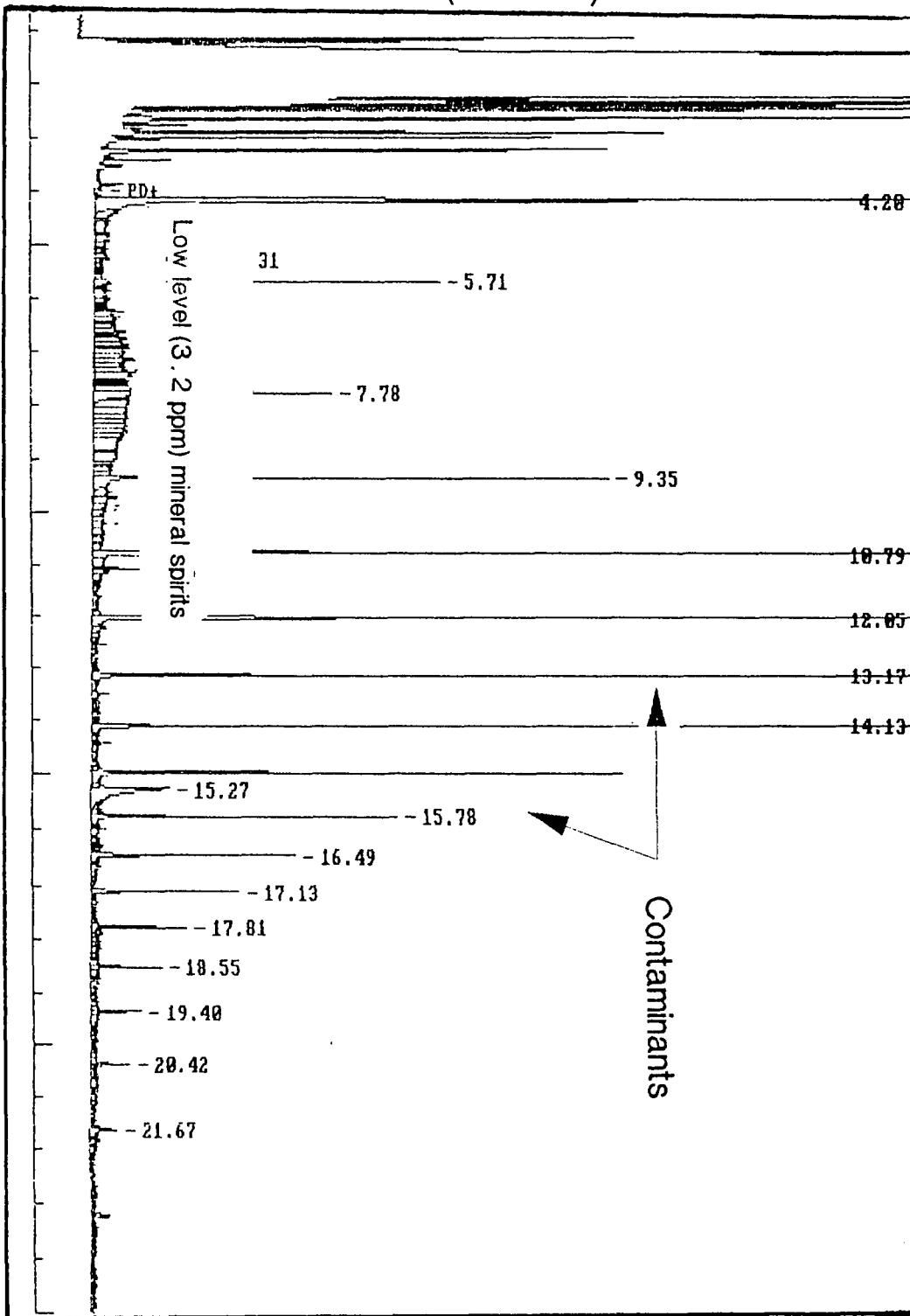
TABLE 1.   RESULTS OF DIESEL HYDROCARBON ANALYSES

SAMPLE NUMBER	BY EPA 3550/8015 (mg/kg)	BY SFE/8015 (mg/kg)		PERCENT MOISTURE
		REPLICATE 1	REPLICATE 2	
1	2800	2280	–	–
2	<1	17	<5	19
3	<1	<5	12	20
4	<1	<5	<5	23
5	<1	<5	<5	19
6	<1	8.5	9.5	12
7	<1	<5	<5	19
8	<1	7.0	7.8	4.7
9	<1	<5	10	21
10	<1	<5	<5	14
11	<1	<5	<5	6.0
12	<1	<5	<5	14
13	<1	<5	<5	22
14	<10	<10	<10	14
15	<1	–	<5	12
16	<1	–	<5	10
17	<1	<5	<5	11
18	46	510	560	17
19	560	635	581	6.6
20	5	<5	<5	14
21	<1	<5	<5	7.2
22	<1	–	17	11
23	6	–	5.2	19
24	<10	<10	<10	13
25	<10	<10	<10	11
26	<1	<5	<5	15
27	<1	<5	<5	15
28	1	<5	14	21
29	<1	<5	<5	23
30	<1	–	<5	25
31	<1	<5	<5	20
32	700	118	112	22
33	<1	<5	<5	22
34	140	65	167	19
35	<1	–	<5	20
36	<1	<5	<5	25
37	30	<5	<5	26
38	<1	<5	<5	18
39	30	55	15	16
40	15	6.6	<5	15
41	<1	<5	<5	18
42	<1	<5	<5	19

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TABLE 2.   EXTRACTS OF SOILS CONTAINING DIESEL HYDROCARBON
LEVELS GREATER THAN THE REPORTING DETECTION LIMIT

SAMPLE NUMBER	BY EPA 3550/8015 (mg/kg)	BY SFE/8015 (mg/kg)
	AVERAGE OF 2 REPLICATES	
1	2800	2280[a]
6	<1	9.0
8	<1	7.4
18	46	535
19	560	608
20	5	<5
22	<1	17[a]
23	6	5.2
32	700	115
34	140	116
37	30	<5
39	30	35
40	15	<5

a) Single extract analysis (no replicate available).

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CREATIVE REVIEW OF "TENTATIVELY IDENTIFIED COMPOUND" DATA USING THE RETENTION INDEX

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INTRODUCTION

Identifying non-target compounds in gas chromatography-mass spectrometry (GC/MS) data is a difficult and time-consuming task, even for those trained in interpretation of mass spectra. It is rare that a compound can be "tentatively identified" with confidence when the only information available is the mass spectrum and the computer library matches.

Aside from prior knowledge of what types of compounds to expect in a particular sample, the only other piece of data available to the data reviewer when interpreting a spectrum is the GC retention time. Because absolute retention times are dependent on a large number of experimental conditions, the retention index was developed to express retention data relative to a standard set of compounds. The original system, called the Kovats index, dates from 1958 and uses the normal alkanes as the retention index standards.

A retention index system was developed in 1979 by Lee and co-authors (1) for use in identifying polycyclic aromatic hydrocarbons (PAH). In the "Lee" retention index system, the retention index standards and their retention indices are naphthalene (I=200.00), phenanthrene (I=300.00), chrysene (I=400.00) and picene or benzo(ghi)perylene (I=500.00). Because the perdeuterated analogs of the first three of these are used as internal standards in the several variations of EPA method 625 for extractable compounds, the Lee retention index can be used NOW by data reviewers in identifying unknown compounds. The Lee retention indices of several hundred compounds of environmental interest are available in the literature (1-5).

CALCULATION OF THE LEE RETENTION INDEX

The Lee retention index, I, is defined as:

$$I = 100 \left(\frac{rt_{unk} - rt_Z}{rt_{Z+1} - rt_Z} \right) + 100 (Z).$$

where rt_{unk} is the retention time of the unknown compound, rt_Z and rt_{Z+1} are the retention times of the bracketing retention index standards, and Z is the number of benzene rings in the retention index standards. To summarize:

Standard	Retention Index	Z
naphthalene	200.00	2
phenanthrene	300.00	3
chrysene	400.00	4

For unknowns which elute before naphthalene or after chrysene, the retention index is "projected" using the two retention index standards closest to the unknown compound.

APPLICATION OF THE LEE RETENTION INDEX TO DATA REVIEW

This paper presents some applications of the Lee retention index system to the identification of compounds in real environmental samples.

The first example (Figure 1) is the spectrum of a dimethylphenol whose experimental I was 194.35. The target compound 2,4-dimethylphenol was also found in this sample at I=190.70. Judging from the known retention indices of the isomeric dimethylphenols, and the measured bias between the experimental index and the known index for the 2,4- isomer, the most probable identification for the unknown is 3,5-dimethylphenol.

Figure 2 shows the spectrum of a polycyclic aromatic hydrocarbon of molecular weight 252. Three of the library matches are target compounds which were also found in the sample at different scan numbers than this unknown. Their scan numbers, and experimental and known retention indices are shown. Based on the known retention order of these compounds (as shown by the retention indices) and considering the experimental bias, the proximity of the unknown to the scan number for benzo(a)pyrene identifies it as benzo(e)pyrene.

Figure 3 shows the spectrum of an unknown with an apparent molecular weight of about 190. Comparison of the experimental spectrum with the library spectra of compounds of MW 192 shows much more intense ions at m/z 190 and m/z 189 in the unknown spectrum. This suggests that the unknown spectrum may not be that of a pure compound, but of two coeluting compounds. In fact, the experimental retention index for the unknown lies just between the known retention indices of the top two library matches, one of which has MW 190 and the other MW 192. Thus both cyclopenta(def)phenanthrene and 9-methylphenanthrene appear to be present in the unknown spectrum.

Figure 4 is the spectrum of another pair of coeluting compounds, this time of dissimilar chemical classes. An isomer of the top library match is present, judging from the retention index. However, a hydrocarbon pattern is also present at m/z 43, 57, 71, 85 etc. The library search results do not suggest the presence of an alkane, but the retention index of pentadecane is close enough to the experimental index that it can also be tentatively identified in this spectrum.

Finally, Figures 5a through 5d show a series of normal alkanes that were found in a sample. As is usual with alkanes, the top library matches are of widely varying chain length. Calculation of the retention index quickly narrows the possibilities to one or two compounds for each spectrum. Note that the tentative identification for each spectrum is not among the top library matches.

CONCLUSIONS

The Lee retention index is an easily calculated bit of information which can be extremely valuable in the identification of unknown compounds. It is useful in identifying specific members of homologous series with identical spectra; coeluting compounds of similar and dissimilar chemical classes; specific positional isomers; and structural isomers. More sophisticated applications of the existing Lee retention index data, using the principles of gas chromatography and structure-retention relationships, are also possible.

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REFERENCES

1. Lee, M.L., Vassilaros, D.L., White, C.M., and Novotny, M., "Retention Indices for Programmed-Temperature Capillary-Column Gas Chromatography of Polycyclic Aromatic Hydrocarbons", *Analytical Chemistry* 51, 768-773, 1979.

2. Vassilaros, D.L., Kong, R.C., Later, D.W., and Lee, M.L., "Linear Retention Index System for Polycyclic Aromatic Compounds. Critical Evaluation and Additional Indices", *Journal of Chromatography*, 252, 1-20, 1982.

3. Willey, C., Iwao, M., Castle, R.M., and Lee, M.L., "Determination of Sulfur Heterocycles in Coal Liquids and Shale Oils", *Analytical Chemistry*, 53, 400-407, 1981.

4. Rostad, C.E., and Pereira, W.E., "Kovats and Lee Retention Indices Determined by Gas Chromatography/Mass Spectrometry for Organic Compounds of Environmental Interest", *Journal of High Resolution Chromatography and Chromatography Communications*, 9, 328-334, 1986.

5. U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Industrial Technology Division, "Analytical Methods for the National.Sewage Sludge Survey. Method 1625, Revision C. Semivolatile Organic Compounds by Isotope Dilution GCMS", August 1988.

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Figure 1

Identification of Specific Dimethylphenol Isomer

Dimethylphenol Isomer	I_{ref}	I_{exp}	Bias
2, 6	184.08		
2, 4 (Target Compound)	192.69	190.70	+1.99
3, 5	196.53	194.35	+2.18
2, 3	198.95		
3, 4	201.49		

LIBRARY SEARCH
08/04/85 16:34:00 + 8:02

DATA: GH057689A16 # 534
ENHANCED (10B 2N 0T)

BASE M/E: 107
RIC: 457727

SAMPLE: 1 UL CC#57689 (8-1-85)

UNKNOWN

1088
SAMPLE

$I_{exp} = 194.35$

PHENOL,2,3-DIMETHYL-   CAS#   526-75-0

C8.H10.0
    1088
M WT 122
B PK 107
RANK 1
 IN 2643
PUR 866

$I_{ref} = 198.95$

PHENOL,3,4-DIMETHYL-   CAS#   95-65-8

C8.H10.0
    1088
M WT 122
B PK 107
RANK 2
 IN 2634
PUR 864

$I_{ref} = 201.49$

PHENOL,2,6-DIMETHYL-   CAS#   576-26-1

C8.H10.0
    1088
M WT 122
B PK 122
RANK 3
 IN 2645
PUR 863

$I_{ref} = 184.08$

50   100   150   200   250   300

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262
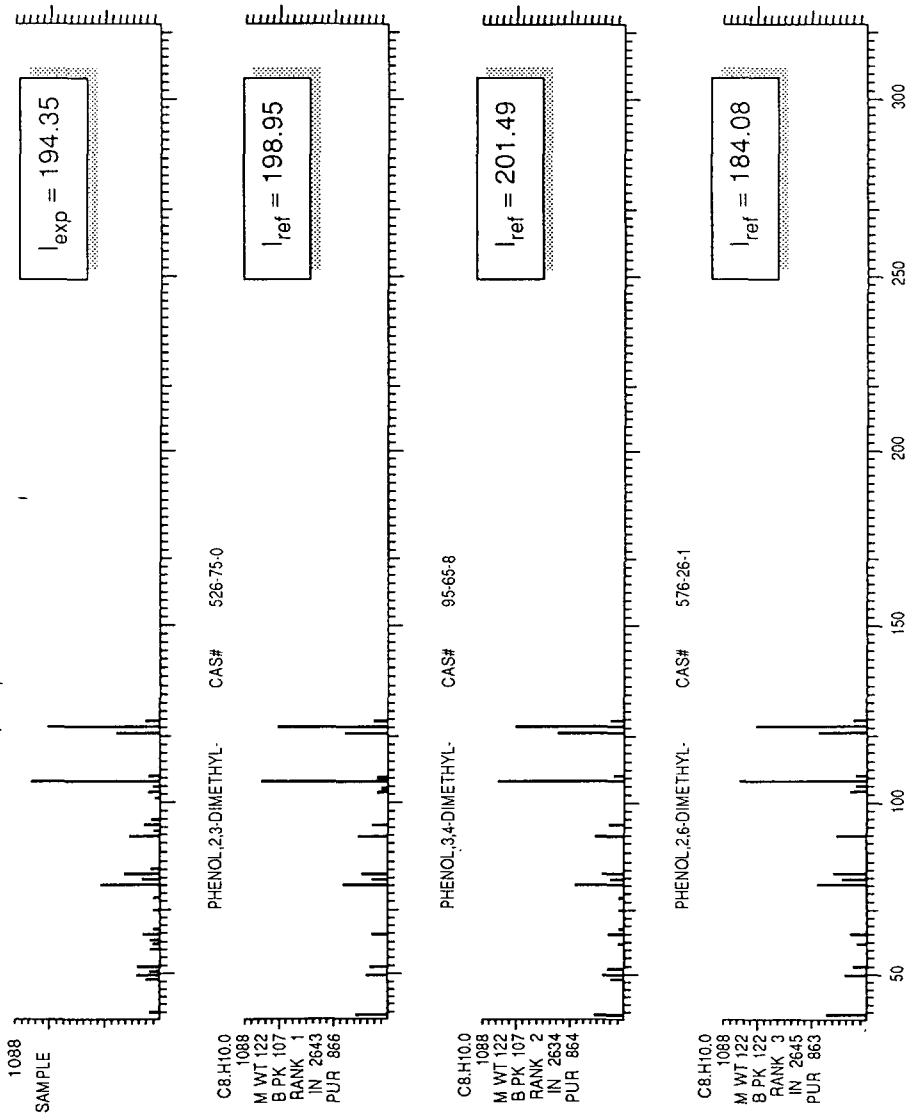
Figure 2

Identification of PAH with Molecular Weight of 252

PAH	I_{ref}	Scan	I_{exp}	Bias
Benzo (j) Fluoranthene	440.92			
Benzo (b) Fluoranthene	441.74	2698	438.03	+3.71
Benzo (k) Fluoranthene	442.56	2703	438.79	+3.77
Benzo (e) Pyrene	450.73	2758	447.12	+3.61
Benzo (a) Pyrene	453.44	2769	448.79	+4.65

LIBRARY SEARCH
06/08/90 6:59:00 + 45:58
SAMPLE: L#1127764

DATA: B1127645 #2758
CALI: B1127645 # 2

BASE M/Z: 252
RIC: 51263

UNKNOWN

$I_{exp} = 447.12$

1237
SAMPLE

BENZO(J)FLUORANTHENE

$I_{ref} = 440.92$

C20.H12
1237
M WT 252
3 PK 252
RANK 1
23964
PUR 923

BENZO(K)FLUORANTHENE

$I_{ref} = 442.56$

C20.H12
1237
M WT 252
3 PK 252
RANK 2
23966
PUR 914

BENZO(B)FLUORANTHENE

$I_{ref} = 441.74$

C20.H12
1237
M WT 252
3 PK 252
RANK 3
23965
PUR 910

BENZO(A)PYRENE

$I_{ref} = 453.44$

C20.H12
1237
M WT 252
3 PK 252
RANK 4
23961
PUR 909

BENZO(E)PYRENE

$I_{ref} = 450.73$

C20.H12
1237
M WT 252
3 PK 252
RANK 5
23962
PUR 905

50   100   150   200   250

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Figure 3

Identification of Coeluting PAHs

PAH	I_{ref}	I_{exp}	MW
2-Methyl-anthracene	321.57		192
Cyclopenta(def)phenanthrene	322.08		190
Unknown		322.99	
9-Methyl-phenanthrene	323.06		192
4-Methyl-phenanthrene	323.17		192
1-Methyl-anthracene	323.33		192

Sample: HQ14   INST C   Injected: 2/07/90 17:02
TIC # 26   Area = 390337.0 Tentative Conc = 510.00
BEST MATCHES
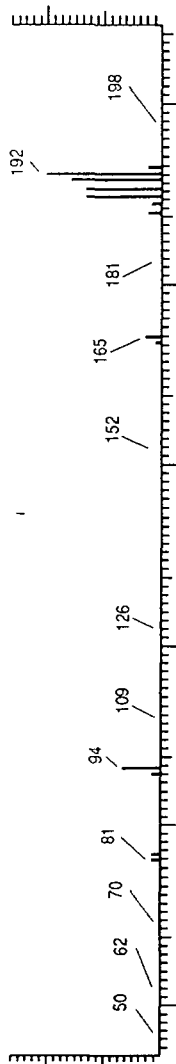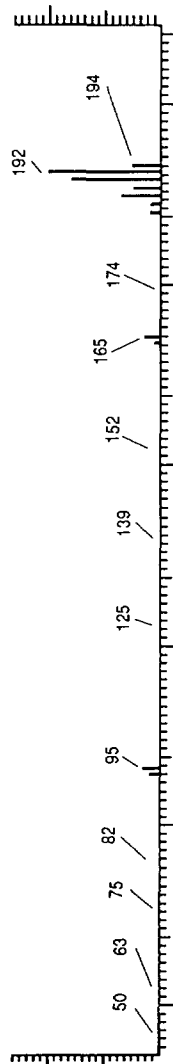
1. Phenanthrene, 9-methyl-   192 C15H12
2. 4H-Cyclopenta(def)phenanthrene   190 C15H10
3. Anthracene, 1-methyl-   192 C15H12
4. 9H-Fluorene, 9-ethylidene-   192 C15H12
5. Phenanthrene, 9-methyl-   192 C15H12
6. Methyl-phenanthrene or Methyl-Anthracene
7. Anthracene, 2-methyl-   192 C15H12 / 192 C15H12

Figure 4

Identification of Coeluting PAH and Alkane

PAH	I_ref	I_exp
2-Methyl-biphenyl	239.84	
Diphenyl-methane	243.35	
3-Methyl-biphenyl	254.33	
4-Methyl-biphenyl	256.12	
Unknown		256.56
Pentadecane (MW 212)	256.75	

Sample: HQ14   INST C   Injected: 2/07/90 17:02
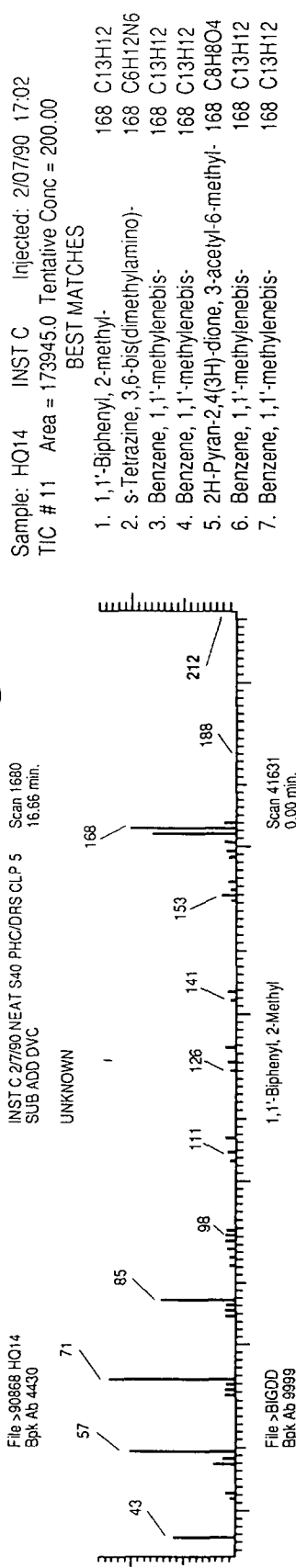TIC # 11   Area = 173945.0 Tentative Conc = 200.00
BEST MATCHES

1. 1,1'-Biphenyl, 2-methyl-   168 C13H12
2. s-Tetrazine, 3,6-bis(dimethylamino)-   168 C6H12N6
3. Benzene, 1,1'-methylenebis-   168 C13H12
4. Benzene, 1,1'-methylenebis-   168 C13H12
5. 2H-Pyran-2,4(3H)-dione, 3-acetyl-6-methyl- 168 C8H8O4
6. Benzene, 1,1'-methylenebis-   168 C13H12
7. Benzene, 1,1'-methylenebis-   168 C13H12

Figure 5a

Identification of Normal Alkanes

LIBRARY SEARCH
08/04/85 14:46:00 + 17:46

DATA: GH057689A16 # 1182
ENHANCED (10B 2N 0T)

BASE M/E: 57
RIC: 1505270

SAMPLE: 1 UL CC#57686 (8-1-85)   UNKNOWN

$I_{exp} = 433.60$

HENEICOSANE   CAS#   629-94-7

$I_{ref} = 347.42$

C8.H10.0
        1081
M WT 296
B PK 43
RANK 1
IN 21792
PUR 798

PENTACOSANE   CAS#   629-99-2

$I_{ref} = 400.45$

C8.H10.0
        1081
M WT 352
B PK 43
RANK 2
IN 25265
PUR 795

PENTATRIACONTANE   CAS#   630-07-9

$I_{ref} = 538.06$
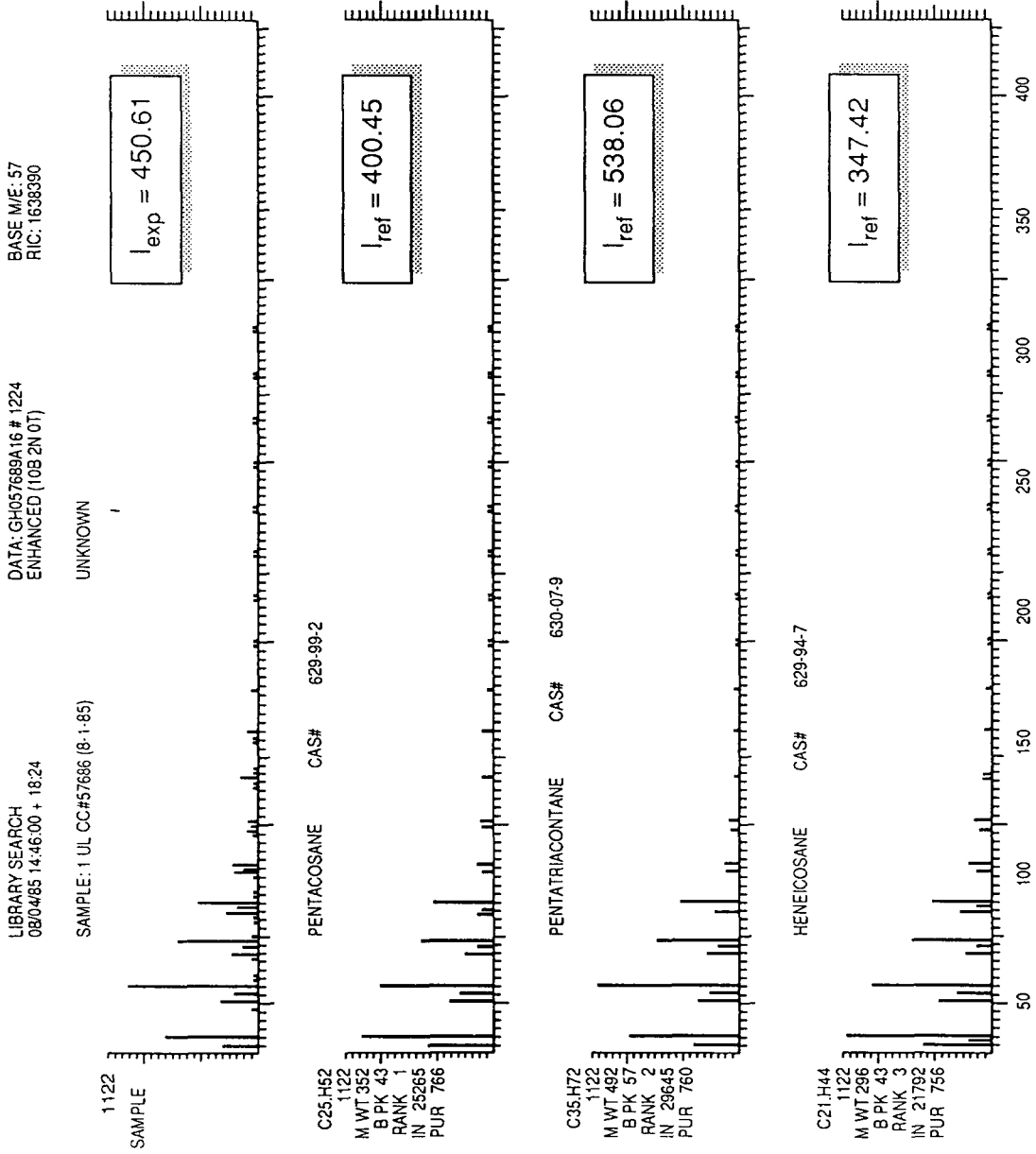
C8.H10.0
        1081
M WT 492
B PK 43
RANK 2
IN 25265
PUR 785

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Figure 5b

Identification of Normal Alkanes

Figure 5c

Identification of Normal Alkanes
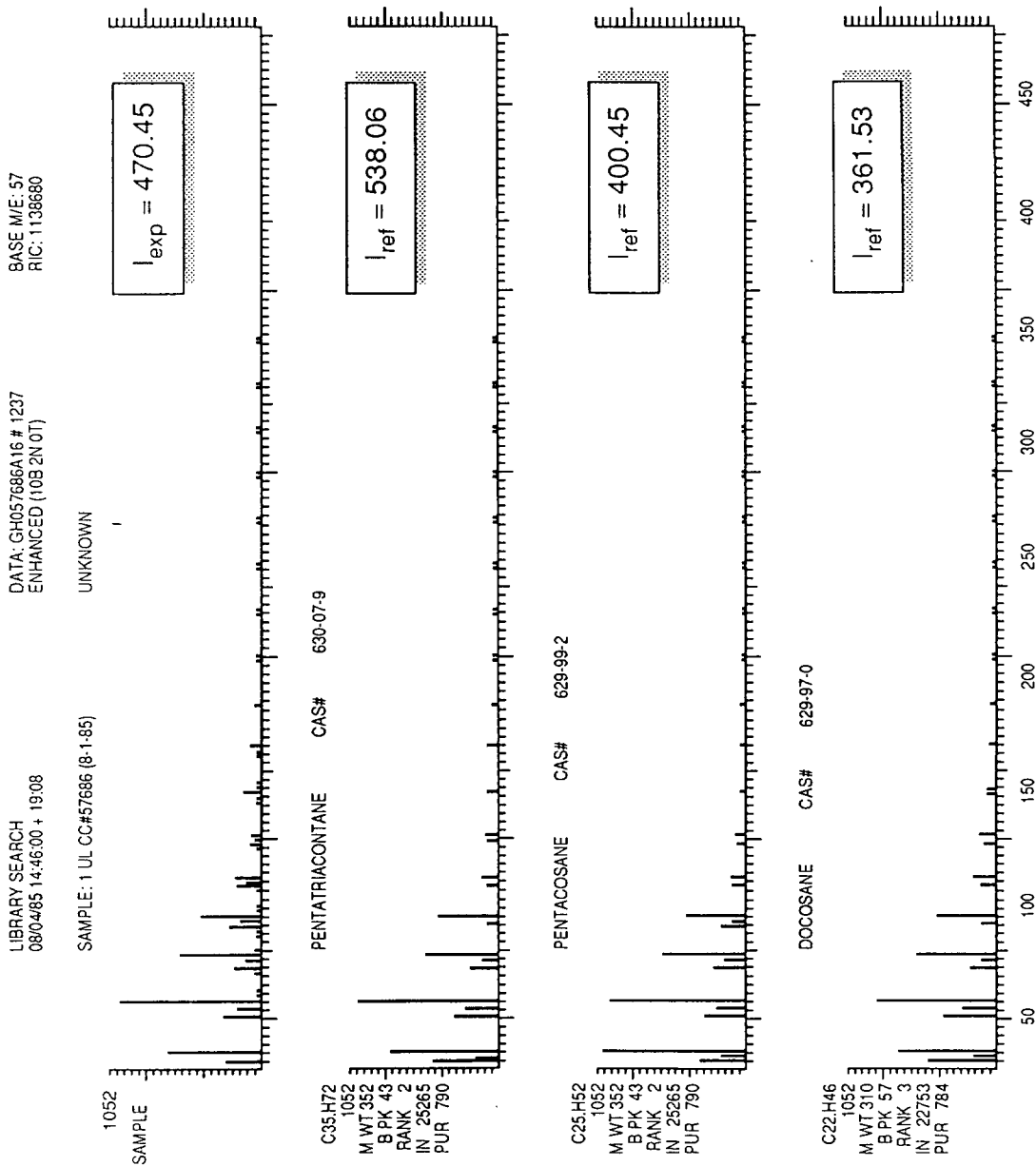
Figure 5d

Identification of Normal Alkanes
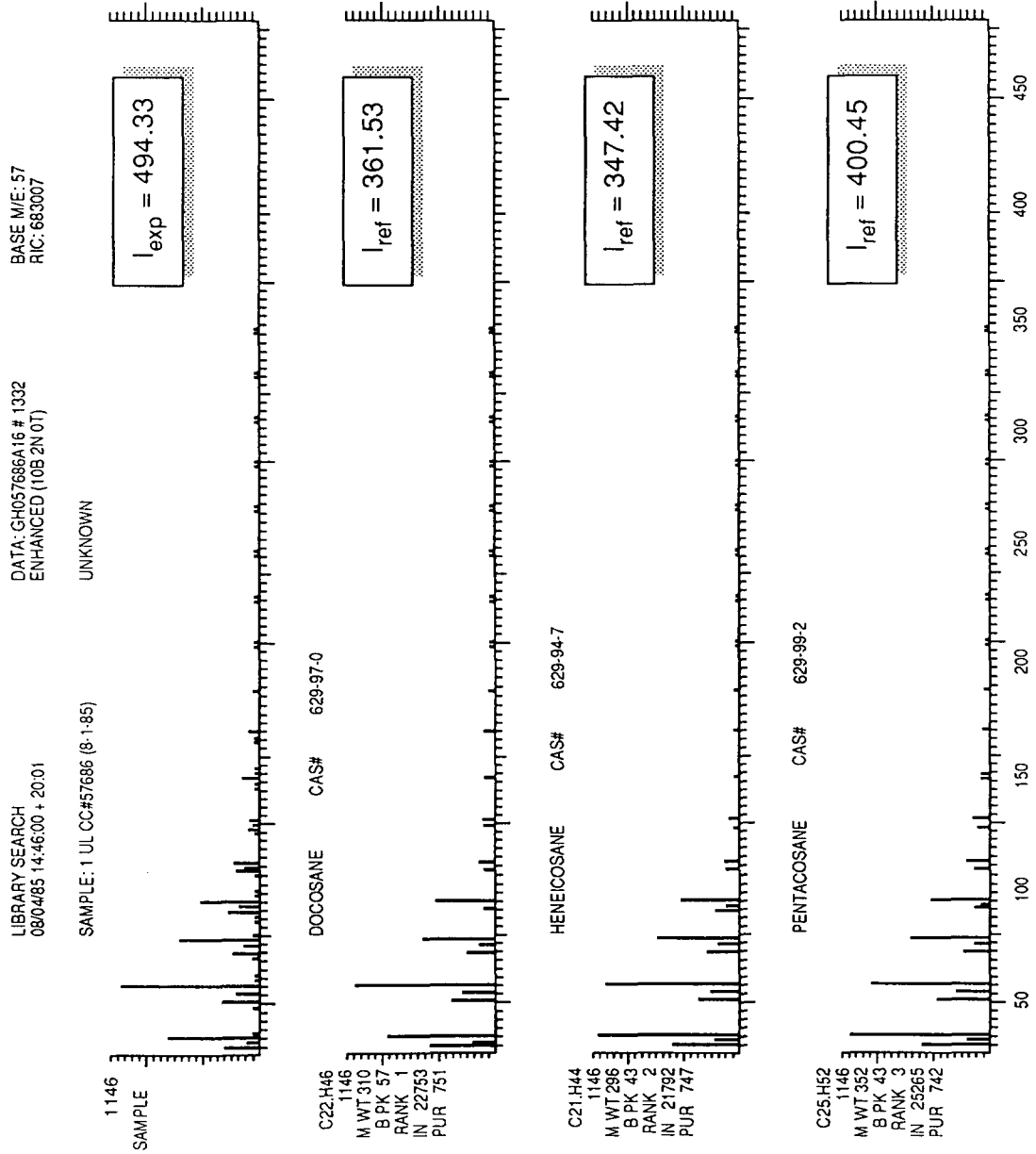
Alkane	I_{ref}	I_{exp}	Spectrum	Bias
n - C_{27}	425.51			
n - C_{28}	437.68	433.60	5a	+4.08
n - C_{29}	448.93	450.61	5b	+1.68
n - C_{30}	460.36			
n - C_{31}	471.96	470.45	5c	+1.51
n - C_{32}	484.94			
n - C_{33}	499.88	494.33	5d	+5.55

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74 HIGH EFFICIENCY GPC CLEANUP OF ENVIRONMENTAL SAMPLES - COLUMN OPTIMIZATION

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ABSTRACT

Gel permeation chromatography (GPC) has been used for almost two decades to remove unwanted high molecular weight compounds from agricultural and environmental samples prior to final analysis. Virtually all of this work has been done with 25mm ID x 40 to 100cm long columns packed with low efficiency 37-75 micron particles.

Using smaller diameter column packing particles produces major gains in column efficiencies, enabling the same separation to be done with much smaller columns. This enables the cleanup to be done in significantly less time using considerably less solvent.

This study was done to determine the optimum grade of GPC packing material and preferred column dimensions for environmental sample cleanup. High efficiency 100A material packed in 19mm x 30cm and 19mm x 15cm columns, as well as the two in series, has performed the cleanup effectively while operating with less solvent and greater throughput than the traditional column. Injecting 5ml samples containing over 310mg of material did not overload the two column set.

INTRODUCTION

GPC clean up of environmental samples is now mandatory for preparing semivolatile and pesticide Superfund samples according to the EPA Contract Laboratory Program Statement of Work. Laboratories which participate in the EPA Contract Laboratory Program and those which follow CLP protocols, doing "CLP-like" work, must use GPC.

Another aspect of environmental testing is concern about the quantities of solvents which are routinely consumed in environmental cleanup and testing procedures. Recently a major refinement of the traditional GPC cleanup procedure produced over 70% reduction in solvent usage and 69% reduction in sample processing time[1], Table 1. This was accomplished by substituting a Waters Ultrastyragel high efficiency, high resolution GPC column for the low resolution column which has been used in the method for almost two decades.

This high resolution column was chosen based on general properties and requirements of the method. Since the work began, a revised set of calibration requirements were issued for the GPC cleanup method, prompting a formal column optimization study. This study was concerned with two main variables - grade of column packing and column dimensions.

REVISED CALIBRATION REQUIREMENTS

The original calibration mix contained corn oil, bis(2-ethylhexyl)phthalate and pentachlorophenol (PCP). The basic requirement of the column was that it provide 85% or better resolution between the corn oil and the phthalate. The corn oil represents the low volatility, high molecular weight material which is removed from the sample before analysis. The work reported by Bumgarner with the high efficiency column met these requirements, Figure 1.

The revised calibration mix still contained corn oil and phthalate but Methoxychlor, Perylene and Sulfur were added in place of PCP. Resolution of 85% or better among each pair of compounds was also specified.

PACKING MATERIAL OPTIMIZATION

The initial high resolution columns studied contained a high efficiency packing material with an exclusion rating of 500A. To determine whether the 500A or the corresponding 100A material is better suited for GPC cleanup work, the relative retention profiles of each were compared to the Bio-Beads[R] packing traditionally used in this method.

Relative retention was defined as the ratio of the retention volume of a calibration compound to the retention volume of sulfur. As indicated in Figure 2, the 100A packing behaved essentially identically to the Bio-Beads. This packing grade was used during subsequent optimization of column dimensions.

COLUMN OPTIMIZATION - RESOLUTION

A 19mm ID x 30cm long column was used originally. It easily met the initial calibration requirements and the revised requirements for all calibration pairs except phthalate and Methoxychlor. To achieve the required level of resolution for all pairs, the column length was increased by using a 19mm ID x 15cm long segment in series with the original 19mm x 30cm column, Figure 3.

COLUMN OPTIMIZATION - MASS LOADING

As indicated in Figure 3, the configuration of a 15cm and 30cm column in series more than satisfies the calibration requirements, with the phthalate and Methoxychlor almost baseline resolved. The concentration of the calibration markers has been increased by 2.5 times to provide the same total mass on column as would have been loaded with a 5ml injection containing the concentrations listed in EPA Method 3640A.

To further demonstrate the resolving power and loading capacity of this preferred column set, a 2ml aliquot of the collected fraction was reinjected into the GPC system, Figure 4. It is estimated that this sample contains about 8-10% of the original mass of the collected peaks. The outstanding capacity of the column is shown again by the similarity in resolution of this diluted fraction and the original 2ml injection.

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COLUMN OPTIMIZATION - VOLUME LOADING

To demonstrate volume loading capacity on the high efficiency column set, a 5ml sample containing about 315mg was injected, Figure 5. The broadened peak shapes are a consequence of the larger injection volume, resulting in more peak overlap. Each peak was collected as a separate fraction with the valley between peaks taken as the cut points.

About 10% of the volume of each fraction was reinjected as a separate fraction, Figure 6. Although the detector sensed what appeared to be considerable peak overlap in the initial injection, rerunning the individual collected fractions shows excellent resolution, well above the calibration requirements. In all of the loading considerations, mass or volume, the actual capacity of the high efficiency column set surpasses the requirements of method.

SPEED, LOADING, RESOLUTION

The availability of 15 and 30cm column sections which can be used alone or in series provides maximum flexibility for cleanup of environmental samples. Used together they provide maximum loading capacity and resolution. With lightly contaminated, low concentration samples the 30cm length may be used alone for maximum throughput and solvent economy. In either case, the high resolution of these columns provides significant gains in operating effectiveness with corresponding reductions in solvent usage versus the low resolution column traditionally used for GPC cleanup.

SUMMARY

High resolution GPC columns have been shown to meet the resolution criteria of EPA Method 3640A and the EPA Contract Laboratory Program Statement of Work for Organics Analysis. They provide major savings in solvent use and processing time relative to the low efficiency columns traditionally used in this work. Maximum resolution and loading capacity for performing GPC cleanup of environmental samples with these high resolution columns is achieved with a 19mm ID x 30cm column in series with a 19mm ID x 15 cm column.

NOTE

Bio-Beads is a registered trademark of Bio-Rad Laboratories.

REFERENCE

1. Bumgarner Jr., J., International GPC Symposium Proceedings, Boston, MA, 1989, Waters Chromatography Division, Millipore Corp., pp.787-793, 1989.

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Table 1

GPC CLEANUP OF ENVIRONMENTAL SAMPLES

COMPARISON OF LOW RESOLUTION COLUMNS VS 500A ULTRASTYRAGEL*

TYPICAL RUN TIMES (MINUTES)

	DUMP	COLLECT	WASH	TOTAL
LOW RESOLUTION	30	36	15	81
ULTRASTYRAGEL	12.5	8.5	4	25

TYPICAL METHYLENE CHLORIDE VOLUMES (ML)

	DUMP	COLLECT	WASH	TOTAL
LOW RESOLUTION	150	180	75	405
ULTRASTYRAGEL	56.25	38.25	18	112.5

*BUMGARNER JR, J., OCTOBER 1989 GPC SYMPOSIUM

Figure 1

ULTRASTYRAGEL COLUMN RUN ON WATERS SYSTEM
SOURCE: BUMGARNER GPC SYMPOSIUM PAPER, 10/89

GPC Calibration Standard
USEPA 2/88 SOW

22.5 minute run time
4.5 ml/minute flow rate
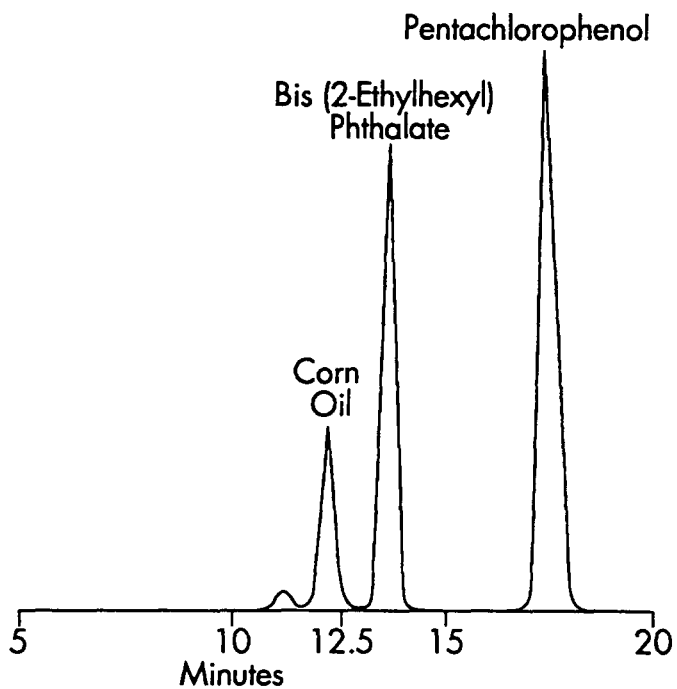
Figure 2

HIGH EFFICIENCY GPC CLEANUP OF ENVIRONMENTAL SAMPLES COLUMN OPTIMIZATION

COMPARISON OF GPC PACKINGS BY RELATIVE RETENTION

O 100 A WATERS
■ 500 A WATERS
● BIO-BEADS™ S-X3

COMPARISON OF GPC PACKING MATERIALS
USING RELATIVE RETENTION TIMES TO
SULFUR AS A TOTAL VOLUME MARKER

CORN OIL   BIS(2-ETHYLHEXYL)   PERYLENE   SULFUR
                  PHTHALATE

1   0.9   0.8   0.7   0.6   0.5   0.4   0.3   0.2   0.1   0

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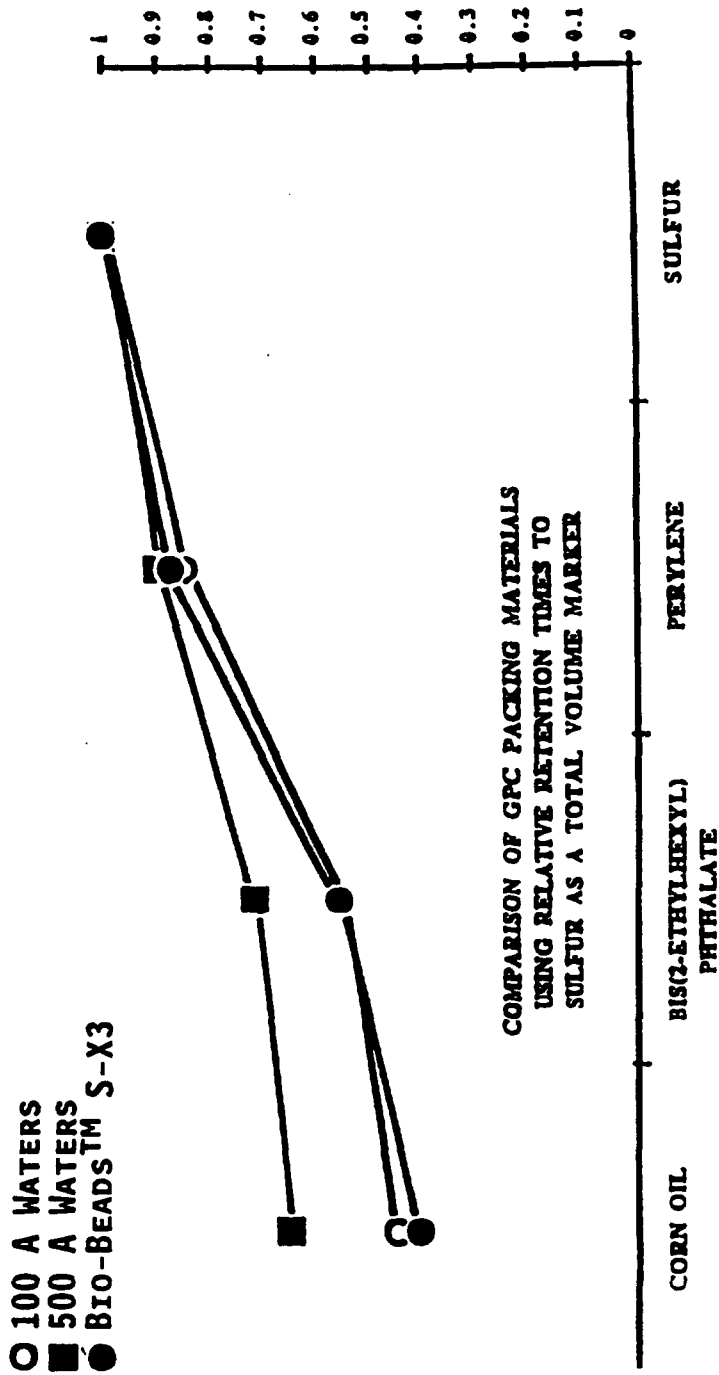
Figure 3

HIGH EFFICIENCY GPC CLEANUP OF ENVIRONMENTAL SAMPLES
COLUMN CALIBRATION AT METHOD LOAD

COLUMN: 100A 19MM X (30CM + 15CM)
SAMPLE: 2000 UL

SOLVENT: METHYLENE CHLORIDE
FLOW RATE: 5ML/MIN
DETECTION: UV @ 254NM, 1.5 AUFS

PEAK ID:
1 CORN OIL, 62.5MG/ML
2 BIS(2-ETHYLHEXYL)PHTHALATE, 2.5MG/ML
3 METHOXYCHLOR, 0.5MG/ML
4 PERYLENE, 0.05MG/ML
5 SULFUR, 0.2MG/ML
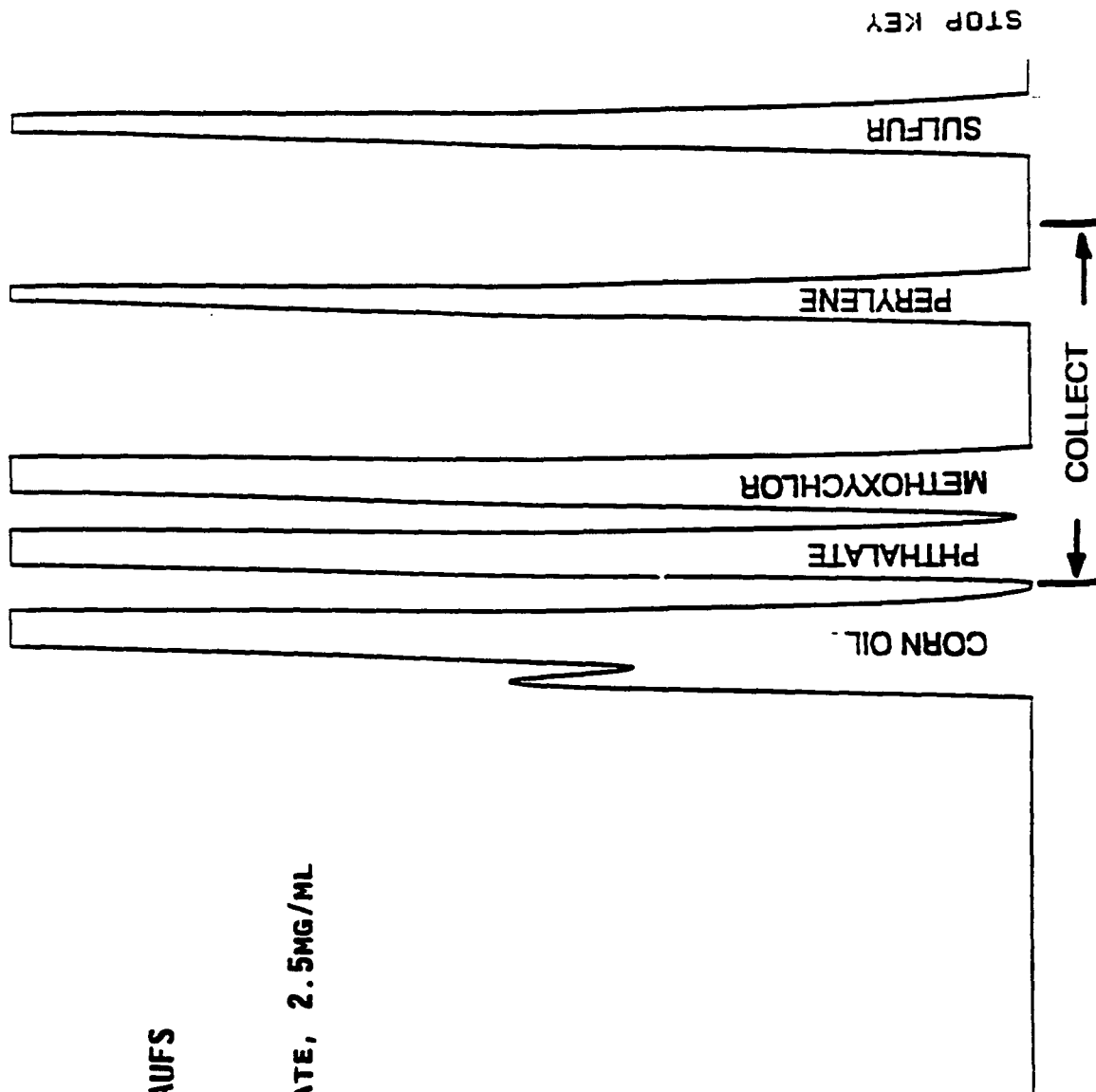
Figure 4

HIGH EFFICIENCY GPC CLEANUP OF ENVIRONMENTAL SAMPLES
COLUMN CALIBRATION AT METHOD LOAD

ALIQUOT OF COLLECTED FRACTION REINJECTED

COLUMN: 100A 19MM x (30CM + 15CM)
SAMPLE: 2000 UL

SOLVENT: METHYLENE CHLORIDE
FLOW RATE: 5ML/MIN
DETECTION: UV @ 254NM, 1.5 AUFS

PEAK ID:

2 BIS(2-ETHYLHEXYL)PHTHALATE, 2.5MG/ML
3 METHOXYCHLOR, 0.5MG/ML
4 PERYLENE, 0.05MG/ML
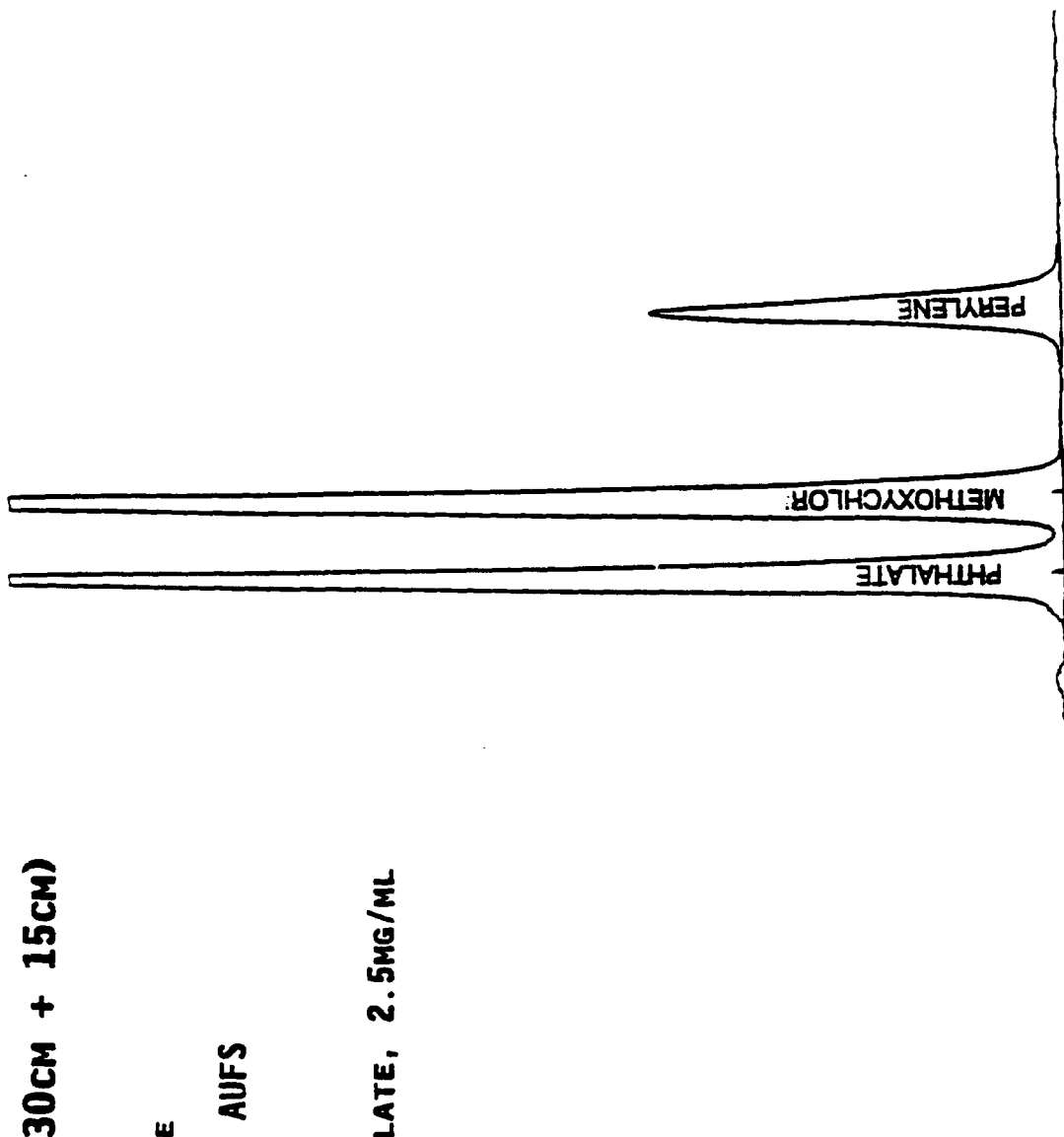
Figure 5

HIGH EFFICIENCY GPC CLEANUP OF ENVIRONMENTAL SAMPLES
COLUMN OPTIMIZATION

5ML TEST MIX INJECTION
COLUMN: 100A 19MM x (30CM + 15CM)
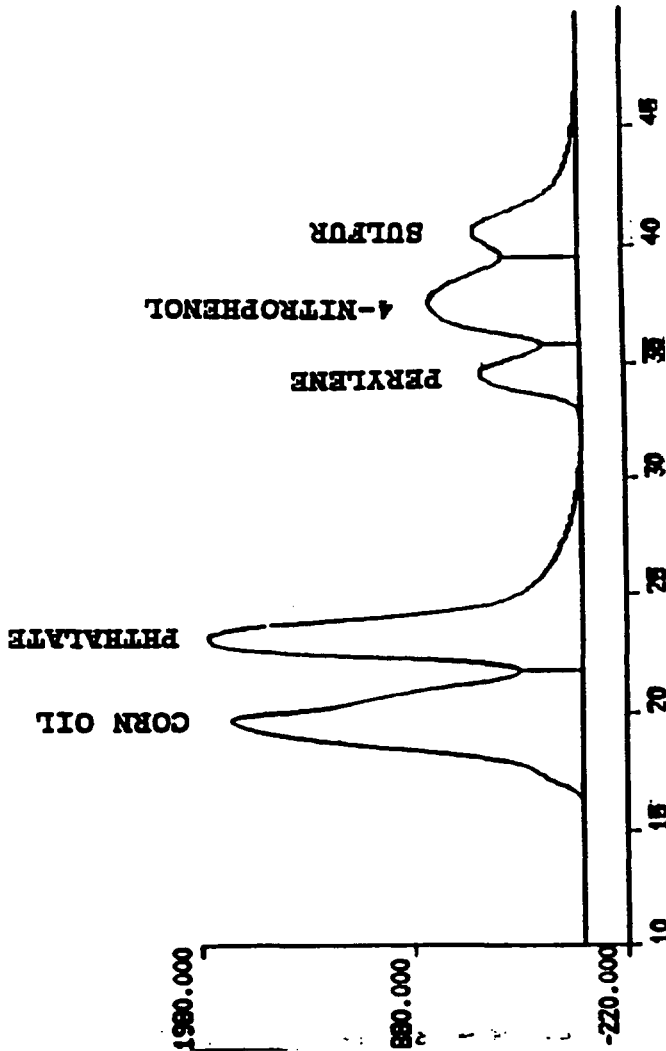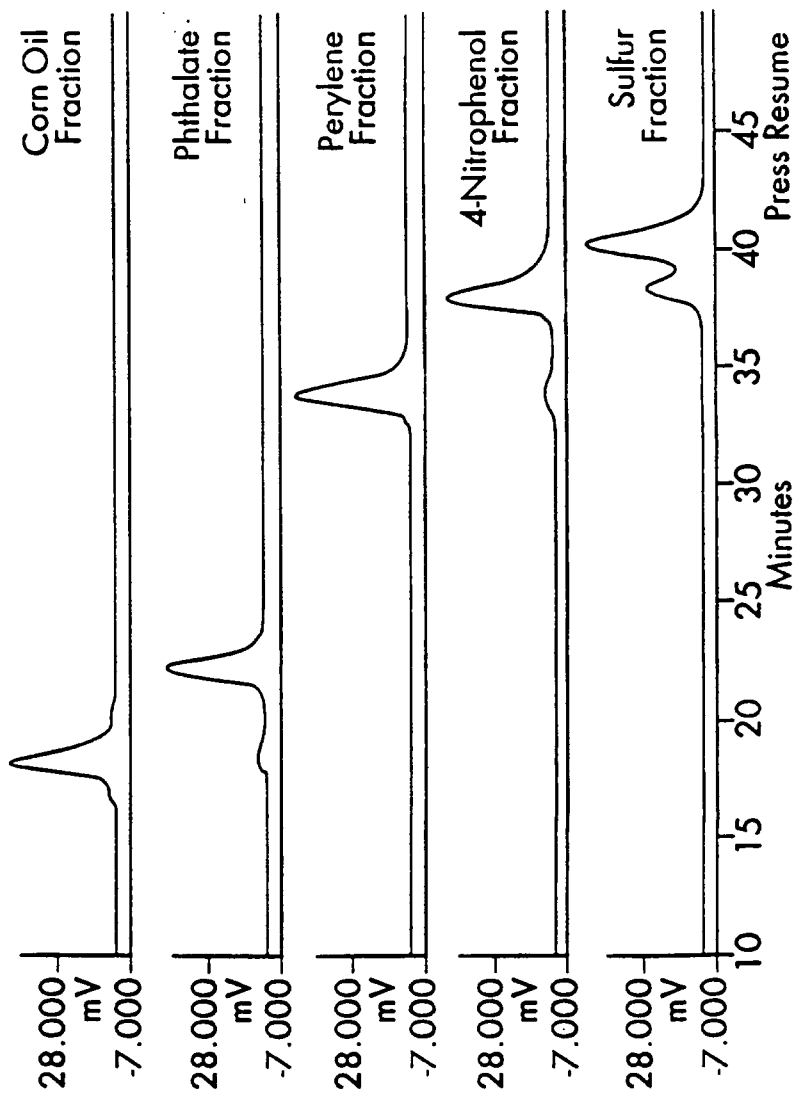

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Figure 6

HIGH EFFICIENCY GPC CLEANUP OF ENVIRONMENTAL SAMPLES
COLUMN OPTIMIZATION

REINJECTED FRACTIONS FROM 5ML TEST MIX INJECTION
COLUMN: 100A 19MM x (30CM + 15CM)

Corn Oil
Fraction

Phthalate
Fraction

Perylene
Fraction

4-Nitrophenol
Fraction

Sulfur
Fraction

Press Resume

Minutes

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75 EFFICIENT AQUEOUS EXTRACTION USING AN EMULSION PHASE CONTACTOR

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ABSTRACT

The Emulsion Phase Contactor (EPC) promotes the efficient liquid/liquid extraction of aqueous samples with organic solvents. Use of transient high intensity electric fields in the liquid/liquid extraction process produces increased interfacial surface area, resulting in more efficient mass transfer. Transient fields also induce droplet motion (distortion and translation) and droplet coalescence, which promote phase transfer and phase separation, respectively.

In the EPC technique, aqueous sample is introduced into a cell, where a voltage is applied to disperse the aqueous phase into the bulk (organic) phase. Mass transfer is facilitated by formation of small (micron-sized) droplets. Contact time of the droplets is increased through the action of additional charged plates, which also aid in the eventual aggregation of dispersed droplets.

EPC data are presented which show excellent methylene chloride extraction recoveries for many priority pollutants, such as would be analyzed using EPA SW-846, Method 8270 (semivolatile organics by GC/MS), or the EPA CLP (Contract Lab Program) Statement of Work (SOW).

The EPC extraction method is suitable for the automation of analytical laboratory sample preparation, and it replaces the more labor intensive extraction methods, such as separatory funnel extraction, or classical liquid/liquid extraction with boiling methylene chloride.

Instrumentation to accomplish the goal of an automated EPC extraction is currently under development at ABC Laboratories. Analytical applications of EPC derive from technology transfer under U.S. Patent No. 4,767,515, "Surface Area Generation and Droplet Size Control in Solvent Extraction Systems Utilizing High Intensity Electric Fields", issued August 30, 1988, which was developed by Scott and Wham at Oak Ridge National Laboratory.

INTRODUCTION

Traditional methods for the liquid/liquid extraction of most environmental samples are both labor and solvent intensive, and have high potential for exposure of laboratory workers to solvents and other hazardous substances. Recent alternatives, such as solid-phase extraction (SPE) cartridges or discs, may not cope well with difficult aqueous matrices. Improvement of ordinary liquid/liquid extraction techniques by automating fluid transfers

and using electrically enhanced mass transfer[1] provides opportunities for superior analyte recoveries and more consistent analytical results, while reducing solvent (and energy) consumption and decreasing the opportunities for exposure of personnel to hazards.

Efficient mass transfer during liquid/liquid extraction depends directly upon the availability of surface area for mass transport. Since organic solvents tend to be essentially nonconductive, charged metal electrodes mounted within a solvent-containing region can be used to polarize water droplets, which leads to droplet shape distortion, rotation, translation, and breakage (Figure 1). This greatly increases phase transfer kinetics for extraction of organic analytes from the aqueous phase.

A device employing this principle for extraction of aqueous samples is diagrammed in Figure 2. Aqueous sample is pumped into the bottom of the solvent-filled chamber, where an electric field causes droplet disruption. A second electric field, situated above the first, induces further droplet motion and also aids coagulation of daughter droplets formed by the action of the first field. Accumulating volume of aggregate aqueous phase (above the two electric fields) overflows to another container. Thus the organic solvent is in equilibrium with only a small portion of the aqueous sample at any time. This contributes to excellent extraction efficiencies.

Efficiency of the EPC is demonstrated by extraction of various environmental pollutants with methylene chloride, followed by analysis of the extract using GC/FID or LC/UV detection.

RESULTS AND DISCUSSION

One liter of simulated field water[2] was spiked with 2.50 mL of a methanol solution that contained 1000 μg/mL each of priority pollutant molecules (analytes were divided into two groups to facilitate chromatographic analysis). The EPC extraction cell was charged with methylene chloride (approximately 400 mL), and plate voltages were set at 15 kV (lower pair) and 10 kV (upper pair). Aqueous sample was introduced into the EPC at a rate of 22 mL/min. After all the sample had traversed the EPC extraction chamber, the methylene chloride layer was drained, and one half was dried with sodium sulfate, then concentrated to 10 mL (to minimize evaporative losses) using a steam bath with the Kuderna-Danish apparatus.

Chromatographic data (FID) were obtained using an HP 5890 Series II temperature programmed gas chromatograph (Hewlett-Packard) plus 3396-A integrator, with one of the following two columns: a 30 meter x 0.25 mm capillary (Supelco DB-5, 0.25 μm film thickness); or a 5 meter x 0.53 mm

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[1]Scott, Timothy C.; Wham, Robert M.; Ind. Eng. Chem. Res. 1989 28, 94.

[2]Prepared by adding 24 mg KCl, 608 mg $MgCl_2$ hexahydrate, 344 mg $CaCl_2$ dihydrate, and 404 mg NaCl to one gallon of reagent water.

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<u>Figure 1</u>. Electric Fields in Extraction

DROP FORMATION
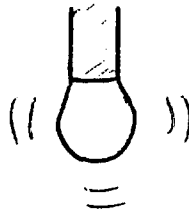
DROP OSCILLATIONS

DROP BREAKUP

DROP-DROP
 INTERACTIONS
 & COALESCENCE
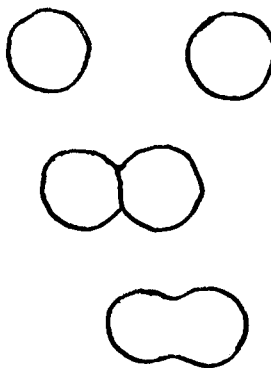
FIGURE 2. EPC EXTRACTION CELL

WATER OUT

METHYLENE CHLORIDE IN

CH_2CL_2 /WATER PHASE BOUNDARY

10 KV ELECTRIC FIELD

S.S. ELECTRODE

15 KV ELECTRIC FIELD

TEFLON BODY

WATER IN

13.5"

METHYLENE CHLORIDE OUT
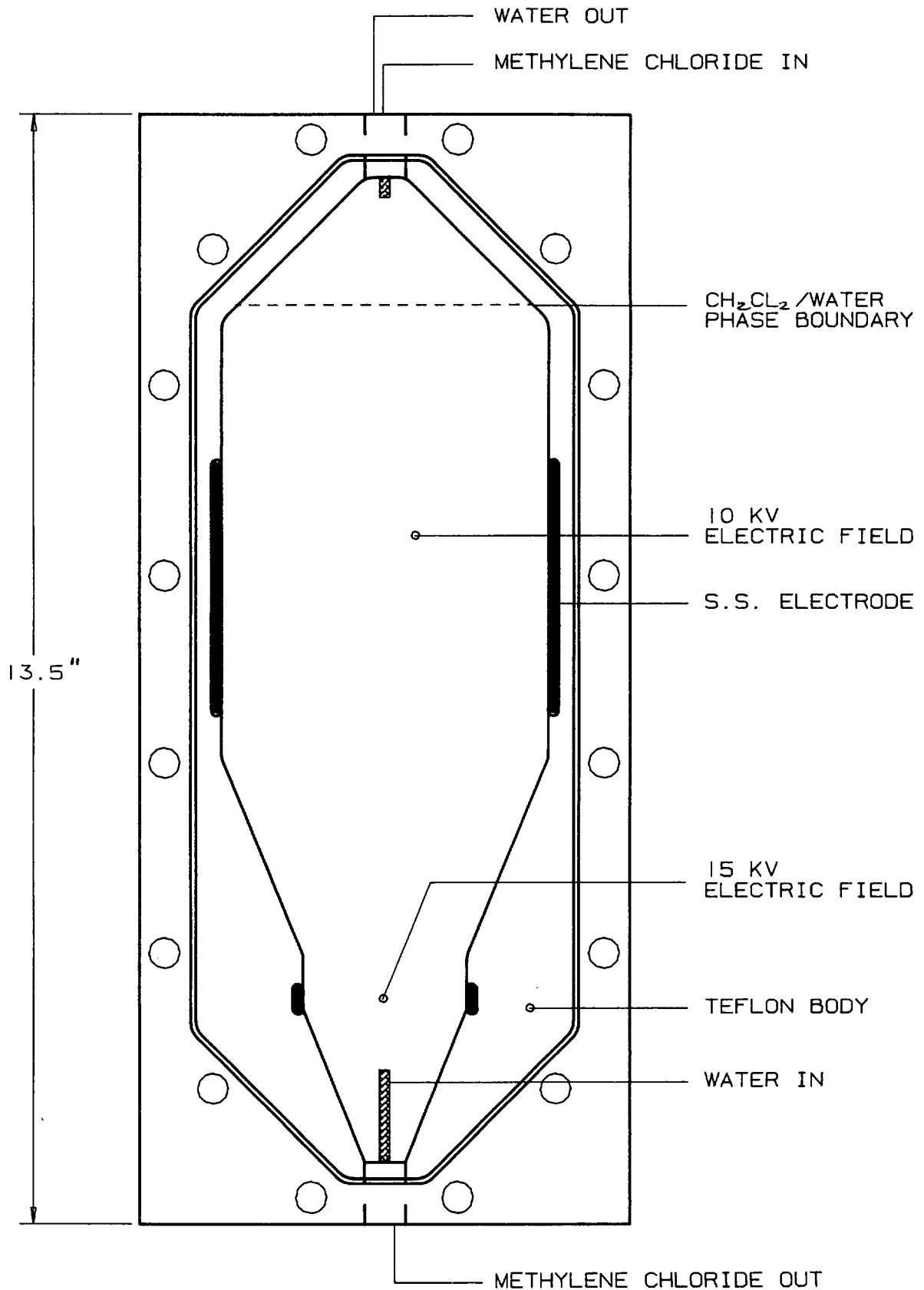
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capillary (HP-1, 2.65 μm film thickness). The recovery data (Table 1) were developed by comparison of peak heights to calibrations with external standards. Recoveries were good to excellent, with excellent precision. One of the two analyte sets was also processed using a lower spiking concentration (250 μL of solution, Table 2) to verify adequate recovery at trace levels. The entire extract from the low level runs was concentrated to 5 mL for analysis.

Calculated recoveries used the average of duplicate extract injections from each of the four extractions. Average recoveries for ten analytes, which represented several classes of chemical pollutants, ranged from 82% to 109%. The largest standard deviation measured was 7.1%, indicating that in addition to good recoveries with faster turnaround time (less than 1 hour per extraction for a 1 Liter sample), EPC methodology furnishes an enhancement in precision, in comparison with more operator dependent techniques.

Influence of pH on the recovery of acidic analytes was assessed by spiking water with 1.00 mL of a solution containing 1000 μg/mL each of phenol, 4-nitrophenol (4-NP), and 2,4-dinitrophenol (2,4-DNP) dissolved in methanol. The pH of the sample was adjusted using 12 $\underline{M}$ HCl. The EPC extraction was carried out at each pH, then HPLC analysis of the extracted water, with UV detection of analytes, was used to measure the concentration of phenols recovered in the extract and remaining in the water.

Data from those extractions at different pHs (Table 3) indicate that the technique is efficient enough to produce reasonably good recoveries of acidic compounds (pK_a values for phenol, 4-NP, and 2,4-DNP are 9.89, 7.15, and 3.96, respectively) with no pH adjustment of samples. Thus 2,4-DNP, although a stronger acid than acetic acid (pK_a 4.75) was recovered in 53% yield from an unadjusted (pH 5.9) sample.

EPC development efforts are now focusing on further reduction of solvent usage, design of particulate-tolerant extraction devices, and continued improvements in sample throughput and analyte recoveries.

SUMMARY

The Emulsion Phase Contactor (EPC) is a very efficient extraction device that electrically enhances mass transfer during liquid/liquid extraction. It provides good recoveries for extraction of a wide range of semivolatile analytes from water samples using methylene chloride, plus greater degree of precision (reproducibility) than can be obtained using less automated techniques. Extraction efficiency is so high that acidic analytes can be recovered without pH adjustment of water samples. Additional advantages are savings in labor and reduced exposure of lab personnel to hazardous substances. Automated EPC equipment is under development for application to SW-846, CLP, and other extraction methods.

Table 1. Recovery Data (% by GC/FID) for Analytes at 2500 μg/L

Analyte	Replicates				Statistics	
	1	2	3	4	x̄	σ
bis(2-Chloroethyl) ether	91	86	94	94	91	3.8
Nitrobenzene	98	94	100	106	100	5.0
bis(2-Chloroethoxy)methane	101	94	96	101	98	3.6
Naphthalene	97	90	93	96	94	3.2
Acenaphthene	98	89	86	101	94	7.1
2-Fluorophenol	91	91	91	90	91	0.5
Aniline	106	110	110	109	109	1.9
1,4-Dichlorobenzene	85	86	87	88	86	1.3
Hexachloroethane	82	80	90	88	85	4.8
2-Fluorobiphenyl	83	83	86	85	84	1.5

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Table 2. Recoveries for Analytes at 250 µg/L

Analyte	**1**	**2**
bis(2-Chloroethyl) ether	100	101
Nitrobenzene	105	103
bis(2-Chloroethoxy)methane	101	104
Naphthalene	98	99
Acenaphthene	88	105

Table 3. Influence of pH on Extraction of Phenolics

Compound	Recovery (%) at Indicated pH		
	pH = 5.9	pH = 3.8	pH = 1.6
Phenol	63	80	181[3]
4-Nitrophenol	59	68	58
2,4-Dinitrophenol	53	75	76

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[3]High result due to chromatographic interference

76 SFE PRACTICAL APPLICATIONS FOR ENVIRONMENTAL AND INDUSTRIAL SAMPLES

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Supercritical fluid extraction (SFE) is a technique that has the potential to revolutionize conventional methods of sample extraction and analysis. When CO_2 is used, SFE is an exceedingly quick, inexpensive, and environmentally safe method of sample preparation for GC, HPLC, UV-VIS, and TLC. SFE can also be used for percent extractable determinations in foods and polymers.

Liquid extractions of analytes from complex matrices often require labor intensive and time consuming methods such as Soxhlet extraction. The matrices must be extracted with large volumes of environmentally hazardous solvents which must be evaporated to the atmosphere or otherwise disposed of.

This presentation will discuss practical SFE applications for a variety of environmental and industrial samples such as soils, polymers, and foods. SFE extraction data will be presented and comparisons will be drawn between SFE and conventional methods of extraction.

INORGANICS

77   Microwave Sample Preparation Methods For Environmental Analysis

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Microwave sample preparation is gaining a wide degree of acceptance and is being applied in EPA methods for elemental analysis. The nature of standard procedures requires that they be readily transferable and reproducible between laboratories[1]. Because microwave sample preparation procedures are quantifiable their reproducibility provides an opportunity to improve data quality. The control and standardization of microwave methods is a matter that must be examined. Calibration of laboratory microwave equipment is required to transfer the methods accurately and precisely. Calibration methods have been evaluated and the error that can be expected in transferring these procedures has been determined.

Microwave sample preparation methods provide a platform to produce procedures that can be used generally for sample preparation in many environmental elemental analyses. Currently, both the RCRA and CERCLA programs share two microwave methods, developed cooperatively, applicable for soils, sediments, sludges, oils, and waters. These methods demonstrate robust microwave procedures that improve precision and are more efficient than many classical methods. These attributes arise from the direct control of energy transfer, and the mechanisms involved in that transfer. Reaction temperatures and their profile control the mineral acid reactions that are necessary to release the elements for analysis. The mechanisms of the energy transfer and the relationships that control these reactions will be discussed relevant to the two current EPA methods.

In addition to manual methods, an automated microwave decomposition system has been developed using a modular design[2]. Three separate portions of the automated microwave sample preparation system will be described as well as a prototype quasi expert system that has been developed to assist in standardizing procedures for microwave dissolution. A file structure has been devised to transfer these procedures from system to system and provides information adaptable to the level of automation in different instrument

configurations. Once a procedure has proven successful, it is stored for future reference and can be sent to other systems where it will automatically reproduce the method. Thus, the system has the ability to "characterize" and "transfer" procedures. A quality control sample log-in system was developed that guides the analyst through data entry, weighing and barcoding of the sample, and creates a sample data file. A computer-controlled microwave unit has been developed for use with this system. The entire system is roboticly integrated and is being tested as the first component of a fully integrated inorganic analysis system. Microwave sample preparation stations following this basic design have been constructed for EPA EMSL-LV and EPA Region 10 using commercial versions of the research system. EPA and NIST are coordinating the testing and evaluation of the systems.

Reference
1. Binstock, David A., Grohse, Peter M., Gaskill, Alvia Jr., Kingston, H. M., and Jassie, L. B., "Development and Validation of a Method for Determining Elements in Solid Waste Utilizing Microwave Digestion", JOAC, 74, 2, 1991.

2. Walter, P., Kingston, H. M., Settle, F. A., Pleva, M. A., Buote, W., and Chrosto, J., "Automated Intelligent Control of Microwave Sample Preparation," in Advances in Laboratory Automation and Robotics 1990, eds. Stramaitis and Hawk, vol. 7, Zymark Corporation, 1991.

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78   COMPARISON OF PROCEDURES FOR TCLP EXTRACT DIGESTION; CONVENTIONAL VS. MICROWAVE

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ABSTRACT

This paper describes a study that compares and evaluates metal data resulting from the analyses of replicate Toxicity Characteristic Leaching Procedure (TCLP) extracts subjected to both the metal acid digestions methods specified in SW-846 and microwave digestion procedures. The TCLP extracts analyzed by Inductively Coupled Argon Plasma (ICP) Spectroscopy for the metals arsenic, barium, cadmium, chromium, lead, selenium and silver were prepared by a CEM Model MDS 81D closed vessel microwave digestion and EPA SW-846 Methods 3010 and 3020.

INTRODUCTION

Method 3010, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy" and Method 3020, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Furnace Atomic Absorption Spectroscopy" found in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, November 1986, Third Edition, USEPA, SW-846 are commonly applied techniques to digest metals from aqueous samples in an open vessel.

As evidenced by the numerous studies reported in the literature, closed vessel microwave acid digestion is receiving considerable attention as a state-of-the-art metal digestion technique. Microwave heating was first reported to speed digestion of samples by acids fifteen years ago[1]. The technique has been used in a variety of sample preparations since then [1-12] and is rapidly gaining recognition as a useful tool in analytical chemistry [13]. Systems designed specifically for laboratory microwave digestion are commercially available. These systems are designed to overcome deficiencies identified by researchers [4,5,9,11,12] who performed their initial work with microwave ovens manufactured for domestic use. Recently, advanced techniques have become available for doing acid digestion of metals in closed TFE vessels by microwave heating [14].

Browning-Ferris Industries Laboratory in Houston, Texas analyzes 150 to 200 Toxicity Characteristic Leaching Procedure (TCLP) metal samples per month with a goal of from two to ten days turnaround time, including the long manual

digestion needed for samples by the traditional hot plate techniques prescribed in SW-846. In order to reduce costs, turnaround time, and to improve the sample handling technique while maintaining QA/QC and laboratory safety, it was decided to investigate the microwave digestion technique.

To accomplish this task, three different TCLP waste extracts of both extraction fluid number one and extraction fluid number 2 were analyzed for metals. The waste descriptions were as follows:
- Soil contaminated with gasoline, diesel and heating oil,
- Soil contaminated with hydraulic and diesel oil,
- Filter press sludge,
- Digested domestic sewage sludge,
- Reactor rake-out residue (magnesium chloride production),
- Sand/urea

All of the Toxicity Characteristic (TC) metals, arsenic, barium, cadmium, chromium, lead, selenium and silver, were at concentrations below their appropriate detection levels. These six extracts were each divided into three samples and spiked with different concentrations each of the TC metals, except for silver. Each of the samples was then further divided into two equal portions. One portion was split into four 50 milliliter (mL) aliquot and microwave digestion was performed on each aliquot in a closed TFE vessel with 3 mL of concentrated nitric acid and 2 mL of concentrated hydrochloric acid for 40 minutes at 90% power (515 Watts). The other portions of the spiked extracts were also subdivided into four aliquots, and each subjected to the hot plate open vessel acid digestion procedure as prescribed by method 3010.

The same procedure was repeated for the TCLP extracts (extraction fluid number one and extraction fluid number two) spiked with silver at three different concentrations. Four 50 mL aliquots of each were microwave digested in closed vessels with 5 mL of nitric acid. Four portions each of the same spiked samples were also digested by the conventional hot plate acid digestion procedure, Method 3020. Method 3020, utilizing only nitric acid, is used by our lab for silver digestion to avoid silver chloride precipitation.

All samples were analyzed by ICP spectroscopy.

Comparison of the data reveals the accuracy, applicability, and performance efficiency of each technique.

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SUMMARY
Results of the study suggest that the Methods 3010 and 3020 can effectively be substituted by the microwave acid digestion procedures utilized.

DISCUSSION

Apparatus
        Microwave Digestion System, CEM Model MDS-81D
        Closed TFE digestion vessels and turntable, CEM Part
No.
            600050
        Capping Station, CEM Part No. 920030
        Hot plates
        Griffin beakers
        Watch glasses, ribbed
Reagents
        Hydrochloric acid, concentrated, spectrograde
        Nitric acid, concentrated, spectrograde
        Water, deionized

Methodology - Six different Toxicity Characteristic (TC) samples, three utilizing extraction fluid number one and three with extraction fluid number two, were spike with the following three concentrations of the metals arsenic, barium, cadmium, chromium, lead, selenium, and silver:
        Concentration level 1 - Maximum regulatory limit, except for barium which was spiked at 5.00 ppm.
        Concentration level 2 - Mid-range of the maximum regulatory limit, except for barium which was spike at 2.50 ppm.
        Concentration level 3 - Five times the respective detection levels of each metal.

The spiked solutions were then divided into two equal portions. To determine accuracy, each portion was subdivided into eight aliquots and four were digested by the microwave method, and four by the conventional hot plate methods.

All samples were analyzed by ICP Spectrometry under SW-846 Method 6010 at the following wave lengths:
        arsenic   189   lead   220
        selenium 196   barium   233
        chromium 205   silver   328
        cadmium   214

Microwave digestion method [3010X] -
o Transfer a 50 mL aliquot of a well mixed sample to a TFE digestion vessel. Add 3 mL of concentrated and 2 mL of concentrated hydrochloric acid. Place the safety pressure relief valve on the vessels and then cap to 12 ft.lbs. torque using the capping station.

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o Weigh the vessel and record its weight in grams. Place it in the MDS-81D turntable and attach the venting tube.

o Repeat the above step until the turntable contains 12 vessels. It is critical that the total volume of the solution equals 660 mL during digestion and that each vessel contains an equal volume of acid. This is necessary to ensure uniform heating of all vessel solutions.

o Turn the microwave unit exhaust on to the maximum fan speed. Activate the turntable so that it is rotating continuously.

o Program the instrument time for 40 minutes and power at 90% (515 watts). Depress the start key and heat the sample mixture for the programmed time.

o At the end of the digestion period, remove the turntable from the microwave unit and allow the sample solutions to cool to room temperature. Shake the vessels to mix the sample solutions. Detach each venting tube and remove the vessels from the turntable.

o Weigh and record the weight of the cooled vessel after digestion. If there is a weight loss greater than 0.5 grams from that recorded prior to digestion, add DI water equal to the weight lost. If there is a significant weight loss (e.g., two to three grams), one should discard the sample, and repeat the digestion procedure.

o Recap the vessel using the capping station and shake the vessel to mix the sample solution.

o Open the vessels and filter the samples to remove any insoluble materials if necessary. Do not rinse or dilute the digested sample.

Microwave digestion method [3020X] -
This procedure is identical to the digestion method [3010X] described above, except that instead of adding 3 mL of concentrated nitric acid and 2 mL of concentrated hydrochloric acid to the sample to be digested, add 5 mL of concentrated nitric acid.

The hot plate digestion methods utilized in this study are those described in SW-846, method 3010 and 3020. Method 3020 is utilized for samples to be analyzed by ICP for silver.

RESULTS

Table I contains the results of the study. The data is divided into two parts to distinguish between the two different TCLP extraction fluids examined. The type of digestion employed is identified for each extract media at the top of the table. The left margin lists the metals and their spike concentrations. The table also lists the concentrations of four replicates and percent recovery.

Table II illustrates the average concentration of the four replicates, and shows the relative percent deviation of the two values obtained by microwave and hot plate digestion methods.

CONCLUSION

The intent of the study was to evaluate the data resulting from the metal analyses of the two TCLP extract solutions digested by both microwave and the conventional hot plate methods.

The data reveal that percent recoveries obtained from microwave digested samples and hot plate acid digested samples are approximately equivalent. In some instances, the lead and barium recoveries are low, probably due to matrix interferences, but overall, the recoveries obtained by means of the two methods are quite comparable.

The relative percent deviation (Table II) shows that hot plate 3010, 3020 methods can be easily substituted by microwave acid digestion method 3010X and 3020X.

The advantages of microwave digestion procedures over those of conventional hot plated methods are: i) it is a rapid and safe way of preparing samples for ICP analysis, ii) the acids do not evaporate from the closed container causing elevated concentrations of trace acid impurities, iii) the digestion acids apparently do not decompose under microwave conditions, iv) there are no acid fumes, v) volatile elements are retained in the sample solution, vi) the method requires less monitoring, and finally, vii) there is less potential for external sample contamination. The only limitation of this method is the time-consuming assembling and cleaning of the digestion vessels.

ACKNOWLEDGEMENTS

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TABLE I
COMPARISON OF PERCENT RECOVERY
MICROWAVE VS. HOT PLATE DIGESTION

EXTRACTION FLUID # 1				EXTRACTION FLUID # 2			
Arsenic at 5.000 ppm							
MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
4.584	92	4.313	86	4.484	90	4.214	84
4.598	92	4.466	89	4.301	86	4.345	87
4.653	93	4.284	86	4.319	86	4.309	86
4.640	93	4.413	88	4.390	88	4.413	88
Arsenic at 2.500 ppm							
MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
2.065	83	2.257	90	2.509	100	2.255	90
2.066	83	2.101	84	2.456	98	2.135	85
2.171	87	2.018	81	2.223	89	2.421	97
2.038	82	2.121	85	2.432	97	2.181	87
Arsenic at 0.500 ppm							
MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.417	83	0.409	82	0.417	83	0.409	82
0.405	81	0.420	84	0.405	81	0.420	84
0.420	84	0.415	83	0.420	84	0.504	100
0.444	89	0.457	91	0.509	102	0.501	100
Selenium at 1.000 ppm							
MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.948	95	0.891	89	1.032	103	0.906	91
1.107	702	0.856	86	1.070	107	0.910	91
0.906	91	0.904	90	1.066	107	0.862	86
0.991	99	0.897	90	1.086	1089	0.897	90
Selenium at 0.500 ppm							
MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.521	104	0.509	102	0.551	110	0.453	91
0.475	95	0.477	95	0.541	108	0.467	93
0.509	102	0.477	95	0.541	108	0.467	93
0.490	98	0.497	99	0.517	103	0.493	99
Selenium at 0.500 ppm							
MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.492	98	0.404	81	0.547	109	0.530	106
0.450	90	0.424	85	0.522	104	0.476	95
0.444	89	0.430	86	0.528	106	0.554	111
0.459	92	0.466	93	0.549	110	0.551	110
Lead at 5.000 ppm							
MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
4.767	95	4.636	93	3.958	79	4.000	80
4.773	95	4.621	92	4.022	80	3.915	78
4.703	94	4.524	90	4.080	82	3.937	79
4.709	94	4.627	93	4.126	83	3.902	78

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TABLE I (CONTINUED)
COMPARISON OF PERCENT RECOVERY
MICROWAVE VS. HOT PLATE DIGESTION

EXTRACTION FLUID # 1

Lead at 2.500 ppm

MicroW	% Rec.	Hot Plate	% Rec.
2.277	92	2.273	91
2.255	90	2.222	89
2.278	91	2.212	88
2.189	88	2.205	88

Lead at 0.500 ppm

MicroW	% Rec.	Hot Plate	% Rec.
0.487	97	0.506	101
0.508	102	0.473	95
0.502	100	0.451	90
0.515	103	0.477	95

Chromium at 5.000 ppm

MicroW	% Rec.	Hot Plate	% Rec.
4.874	97	4.438	89
4.844	97	4.438	89
4.862	97	4.476	90
4.844	97	4.325	87

Chromium at 2.500 ppm

MicroW	% Rec.	Hot Plate	% Rec.
2.401	96	2.210	88
2.394	96	2.170	87
2.417	97	2.187	87
2.354	94	2.240	90

Chromium at 0.250 ppm

MicroW	% Rec.	Hot Plate	% Rec.
0.283	113	0.280	112
0.264	106	0.261	104
0.257	103	0.277	111
0.237	95	0.275	110

Barium at 5.000 ppm

MicroW	% Rec.	Hot Plate	% Rec.
4.618	92	4.573	91
4.466	89	4.642	92
4.519	90	4.488	90
4.560	91	4.627	92

Barium at 2.500 ppm

MicroW	% Rec.	Hot Plate	% Rec.
2.375	95	2.346	94
2.355	94	2.391	96
2.397	96	2.379	95
2.261	90	2.345	94

EXTRACTION FLUID # 2

MicroW	% Rec.	Hot Plate	% Rec.
1.914	77	1.964	79
1.872	75	2.067	83
1.918	77	1.846	74
1.939	78	1.946	78

MicroW	% Rec.	Hot Plate	% Rec.
0.487	97	0.506	101
0.508	102	0.473	95
0.501	100	0.451	90
0.510	102	0.477	95

MicroW	% Rec.	Hot Plate	% Rec.
4.488	90	4.924	98
4.600	92	5.085	102
4.508	90	4.427	89
5.035	100	4.215	84

MicroW	% Rec.	Hot Plate	% Rec.
2.262	90	2.100	84
2.463	98	2.228	89
2.490	99	2.289	92
2.476	99	2.218	89

MicroW	% Rec.	Hot Plate	% Rec.
0.283	113	0.261	104
0.264	1.06	0.277	111
0.257	103	0.275	110
0.238	95	0.280	112

MicroW	% Rec.	Hot Plate	% Rec.
4.412	88	4.287	86
4.480	90	4.403	88
4.473	89	4.296	86
4.464	89	4.295	86

MicroW	% Rec.	Hot Plate	% Rec.
2.356	94	2.246	90
2.328	93	2.253	90
2.365	95	2.371	95
2.360	94	2.186	87

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TABLE I (CONTINUED)
COMPARISON OF PERCENT RECOVERY
MICROWAVE VS. HOT PLATE DIGESTION

EXTRACTION FLUID # 1				EXTRACTION FLUID # 2			

Barium at 0.100 ppm

MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.094	94	0.095	95	0.899	90	0.891	89
0.094	94	0.092	92	0.909	91	0.874	87
0.095	95	0.087	87	0.913	91	0.877	88
0.095	95	0.099	99	0.913	91	0.889	89

Cadmium at 1.000 ppm

MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.946	95	0.913	91	0.829	83	0.828	83
0.953	95	0.944	94	0.853	85	0.841	84
0.943	94	0.894	89	0.845	85	0.831	83
0.955	95	0.915	91	0.848	85	0.828	83

Cadmium at 0.500 ppm

MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.443	89	0.429	86	0.375	75	0.380	76
0.431	0.86	0.419	84	0.399	80	0.386	77
0.439	88	0.416	83	0.393	79	0.399	80
0.425	85	0.415	83	0.406	81	0.380	76

Cadmium at 0.100 ppm

MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.110	110	0.104	104	0.106	106	0.101	101
0.109	109	0.106	106	0.104	104	0.098	98
0.107	107	0.105	105	0.103	103	0.103	103
0.105	105	0.106	106	0.098	98	0.100	100

Silver at 5.000 ppm

MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
5.022	100	4.230	85	5.022	100	4.440	89
4.983	99.6	4.275	86	5.088	102	4.305	86
5.065	101	4.040	81	5.049	101	4.165	83
5.027	101	4.325	87	5.093	102	4.230	85

Silver at 2.500 ppm

MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
2.431	97	2.200	88	2.407	96	2.367	95
2.420	97	2.130	85	2.591	104	2.476	99
2.430	97	2.340	94	2.604	104	2.564	103
2.542	102	2.136	85	2.453	98	2.314	93

Silver at 0.250 ppm

MicroW	% Rec.	Hot Plate	% Rec.	MicroW	% Rec.	Hot Plate	% Rec.
0.240	96	0.225	90	0.249	100	0.223	92
0.239	96	0.227	90	0.243	97	0.206	82
0.231	92	0.235	94	0.251	100	0.223	89
0.240	96	0.223	89	0.244	98	0.215	86

TABLE II
COMPARISON OF RELATIVE PERCENT DEVIATION
MICROWAVE VS. HOT PLATE DIGESTION

EXTRACTION FLUID # 1						EXTRACTION FLUID # 2					

Arsenic

MW	H P	MW	H P	MW	H P	MW	H P	MW	H P	MW	H P
4.619	4.369	2.085	2.124	0.422	0.425	4.374	4.322	2.405	2.248	0.438	0.459
RPD 5.6%		1.9%		0.71%		1.2%		6.7%		4.7%	

Selenium

MW	H P	MW	H P	MW	H P	MW	H P	MW	H P	MW	H P
0.966	0.887	0.499	0.488	0.461	0.431	1.064	0.894	0.521	0.466	0.536	0.528
RPD 8.5%		2.2%		6.7%		17.4%		11.1%		1.5%	

Lead

MW	H P	MW	H P	MW	H P	MW	H P	MW	H P	MW	H P
4.738	4.602	2.250	2.228	0.503	0.477	4.047	3.939	1.911	1.956	0.502	0.477
RPD 2.9%		0.98%		5.3%		2.7%		2.3%		5.1%	

Chromium

MW	H P	MW	H P	MW	H P	MW	H P	MW	H P	MW	H P
4.856	4.419	2.391	2.202	0.260	0.273	4.659	4.663	2.423	2.210	0.261	0.273
RPD 9.4%		8.2%		4.88%		0.09%		9.1%		4.8%	

Barium

MW	H P	MW	H P	MW	H P	MW	H P	MW	H P	MW	H P
4.541	4.583	2.347	2.365	0.094	0.093	4.457	4.320	2.352	2.264	0.909	0.883
RPD 0.94%		0.76%		1.07%		3.1%		3.8%		2.9%	

Cadmium

MW	H P	MW	H P	MW	H P	MW	H P	MW	H P	MW	H P
0.949	0.917	0.435	0.420	0.108	0.105	0.844	0.830	0.393	0.386	0.103	0.101
RPD 3.4%		3.5%		2.8%		1.7%		1.8%		2.0%	

Silver

MW	H P	MW	H P	MW	H P	MW	H P	MW	H P	MW	H P
5.025	4.218	2.456	2.202	0.238	0.228	5.063	4.285	2.574	2.430	0.247	0.217
RPD 17.5%		10.9%		4.3%		16.6%		3.4%		12.9%	

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79 Sample Decomposition In Closed Vessels With A Pressure Controlled Microwave Oven.

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Wet-chemical sample decomposition in closed vessels is one of the most efficient methods for trace element analysis. Temperatures of at least 300°C are required. In order to guarantee the complete decomposition of organic matter with nitric acid. For that purpose the decomposition must be done under high pressure of up to 80 bar. The currently available high-pressure vessels for microwave decomposition do not permit control of the microwave energy and therefore unknown sample materials can cause the vessel to rupture at excessive internal pressure. The high-pressure microwave decomposition vessels we developed permit the control of microwave energy by the internal pressure. Thus also unknown sample materials can be decomposed quickly and without problems.

80 STATE-OF-THE-ART OF MICROWAVE DIGESTION METHODS FOR ENVIRONMENTAL ANALYSIS

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ABSTRACT

The closed vessel microwave digestion methods approved by EPA for the preparation of waters and soils for trace metal analysis require a two stage microwave power program that is designed to achieve an initial target temperature of the digestion acid followed by a slow rise to a final temperature. There are inherent problems with this method that arise from the fact that the digestion acid temperatures are functions of vessel type, microwave power, line voltage and the number of vessels. In-situ temperature measurement of the acid during digestion requires the use of an expensive fiber-optic probe device that is beyond the budget of most environmental laboratories. Therefore, users will be "flying blind" when attempting to reach target temperatures. This paper will present data that depicts in-situ temperature-time curves that demonstrate the effect of vessel design and increased microwave power on target temperatures.

INTRODUCTION

The approved EPA CLP and the proposed EPA SW-846 closed vessel microwave digestion procedures are based on very rigid formats regarding power-time programming and the number and type of vessels used (1). The EPA methods for the digestion of water samples requires the use of 5 vessels all containing 45 mls of water sample and 5 mls conc. nitric acid with a two stage power program of 545 Watts for 10 minutes followed by 344 Watts for an additional 10 minutes. This program is designed to allow the acidified samples to reach a target temperature of 160 $\pm$ 4 $^{\circ}$C by the end of the first 10 minutes and to allow for slow rise to 165 - 170 $^{\circ}$C within the next 10 minutes. The EPA methods for the digestion of soil samples requires the use of either 2 vessels containing the samples and 10 mls conc. nitric acid with a one stage power program of 344 Watts for 10 minutes or 6 vessels containing the samples and 10 mls conc. nitric acid with a one stage power program of 574 Watts for 10 minutes. This program is designed to allow the acidified samples to reach an inital target temperature of 175 $^{\circ}$C in less than 5.5 minutes and remain between 170 - 180 $^{\circ}$C for the balance of the 10 minute time period. The above microwave programs are based on the use of 120 ml single walled teflon vessels.

If the user deviates from the above conditions, i.e. uses more than the prescribed number of vessels, uses double walled instead of single walled vessels, uses a higher power wattage than prescribed, then the methods as written will not work as they will not reach the initial and final target temperatures in the prescribed time. The proposed SW-846 Methods 3015 and 3051 allow users to use higher wattage ovens to digest more than the prescribed number of samples at one time and allow the users to use alternative vessel designs. However, the methods allow these changes only if the user can document that the temperature-time profiles remain unaltered. This requires the use of an expensive fiber-optic temperature probe that requires experience and can be dangerous if not used properly with pressurized vessels containing acid. Therefore, this author considers the SW-846 allowed changes to be a moot point for most environmental laboratories.

The basic equation used to calculate microwave power absorbed by acid matrices (2) is shown in Equation 1:

$$P_{(absorbed)} = [(K)(C_p)(m)(dT)]/t$$

This author receives feedback from users that are under the impression that Equation 1 can be used to predict the final temperature reached in a specific time if they know the number of vessels to be used. This, in fact, is not the case since this equation does not take into account cooling effects. In fact, the power-time programs developed for the EPA CLP and SW-846 methods had to be developed empirically using an expensive fiber-optic temperature probe (3). Again, without such a probe, users cannot develop their own microwave digestion methods to stay within the EPA required temperature-time confines.

As yet, manufacturers of microwave digestion systems have not provided the information needed to alter conditions while remaining within the temperature-time guidelines. Therefore, this author conducted the following experiments to document the effect of varying the types of vessels and the power on reaching the initial and final target temperatures for the microwave digestion of water samples. This study used a Luxtron Model 750 fiber-optic temperature probe for in-situ temperature monitoring and a Floyd Model RMS-150 microwave digestion oven (4).

Figure 1(a) depicts the temperature-time curve for the typical CLP and SW-846 type water digestion microwave program. It uses 5 single-walled vessels, each containing 45

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mls deionized water and 5 mls conc. nitric acid, using the prescribed 2 stage program of 545 Watts for 10 minutes followed by 344 Watts for 10 minutes. The temperature profile, as expected met the required target values.

Figure 1(b) depicts the temperature-time curve developed empirically using 5 double walled vessels, each filled with 45 mls deionized water and 5 mls conc. nitric acid. A 2 stage program of 480 Watts for 10 minutes followed by 234 Watts for 10 minutes met the required target temperatures. The reduction in power to meet the temperature targets was a result of the greater insulation afforded by the double walled vessels. Again, it is stressed that this alteration to the EPA prescribed microwave power-time program would have been impossible without the use of the fiber-optic temperature probe.

Figure 1(c) depicts the temperature-time curve when 5 double walled vessels containing 45 mls deionized water and 5 mls conc. nitric acid, instead of 5 single walled vessels, were used with the EPA power-time program of 545 Watts for 10 minutes followed by 344 Watts for 10 minutes. As shown, by using more insulated vessels, the temperatures reached far exceed the EPA required target temperatures.

As stated previously, predicting target temperatures must be done empirically. This author wanted to predict how many more doubled walled vessels could be used for water digestions if a higher wattage (745 W) microwave oven were used. Figure 2(a) depicts the temperature-time curve for 12 vessels all filled with 45 mls deionized water and 5 mls conc. nitric acid were heated at full power. As depicted, it required 16 minutes for the samples to reach the initial target temperaure of 160 °C. From this curve, the number of double walled vessels that can be used to reach 160 °C in 10 minutes using 745 Watts of power can be predicted as follows:

Step 1: Using Equation 1, determine the actual power absorbed over the 16 minute period. In this case, m = 624 gm [(12 x 45 ml water x 1 gm/ml) + (12 x 5 ml nitric acid x 1.4 gm/ml)]; C_p = 0.9297 (estimated from reference (2)); dT = 160 - 24.2 = 135.8 °C; t = 16 minutes x 60 second/minute = 960 seconds; K = 4.184. The actual power absorbed is therefore:

$$P_{(absorbed)} = \frac{(4.184)(0.9297)(624)(135.8)}{960} = 343 \text{ Watts}$$

Step 2: Using the empirically determined power absorbed of 343 Watts, determine how many vessels containing 45 mls deionized water and 5 mls conc. nitric acid (52 grams total mass/vessel) can be heated from 24 °C to 160 °C in 10 minutes:

(a) $m = [(P)(t)]/[(K)(Cp)(dT)] = [(343)(600)]/[(4.184)(0.9297)(136)] = 389$ grams

(b) (389 grams)/(52 grams/vessel) = 7.5 = 8 vessels

Figure 2(b) verifies that the prediction of 8 vessels is correct since the actual temperature-time curve for 8 vessels containing 45 mls deionized water and 5 mls conc. nitric acid using 574 Watts reaches 160 °C in 10 minutes.

SUMMARY

The interest by EPA in converting from hot plates to microwave ovens for the preparation of samples for trace metal analysis is to be commended. However, the confusion at the outset when SW-846 approves methods 3015 and 3051 is expected to be, in this author's opinion, overwhelming. Without expensive in-situ temperature monitoring probes and without documentation from the microwave manufacturers on how to deviate from the rather rigid temperature-time profiles as prescribed by EPA, users are expected to be confused. The announcement of in-situ temperature monitoring capabilities built into the next generation of microwave ovens will go a long way to reduce this confusion.

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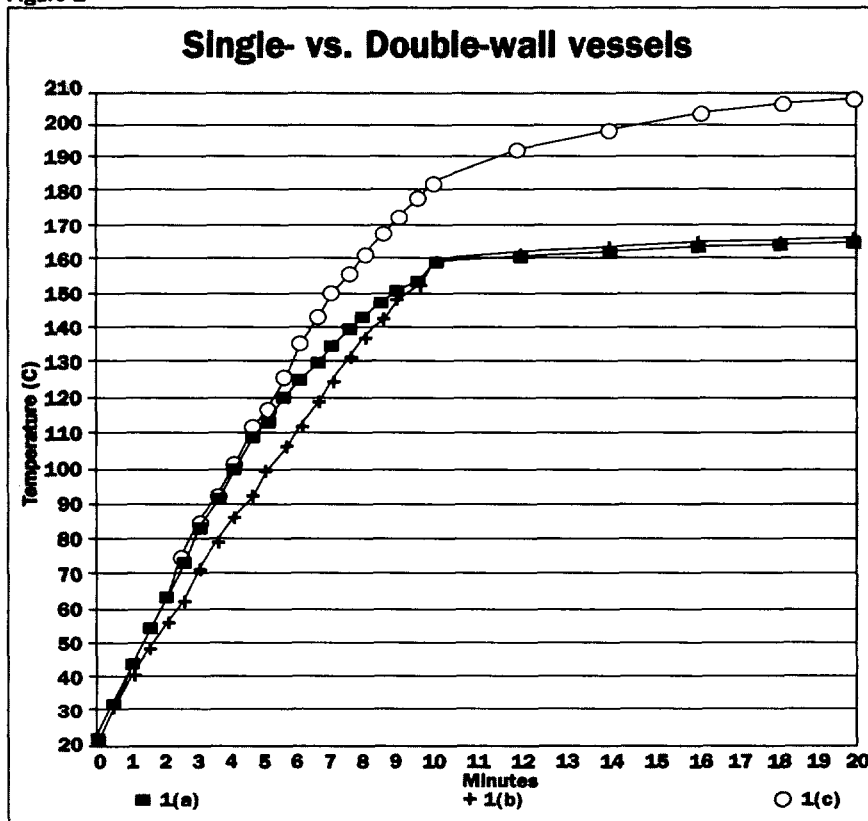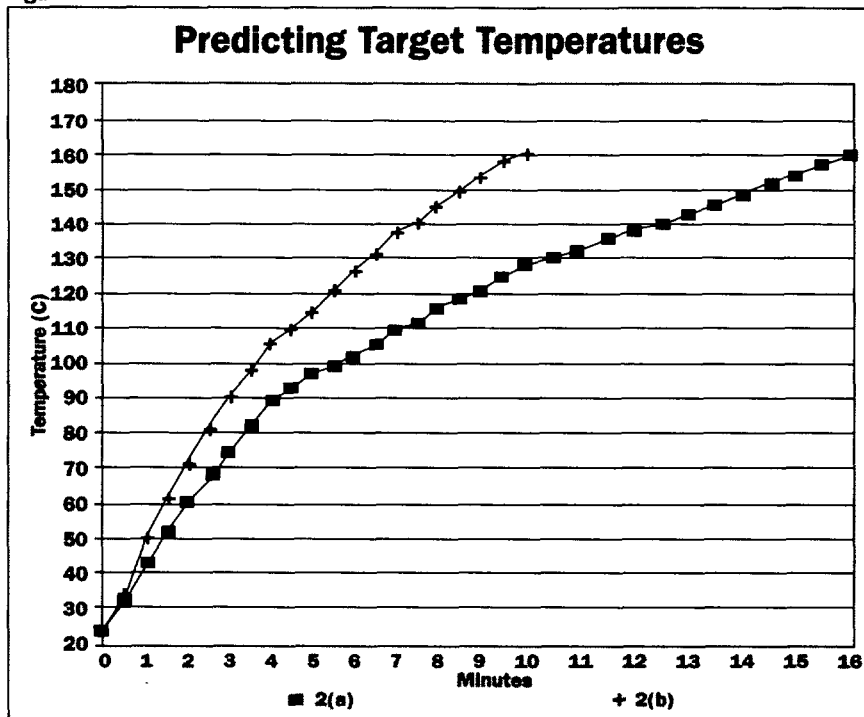4. M.E. Tatro, From hot plates to microwaves. *Environmental Lab*, 3(1), 28 (1991).

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Figure 1

Single- vs. Double-wall vessels

■ 1(a)   + 1(b)   ○ 1(c)

Figure 2.

Predicting Target Temperatures

■ 2(a)   + 2(b)

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81 THE APPLICATION OF X-RAY FLUORESCENCE SPECTROSCOPY FOR RAPID HAZARDOUS WASTE CLASSIFICATION AND SCREENING

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ABSTRACT

X-ray fluorescence spectroscopy (XRF) with pattern recognition data interpretation provides immediate elemental screening capabilities for the comparison of sales sample metal composition with compositional data from loads received at hazardous waste sites.

The proper disposal of hazardous waste through stabilization processes requires information about the elemental composition of the waste stream. Based on the stream's elemental composition, which is both waste code and generator specific, processing decisions are made to select the most effective waste stabilization procedure. Current procedures utilize SW-846 methods to generate elemental compositional data. The analytical method turnaround time creates significant process delays and costs for materials received at CWM sites. XRF can rapidly provide information regarding RCRA elemental analyte composition in hazardous waste streams, enabling processing decisions to be made on a comparatively realtime basis and provide assurance of effective stabilization.

Advances in energy-dispersive (ED) XRF instrumentation with computer software have greatly increased interest in the technology. Advantages for hazardous waste analysis include minimal sample preparation, applicability to a broad range of liquid, solid or semi-solid samples and simultaneous multi-element analysis over a broad concentration range with no elemental carryover. The study generated elemental pattern data for K061 and F006 wastes, produced by specific generators. Fourteen elements were selected for the study: calcium, chromium, iron, nickel, copper, zinc, arsenic, selenium, silver, cadmium, barium, mercury, thallium and lead. ICP analyzed K061 wastes were used as quantitation standards.

Univariate elemental analysis using a one standard deviation comparative criterion demonstrates the effectiveness of XRF technology for distinguishing among waste codes and generators. Multivariate analysis using the Mahalanobis distance technique improves the comparison by utilizing specific elements or the entire X-ray spectrum for recognition of XRF patterns. We conclude that ED-XRF is able to provide data critical for the decision process at hazardous waste disposal sites, while reducing the overall cost of operation.

INTRODUCTION

All wastes received at Chemical Waste Management (CWM), both for waste disposal decisions and as received loads at our disposal sites are subjected to a "fingerprint" analysis. The purpose of this rapid test series is to verify that the material received for disposal matches the profile for that generator produced by the sales samples. Screening tests are in place for nine parameters, and it would improve the quality of the screening process and streamline disposal operations if metals could be included in the fingerprint screening process. This study was undertaken to determine if x-ray fluorescence spectroscopy (XRF) could provide a reasonable and rapid metals-based fingerprint analysis to augment the current series.

An important factor in any fingerprint screen is that it be rapid and sensitive enough to screen the hazardous parameter at the appropriate level of quantitation. XRF is an excellent screening choice for this research, since samples require little or no sample preparation and data can be generated within minutes.

PROJECT PURPOSE

The purpose of this project is to determine the applicability of XRF analysis to fingerprint screening of sales and received samples. The project will proceed through the generation of quantitative analytical data to determine the feasibility of a univariate pattern recognition process in differentiating among waste codes and generators. The work will continue using a multivariate process based on a Mahalanobis distance technique, which will eliminate the need for the generation of quantitative analysis.

TECHNICAL OVERVIEW

In XRF, electrons in the lowest energy orbitals near the nucleus of the atom are energized by external radiation and escape from the atom. Electrons from higher energy orbitals fill the empty orbital and the energy lost in dropping to a lower

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energy orbital is emitted as an x-ray. Because the emitted x-rays are always at a lower energy than the activating radiation, the process is called "x-ray fluorescence." Each element has characteristic electron orbitals of specific energy and therefore a characteristic x-ray fluorescence pattern. Because inner orbital rather than valence electrons are involved in this method, the chemical form of the element has little or no influence. The method is applicable for qualitative and quantitative analysis for chemical elements higher in the periodic chart than oxygen.

Although the technique of ED-XRF has been known for about 40 years, recent advances in instrumentation and especially computer software have greatly increased interest in the technique. XRF advantages include minimal sample preparation, applicability to liquid, semi-solid or solid samples, simultaneous multi-element analysis over a wide concentration range, no carryover to the succeeding sample, rapid quantitation and potential to optimize the system for specific elements.

The XRF spectrometer records counts received in individual channels of a multi-channel analyzer. Each channel counts a small range of energies so that a spectrum of counts at specific energies is obtained. On the basis of known energy values for individual elements, specific ranges are assigned to certain elements.

EXPERIMENTATION

Instrument Selection

The Kevex 770 XRF spectrometer was chosen as the most applicable instrument based on its sensitivity, flexibility and speed of analysis. The instrument was purchased with a DEC VAX 11-57 computer, TSX operating system and Toolbox software.

Sample Preparation

Sample preparation for this technique is minimal. Dry powdered materials may be placed directly in an XRF cup. Liquid or semisolid samples may be run as received or be dried in an oven and then analyzed as a dried powder. Claylike damp samples can be packed into the cup and tamped gently to remove the air spaces.

Instrument Calibration

As a starting point for this work the instrument was calibrated using a large set of K061 wastes from a single generator. The set of K061 wastes were first analyzed

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for the following 14 elements using conventional ICP and AA methodology:

Calcium	Chromium	Iron
Nickel	Copper	Zinc
Silver	Cadmium	Barium
Arsenic	Selenium	Mercury
Thallium	Lead	

These data are presented in Table 1. The high values of thallium and arsenic were found to arise from elemental interferences and were not considered in the pattern recognition process. Additionally, values for calcium and iron were not included, since their consistently high values overshadowed the metals of interest.

A critical consideration for this work is that the instrument was not calibrated to produce quantitative data but consistent data among the matrices encountered.

Analytical Precision

A single K061 sample was run repeatedly under the same activation conditions to show the precision of the method. The sample was run under the activation conditions used for elements calcium, chromium, iron, nickel, copper, and zinc. The sample was stirred every few runs to expose a different portion of the sample to the analytical procedure. Results are shown in Table 2. Again close agreement for each element is seen so that precision is acceptable for waste samples.

X-Ray Analysis

The following samples were analyzed by x-ray using the calibration curves produced by the K061 materials.

Number of Samples	Sample Type	Generator
24	K061	A
4	K061	B
7	F006	C

It was recognized that changing the sample type changed the matrix, which in turn reduced the data's quantitative quality. Again, the project goals were not data quantitation but pattern recognition, using elemental analysis as a guide. Varying the calibration curves only adds an additional degree of freedom.

The analytical data for Generators A, B and C are presented in Figures 1-4 a and b, in a bar graph format. The "a" portion of the Figure presents the composition in percent, while the "b" portion presents the ppm information. The brackets on each bar in Figure 2 show the compositional variation of the 24 K061 wastes at one standard deviation. In a univariate pattern recognition approach, if the elemental concentrations for the sample fall between the brackets defined in Figure 2, there is a 65% probability that the waste is a K061 from Generator A.

A visual comparison of the bar graphs in Figures 2 and 3 show that the overall elemental pattern is reasonably similar for the K061 wastes from generators A and B. But, since the lead, cadmium and barium concentrations fall outside of the defined brackets, there is a high probability that the waste is not a K061 from Generator A.

Comparing the elemental pattern data between Generators A and C, K061 and F006 wastes, the basic elemental pattern is extremely different. No lead appears in the samples from Generator C, but there are significant amounts of barium and nickel. XRF can differentiate among waste codes and generators based on the univariate elemental pattern.

CONCLUSIONS

1. XRF coupled with univariate analysis can generate unique elemental data patterns, within 15 minutes for specific waste codes and generators. Wastes from an individual generator are quite characteristic.

2. The method is rapid enough to be applicable for the purpose of fingerprint screening.

3. The data are also applicable to process related decisions which are a function of elemental distribution.

TABLE 1
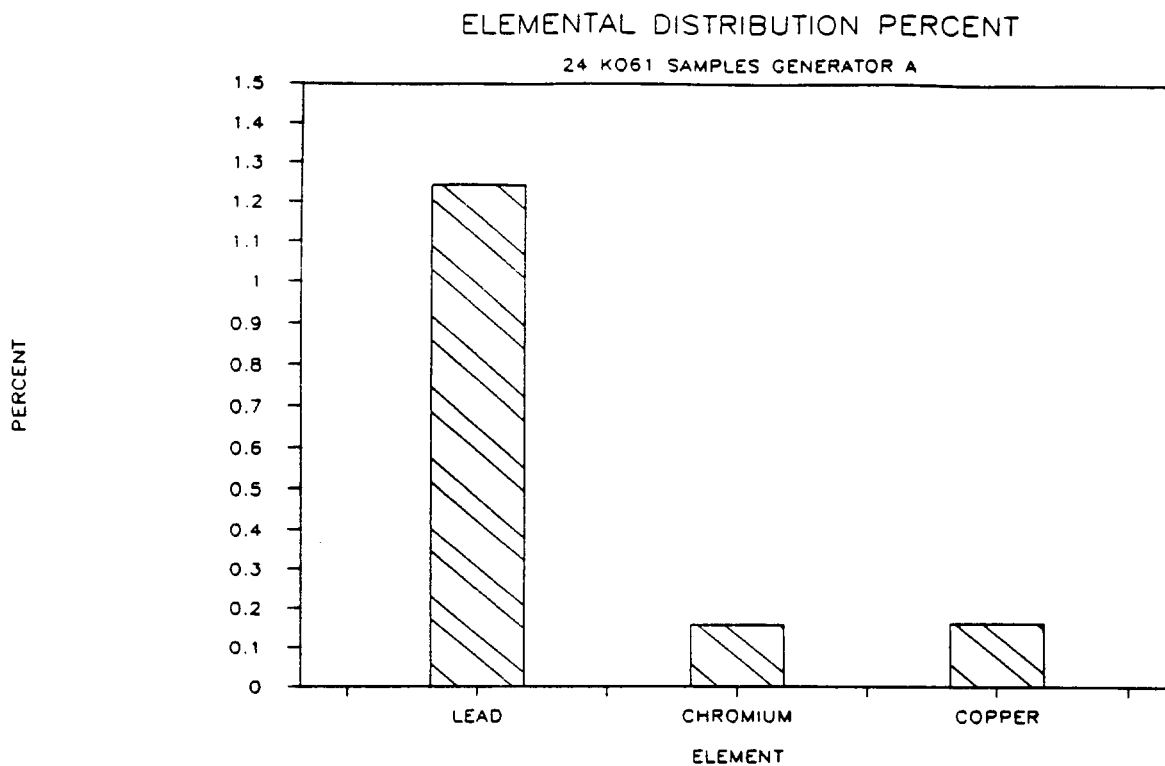## ANALYTICAL DATA FOR 24 K061 WASTES FROM GENERATOR A

LEAD %	CHROMIUM %	COPPER %	CADMIUM PPM	BARIUM PPM	NICKEL PPM	SILVER PPM	MERCURY PPM	SELENIUM PPM
1.40	0.15	0.19	152	161	99.8	36.2	0.10	0.53
1.47	0.16	0.18	131	118	76.2	36.6	0.10	0.53
1.26	0.12	0.16	148	155	76.2	35.9	0.10	0.53
1.33	0.14	0.18	129	123	76.2	35.7	0.10	0.53
1.65	0.18	0.19	161	130	91.2	36.6	0.72	0.53
1.92	0.17	0.19	123	115	115.0	37.3	0.10	0.53
1.70	0.17	0.20	221	159	102.0	37.5	0.10	0.53
1.22	0.16	0.19	201	135	99.2	41.2	0.10	1.76
1.22	0.14	0.15	157	122	84.4	36.4	0.10	0.53
1.33	0.14	0.13	239	144	87.3	38.0	0.75	0.53
1.25	0.16	0.15	227	141	94.2	40.0	0.10	1.69
1.40	0.14	0.14	224	116	76.2	36.9	0.10	1.79
1.15	0.18	0.13	219	118	76.2	35.6	0.10	0.53
1.36	0.18	0.18	223	165	107.0	38.2	0.10	1.50
1.43	0.18	0.16	226	111	112.0	38.7	0.10	1.36
1.31	0.18	0.13	233	116	124.0	35.4	0.10	0.53
0.84	0.14	0.13	190	123	76.2	35.5	0.10	0.53
0.77	0.15	0.17	148	126	98.3	36.0	0.70	0.53
1.32	0.16	0.14	223	115	107.0	37.8	0.10	0.53
1.13	0.17	0.14	257	117	102.0	36.7	0.10	1.80
0.78	0.16	0.15	175	164	76.2	35.4	0.52	1.50
1.01	0.14	0.20	208	164	76.2	34.7	0.10	2.58
0.89	0.14	0.15	195	180	95.2	35.7	1.01	0.53
0.67	0.14	0.13	133	158	97.0	36.0	0.10	0.53
AVERAGE 1.242	0.156	0.161	189.292	136.500	92.717	36.833	0.229	0.936
STD DEV 0.298	0.017	0.024	40.345	20.831	14.231	1.513	0.272	0.608
RANGE 1.541	0.173	0.185	229.637	157.331	106.948	38.346	0.502	1.544
0.944	0.139	0.137	148.947	115.669	78.485	35.321	-0.043	0.328
RSD 68% 24.032	10.901	15.115	21.314	15.261	15.349	4.107	118.870	64.996
RSD 95% 48.064	21.802	30.230	42.627	30.521	30.669	8.213	237.740	129.992
RSD 99% 72.096	32.702	45.345	63.941	45.782	46.048	12.320	356.610	194.988

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TABLE 2

ANALYTICAL DATA PRECISION FOR KO61

CALCIUM %	ARSENIC ppm	IRON %	NICKEL ppm	COPPER %	ZINC %
7.13	0.17	42.8	103	0.19	9.09
7.08	0.16	43.0	88.9	0.17	9.15
7.07	0.15	42.8	88.9	0.17	9.01
7.03	0.17	42.9	88.9	0.17	9.05
7.13	0.15	42.8	107	0.15	9.08
7.13	0.15	42.9	99.2	0.17	9.15
7.01	0.19	43.1	122	0.18	9.13
7.05	0.15	42.9	119	0.19	9.13
7.04	0.18	42.9	117	0.21	9.18
7.15	0.17	43.0	93.3	0.17	9.03
7.08	0.17	43.0	97.3	0.15	9.07
7.15	0.18	43.4	108	0.18	9.24
7.00	0.18	43.2	102	0.23	9.24
7.08	0.17	43.5	111	0.16	9.15
Average 7.08	0.17	43.01	103.25	0.18	9.12
StdDev 0.049	0.013	0.210	10.875	0.021	008
RSD%: 0.69	7.6	0.48	10.5	1.16	0.74

FIGURE 1A

ELEMENTAL DISTRIBUTION PERCENT

24 KO61 SAMPLES GENERATOR A

FIGURE 1B

ELEMENTAL DISTRIBUTION PPM

24 KO61 SAMPLES GENERATOR A

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FIGURE 2A

ELEMENTAL DISTRIBUTION PERCENT

24 K061 SAMPLES GENERATOR A

FIGURE 2B

ELEMENTAL DISTRIBUTION PPM

24 K061 SAMPLES GENERATOR A

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FIGURE 3A

ELEMENTAL DISTRIBUTION PERCENT

4 KO61 SAMPLES GENERATOR B

FIGURE 3B

ELEMENTAL DISTRIBUTION PPM

4 KO61 SAMPLES GENERATOR B

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FIGURE 4A

ELEMENTAL DISTRIBUTION PERCENT

7 F006 SAMPLES GENERATOR C

FIGURE 4B

ELEMENTAL DISTRIBUTION PPM

7 F006 SAMPLES GENERATOR C

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82   SEMI-QUANTITATIVE DETERMINATION OF INORGANIC CONSTITUENTS IN SPECIFIC AND NON-SPECIFIC CATEGORICAL WASTESTREAMS USING EDXRF

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ABSTRACT

X-Ray fluorescence spectroscopy was used to determine several inorganic constituents and associated interferences in F006 and K061 wastestreams. The primary objective was the optimization of stabilization reagents and materials by analyzing incoming waste loads prior to stabilization. By applying EDXRF techniques to the pre-accepted waste loads, an overall increase in site stabilization efficiency can be realized. Total metal disparities between the pre-acceptance sample from the generator and the actual load sample are ubiquitous and problematic. Presently, there exists a paucity of quantitative data concerning the role of EDXRF as a useful analytical tool applied to the environmental analysis of categorical solid waste. Wastestreams that were approved for treatment, stabilization and disposal were randomly sampled and subjected to salient preparation methods. Three instrumental calibration techniques were investigated using the K061 samples: fundamental parameters (FPT), single similar standard and simple linear regression calibration. Because of the extreme variation of the F006 samples, only two instrumental calibration techniques were investigated on these samples: FPT, and a sorting program developed for alloy analysis. Sample characterization using these techniques can be both semi-quantitative and quantitative depending on several parameters, notably, the analyte, method of sample preparation and interferences. The sensitivity inherent to

this analytical technique was sufficient to meet our objectives and provided a certain degree of direction for further study. Moreover, pre-stabilization profiling or analysis of these types of wastestreams optimizes the use of proprietary additives while reducing the total volume of waste placed in the landfill. A complex database can be structured and implemented to work in concert with our rigorous stabilization program furthering our expertise in the field of waste management.

83 IDENTIFYING SOURCES OF ENVIRONMENTAL CONTAMINATION THROUGH LASER SAMPLING ICP-MASS SPECTROMETRY

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ABSTRACT

Laser sampling ICP-mass spectrometry (LS-ICP-MS) is shown to be an effective technique for helping to identify sources of environmental contamination. This rapid, sensitive elemental analysis technique requires little or no sample preparation and provides elemental fingerprints of solid samples in a few minutes. In this study, LS-ICP-MS was used to analyze high-volume air filters and sludge samples, with emphasis placed on obtaining elemental isotopic fingerprints of all the samples and semiquantitative analysis results for the air filter samples.

INTRODUCTION

Determining the elemental composition of environmental contaminants or contaminated materials is one of the many concerns of environmental regulatory agencies and the analytical chemistry community. For many sample analyses, the analysis goal is to determine accurately, a specific list of elements. These analyses usually have rigid, well-defined analysis protocols and specified maximum levels for the elements to be determined. For some analyses, however, it can instead be more advantageous to obtain a full elemental profile of the samples, without the need for a high degree of accuracy. For other samples, it may also be advantageous to know the isotopic abundances for specific elements. Such elemental profiles and isotopic information can often be used as a "fingerprint" to help identify a source of environmental contamination.

As an example, the presence of smog and particulate matter in air is an important environmental concern. Determining the relative elemental compositions of the smog and particulates will help regulatory agencies decide what elements need to be monitored and regulated. Also important, however, is identifying the point sources of the emissions so that proper controls can be placed on these sources. This example can likewise be extended to ground and water contamination.

In this study, laser sampling inductively coupled plasma mass spectrometry (LS-ICP-MS) has been used to analyze sludge samples of domestic and industrial origins and high-volume air filters from various locations in a metropolitan area. By comparing and combining the analysis results with other information, these results can then be used to help establish the sources of environmental contamination.

The well-established ICP-MS technique has the ability to measure rapidly as many as eighty elements. Besides the vast numbers of determinations that can be made in

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a relatively short time using the technique, ICP-MS is known for its high sensitivity, with detection limits generally in the parts-per-trillion range for solution sampling. As a mass spectrometry-based technique, it also has the advantage of being able to determine isotope ratios for certain elements present in a sample.

Using laser sampling, as opposed to solution sampling, as the sample introduction technique, has the advantage of eliminating the usually tedious sample dissolution step required for most atomic spectrometry techniques. This is accomplished by focussing a high-power laser beam onto the sample, thereby creating a sample vapor directly from the solid state. This vapor is then transported to and analyzed by the ICP-mass spectrometer. Sample results can normally be obtained in a few minutes. Among the other advantages are its ability to provide spatially resolved sample information in the form of lateral distributions and depth gradients of elements in a solid. An increasingly important advantage of eliminating the sample dissolution step is avoiding the need to work with concentrated acids and to dispose of acid wastes. A thorough review of the LS-ICP-MS technique has been recently published [1].

LS-ICP-MS has been shown previously to be a good technique for rapid, semiquantitative analysis of various geological materials [2] and several materials of environmental interest [3], as well as many other sample types. Given proper calibration standards for the elements of interest, LS-ICP-MS can also be used for quantitative analysis of many materials. However, like many other solid sampling techniques, the availability of appropriate solid calibration standards can limit the quantitative aspect of LS-ICP-MS for some analyses.

The primary interest in this study was to use LS-ICP-MS to obtain elemental fingerprints of the various samples analyzed. Such fingerprints indicate the relative elemental compositions of the samples without regard for the absolute element concentrations. While some interpretation of the mass spectra is required to compensate for spectral interferences, subsequent quantitation using the element intensities, and thus calibration of the system, is not required.

Of secondary interest in this study was to quantitate the results from the analysis of the high-volume air filters. In order to accomplish this task, a calibration method appropriate for laser sampling of the air filters had to be developed.

EXPERIMENTAL

Instrumentation

Two different LS-ICP-MS systems were used for data collection in this study. The first system consisted of a Perkin-Elmer SCIEX Model 320 Laser Sampler coupled to a P-E SCIEX ELAN 500 ICP mass spectrometer. The laser sampler consists primarily of a pulsed, Q-switchable Nd:YAG laser; an enclosed sample cell mounted on a three-axis translation stage; and a closed-circuit video monitoring system. The laser and translation stages are all computer controlled. The ICP-MS was controlled using an IBM PS/2 Model 70 microcomputer running the P-E SCIEX ELAN 5000 software under the Xenix operating system. The laser sampler

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was controlled by an 80286-based microcomputer running the P-E SCIEX laser sampler software under Windows and DOS.

The second LS-ICP-MS system consisted of a Model 320 Laser Sampler coupled to a P-E SCIEX ELAN 5000 ICP mass spectrometer. Both the ICP-MS and the laser sampler were controlled from a single IBM PS/2 Model 70 microcomputer. The software used was the same as for the first system except that the laser sampler software was run under Windows and VP/ix. A block diagram of the laser sampler/ICP-MS system is shown in Figure 1.
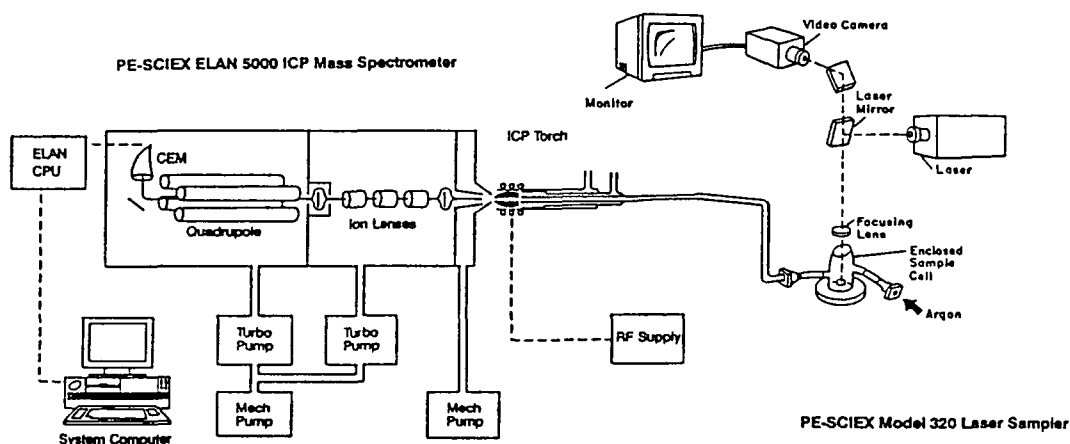

Figure 1. Diagram of laser sampling ICP-MS system.

Methodology

Standard and Sample Preparation. For the sludge analysis, the certified reference materials studied were combined with an X-ray fluorescence binding agent, SpectroBlend (Chemplex Industries, Inc.), at a sample:binder ratio of 3:1. These mixtures were shaken well and then pressed into 0.5 g pellets using an IR pellet dye and a 12-ton press. Had the reference materials not been finely powdered, they first would have been ground to a 350 to 400 mesh before mixing with the binding agent.

Standards were prepared for the high-volume air filters analysis by evenly loading measured amounts of standard reference materials (SRM) onto 1.5 x 3.0 cm pieces of blank filters of the same type used for the air sampling. In order to keep the SRM's from leaving the surface of the filters prematurely when sampled by the laser, the filter standards were coated with an aerosol-based binding agent. The air filter samples were cut into 1.5 x 3.0 cm pieces and also coated with the binding agent before laser sampling. For solution sampling, 3.0 x 3.0 cm pieces of the filter samples were leached in 20% nitric acid. The leachate for each sample was then diluted 20x before analysis. Appropriate blanks were prepared in the same manner as the respective laser and solution sampling filters samples.

Analysis Procedures - General. Standard laser-sampling operating conditions for the ICP-MS instruments were used for all the analyses. For the semiquantitative

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analyses, the LS-ICP-MS system was calibrated by analyzing a prepared standard for several certified elements using the TotalQuant routine of the ELAN 5000 software. The TotalQuant routine then used the results for the certified elements to calibrate the system for the other elements of interest, for a total of up to eighty elements. The TotalQuant routine was also used to produce the fingerprint spectra resulting from the analyses.

Sampling Procedures - Sludges. The reference material pellets were sampled with the laser in the Q-switched mode, with an energy of 50 mJ/pulse and a repetition rate of 10 Hz. The laser beam was scanned back and forth across the sample on a 5-mm line for a 20-second pre-measurement period followed by a 60-second data collection period. Since only relative sample intensities were desired for this part of the study, no concentration calibration was performed.

Sampling Procedures - Air Filters. The standard and sample air filters were sampled with the laser in the Q-switched mode, with an energy of approximately 10 mJ/pulse and a 10-Hz repetition rate. A 6 x 7 mm area of each filter was sampled using a z-pattern raster with the laser beam. A 30-second pre-measurement sampling time was used, followed by 3 successive 60-second data collection periods for each determination.

RESULTS AND DISCUSSION

Sludge Samples

Spectral fingerprints for the two sludge materials studied were obtained easily using the described technique. Figures 2 and 3 show the single point per dalton "mass histograms" for the sludge samples. These spectra were interpreted and elemental intensities were automatically calculated by the TotalQuant software routine. The element intensities were then normalized to each sample's total element intensity so that any differences in laser sampling efficiency could be nullified. The resulting normalized elemental fingerprints for the sludges are shown in Figures 4 and 5.
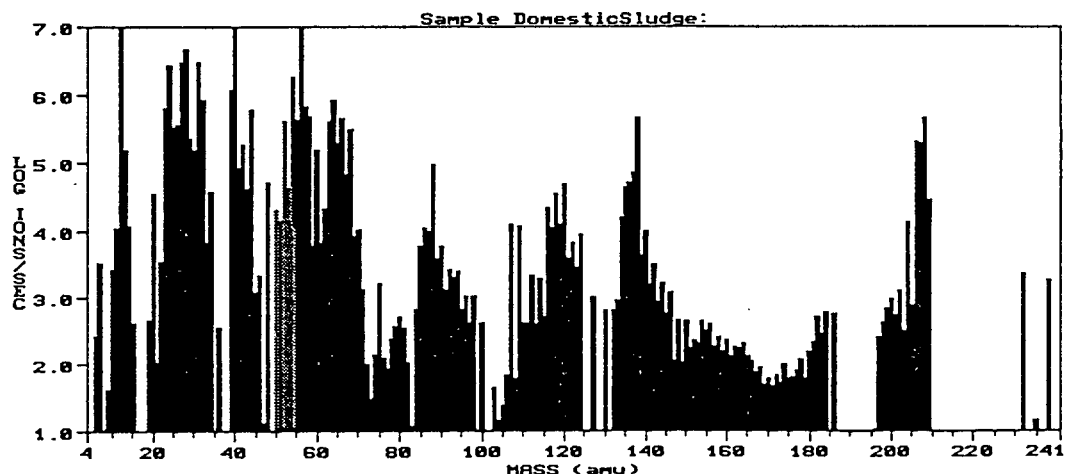

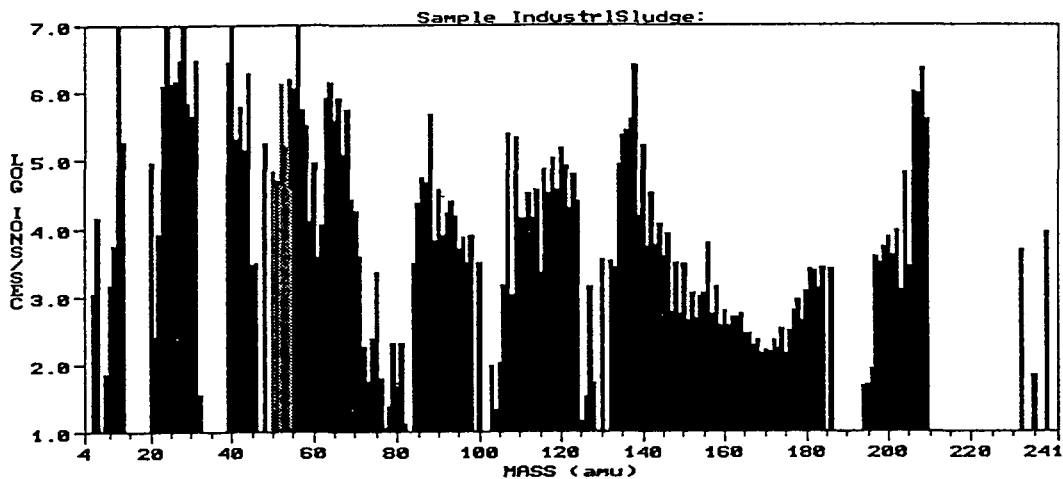**Figure 2.** LS-ICP-MS spectral fingerprint for domestic sludge sample.

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Figure 3. LS-ICP-MS spectral fingerprint for industrial sludge sample.
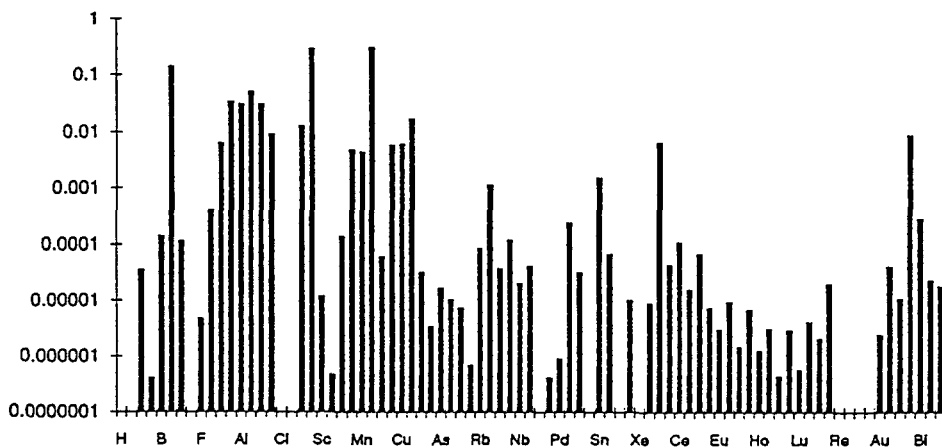

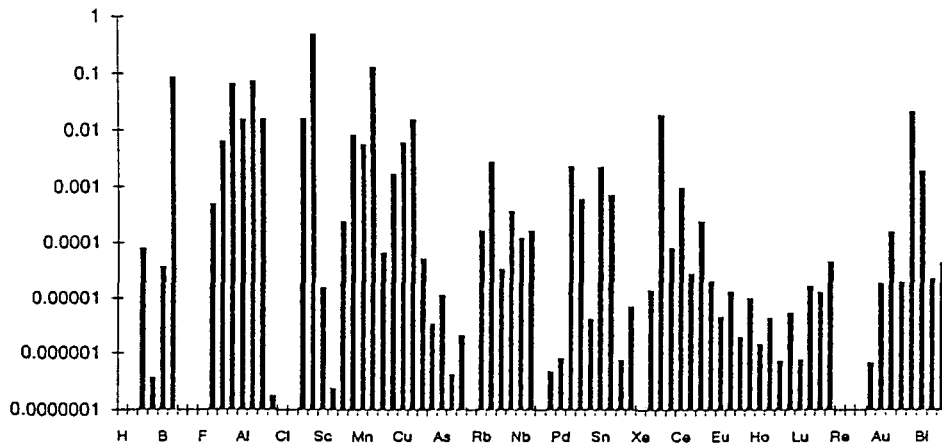**Figure 4.** Normalized elemental fingerprint for domestic sludge sample.

Figure 5. Normalized elemental fingerprint for industrial sludge sample.

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At first glance, the two sludge elemental fingerprints appear quite similar. However, upon closer examination, some differences can be seen. In order to make these difference more apparent, the two elemental fingerprints were ratioed to one another. Figure 6 shows the ratios of the domestic sludge fingerprint to the industrial sludge fingerprint. From these ratios, it appears that the domestic sludge has a higher content of N, F, S, and Se, while the industrial sludge is higher in In, Te, Pt, and Bi.
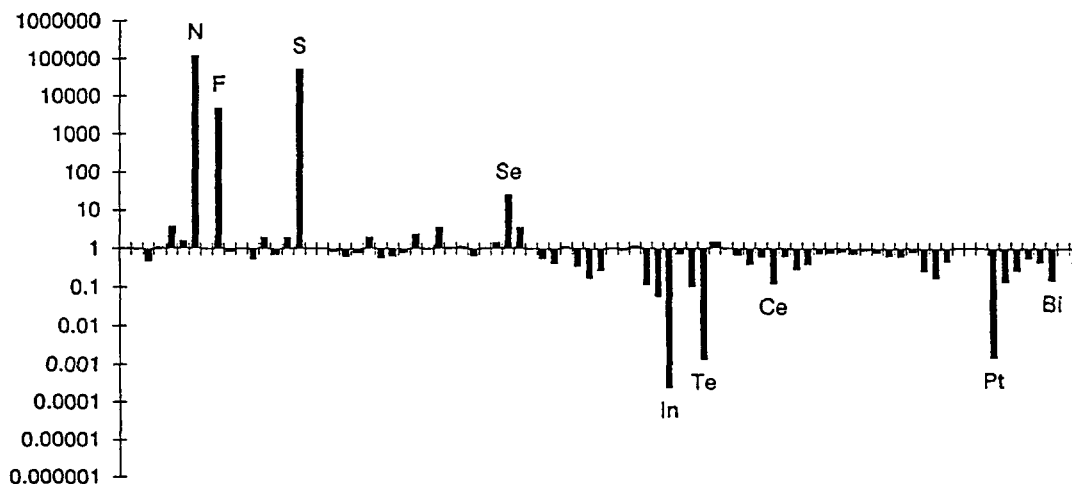

Figure 6. Ratios of normalized results for sludges, domestic:industrial.

Because the ratio of two small numbers can still turn out to be a large (or very small) number, however, it was necessary to apply a filter function to the fingerprint data before the ratios were calculated. Figure 7 shows the domestic:industrial sludge ratios after a 1e-06 filter function was applied to the data. While the significant elements on the domestic sludge side didn't change much, the significant elements for the industrial sludge now appear to be Cd, Sb, Ce, Au, and Bi.

The utility of data such as these goes beyond the ability to determine rapidly the content of a sample. For the case of the domestic sludge, one might expect a high organic content, and thus look for carbon as a major constituent. While the domestic sludge did contain a large amount of carbon, Figure 7 shows that it was not much higher than was found in the industrial sludge. However, while the nitrogen and sulfur content of the domestic sludge was much lower than the carbon content, the relative concentrations of these elements were much higher than those in the industrial sludge. Therefore, it should be possible to use nitrogen and sulfur as indicators of the organic content of a sample. Likewise, it appears that the heavy metals, rare earths, and precious metals may be good tracers for industrial waste. While these data certainly do not comprise a comprehensive study, combining such data with methods of principle components analysis shows great promise for helping environmental scientists to categorize waste types and even pinpoint sources of environmental contamination.
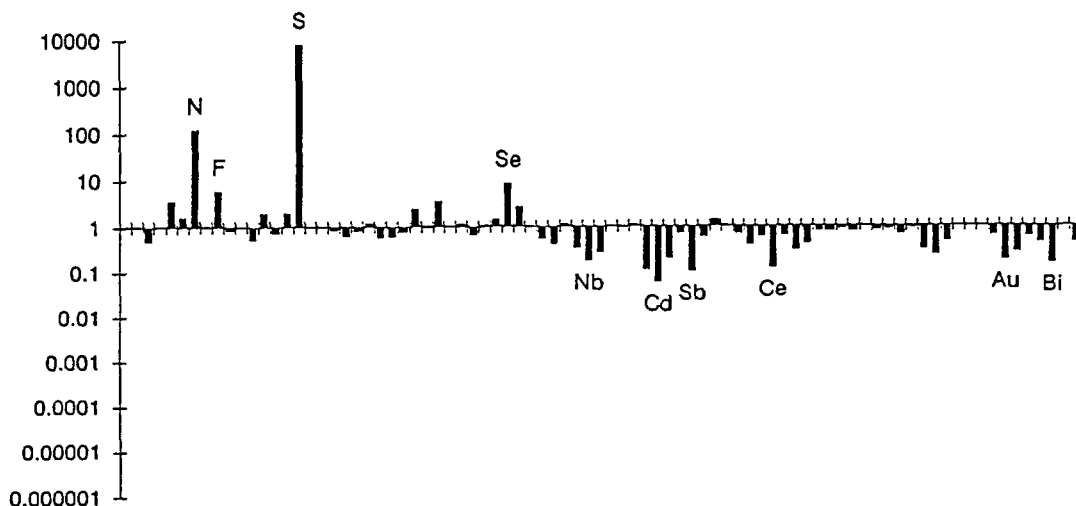
Figure 7. Domestic:industrial sludge ratios after 1e-06 filter function.

High-Volume Air Filters

In this part of the study, several high-volume air filters from a metropolitan area were analyzed. These filters sampled the air in various locations in the area and were designated as "downtown," "North," "petroleum plant," and "airport." There was also a filter that sampled the output from a point emission source.

Obtaining reproducible spectral and elemental fingerprints of the high-volume air filters was not quite as straightforward initially as is was for the sludge samples. Because of the fragility of the glass fiber filters used for this application and the relatively low laser power with which they could be ablated, the laser sampling conditions for this application had to be carefully controlled. Once the proper sampling conditions were established, however, good fingerprints could be produced readily. The spectral fingerprint for the "downtown" filter is shown in Figure 8.

Quantitating the results from the air filter analysis required producing an appropriate calibration standard and analysis method. Previous attempts made in our laboratories, and those of other workers [4], to provide a proper calibration standard have included soaking filters with standard solutions, using a mylar-based filter standard, and coating filters with slurries of reference materials.

Using the first two methods have the disadvantage of having the calibration species entrained throughout the filter material, whereas the sample filters have the analyte particles mostly on the surface of the filter. Because the filters used in this application can contain relatively high levels of some of the elements of interest, the goal of the laser sampling process is to remove particles from the filter surface while removing as little of the filter as possible. In addition, removing too much filter material can leave filter particles deposited throughout the sample transport line,

causing memory effects. Another possible problem with the solution-spiked filters is that the chemical forms of the analyte species in the standards and sample are likely to be quite different. This can cause some differences in the sampling efficiencies for the species, although using a Q-switched laser should help to reduce the differences. Finally, there has been no proof to date that this calibration method is valid for the air filters analysis.
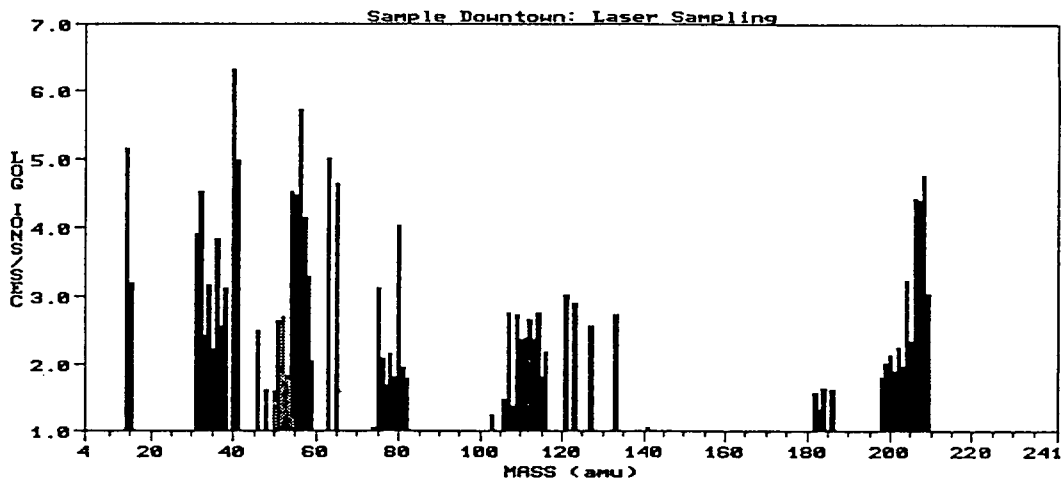

**Figure 8.** LS-ICP-MS spectral fingerprint for "downtown" air filter.

Advantages of the slurry-coating approach are that the species of interest are deposited onto the surface of the filter and are more likely to be in the same chemical form as they are on the sample filters. One potential problem with this approach, however, is that some analyte species could be leached from the reference material particles and either be left in the container the slurry was made in or soaked into the bulk of the filter. Another practical problem with sampling slurry-coated filters with the laser is that a relatively wide area, up to several millimeters in diameter, of the reference material is removed by the shock wave produced by the laser-solid interaction. This may seem to be an advantage at first, since the sampling efficiency would be large. However, much of the material removed in this manner is not vaporized by the laser, but instead is removed as particles that are too large to be analyzed well by the ICP-MS or simply fall out of the carrier stream and are deposited in the sample line.

The approach used in this study was to load various dry, powdered reference materials directly onto blank filters. The filters, which were cut to a specific size, were weighed before and after the reference materials were added so that a loading factor could be calculated for each filter. This loading factor was then used with the certified concentrations to determine the loading, in ng cm^{-2}, for the elements of interest on the filter surface.

When filters prepared in this way were sampled with the laser, the problem with the wide sampling area, described above, was encountered. To counteract this effect, the filters were coated with an aerosol-based binding agent and dried. Subsequent

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sampling of the filters was then confined to the immediate area of the laser beam. Another advantage of this method is that less of the filter substrate was sampled by the laser, also. Analysis of blank filters coated with the binder only showed that the binder did not contribute to the background levels of the elements of interest.

Figure 9 shows the semiquantitative analysis results from the laser sampling analysis of several SRM-coated filters. A filter coated with NIST SRM 1648, Urban Particulate Matter, was used as the calibration standard for this analysis. SRM's on the analyzed filters included Coal Fly Ash and Estuarine Sediment. Also included are results from analysis of a filter coated with the Urban Particulate Matter SRM, but with a different loading factor than the standard filter. While these results indicate that this approach used for calibration has some validity, it is clear that more work needs to be done to refine the technique.
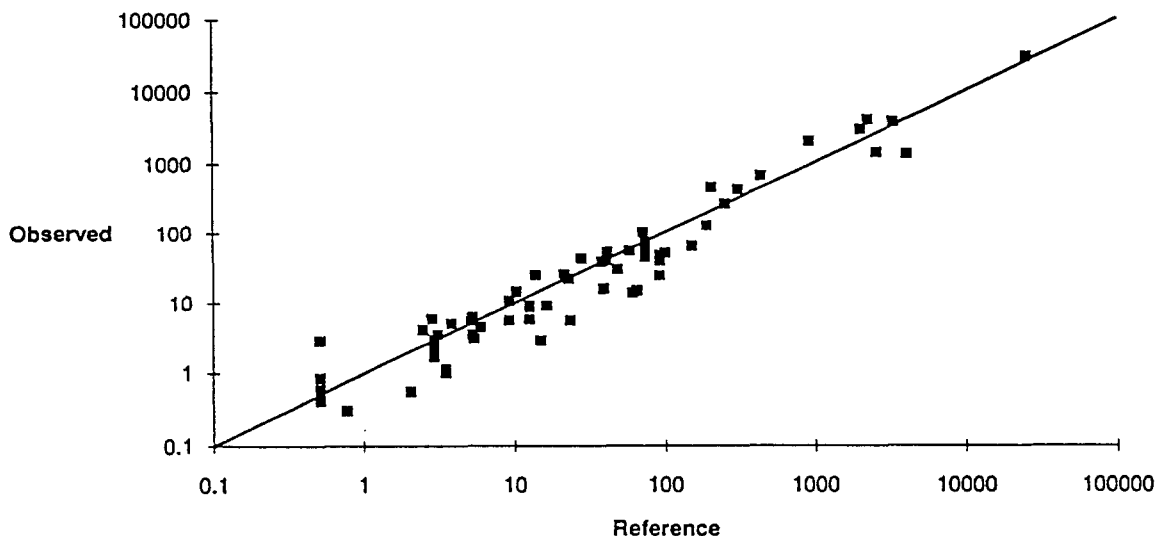
Figure 9. Semiquantitative analysis results (ng cm^{-2}) for SRM-coated filters.

All of the sample filters were also analyzed against the SRM 1648 standard filter. Figure 10 shows the semiquantitative elemental fingerprint for the "downtown" sample. Of note are the relatively high results for As, Cd, Hg, and Pb. The other filters showed similar results. While it was not done in this study, these results could be compared in the same manner as the sludge results to determine what elements show the most significant differences and could be used as tracer elements to help track sources of pollution.

Comparison to Solution Sampling

The analysis of air filters using atomic spectrometry techniques is in wide practice. While X-ray fluorescence can be used to analyze these filters directly, most analyses are performed using atomic absorption and ICP techniques which require the sample to be in a solution form. The most widely-used technique for getting the samples into solution is to use a nitric acid leaching procedure. In fact, it is because of this leaching procedure that the glass fiber filters are used instead of the more common cellulose fiber filter papers.
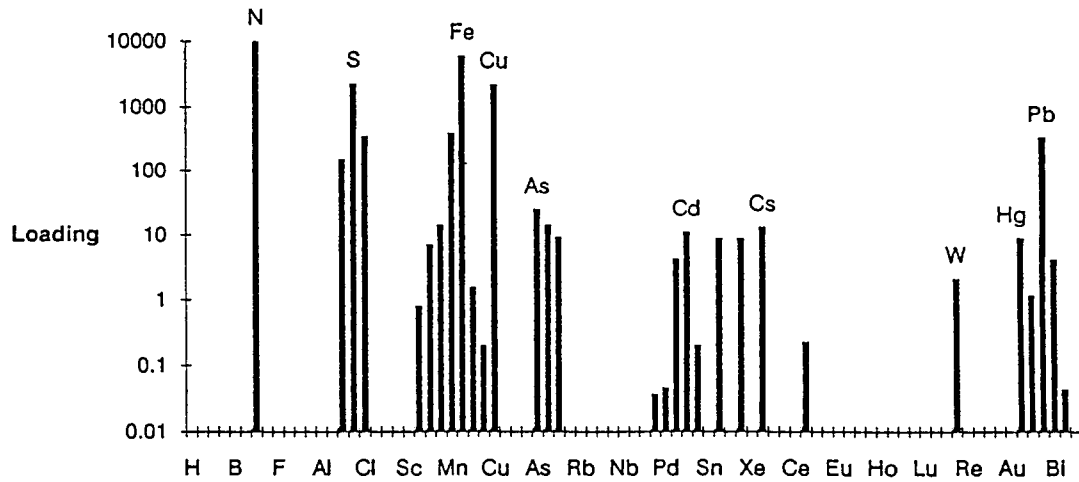
Figure 10. Semiquantitative elemental fingerprint for "downtown" air filter. (Loading in ng cm^{-2})

The results for laser sampling ICP-MS were compared to results obtained from solution sampling ICP-MS for the same filter samples. After nitric acid leaching procedures were performed on the filters, the leachate solutions were diluted to a factor that would give ICP-MS results in the same intensity range found for laser sampling. Figure 11 shows the solution sampling spectral fingerprint for the "downtown" filter sample. Many features of this fingerprint are similar to those found for the laser sampling fingerprint of this filter (Figure 8).

Figure 11. Solution sampling ICP-MS spectral fingerprint for "downtown" air filter.

In order to make comparison of the solution and laser sampling results easier, the results were normalized and ratioed in the same manner as the sludge samples. Figure 12 shows the ratios comparing the solution and laser sampling results for the

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"downtown" filter sample. Of particular note from these results is that the laser seems to have provided a more complete sampling for N, S, Cl, Br, and Hg. It is not surprising that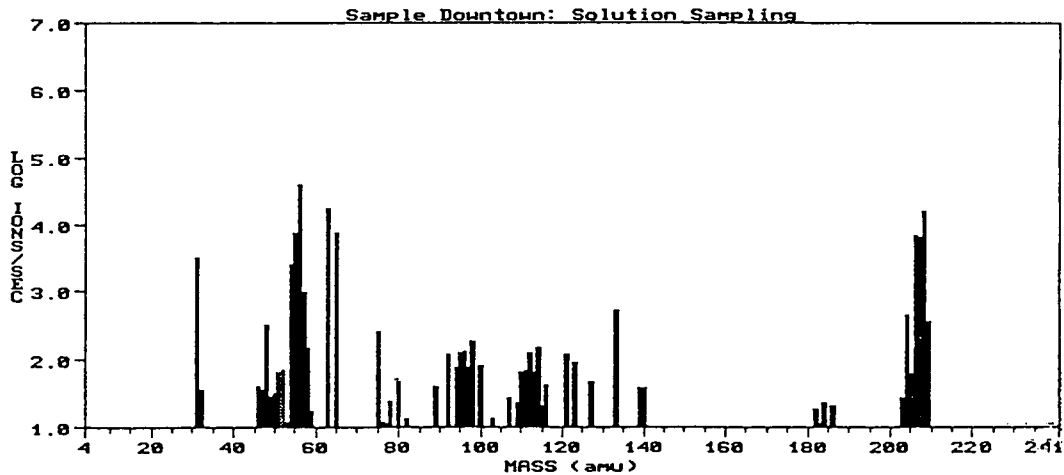 these elements were either not leached well from filters using the nitric acid procedure or did not remain in solution.
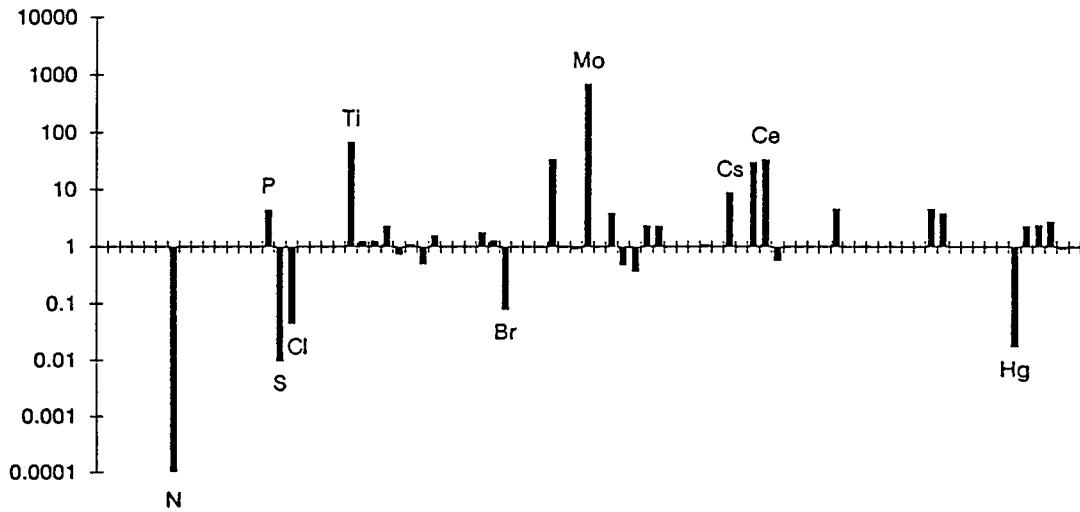
Figure 12. Ratios of solution sampling:laser sampling results for "downtown" air filter.

Because of specific interest in determining sulfur for the filters, the laser sampling results for sulfur were examined more closely. This interest is compounded by the fact that X-ray fluorescence determinations for sulfur are suspect in their accuracy. Figure 13 shows an intensity versus sulfur loading plot for the semiquantitative analysis of the SRM-coated filters. While this is not a perfect calibration curve, it does show promise for laser sampling ICP-MS (or LS-ICP-AES) as a method for determining sulfur on the filters.

Sulfur Loading (ng cm-2)
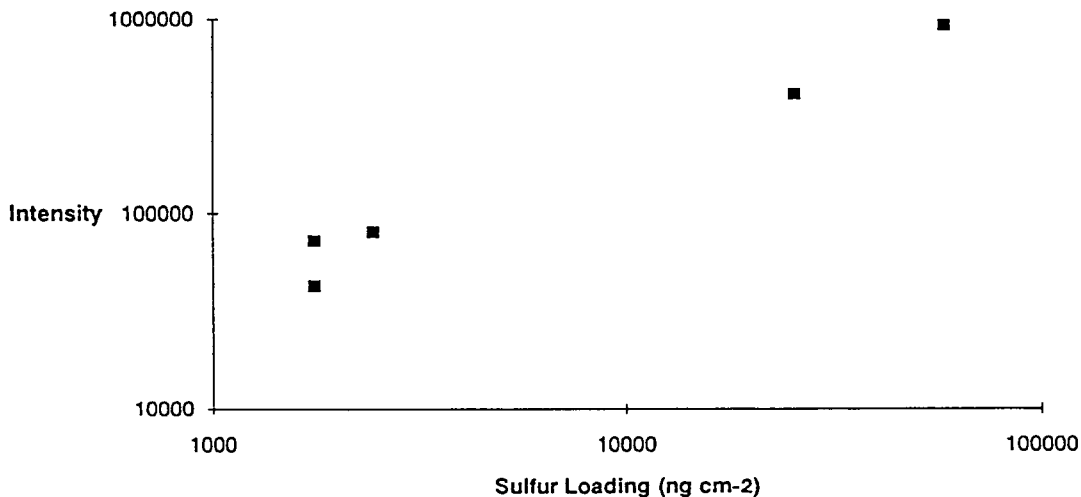
Figure 13. Intensity (counts/sec) versus sulfur loading results for SRM-coated filters.

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Solution and laser sampling results were also compared for the point emission source filter sample, since this sample contained high levels of several difference elements. These results are shown in Figure 14. On the solution side, it was found that Zn and Ba could be determined better by solution sampling than with the laser. This is because the blank filters used in this application contained high levels of these elements which, when sampled by the laser, produced very high background signals that made them difficult to determine.
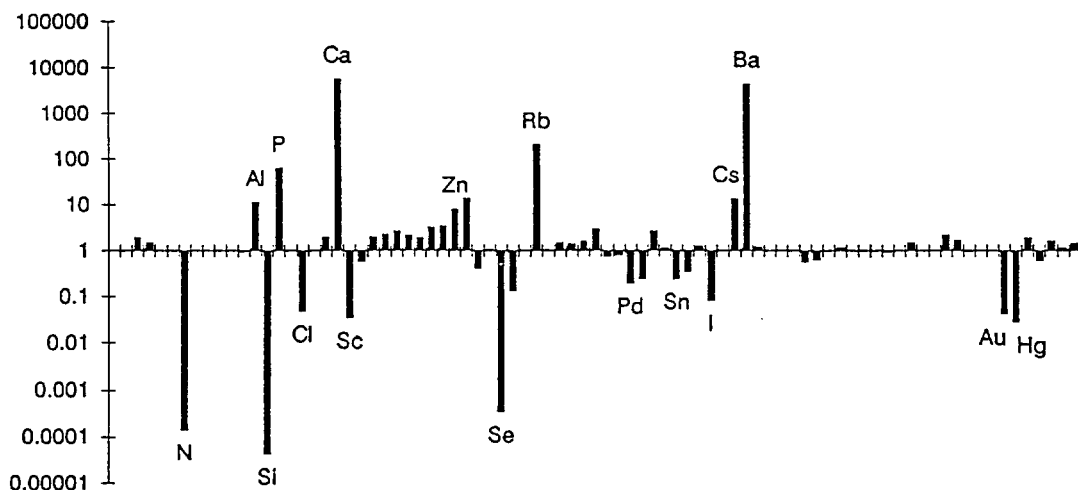

Figure 14. Ratios of solution sampling:laser sampling results for point source filter.

For laser sampling of the point source filter, once again the laser seems to be more proficient for N, Hg, and the halogens. Also note that Au and Pd were sampled better with the laser. Figures 15 and 16 show the spectral fingerprint data from 170 to 240 daltons for solution and laser sampling of the point source filter. The difference in the Hg isotope intensities in the 196 - 204 range for the two methods can be seen clearly, while intensities for Pb (204 - 208), Tl (203 & 205), Re (185 & 187), W (180 - 186), Th (232), and U (238) are quite similar. Also, the Au signal at 197 is quite strong for laser sampling while essentially absent from the solution sampling data.

As indicated in the sludge application, N, S, and the precious metals may be important elements for helping to identify and track sources of environmental contamination. The ability of laser sampling ICP-MS to determine these elements, even semiquantitatively, could be quite important for this type of application. For toxic elements such as As, Cd, Pb, and Hg, the importance of the more complete sampling using the laser is even more apparent. Had solution sampling techniques alone been used for these samples, it is possible that important elemental information would not have been uncovered.

Another advantage of using laser sampling for the analysis of air filters is that by eliminating the sample leaching step, the need for using the glass fiber filters, as

opposed to cellulose fiber filters, is also eliminated. During methods development for this application with the laser sampler, it was found that cellulose filters coated with SRM's could be sampled more easily and reproducibly than the glass filters. The semiquantitative analysis results for laser sampling of an SRM-coated cellulose filter are shown in Figure 17. Besides the generally good agreement between the observed and certified values, note that zinc could be determined using these filters, whereas it could not be determined on the glass filters because of the high background levels.
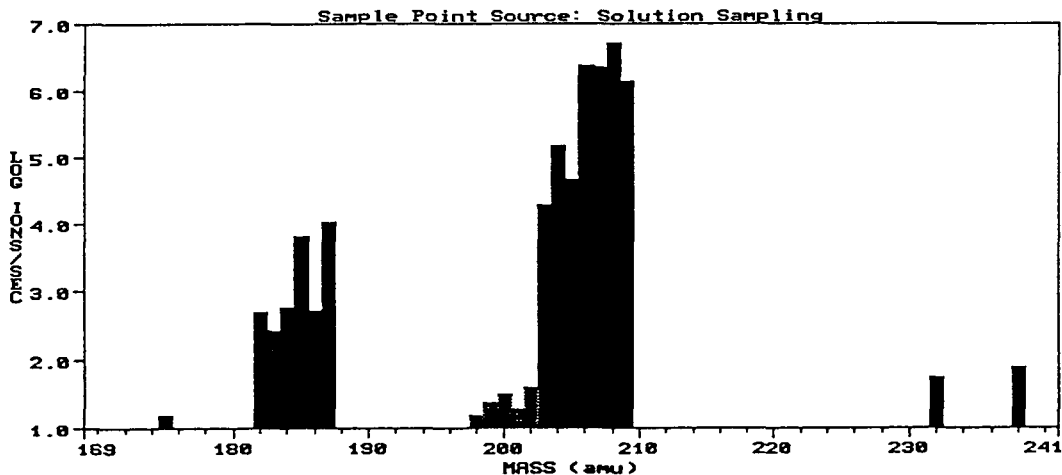
Figure 15. Spectral fingerprint from 170 - 240 dalton region for solution sampling analysis of point source filter.
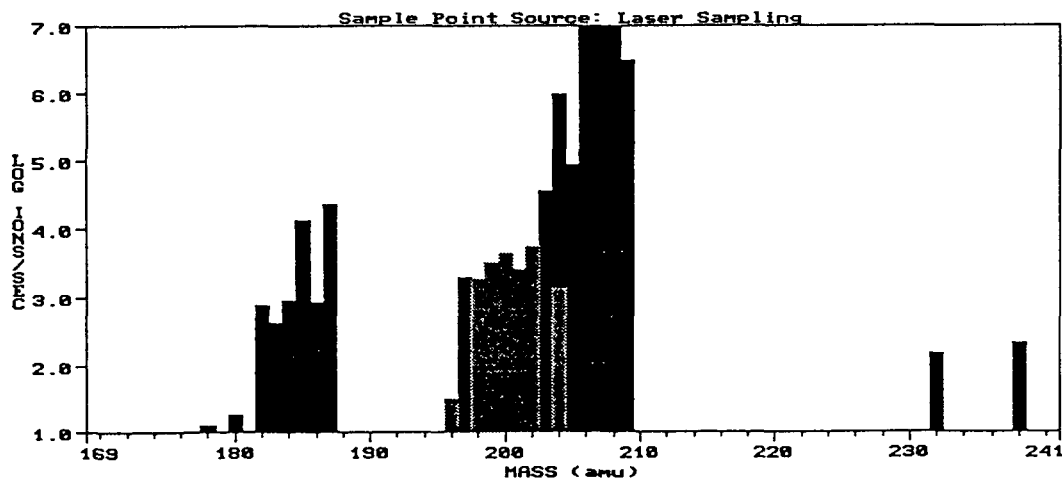
Figure 16. Spectral fingerprint from 170 - 240 dalton region for laser sampling analysis of point source filter.
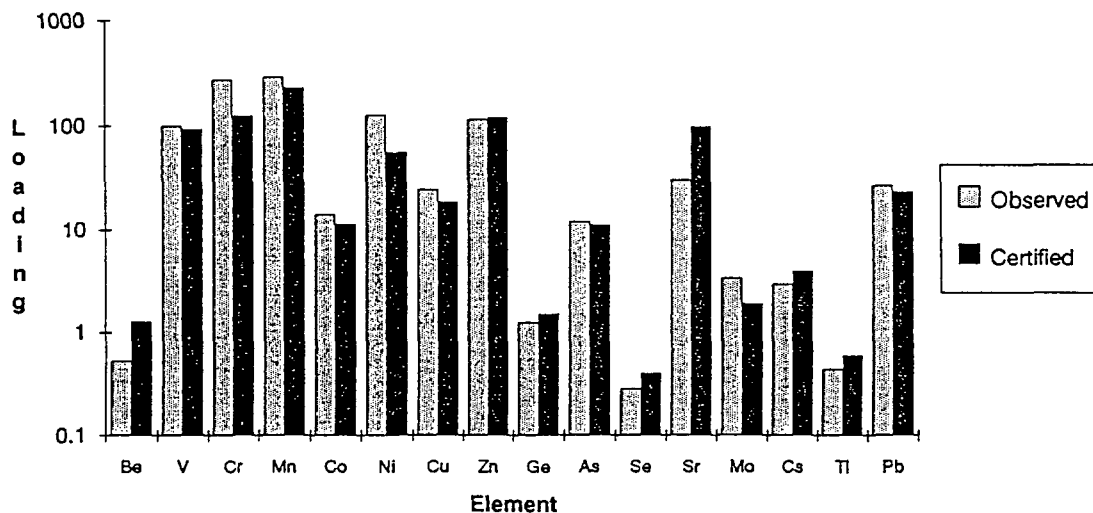
Figure 17. Semiquantitative LS-ICP-MS results (ng cm^{-2}) for an SRM-coated cellulose filter.

SUMMARY

Laser sampling ICP-mass spectrometry can be used to produce full, semiquantitative elemental profiles for elements present at trace to major levels in a wide variety of samples. In this study, the LS-ICP-MS technique has been applied to the analysis of solid sludge samples and high-volume air filters. The elemental fingerprints produced by the technique can be used to help identify which elements may be important to monitor in order to identify sources of environmental contamination. The technique also shows great promise in being able to determine important elements that are difficult to determine by other techniques.

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ICP/MS ANALYSIS OF
TOXIC CHARACTERISTIC LEACHING PROCEDURE (TCLP) EXTRACT
ADVANTAGES AND DISADVANTAGES

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Paul Roettger, Isaiah Murshak and Dan Edelman

ABSTRACT

The use of the ICP/MS analytical technique is growing for various analytical applications. The authors of this work describe the advantages and disadvantages of the ICP/MS analysis of toxic characteristic leaching procedure (TCLP) extract. This aqueous extract buffered with acetic acid may cause interferences with the ICP/MS qualitative and quantitative analyses.

This study presents the matrix spike recoveries for all of the RCRA metals except mercury (Hg). These metals include: arsenic (As), barium (Ba), cadmium (Cd), lead (Pb), selenium (Se), and silver (Ag), as well as zinc (Zn) and copper (Cu). In addition, these results are compared to ICP/AES recoveries. Based on these recoveries and other observations in our laboratory, we conclude that the ICP/MS is appropriate and convenient for the analysis of TCLP extract.

INTRODUCTION

The recent change in toxic characteristic analysis from EP Toxicity to the toxic characteristic leaching procedure (TCLP) provides analytical environmental chemists with another matrix for analysis. Traditionally environmental laboratories have performed analyses for metals in the TCLP leachate with atomic absorption spectrometry and inductively coupled plasma Atomic Emission Spectrometry (ICP/AES).

Our laboratory has used ICP/AES since 1988 to perform analyses on the TCLP extract. In 1989 we installed an ICP/MS to perform analyses of metals. Our incentive for installing the ICP/MS was the low detection limits the method provides using traditional aspiration for sample introduction. In addition, the ICP/MS performs the simultaneous qualitative and quantitative analyses of up to 70 or so elements. This allows for rapid sample through put. However, we soon discovered many other advantages of ICP/MS and it became the analytical method of preference for metal analyses in our laboratory.

This work discusses observations made in our laboratory regarding the advantages and disadvantages of analyzing TCLP extract for metals with an ICP/MS. They are based on real life samples submitted to our laboratory by clients. Thus, this ICP/MS work did not involve a predesigned experiment as would be done in academic research.

ANALYTICAL METHOD

The inductively coupled plasma spectrometer (ICP/MS) in use at FECL is the SCIEX ELAN model 250, converted to a model 500 capability (Perkin Elmer, Norwalk, Connecticut). FECL also has a Perkin Elmer Plasma 40 Spectrometer (ICP). The ICP/MS system components include Xenic System V Software, and IBM Personal System 2 computer and an Epson LQ-850 printer. The various features and conditions of the system are shown in Table 1.

For standard preparation equal volumes of 10 ppm multielement stock solution and 10 ppm silver stock solution are added together resulting in a 5 ppm solution for all metals. The stock solutions are obtained from PlasmaChem Associates, Bradley Beach, New Jersey.

Under FECL's Standard Operating Procedures, samples of 50 ml each are spiked with 1 ml of 5 ppm solution resulting in a 0.1 ppm spike concentration for the various elements. To each of the samples, 2.5 ml of 70% nitric acid (HNO_3) is added. Spiked and unspiked samples are subsequently digested in a microwave oven for 30 minutes at medium power. After the samples have cooled down following digestion, they all receive 1 ml of 25 ppm internal standard. The samples are diluted to their final volume of 50 ml yielding a 0.5 ppm concentration. The samples are then ready for internal standard ICP/MS analysis.

The internal standard is made up by combining 10 ml of the 1000 ppm solutions for each of the five standards, i.e. In, Se, Y, Rh and Re. The total volume is diluted to 400 ml of 25 ppm concentration. The internal standards are supplied by Inorganic Ventures, Inc. of Toms River, New Jersey.

For instrument calibration, two calibration solutions of 0.50 ppm and 0.10 ppm, respectively, are prepared weekly from the multielement stock solution and internal standard. For the 0.5 ppm calibration solution 5 ml of 10 ppm multielement stock solution are mixed with 2 ml of 25 ppm internal standard and bringing the mixture to a final volume of 100 ml. The 0.1 ppm calibration solution combines 10 ml of 1.00 ppm

TABLE 1

ICP/MS Operating Conditions

ICP torch	Ames laboratory design (28); outer tube extended 30 mm from inner tubes
Forward power	1.25 kW
Argon flowrate (L/min)	
Outer	12
Auxiliary	0.5
Aerosol gas	1.0 - 1.2
Sampling position	22 mm above load coil, on center
Sampler	Nickel, 1.2 mm orifice
Skimmer	Platinum, 0.90 mm orifice
Ion lens settings	Upgraded ion optical system
Bessel box barrel	$+30 \pm 5$ V
Bessel box plate lens	-13 ± 3 V
Einzel lenses 1 & 3	-70 V
Einzel lens 2	-130 V
Bessel box stop	-30 ± 5 V
Operating pressure	
Interface	1 torr
Quadrupole chamber	2.3×10^{-5} torr
Data acquisition	Multi-element monitoring mode, normal resolution setting; three measurements per peak spaced 0.1 m/z units about peak top; dwell time at each position is 20 ms, with total measurement time of 0.17 s allows detection of three analytes per injection without missing tops of peaks.
Isotopes monitored	^{52}Cr, ^{63}Cu, ^{66}Zn, ^{75}As, ^{78}Se, ^{82}Se, ^{107}Ag, ^{111}Cd, ^{137}Ba, ^{208}Pb

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multielement solution and 2 ml of 25 ppm internal standard and diluting to a volume of 100 ml. A calibration blank and check standard are also prepared weekly. The blank is made up of 5 ml of 1.00 ppm multielement solution and 2 ml of 25 ppm internal standard. The mixture is added to 100 ml of deionized water to result in a 0.05 ppm concentration. The check standard of 0.2 ppm is prepared by diluting 2 ml of 10 ppm multielement solution and 2 ml of 25 ppm internal standard to 100 ml. The check standard is used each time after five to seven samples are run as an independent calibration solution.

Operation of the ICP Atomic Emission Spectrometer (ICP/AES) is similar to that of the ICP/MS except the spiking level of samples is higher. The ICP samples are spiked with 5 ml of 10 ppm multielement stock solution to an element concentration of 1 ppm.

We use EPA method 200.7 for ICP/AES analysis and EPA method 200.8 for ICP/MS analysis. Furthermore, we use EPA method 1311 for the TCLP extraction.

The data presented herein are grouped by sample type and type of extraction fluid. Method 1311 requires Fluid #1 which is more buffered for samples with low pH (pH <5). The method requires Fluid #2 when a special HCl test yields a pH of greater than five. Figure 1 shows a flow chart of the TCLP procedure.

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Figure 1
TCLP EXTRACTION PROCEDURE

```
┌──────────────────┐
│    Determine     │
│    Sample pH     │
└──────────────────┘
         │
┌──────────────────┐
│    See Start     │          filtrate <0.5%
│    Procedure     │          of total mass
│    Below         │
└──────────────────┘
         │
┌──────────────────┐    ┌──────────────┐    ┌────────────────────┐
│    Determine     │────│  Filter and  │────│  No Extraction     │
│    Sample Type   │    │  Weigh       │    │  Necessary; Filter │
└──────────────────┘    │  Filtrate    │    │  and Continue as is│
   solid │    solid portion└──────────────┘    └────────────────────┘
┌──────────────────┐    ┌──────────────┐
│  Place Solid     │◄───│    Store     │
│  Portion into    │    │  Filtered    │
│  Borosilicate jar│    │  Liquid      │
└──────────────────┘    └──────────────┘
  pH > 5 │          pH < 5 │
┌──────────────────┐    ┌──────────────────┐
│ Add (2L x %Filtrate)│ │ Add (2L x %Filtrate)│
│ of Fluid #2      │    │ of Fluid #1      │
└──────────────────┘    └──────────────────┘
         │
┌──────────────────┐
│   Tumble for     │
│   18 Hours       │
└──────────────────┘
         │
┌──────────────────┐
│  Remove from     │
│  Tumbler         │
└──────────────────┘
         │
┌──────────────────┐    ┌──────────────────┐
│  Measure pH      │────│  Re-add Filtered │
│  of Extracted Fluid   │  Portion to Jar  │
└──────────────────┘    └──────────────────┘
  if solid │
┌──────────────────┐
│   Let Settle     │
│   (as Necessary) │
└──────────────────┘
         │
┌──────────────────┐
│     Filter       │
└──────────────────┘
         │
┌──────────────────┐
│  Store 250ml     │
│  of Filtrate in  │
│  Plastic Bottle  │
└──────────────────┘
         │
┌──────────────────┐
│  Proceed to      │
│  Digestion       │
└──────────────────┘
```

NOTES:

1. Fluid #1: 5.7ml HOAc/L
   + 64.3ml NaOH/L.

2. Fluid #2: 5.7ml HOAc/L

Start Procedure:

Add 5g sample to 96.5ml
DI Water. If pH > 5,
add 3.5ml HCl. Heat to
60 C and recheck pH.
Use this pH value to
determine extraction
fluid needed.

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ANALYTICAL RESULTS

Table 2 summarizes the detection limits established according to CFR 136 Appendix B for ICP/MS and ICP/AES analysis of the TCLP analytes. It also provides detection limits from the analytical methods published in EPA method 200.7 and 200.8 for comparison. Note, for most of the metals presented there is a significantly lower detection limit for the ICP/MS. Indeed in many cases, it is one hundred times lower, than ICP/AES detection limits. But, in every case, the ICP/MS detection limit is at least a factor of ten lower. These lower detection limits offer one of the significant advantages of the ICP/MS. That is, the ICP/MS has the ability to analyze a sample diluted to the point where matrix effects are minimized and still yields an acceptable detection limit.

Tables 3, 4, and 5 summarize the performance of the ICP/MS for known and blank spike samples. The knowns are standards obtained from outside our laboratory certified for the concentrations shown in the table. The blank spikes were dilutions of our standard solutions. The diluted concentrations are shown in Table 4.

Tables 3 and 4 show the accuracy obtained with the ICP/MS. Standard deviations of less than nine percent are obtained in every case. Table 5 shows the precision of the ICP/MS from the analysis of duplicate blank spikes. These tables summarize the accuracy and precision that we routinely observe with the ICP/MS on these standards.

Tables 6, 7 and 8 show the percent recoveries for the metals using the ICP/MS and ICP/AES. These tables are grouped by sample type and the type of extraction fluid used in the TCLP. In Tables 6 and 8 the standard deviations for all of the metals, except for arsenic, copper and zinc in Table 6 and for cadmium and selenium in Table 8 are lower with the ICP/MS. For the soil matrix in Table 7 ICP-40 provided lower standard detections for most of the metals. However, the ICP/MS samples were spiked with 0.1 ppm of analyte compared to 5 ppm for the ICP/AES analysis.

The ICP/AES, of course, is an established method for toxic characteristic analyses. So, these observations indicate that the ICP/MS is also a useful method for these analyses.

Tables 9, 10, 11 and 12 show the spike recoveries from the ICP/MS analysis of TCLP extract for four of our most common sample types. Again, these tables group similar extraction fluid and sample types. Table 9 presents the

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TABLE 2
Method Detection Limits

	ICP-MS (mg/l)		ICP-40 (mg/l)	
	Calculated[1]	EPA Estimated[2]	Calculated[1]	EPA Estimated[3]
As	0.0015	0.0009	0.20	0.053
Ba	0.0015	0.0005	0.02	0.002
Cd	0.0009	0.0001	0.01	0.004
Cr	0.0005	0.00007	0.04	0.007
Cu	0.0012	0.00003	0.01	0.006
Pb	0.0007	0.00008	0.08	0.042
Se	0.0047	0.0050	0.50	0.075
Ag	0.0032	0.00005	0.05	0.007
Zn	0.0032	0.0002	0.02	0.002

1. Using CFR136 Appendix B. Based on 10 Blank Spikes of 0.01ppm.

2. From EPA Method 200.8.

3. From EPA Method 200.7.

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TABLE 3

Quality Control Knowns by ICP/MS % Recovery

ICP/MS

QC-ICP Knowns

	mg/l	SET #1	SET #2	SET #3	SET #4	SET #5	Mean	S*
As	0.2	97	104	96	96	101	98.80	3.56
Ba	0.2	99	106	98	105	98	102.00	4.06
Cd	0.2	98	103	95	98	102	98.50	3.36
Cr	0.2	97	104	97	98	99	99.00	2.92
Cu	0.2	99	102	98	96	99	98.75	2.17
Pb	0.2	101	103	101	96	101	100.25	2.61
Se	0.2	101	104	98	113	104	104.00	5.61
Ag	0.2	103	100	94	111	114	102.00	8.57
Zn	0.2	100	96	97	95	107	97.00	5.34

TABLE 4

Blank Spikes by ICP/MS % Recovery

	mg/l	SET #1	SET #2	SET #3	SET #4	SET #5	Mean	S
As	0.05	104	100	96	108	94	100.40	5.73
Ba	0.05	104	102	104	105	102	103.75	1.40
Cd	0.05	110	100	100	96	99	101.50	5.32
Cr	0.05	100	98	94	95	100	96.75	2.89
Cu	0.05	108	99	100	98	99	101.25	4.12
Pb	0.05	108	100	104	98	100	102.50	4.04
Se	0.05	108	114	98	98	97	104.50	7.80
Ag	0.05	110	100	107	100	96	104.25	6.02
Zn	0.05	108	111	95	99	100	103.25	6.70

TABLE 5

Blank Spike Difference in Duplicates by ICP/MS

	mg/l	SET #1	SET #2	SET #3	SET #4	SET #5	Mean	S
As	0.05	0	0	0	0	0	0.00	0.00
Ba	0.05	0	3.4	0	4.1	1.2	1.88	1.92
Cd	0.05	0	0	0	0	0	0.00	0.00
Cr	0.05	0	0	0	0	0	0.00	0.00
Cu	0.05	0	0	1.9	0	5.9	0.47	2.83
Pb	0.05	0	0	0	0	1.0	0.00	0.50
Se	0.05	0	0	0	0	0	0.00	0.00
Ag	0.05	0	0	0	0	0	0.00	0.00
Zn	0.05	0	4.8	1.6	0	6.8	1.60	3.26

*S = Standard Deviation

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ICP-40 & ICP/MS

TABLE 6

Spike Recoveries in % for TCLP Analysis of Industrial Paint Sludge
Comparison Between ICP/MS and ICP-40

SET #4
ICP/MS
INDUSTRIAL PAINT SLUDGE

EXTR.#	1	1		Mean	S*
	6711-E1	6711-E2			
Sample	1	2			
As	180	168		174.00	8.49
Ba	80	92		86.00	8.49
Cd	100	100		100.00	0.00
Cr	110	98		104.00	8.49
Cu	80	98		89.00	12.73
Pb	90	84		87.00	4.24
Se	175	160		167.50	10.61
Ag	82	80		81.00	1.41
Zn	170	90		130.00	56.57

ICP-40
INDUSTRIAL PAINT SLUDGE

EXTR.#	1	1		Mean	S*
	6711-E1	6711-E2			
Sample	1	2			
As	85	88		86.50	2.12
Ba	114	88		101.00	18.38
Cd	86	75		80.50	7.78
Cr	98	83		90.50	10.61
Cu	93	78		85.50	10.61
Pb	90	69		79.50	14.85
Se	130	107		118.50	16.26
Ag	10	7		8.50	2.12
Zn	94	80		87.00	9.90

TABLE 7

Spike Recoveries in % for TCLP Analysis of Soils
Comparison Between ICP/MS and ICP-40

ICP/MS
SOILS

EXTR.#	2	2	2	Mean	S*
	6704-E1	6704-E2	6734-E1		
Sample	1	2			
As	149	136	118	134.33	15.57
Ba	REJ	100	90	95.00	7.07
Cd	106	100	80	95.33	13.61
Cr	110	94	76	93.33	17.01
Cu	94	85	73	84.00	10.54
Pb	99	93	75	89.00	12.49
Se	159	131	123	137.67	18.90
Ag	81	80	38	66.33	24.54
Zn	190	70	80	113.33	66.58

ICP-40
SOILS

EXTR.#	2	2	2	Mean	S*
	6704-E1	6704-E2	6734-E1		
Sample	1	2			
As	99	110	87	98.67	11.50
Ba	169	108	71	116.00	49.49
Cd	90	91	78	86.33	7.23
Cr	94	100	74	89.33	13.61
Cu	90	93	77	86.67	8.50
Pb	88	80	73	80.33	7.51
Se	87	105	116	102.67	14.64
Ag	64	13	107	61.33	47.06
Zn	107	91	74	90.67	16.50

*S = Standard Deviation

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TABLE 8

Spike Recoveries in % for TCLP Analysis of WWTP Sludge
Comparison Between ICP/MS and ICP-40

SET #5
ICP/MS   ICP-40
WWTP SLUDGE   WWTP SLUDGE

EXTR.#	1	1	1	1			EXTR.#	1	1	1	1		
	6613-E1	6613-E2	6613-E3	6613-E4	Mean	S*		6613-E1	6613-E2	6613-E3	6613-E4	Mean	S*
Sample	1	2					Sample	1	2				
As	110	105	100	104	104.75	4.11	As	104	94	103	76	94.25	12.97
Ba	100	100	100	100	100.00	0.00	Ba	58	74	89	59	70.00	14.63
Cd	78	74	80	80	78.00	2.83	Cd	86	85	85	81	84.25	2.22
Cr	141	141	141	135	139.50	3.00	Cr	100	96	89	87	93.00	6.06
Cu	90	84	77	75	81.50	6.86	Cu	104	85	89	85	90.75	9.03
Pb	77	75	78	77	76.75	1.26	Pb	86	87	75	78	81.50	5.92
Se	89	81	128	130	107.00	25.63	Se	100	100	86	90	94.00	7.12
Ag	68	69	70	70	69.25	0.96	Ag	47	15	20	4	21.50	18.27
Zn	100	100	100	100	100.00	0.00	Zn	85	62	70	67	71.00	9.90

*S = Standard Deviation

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TABLE 9

Spike Recoveries in % on TCLP Extract of soils by ICP/MS
with Mean and Standard Deviation(s)

SOILS

EXTR*	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	Mean	S**
As	112	117	119	130	179	104	124	146	105	121	116	106	94	112	97	118	136	149	121.39	20.24
Ba	140	220	270	100	117	100	100	100	100	100	100	72	100	100	100	90	100	149	118.18	48.78
Cd	100	96	103	102	116	104	94	112	95	109	103	99	101	98	103	80	100	106	101.17	7.54
Cr	135	145	130	118	133	126	115	145	128	128	126	109	103	114	107	76	94	110	119.00	17.13
Cu	95	103	100	82	89	100	82	89	76	83	92	78	76	79	78	73	85	94	86.33	9.02
Pb	100	60	73	76	79	95	74	84	74	81	83	79	82	77	82	75	93	99	81.44	9.79
Se	147	142	153	157	199	130	127	116	96	116	106	103	98	100	99	123	131	159	127.89	26.88
Ag	79	70	77	71	72	90	86	96	91	86	90	79	91	76	89	38	80	81	80.11	12.67
Zn	100	80	95	80	105	100	59	72	50	86	140	100	71	54	80	80	70	190	89.56	31.98

TABLE 10

Spike Recoveries on TCLP Extract of WWTP sludge
with Mean and Standard Deviation(s)

WWTP SLUDGE

EXTR*	1	1	1	1	1	1	1	1	1	1	1	1	Mean	S**
As	94	97	102	137	117	135	130	80	110	105	100	104	109	16.7
Ba	106	35	99	108	100	100	94	82	100	100	100	100	94	18.7
Cd	103	102	100	100	92	99	106	82	78	74	80	80	91	11.2
Cr	94	100	101	117	111	128	104	106	141	141	141	135	118	17.2
Cu	91	88	86	92	76	85	86	80	90	84	77	75	84	5.7
Pb	79	82	80	84	55	70	52	82	77	75	78	77	74	9.9
Se	118	122	135	154	148	141	86	72	89	81	128	130	117	26.8
Ag	114	109	105	115	84	101	86	74	68	69	70	70	89	18.1
Zn	185	85	80	88	160	100	100	100	100	100	100	100	108	30.0

*EXTR = TCLP Extraction Fluid # (i.e. Fluid #1 or Fluid #2)
**S   = Standard Deviation

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TABLE 11

Spike Recoveries on TCLP Extract of Industrial sludge
with Mean and Standard Deviation(s)

INDUSTRIAL SLUDGE

EXTR*	1	1	1	1	1	1	Mean	S**
As	135	116	104	120	180	168	137	27.8
Ba	110	100	98	100	80	92	97	9.1
Cd	95	104	104	91	100	100	99	4.7
Cr	130	100	106	104	110	98	108	10.6
Cu	89	92	90	96	80	98	91	5.8
Pb	74	120	72	72	90	84	85	16.9
Se	147	96	114	125	175	160	136	27.2
Ag	91	100	92	84	82	80	88	6.9
Zn	100	96	100	34	170	90	98	39.5

TABLE 12

Spike Recoveries on TCLP Extract of Industrial sludge
with Mean and Standard Deviation(s)

INDUSTRIAL SLUDGE

EXTR*	2	2	Mean	S**
As	138	91	115	23.5
Ba	100	100	100	0.0
Cd	102	100	101	1.0
Cr	86	89	88	1.5
Cu	100	80	90	10.0
Pb	86	77	82	4.5
Se	145	89	117	28.0
Ag	100	109	105	4.5
Zn	100	100	100	0.0

*EXTR = TCLP Extraction Fluid # (i.e. Fluid #1 or Fluid #2)
**S   = Standard Deviation

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percent spike recoveries for soils extracted with Fluid #2. The highest standard deviation of all the metals shown is for barium. It is 1.5 times the next higher standard deviation (44 vs. 32). However, in Tables 10, 11 and 12 the standard deviations for Barium are more than two times lower. We cannot explain this.

The standard deviation for wastewater treatment plant sludge (Table 10) and industrial sludge extracted with Fluid #1 (Table 11) and Fluid #2 (Table 12) show standard deviations less than 30 percent for all metals. This is at sample spike levels of 0.1 ppm analyte concentration.

The percent spike recoveries presented here are typical of those we observe in our TCLP analysis. Please note that none of these samples have been tested for matrix interferences. Indeed, the samples themselves have a significant impact on the recovery of the metals. The ICP/MS performs about the same for each of the four sample types.

CONCLUSIONS

Based on the data summarized in this work and on other observations made in our laboratory we find the ICP/MS to be an appropriate and convenient method for analyzing TCLP extracts. We find the advantages of the method out-weigh the disadvantages. The major advantages and disadvantages of the ICP/MS analysis which we've identified are summarized in Table 13.

TABLE 13

ICP/MS Analysis of TCLP Extracts

Advantages and Disadvantages

Advantages:

- Fast - 3 readings per sample for 10 metals in less than 20 seconds
- Able to verify calibrations at any place in the run and then continue
- Recalibration to compensate for drift by internal standards takes only a few seconds
- High sensitivity allows diluting to minimize matrix effects
- Avoids atomic emission interferences
- Uses only 2 ml of sample for analysis
- Able to screen samples semi-quantitatively

Disadvantages:

- High sensitivity requires significant diluting of higher analyte concentrations to be within the calibration range (or switch to high concentration mode)
- Operator must be knowledgeable in recognizing and correcting interferences

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SEVENTH ANNUAL WASTE TESTING
AND QUALITY ASSURANCE SYMPOSIUM

ABSTRACT

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Title:

Chromium VI; An Overview of Its Relevant Environmental Occurrence, Analytical Methods of Quantitation, and Report on Recent Ion Chromatography Methods Development and Validation Activities.

This presentation covers the various forms of chromium found in nature and those that are significant in environmental samples and to human and ecosystem health. The interconversion of trivalent and hexavalent chromium in the environment and related problems associated with sample collection, preservation and quantitation of the various species is discussed. Topics covered include the current analytical methodology that utilizes chelation/extraction or coprecipitation with iron or lead. These approaches have several potential chemical interferences or deficiencies that are discussed.

A description of recent methods development studies, utilizing ion chromatography and inductively coupled plasma mass spectroscopy, for the determination of total and hexavalent chromium in incinerator particulate emissions is presented. The ion chromatography method developed in this study was adapted for use in aqueous environmental samples and is now available for use in the Environmental Protection Agency's compliance monitoring programs. The water method is identified as Method 218.6, " Determination of Dissolved

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Hexavalent Chromium in Drinking Water, Ground Water and Industrial Effluents by Ion Chromatography". Results of a recently completed multi-laboratory method validation study conducted in cooperation with ASTM are presented.

Additional efforts needed in the area of sample processing to extend application of the technique to a wider variety of sample types will also be presented.

86 Rapid High Performance Microwave Digestion

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Microwave Digestion Techniques have reduced the time required to place a sample in solution. However, there are still limitations in sample handling, cooling and recoveries of elements. In this paper we will present several different types of Digestion Systems and show how each of them addresses the above mentioned problems. To be covered in the study are: Closed Vessel Microwave Ovens; Open Vessel Microwave; High Pressure Conventional Digestion, and High Pressure Microwave Digestion. Comparisons are made based upon what we consider the two most important operating factors: throughput and recovery. Throughput encompasses all of the cost factors such as speed of digestion, speed of cooling, number of samples per batch, amount of reagents and operator time. Recovery, especially its reproducibility, defines the success or failure of the procedure.

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THE PERFORMANCE OF A LOW COST ICP-MS
FOR THE ROUTINE ANALYSIS OF ENVIRONMENTAL SAMPLES

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ABSTRACT

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is rapidly being recognized as the choice of instrumentation for trace element analysis of environmental samples. It possesses a number of distinct advantages when compared with other established techniques: sensitivity, speed and versatility.

This presentation will demonstrate the performance and cost effectiveness of the new Fisons PQe ICP-MS. The system was designed to meet the specific and varying needs of laboratories concerned with analyzing environmental samples. Data will be presented on water and soil samples according to USEPA Methodology 6020 showing the PQe's multi-element capability and determination of all elements in a single acquisition. Detection limit studies will be presented along with information on the profit potential of the PQe when used to perform contract analysis of environmental samples.

INTRODUCTION

For a laboratory to enter the Environmental Protection Agency's Contract Laboratory Program, it must have the capability to determine 22 metals in water and soils. Until recently, most laboratories have been using a combination of ICP-OES and GFAA instrumentation. The choice of instrumentation is made on the basis of the CLP contract required detection limits (CRDL's). The ICP-MS technique is particularly suitable for environmental analysis due to its exceptional multi-element sensitivity. ICP-MS can meet or exceed the CRDL's for all 22 elements in Method 6020 (with the exception of Se in soil) and perform the analysis in one sample cycle. Two instruments are now combined in one.

PROFIT POTENTIAL AND DESIGN

Laboratories performing high through-put routine environmental analysis have been reluctant to invest in such technology because of the high capital cost of current ICP-MS instrumentation. However, using a completely new approach to ICP-MS, Fisons has introduced the new PQe. A customized, low-cost ICP-MS instrument specifically aimed at the environmental market. The instrument is based on a radical new design which emphasizes robustness of hardware and simplicity of operation. A completely new mass spectrometer and detector system is employed and the benefits to the analyst are detection limits and a dynamic range more than sufficient to meet EPA legislative requirements[1]. Profitability projections will be presented in this poster/paper to help illustrate the cost effectiveness of the new ICP-MS design.

ANALYTICAL REQUIREMENTS FOR WATER ANALYSIS

The term "water analysis" covers a wide variety of sample types and matrices. In particular, environmental water samples may vary significantly in terms of inorganic and organic dissolved solid content

and suspended material. The PQe has a range of features which enable it to deal routinely with this wide range of sample types, for example matrix independent calibration and wide linear dynamic range.

Matrix independent calibration
The PQe requires only a single set of calibration standards, even for the analysis of different sample matrix types, such as rain water, riverine waters and effluent. Matrix independent calibration obviates the need to run different standards for each type of matrix, or perform standard additions on each sample, thus saving valuable analysis time.

Wide Linear Dynamic Range
Environmental water samples may include analytes at high concentrations e.g. Na, Mg, K and Ca as well as the trace and ultra-trace components e.g. Cr, Cd, Tl and U. For efficient sample analysis, it is essential that all the elements of interest should be determined in the same solution, without the need for preconcentration, separation or dilution. The wide linear dynamic range of the PQe allows the determination of major, minor and trace elements in a single acquisition, without the need for operator input. Furthermore, there is no necessity to match the concentration of each analyte in the calibration standard to the expected sample concentration, thus simplifying calibration procedures and further improving sample through-put[2].

ANALYTICAL PERFORMANCE

A series of experiments were carried out to assess the performance of the PQe in terms of accuracy, precision, spike recovery, stability, dynamic range and detection limits. Data will be presented on certified materials as well as routine water and soil digested samples.

SUMMARY

The EPA Contract Laboratory Program protocol for inorganics is a complicated program to enter successfully. With the help of low cost, simplified, and high sample through-put instrumentation, it becomes a straight forward and profitable task.

References:

[1]Tye, C.T., et al, 1991 Pittsburgh Conference, March 3-8, 1991

[2]PQe Technical Note 2, VG Elemental, Winsford, Cheshire, UK, 1990

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88 Robotics For Automated Digestion Of Environmental Samples

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Microwave Ovens are ideal for preparation of Environmental samples for metals analysis. However, the oven does present problems of vessel handling and storage. A new robotic system, utilizing several microwave stations, has been configured to digest samples, at a sufficiently high rate, to enable the digestion to keep up with the pace of a simultaneous ICP system. Protocols for many different types of samples can be stored, recalled, and implemented, in order to allow the robotics to accept many different samples of various sizes and consistencies. In our paper we will describe the software and protocols and show how they can be utilized to accommodate the day to day changes in the types and quantities of samples encountered in the typical environmental laboratory.

89 APPLICATION OF LASER SAMPLING ICP-MASS SPECTROMETRY TO ENVIRONMENTAL ANALYSIS

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Laser Sampling ICP-Mass Spectrometry is increasingly becoming recognized as an analytical tool for the direct analysis of solid samples. Early work with LS-ICP-MS focused mainly on geological and metallurgical type applications mainly because of the ability to bypass the lengthy sample dissolution stage.

However as the technique progresses, other application areas for LS-ICP-MS are becoming more and more attractive. One such area is in the analysis of environmental type applications. The ability to bind and/or press samples into a small pellet allows LS-ICP-MS to be used for the analysis of samples such as urban particles or river sediments.

This work will discuss some of the capabilities and limitations of LS-ICP-MS for the analysis of these type of environmental samples. In addition, approaches to the difficult problem of sampling some of these materials will be discussed.

RT:td.329

REGULATORY COMPLIANCE

Status of Developing Land Disposal Restrictions for Superfund Soils

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ABSTRACT

RCRA Land Disposal Restrictions (LDRs) for contaminated soil and debris at Superfund sites are currently being developed. This paper will present the current status of the EPA sponsored testing and the design of an integrated data base for both technology transfer and the development of the LDRs.

The unique physical and chemical characteristics of Superfund soil and debris make these wastes more difficult to treat than more homogeneous industrial process wastes. The National Contingency Plan acknowledges that Best Demonstrated Available Technology (BDAT) standards are generally inappropriate for Superfund soils. In response to this, EPA is in the process of developing separate LDR standards for contaminated soil and debris (CSD). LDRs for CSD are being developed under section 3004 of the Hazardous and Solid Waste Amendments of 1984 to RCRA.

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Until the final CSD standards are in place, treatability variance levels, also based on the actual treatment of soil, will be used.   In addition, the paper will discuss some preliminary findings on the treatment of debris, and the analytical methods used for determining the BDAT for CSD.

1.0   INTRODUCTION

Section 3004(m) of the Resource Conservation and Recovery Act (RCRA) mandates that the U. S. Environmental Protection Agency (EPA) require treatment of hazardous wastes prior to land disposal.   Known as the "land disposal restrictions" (LDRs), these regulations were designed for industrial process wastes defined to be hazardous under RCRA.   They apply as well to contaminated soil, sludge and debris from RCRA facilities and Superfund sites.   RCRA requirements for treatment are mandatory and self-implementing at all RCRA regulated facilities, but apply at a CERCLA site only if a) the waste is a RCRA listed or characteristic waste; b) the CERCLA activity constitutes treatment of RCRA hazardous waste, as defined under RCRA; and c) the treatment activity constitutes "placement."

The Office of Solid Waste (OSW) is responsible under EPA's Office of Solid Waste and Emergency Response (OSWER), for responding to directives under RCRA, and therefore, prepares and presents the LDR standards to the regulated community.

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The Office of Emergency and Remedial Response (OERR) is responsible under OSWER for responding to directives under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund activities. As the majority of soil and debris contaminated with hazardous wastes are found on Superfund sites, LDRs have a profound potential effect on the government's efforts at site remediation.

OSWER has recognized that contaminated soil is more difficult to treat than RCRA industrial process wastes, and that it is not likely that these wastes can be treated to meet the LDRs developed for RCRA listed wastes because of the physical and chemical complexity of contaminated soils. In response, OSWER initiated a program to develop Treatability Variances, which are alternate treatment standards based on actual treatment of Superfund and RCRA soil and debris. Data was collected, and in 1989, treatability variance levels were established for soils utilizing 67 data sets (Superfund LDR Guides #6A and #6B).

OSWER developed a strategy for calculating variance levels from a quantity-limited data base. The data are categorized into 13 "contaminant groups" which are groups of contaminants having similar chemical and physical characteristics. Examples of contaminant groups include non-polar halogenated aromatics, and PCBs/dioxins/furans and their precursors. The variance levels

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that were developed quantified the effectiveness of various available technologies on the contaminant groups.

EPA OSWER determined that the existing soil treatment data base was not comprehensive enough to support a formal set of LDRs for CSD. Several available technologies had insufficient performance data to develop regulations. EPA therefore implemented a research program to obtain all of the necessary data to support the development of LDRs for CSD. In 1988, OSWER's OERR, OSW, and Technology Innovation Office (TIO), and the Office of Research and Development's (ORD) Risk Reduction Engineering Laboratory (ORD-RREL) in Cincinnati, Ohio established a work group to develop BDAT standards for CSD. The work group objectives include a review of the current data base, recommendations for additional studies on treatment performance, implementation of treatability studies, collection of new available data, and development of BDAT regulations based upon new and available data. There has been significant progress with these efforts.

2.0 DATA COLLECTION/DATA BASE DESIGN AND OPERATIONS

OSWER, in its initial data collection effort, collected and examined over 500 studies conducted by the EPA, federal agencies, industries and universities. These studies formed the basis for the development of treatability variances. Of these studies, 67 met the criteria established for the development of variance

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levels for contaminated soils. The established criteria required that the: (1) data be of sufficient quality; and (2) untreated and treated soil contamination be measured. The current criteria for setting final LDR treatment standards are more rigorous than the criteria for variance levels. They require more documentation of quality assurance/quality control (QA/QC) procedures as well as bench, pilot and full-scale testing data. A formal data summary form (DSF) has now been developed by OSWER to extract pertinent data from all studies reviewed for inclusion into the data base.

EPA utilizes a four-tiered project category approach in its QA program in order to more effectively focus QA. Category I involves the most stringent QA approach, whereas Category IV represents the least stringent. Category II projects are those producing results that complement other inputs and are designed for use in rulemaking, regulation making, or policy making. Therefore, all data used to support the CSD LDRs should have a Category II objective designed into the QA project plan (QAPjP).

After a thorough QA review using the established criteria, only 13 of the 67 studies used for variance levels were determined to be adequate for consideration in the development of LDR treatment standards. However, all studies reporting data are accepted as Category IV data and included in the data base for technology transfer purposes.

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Lack of soil treatment data prompted an aggressive data collection effort by OSWER and ORD. Figure 1 shows the system for data collection and treatment research in the CSD program. Additional data will be collected from recent remedial/removal actions, including DOD and DOE actions, SITE program demonstrations, and treatability tests conducted by the CSD program. Currently the new data base is planned to contain not only the original data base, but studies that have been collected since the variance levels were published as well. OSWER will also use the data base to manage technology transfer information collected during this project.

This new EPA data base, the Superfund Soil Data Management System (DMS) is an important tool for fostering technology transfer involving contaminated soil, debris and sludge and relating the information to applicable LDRs of HSWA which are applicable or relevant and appropriate requirements (ARARs) to Superfund actions. The Superfund Soil DMS will allow maximum utility of the data obtained from any source. Data meeting a minimal criterial will be included in the data base.

The data base construction allows for easy user access and tailoring of reports to individuals' needs. Sorting will allow questions concerning technology, waste characteristics, soil matrix and other parameters to be addressed.

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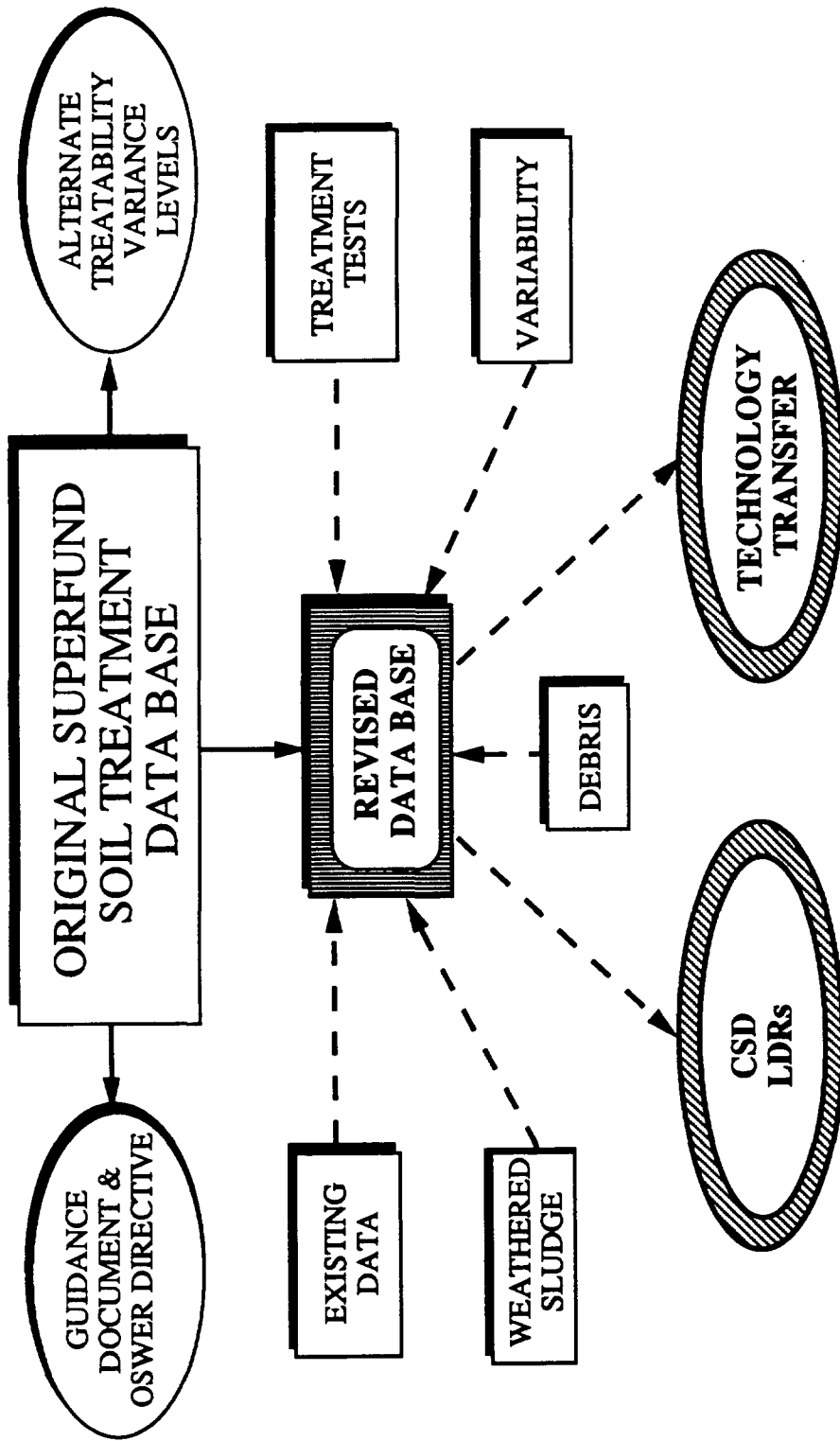
Figure 1. EPA OSWER Data Collection and Research Approach

Outside access to the Superfund Soil DMS will be through a central EPA system. At this time this is envisioned to be the Agency's ATTIC System which is being managed at the Agency's Edison NJ laboratory facility.

3.0 SOIL TREATMENT TESTS

The CSD Program reviewed existing data and identified technologies that lacked treatment performance data, but would be available technologies for treating CSD (Table 1). Twelve treatment tests are planned. The technologies that will be tested include slurry bioremediation, low temperature thermal desorption, chemical extraction, soil washing, and stabilization (Table 2). The technologies are applied to different types of soils and wastes. For example, the biotreatment tests will be conducted on three soil types. The soil classifications range from sandy to clay type soils. In addition, different types of wastes, including wastes high in PNAs, PCBs and metals, will be tested. The stabilization technology will be tested as both a primary technology and as a residual treatment.

The treatability tests will be conducted according to the OSW Quality Assurance Project Plan for Characterization Sampling and Treatment Tests Conducted for the Contaminated Soil and Debris Program (QAPP) and site specific Sampling and Analysis Plans. The individual sampling plans specify holding times, analytical

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TECHNOLOGY / TREATABILITY GROUP	BIOREMEDIATION	IMMOBILIZATION	DECHLORINATION	CHEMICAL EXTRACTION	THERMAL DESTRUCTION	LOW TEMPERATURE THERMAL DESORPTION	SOIL WASHING	MISCELLANEOUS TECHNOLOGIES
NON-POLAR HALOGENATED AROMATICS (W01)	▨			▨		▨		
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECURSORS (W02)	▨		▨			▨	▨	
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	▨			▨		▨	▨	
HALOGENATED ALIPHATIC COMPOUNDS (W04)	▨	✕	▨			▨	▨	
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	▨					▨		
NITRATED COMPOUNDS (W06)			✕					
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	▨	✕	✕	▨		▨	▨	▨
POLYNUCLEAR AROMATICS (W08)	▨		✕	▨		▨	▨	▨
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	▨		✕					
NON-VOLATILE METALS (W10)	✕		✕	▨	✕	✕		▨
VOLATILE METALS (W11)	✕	▨		▨	✕	✕		▨
ARSENIC (W11)						▨	▨	
CYANIDE (W12)								

Legend:

☐ EXISTING DATA EXPECTED

▨ CS&D TEST DATA

✕ INDICATES TECHNOLOGY IS NOT EXPECTED TO BE EFFECTIVE

Table 1: Available Soil Treatment Technologies

SITE	SOIL TYPE	CONTAMINANTS	TECHNOLOGY
Jennison-Wright	Clayey	Organics	Bioremediation
Jennison-Wright	Clayey	Organics	LTTD
Jennison-Wright	Clayey	Organics	Solvent Extraction
Bayou Bonfouca	Silty	Organics	LTTD
Bayou Bonfouca	Silty	Organics	Solvent Extraction
New Hampshire	Silty	Metals	Soil Washing
Brown's Battery	Silty	Metals	Stabilization
Burlington Northern	Silty, Sandy	Organics, Metals	Bioremediation
Burlington Northern	Silty, Sandy	Organics, Metals	LTTD
Ninth Ave.	Sandy	Organics, Metals	Bioremediation
MIDCO	Sandy	Organics, Metals	Sandy
C&R Battery	Sandy	Metals	Soil Washing

Table 2. Planned Treatment Tests

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methods, chain of custody, and quality control measures, such as blanks and spikes. The tests will include measurements of contaminant concentrations before and after treatment, and measurements of the waste characteristics that affect the performance of soil treatment technologies. Examples of waste characteristics that affect treatment performance such as moisture content, oxidation/reduction potential, and particle size distribution are listed in the QAPjP.

4.0 DEBRIS

OSWER collected existing data on debris treatment in their data collection program. The study determined that debris could constitute as much as fifty percent of the contaminated media, such as at a wood preserving site. The study also found that the sampling procedures were not well documented. Recognizing the importance of debris, the CSD Program has implemented a comprehensive review of debris sampling, analysis and treatment. The characteristics of debris that have been determined to affect treatment include permeability and destructibility. The potential treatment technologies have been generalized into three categories for debris: 1) destruction, 2) extraction and removal, and 3) sealing/solidification (Table 3). The Agency will discuss the use of specified-technology standards for debris remediation in an upcoming Advanced Notice of Proposed Rulemaking (ANPRM).

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CONTAMINANT GROUPS / DEBRIS MATRICES	ORGANICS * (EXCEPT NITRATED ORGANICS)	NITRATED COMPOUNDS	METALS	CYANIDE
PERMEABLE DESTRUCTIBLE	Destruction	Destruction	Chemical Extraction, Physical Removal, Sealing/Solidification	Destruction
PERMEABLE NON-DESTRUCTIBLE	Chemical Extraction, Physical Removal, Sealing/Solidification	Chemical Extraction, Physical Removal	Chemical Extraction, Physical Removal, Sealing/Solidification	Chemical Extraction, Physical Removal, Sealing/Solidification
NON-PERMEABLE DESTRUCTIBLE	Chemical Extraction, Physical Removal, Destruction, Sealing/Solidification	Chemical Extraction, Physical Removal, Destruction	Chemical Extraction, Physical Removal, Sealing/Solidification	Chemical Extraction, Physical Removal, Destruction, Sealing/Solidification
NON-PERMEABLE NON-DESTRUCTIBLE	Chemical Extraction, Physical Removal, Sealing/Solidification	Chemical Extraction, Physical Removal	Chemical Extraction, Physical Removal, Sealing/Solidification	Chemical Extraction, Physical Removal, Sealing/Solidification

Table 3. Potential Management Practices for Debris Decontamination

* Organics include volatile, acid extractable, and base neutral organics, pesticides, dioxins and PCBs

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5.0 SLUDGE

The previous OSWER survey of Superfund sludge data found that sludges are not consistently defined in the literature. However, sludges, when identified, had higher concentrations of contaminants than soils, and as a result, did not meet variance level standards as frequently as soil. Of the OSWER survey data, 55% of the sludges treated met variance levels, while 78% of the soils treated met variance levels. OSWER believes that to fully characterize the treatment of sludge much additional work will be required. To this end, OSWER, in conjunction with ORD, is fully characterizing sludges from several hazardous waste sites on sludge later this year. In addition, EPA is holding a symposium during the summer of 1991 to broaden the background information and share collective views on this topic. Additional information on the symposium will be made available to any interested parties by contacting the authors of this paper.

6.0 VARIABILITY

The OSWER study of Superfund soil treatability has found an order of magnitude difference in treatability between remedy selection testing and full scale treatment. As a result, treatability tests must achieve an order of magnitude better treatment than the standards in order to achieve compliance with the full scale process. The factors that affect treatment effectiveness include

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mixing effectiveness, homogeneity of the soil matrix, feed specifications, and contaminant concentrations. Variability of the treatment results for the relatively homogeneous RCRA waste streams has been accounted for by using classical statistics which assume a less variable data set than Superfund soils.

EPA has begun a study to determine whether the soil matrix presents unique problems in specific treatment methods and types of wastes. EPA's study will use "clean" soils of similar characteristics as the contaminated soil and artificially "mark" the soil with a non-hazardous contaminant. Soils will then be mixed and analyzed to determine the efficiency of mixing as a treatment condition. The results of the study are expected to show whether variability mixing effectiveness exists as a function of soil type, equipment scale or moisture content, which is representative of different treatment technologies. The results of the study are not expected to conclusively show what the variability function is or to allow for a direct correlation into the LDR. Additional experimentation will be required to assess the magnitude of the variability as it impacts on the treatment standards for contaminated soil.

7.0 CONCLUSIONS

The current schedule provides for completion of data collection and data analysis in the fall of 1991. We are soliciting

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existing treatment data, and new tests which may meet these needs. We welcome comments on the above described program to advance this study effort on soils, sludges, debris and variability. If you have data, comments or questions regarding the LDRs for contaminated Superfund soils and debris please contact:

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8.0 References

1. Superfund LDR Guide #6A: Obtaining a Soil and Debris Treatability Variance for Remedial Actions. 1989, Revised 1990. Office of Solid Waste and Emergency Response, USEPA. Directive: 9347.3-06FS.

2. Superfund LDR Guide #6B: Obtaining a Soil and Debris Treatability Variance for Removal Actions. September, 1990. Office of Solid Waste and Emergency Response, USEPA. Directive: 9347.3-06BFS.

3. Quality Assurance Project Plan for Characterization Sampling and Treatment Tests Conducted for the Contaminated Soil and Debris (CSD) Program. November, 1990. Office of Solid Waste and Emergency Response, USEPA.

91   Certification Protocol for Meeting Organic Treatment Standards for Incineration Ash

SEVENTH ANNUAL WASTE TESTING & QUALITY ASSURANCE SYMPOSIUM

American Chemical Society
Washington, D. C.

July 8-12, 1991

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Certification Protocol for Meeting Organic Treatment Standards for Incineration Ash

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ABSTRACT

The Hazardous and Solid Waste Amendment of 1984 (HSWA) of the Resource Conservation and Recovery Act (RCRA) requires the treatment of hazardous waste to a specified treatment standard prior to land disposal. Testing to verify that treatment residuals (i.e., incinerator ash and scrubber sludge/filter cake) meet treatment standards is an expensive and time consuming process, especially for commercial incinerators in which each batch of residuals has a different set of EPA waste codes and consequently different treatment standards.

The challenge is to develop a testing approach or protocol which will simultaneously provide: (1) a high level of assurance that treatment standards are being consistently met while (2) holding testing and residual storage costs and testing turnaround time at reasonable levels and (3) insuring that permitted residual storage limits are met.

Chemical Waste Management has developed a practical testing protocol based on EPA developed or supported concepts which is sufficiently flexible to fit the widely varying incinerator facilities within our system. In concept, the universe of EPA waste codes is divided into "treatability groups" based on chemical and physical similarities. Each treatability group is then represented by one or more "indicator waste code(s)" selected on the basis of: (1) treatment standard chemical species and acceptance levels, (2) volume of waste with that code needing treatment, (3) volatility and thermal stability of the chemical species present in the waste, (4) matrices effects and (5) related issues.

A demonstration or "trial burn" is conducted in which the incinerator is operated within an "operating envelope" and under a "quality assurance/quality control system"

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which will assure operation within the envelope.

If the incineration residuals meet treatment standards for the carefully selected indicator codes, then compliance with treatment standards for the subject chemical species are assumed for other codes within the treatability group which have treatment standards ar or above the level detected on the demonstration test residuals.

Spot tests are conducted on at least a quarterly basis to confirm continued compliance. New demo burns are initiated whenever the operating envelope is changed in a manner in which would be detrimental to the destruction or removal of organics from residuals.

This approach has been successfully used with all three CWM incinerator facilities. Other aspects of the protocol will be discussed in the presentation.

INTRODUCTION - DEFINITION OF THE PROBLEM

With the implementation of the HSWA (Hazardous and Solid Waste Amendment of 1984) of the RCRA (Resource Conservation and Recovery Act) landbans and the gradual elimination of the remaining variances, a large fraction of the hazardous waste generated in the U. S. must be treated to meet stringent BDAT (Best Demonstrated Available Technology) treatment standards before it can be land disposed. For hazardous waste containing organics, sufficient treatment frequently requires incineration to destroy the organic and cyanide compounds. The resulting solid residuals (ash and scrubber cake) are then stabilized to chemically immobilize any regulated metals present prior to landfilling.

A great deal of effort has been invested in the hazardous waste management industry to develop a practical and reliable method to verify that each treatment step has met the HSWA treatment standards. In the case of organics contaminated waste, this is frequently a two stage process: (1) verification that the incinerator ash and filter cake meet organic and cyanide standards for all EPA waste codes present followed by (2) verification that metal mobility or leachability has been sufficiently reduced in the stabilization process to meet TCLP (Toxic Constituent Leaching Procedure) limits for metals.

The focus of this paper is the certification protocol for organics in residuals from a commercial hazardous waste incinerator; a simplified version of this protocol would apply to captive incinerators. The protocol is described in toto; however, no attempt will be made to cover every possible contingency which can occur when attempting to satisfy, with total regulatory compliance, a program as exacting and complex as the EPA landban regulations.

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The challenge in developing a practical and reliable protocol can be seen by considering the following facts:

1. The EPA landban program presently contains a total of 1,467 variations of waste codes, categories, and subcategories. There are typically 20 to 40 EPA waste codes associated with a given batch of solid residuals from a commercial incinerator; these codes can change dramatically with time. Consequently, the required treatment standards which the residuals must meet also change with time.

2. EPA has established treatment standards for one or more organic/cyanide compounds (target compounds) for each waste code which requires incineration. (There is typically one target organic compound for U, P, and D codes, 5 to 12 for each F and K code and from dozens of target compounds for F001-5 codes to hundreds for F039 codes.)

3. Frequently the same target compound will appear associated with two or more waste codes present in a batch of residuals and typically the treatment standard level will vary from code to code even for the same target compound. Thus, the lowest treatment standard present must be simultaneously met for every target compound present before a batch of residuals can be certified as having met BDAT.

4. There is no on-line method of testing incineration residual for organics and cyanides - one or more different extraction protocols must be completed on each sample, typically, followed by multiple GC scans, GC/MS volatile and semi-volatile scans and other testing depending on which EPA waste codes are present.

This an analogous situation to the use of EPA Modified Method 5 sampling of an incinerator stack in a trial burn and subsequent extractions and analyses as a means of verifying that the incinerator met the required minimum destruction and removal efficiency (DRE) during the trial burn; thus, CWM as the permittee is authorized to infer that the unit is meeting DRE requirements during subsequent commercial operations as long as the unit is operating within the permitted operating envelope.

5. The sampling and analysis turnaround time for HSWA residual testing is extremely slow, very complicated and disruptive to the residual management process (e.g., one week, under ideal circumstances, to a more typical 30 to 60 days). In addition, the cost is quite expensive (e.g., $3,000 - 10,000 per event).

6. HSWA requires the treater (in this case the incinerator owner/operator) to "certify under penalty of law" to the land disposal facility where the ash will be landfilled that the waste has met applicable organics treatment standards. Thus,

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boxes of ash can not be shipped until the certification can be completed.

7. A commercial incinerator typically generates 2-6 boxes of ash and other solid residuals during a normal operating day and with larger volumes being frequently generated during maintenance turnarounds. As a point of interest, the CWM Port Arthur incinerator has the physical capacity and permitted authority to process sufficient waste to produce up to 20 boxes of residuals per day.

A quick review of these facts indicates that if every box of residuals must be sampled and analyzed for the applicable target compounds, this would result in ongoing inventories of at least 50 - 100 boxes of uncertified residuals and would disrupt the ability to manage residual in a timely and environmentally sound manner. In addition, analysis of each box would result in analytical cost in the order of hundreds of thousands to millions of dollars a year, diverting resources from areas that would afford more protection to the environment.

DEVELOPMENT OF A CERTIFICATION PROTOCOL - CONCEPTS AND RATIONALE

The factors which affect the degree to which organics are destroyed on or vaporized from solid residuals in a given hazardous waste (typically rotary kiln) incinerator include (see Figure 1 for a schematic diagram of an incinerator process):

1. Residence time of the solid in the hot zone (i.e., rotary kiln length, waste loading and RPM).

2. Temperature in the hot zone (i.e., kiln temperature).

3. Oxygen concentration (i.e., % excess air).

4. Degree of agitation of the organic contaminated solid (i.e., kiln RPM)

5. Solids loading (i.e., feed rates of solids bearing waste).

6. Volatility of organic compound (i.e., vapor pressure of target compounds).

7. Thermal stability (i.e., thermodynamic stability of target compounds).

8. Nature of solid substrate or matrix factor (i.e., Is the waste liquid, sludge or solid? Is contamination a surface or depth phenomenon?).

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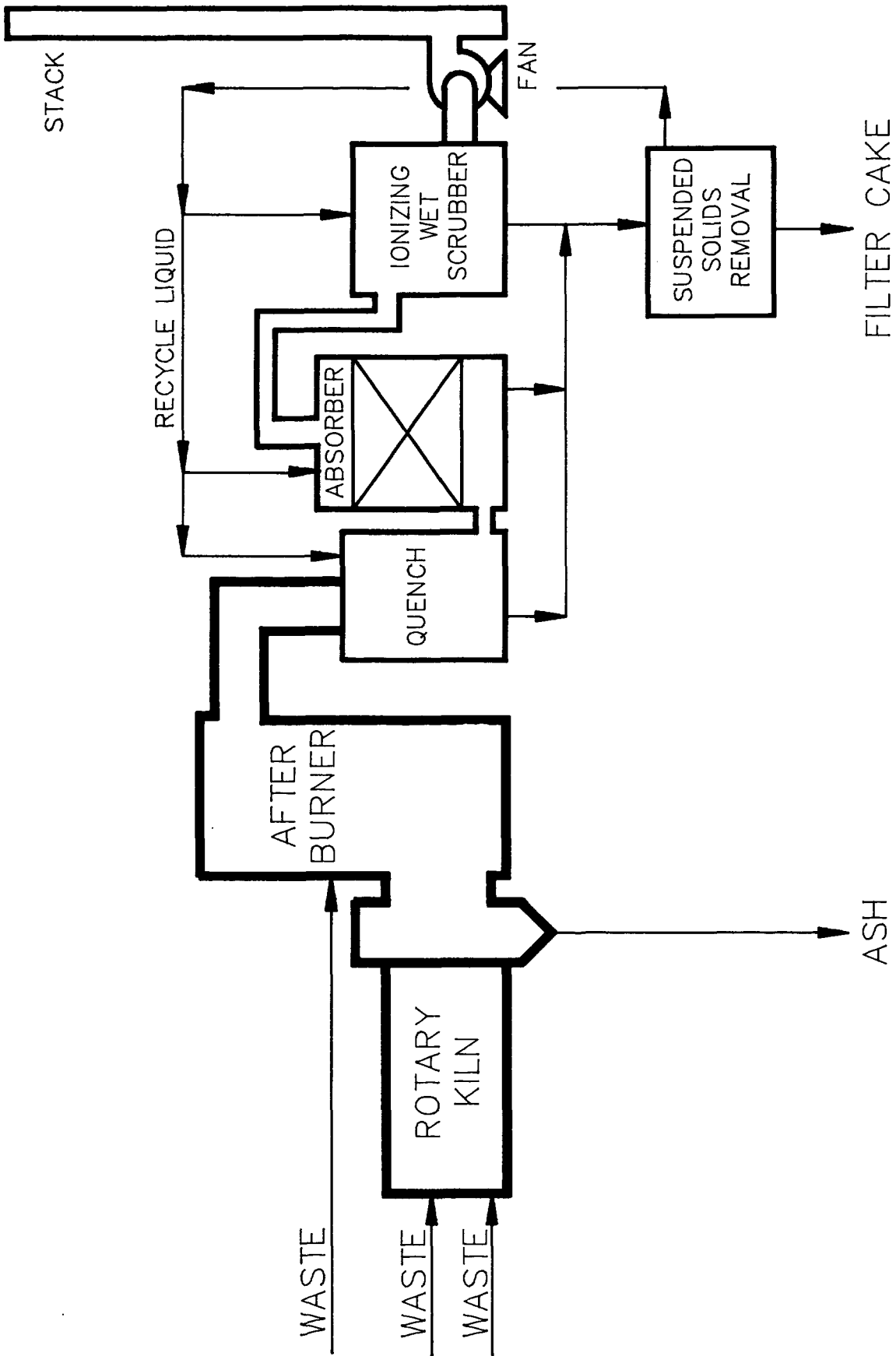
FIGURE 1   A schematic diagram of a typical hazardous waste incinerator with a wet, acid gas absorber.

The process variables (i.e, temperature, oxygen concentration, solids residence time, loading, and agitation) are controlled directly or indirectly by the permit limits and/or the incinerator design. The matrix factor is waste stream specific and volatility and thermal stability is determined by the molecular structure of the target compound. Thus, a protocol could be based on: (1) direct measurement and control of the pertinent process variables while controlling (2) the waste streams selected to provide a range of matrix types (i.e., solid organics, inorganic solids contaminated by organics, particle size, liquids, etc., and (3) waste codes selected to provide target compounds covering a range of volatilities and thermal stabilities.

A calibration test (or demonstration burn) would then be conducted which would establish that the treatment (incinerator) system meets the treatment standards for the codes present while operating within permit/design limits. The idea being that an incinerator destroys organic compounds without regard to the waste codes associated with those compounds.

This approach is quite analogous to the EPA trial burn approach to demonstrating that a given incinerator will meet DRE requirements as long as the incinerator operates within its permitted operating envelope.

In developing the RCRA/HSWA landban treatment standards EPA drew on several concepts which are equally useful here. These concepts are: "treatability groups" based on chemical and physical similarities among wastes with certain codes, "transference of data" on treatment efficiency in an incinerator from waste code to another code in the same treatability group, i.e., the use of one waste code as an "indicator code" for other codes within the same treatability group. CWM has used these concepts to develop a certification protocol.

The universe of all EPA waste codes was divided into 16 treatability groups along the same chemical similarity lines EPA used in the RCRA/HSWA third third regulations (see Table I for a listing of waste codes in each treatability group).

From each treatability group one (or more) code(s) were selected as indicator codes based on the following criteria:

1. The number and type of target compounds for that code.

2. Treatment standard levels for that code.

3. The thermal stability and incinerability of the target compound(s) of that code compared to the stability and incinerability of the target compounds of other codes

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TABLE 1   EPA waste codes[1] assigned to each treatability group.

GROUP 1 - Solvents and Dioxin: F001-05, F020-23, F026-28

GROUP 2 - Halogenated Pesticides: D012-17, K032-34, K041, K097-98, P004, P037, P050-51, P059-60,
P123, U036, U060-61, U128-130, U142, U240, U247

GROUP 3 - Chlorobenzene: K042, K085, K105, U037, U070-72, U127, U183, U185, U207

GROUP 4 - Halogenated Phenolics: U039, U048, U081-82

GROUP 5 - Brominated Organics: U029-30, U066-68, U225

GROUP 6 - Miscellaneous Halogenated Organics: P024, U024-25, U027, U043,
U045, U047, U075, U121, U138, U158, U192

GROUP 7 - Aromatic & Other Hydrocarbons: U019, U220, U239

GROUP 8 - Polynuclear Aromatic Hydrocarbons: K001, K015, K022, K035, K048-52, K060, K087,
U005, U018, U022, U050-51, U063, U120, U137, U157, U165

GROUP 9 - Phenolics: P020, P047-48, U052, U101, U170, U188

GROUP 10 - Oxygenated Hydrocarbons & Heterocyclic: K023-24, K086, KO93-94, U002, U004, U028,
U031, U069, U088, U102, U107-08, U112, U117-18, U140, U159, U161-62, U190

GROUP 11 - Organo-Nitrogen Compounds: K011, K013-14, K083, K101-04, P069, P077, P101, U003,
U007, U009, U012, U105-06, U111, U152, U169, U172, U174, U179-81, U196

GROUP 12 - Halogenated Aliphatic: F025, K009-10, K016-21, K028-30, K073, K095-96, U043-44, U076-
80, U083-84, U131, U184-85, U208-11, U226-28, U243

GROUP 13 - Other Chlorinated Organics: F024, K043, K099

GROUP 14 - Organo-Sulfur Compounds: K036-38, K040, P039, P071, P089, P094, P097, U235

GROUP 15 - Pharmaceuticals: U141, U155, U187, U203

GROUP 16 - Cyanide: F006-12, F019, P013, P021, P029-30, P063, P074, P098-99, P104, P106, P121

1 Waste codes with BDAT specified technology of incineration (INCIN) are not listed.

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within that group.

4. The volatility of the target compounds of this code compared to the other codes in the group.

5. The volume of waste with this code in the market place, i.e., the commercial significance of the code compared to other codes in the group. In this and numerous other ways CWM has attempted to conduct these tests in a manner which would simulate routine, day to day operating conditions.

Once this list of indicator codes is developed one or more waste streams are selected for each code based on commercial significance and matrix effects. Waste inventories are collected and used in a trial burn type demonstration in which the waste is burned in the treatment process under normal operating envelop conditions and with a defensible QA/QC program in effect.

In the case of the CWM Port Arthur incinerator the incinerator is controlled by a computer which continuously monitors all permit limited parameters. If a single operating parameter moves outside of its permitted range or operating envelope, the computer automatically discontinues waste feeds.

In planning the demonstration test, we generally will want wide ranges of thermal stabilities, volatilities, matrix effects and treatment standard levels represented; however, for the sake of minimizing uncertainty or risk, we have tended to choose waste codes with less volatile, highly stable target compounds in solid substrates with quite low treatment standard levels. (See Table II for the selected indicator codes for each treatability group.)

The concept is that waste with the indicator codes will incinerate in a like manner to other wastes within the same treatability group, i.e., we can transfer data concerning how well the treatment process incinerated one waste code to the other codes with chemical similarities.

Once the demonstration test is completed and the resulting residuals are carefully sampled and analyzed (in triplicate), then waste codes from a represented treatability group with treatment standards at or above the level of target compound(s) detected in the demonstration test residuals can be certified as long as the process is operated within the operating envelope and the QA/QC system is maintained. Conversely, codes with treatment standards which are lower than the residual concentrations found in the demonstration burn could not be certified without process adjustments as needed followed by a successful new demonstration test.

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TABLE II Indicator code(s) selected for each treatability group.

TREATABILITY GROUP	INDICATOR CODE(S)
1. SOLVENT & DIOXIN	F001-5
2. HALOGENATED PESTICIDES	U129, P123
3. CHLOROBENZENE	U070, UO72
4. HALOGENATED PHENOLICS	
5. BROMINATED ORGANICS	U029
6. MISC. HALOGENATED ORGANICS	(K019, F001, F002)[1]
7. AROMATIC & OTHER HYDROCARBONS	U220
8. PNA HYDROCARBONS	U165
9. PHENOLICS	P020
10. OXYGENATED HC & HETEROCYCLIC	U002, U069, U190
11. ORGANO-NITROGEN	K011, K013, U012
12. HALOGENATED ALIPHATICS	K019, K020
13. OTHER CHLORINATED ORGANICS	
14. ORGANO-SULFUR	P039, P071, P089, P094
15. PHARMACEUTICALS	
16. CYANIDES	F0007, F008

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TABLE III   Permit and other limitations which the 1990 operating envelope for the CWM Port Arthur incinerator

HOURLY TOTALS	PERMIT LIMIT	
CHLORINE	1,690	LBS/HR
SULFUR	250	LBS/HR
ORGANIC HALOGEN	1,352	LBS/HR
ASH (SCC)	240	LBS/HR
TOTAL ORGANIC CONTENT	20,000	LBS/HR
POLYCHLORINATED BIPHENYLS	3,172	LBS/HR
WASTE AND FUEL FEEDS	50,270	LBS/HR
ENERGETIC LIQUIDS (KILN)	3,000	LBS/HR
ENERGETIC LIQUIDS (SCC)	8,900	LBS/HR
ENERGETIC SLUDGE	5,300	LBS/HR
NON-ENERGETIC SLUDGE	10,000	LBS/HR
ENERGETIC SOLIDS	3,000	LBS/HR
NON-ENERGETIC SOLIDS	41,475	LBS/HR
AQUEOUS WASTE	(determined by DCS)	
MINIMUM KILN HEAT VALUE	47.9 MM BTU/HR	
MAXIMUM KILN HEAT VALUE	79.5 MM BTU/HR	
MINIMUM SCC HEAT VALUE	35.0 MM BTU/HR	
MAXIMUM SCC HEAT VALUE	77.2 MM BTU/HR	
MINIMUM TOTAL HEAT VALUE	79.0 MM BTU/HR	
MAXIMUM TOTAL HEAT VALUE	150.0 MM BTU/HR	
ACRYLAMIDE	900	LBS/HR
CHLOROMETHYLMETHYLETHER	660	LBS/HR
1,2-DIBROMO-3-CHLOROPROPANE	79	LBS/HR
SYM-DICHLOROMETHYLETHER	79	LBS/HR
DICTROTOPHOS	1,330	LBS/HR
DIMETHYL CARBAMOYL CHLORIDE	660	LBS/HR
DIPHENYLMETHANE DIISOCYANATE	1,330	LBS/HR
ISOPROPYL MERCAPTAN	240	LBS/HR
ISOPHORONE DIISOCYANATE	1,330	LBS/HR
N-NITROSODIETHANOLAMINE	130	LBS/HR
N-NITROSODIETHYLAMINE	130	LBS/HR
PHOSPHINE	1,660	LBS/HR

CWM OPERATIONAL LIMITATIONS

LEAD (FEED RATE LIMITS)		1,350.0	LBS/HR
CADMIUM	"	240.0	LBS/HR
VANADIUM	"	240.0	LBS/HR
MERCURY	"	240.0	LBS/HR
ARSENIC	"	48.0	LBS/HR
BERYLLIUM	"	17.5	LBS/HR
CHROMIUM	"	900.0	LBS/HR
NICKEL	"	135.0	LBS/HR

[1] Although K019, F001, and F002 are EPA waste codes which do not appear in treatability Group 6, these codes have target components in common with codes from Group 6. Since K019, F001, and F002 were fed during the demonstration test and the residual values for the target compounds were found to be lower than all the treatment standard levels specified for these three codes and for Group 6 codes, the common compounds could and have been used to certify Group 6.

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A SPECIFIC EXAMPLE - PORT ARTHUR INCINERATOR, 1990

Shortly after the third landbans became effective in 1990 a broad based demonstration burn was conducted on the CWM Port Arthur (Texas) incinerator; the results are summarized here as an example.

Appropriate streams could not be found for groups 4, 13, and 15. The test took place over approximately 24 hours. Table III defines the operating envelope in effect at the time of the test. Three samples were carefully collected to represent three eight hour time periods, independently extracted and analyzed per SW846.

Organic concentrations were below the practical quantitation levels (QL) in almost all cases; exceptions were:

TARGET COMPOUND	PQL	MIN TREAT[1] STANDARD	TEST RESULTS 1	2	3
ACETONE	0.010	0.590	0.010	0.043	0.011
TRICHLOROTRIFLUOROETHAN	0.005	28.000	7.865	6.100	0.955
CARBON TETRACHLORIDE	0.005	5.600	[2]	0.105	[2]
IODOMETHANE	0.005	65.000	0.055	0.115	0.108
ISOBUTYL ALCOHOL	0.100	170.000	[2]	1.145	[2]
ETHYL CYANIDE	0.010	360.000	[2]	[2]	0.560
TRICHLOROFLUOROMETHANE	0.005	33.000	0.070	0.200	0.115
DISULFOTON	0.010	0.100	0.020	0.020	[2]
DIS-N-BUTYL PHTHALATE	0.330	3.600	[2]	[2]	0.363
FAMPHUR	0.100	0.100	0.100		[2]
TOTAL CYANIDE	1.000	57.000	1.800	[2]	1.300

All numbers are expressed as TCA (mg/Kg) except Acetone which is expressed as TCLP (mg/L).

[1] These are the lowest treatment standards within the landban program for these target compounds regardless of waste code.

[2] The results were below the practical quantitation level (PQL) of the analytical instruments used.

Inspection of these data indicates that this test was successful on all compounds of the codes/treatability groups tested. Thus, based on these results the Port Arthur facility was able to certify that ash generated with codes from the tested treatability groups meets all applicable organic and cyanide treatment standards as long as the unit is within the operating envelope and the QA/QC program is maintained.

An additional demonstration burn would be required to qualify codes/treatability groups not covered in this initial effort or to requalify the treatment system if one or more conditions were changed in a manner which could reduce the incinerator system's ability to produce clean treatment residuals.

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ABSTRACT

Factors Affecting the Admissibility
and Weight of Environmental Data as Evidence

Jeffrey C. Worthington, Director of Quality Assurance; Kerri G. Luka, Audit Programs Manager, TechLaw, Inc. 12600 West Colfax Avenue, Suite C-310, Lakewood, Colorado 80215.

Many factors may affect the potential admissibility of environmental data in litigation. These factors include but are not limited to:

o Integrity of the sampling method

o Integrity of the analytical method

o Comparability to other sets of environmental data

o Documented sample custody

o Documented quality control results

o Authenticity of the data

These same factors may also enter into the weight of the data as evidence. For example, some data may include rigorous quality control including the use of performance evaluation samples with each batch of samples from the field; other data may include less rigorous quality control. The first set of data may be given greater weight by the trier of fact.

The admissibility and weight of environmental data evidence may figure prominently into pre-trial settlement discussions. Data is not often accepted at "face value". Litigants usually need to address all the issues concerning the environmental data before proceeding to other litigation matters.

The authors present a discussion of these factors and summarize several cases where the admissibility and weight of the data as evidence were items of concern.

93   REVIEW OF GROUNDWATER MONITORING REQUIREMENTS AT RCRA SITES

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ABSTRACT

This paper summarizes the groundwater monitoring requirements for RCRA facilities under both interim status and operating permit conditions. In addition, it highlights the major differences in the regulations for facilities subject to both interim status as well as permit requirements. Along with this overview, this paper addresses how these regulations are enforced and what mechanisms are set up to ensure that facilities are in compliance with the groundwater requirements under the RCRA program.

INTRODUCTION

Subtitle C of the Resource Conservation and Recovery Act of 1976 (RCRA) regulates hazardous waste treatment, storage, and disposal facilities (TSDFs). Section 3004 of RCRA requires owners and operators of hazardous waste TSDFs to comply with standards established by EPA. Section 3005 provides for implementation of these standards under permits issued to owners and operators by EPA or authorized States. Section 3005 also provides that owners and operators of existing facilities that comply with applicable notice requirements may operate as " interim status" facilities until a permit is issued or denied. Owners and operators of interim status facilities also must comply with standards set under Section 3004.

EPA promulgated regulations for permitted facilities in 1982 (47 <u>FR</u> 32274, July 26, 1982), codified in 40 CFR part 264, Subpart F and 40 CFR part 270, Subpart B. These regulations establish programs for protecting groundwater from releases of hazardous wastes or constituents from treatment, storage, and disposal units.

BASIC GROUNDWATER MONITORING REQUIREMENTS

The basic groundwater monitoring program under RCRA consists of three main components: Interim status requirements, permit application requirements and operating permit requirements (see figure 1). Each of these components contains specific requirements and is designed to follow a sequence of applications as a facility moves into different segments of the regulatory process.

INTERIM STATUS GROUNDWATER MONITORING REQUIREMENTS

On May 19, 1980, EPA promulgated comprehensive standards under 40 CFR part 265 for owners and operators of hazardous waste treatment, storage, and disposal facilities (TSDF's) that qualify for interim status. A facility owner or operator who has fully complied with the requirements for interim status specified in Section 3005(e) of RCRA and 40 CFR 270.70 may comply with the part 265 regulations in lieu of part 264 pending final disposition of the permit application. Part 265 Subpart F contains groundwater monitoring requirements applicable to owners and operators of interim status landfills, surface impoundments, and land treatment facilities. The goal of the interim status groundwater monitoring program is to evaluate the impact that the facility may have on the uppermost aquifer underlying the site. The regulations establish a two-stage groundwater monitoring program designed to detect and characterize the migration of any wastes that may have contaminated the groundwater. Stage I consists of a **detection** monitoring phase where the objective is to determine if hazardous wastes have leached into the uppermost aquifer in quantities sufficient to cause a significant change in groundwater quality. Stage II is an **assessment** monitoring phase that is initiated when a significant change in water quality has been detected at a hazardous waste facility and contamination is suspected. The assessment monitoring program is directed at characterizing the rate and extent of contaminant migration. Assessment monitoring under Section 265 entails a determination of both the vertical and horizontal concentration profiles of all hazardous waste constituents in the plume(s) that escape from the hazardous waste management areas. Figures 2, 3 and 4 outline the major features of interim status groundwater monitoring.

PART 270 - PERMIT REQUIREMENTS

Part 270.14(c) establishes permit application requirements (Part B), that an owner/operator must submit in order for EPA to determine if the facility is in compliance with the part 264 standards. Part 270.14(c) requires the applicant to establish the nature of the facility's impact on the groundwater, as well as the hydrogeologic characteristics of the site's subsurface and the extent of the waste management area.

OPERATING PERMIT REQUIREMENTS

The part 264 Subpart F groundwater monitoring requirements apply to owner/operators that treat, store, and or dispose of hazardous waste in surface impoundments, waste piles, land treatment units, or landfills that receive waste after July 26, 1982. Such units are referred to as "regulated units." These requirements are

effective only at facilities that have failed to qualify for
interim status (see Part 270). An interim status land TSD
facility would not be subject to part 264 standards until a
permit is issued to that facility and unless waste was received
after July 26, 1982.

Groundwater Monitoring at permitted facilities has three phases:

1. **Detection** - of indicator parameters, waste constituents, or
reaction by-products in the uppermost aquifer.
2. **Compliance Monitoring** - to better define the extent of aquifer
contamination by identifying which hazardous waste constituents
are present in the groundwater and by describing the shape and
concentration of the contaminant plume
3. **Corrective Action** - to remove hazardous waste constituents
from the groundwater or to treat them in place.

Typically, a facility employs a detection monitoring program
until there's a statistically significant increase in that
program's parameters or constituents, after which a compliance
monitoring program begins. If there's a statistically
significant increase in the concentrations established in the
compliance monitoring program, i.e., if the groundwater
protection standards have been exceeded, the facility must enter
a corrective action program. However, a facility need not begin
with detection monitoring - if there is existing evidence of
groundwater contamination (such as from an interim status
monitoring program), the facility can be put directly into a
compliance or corrective action program when the facility's
permit is issued. Figures 5 and 6 illustrate the main components
of groundwater monitoring for facilities with operating permits.

SUMMARY

The part 264 groundwater monitoring standards differ from those
in part 265 in that the part 264 standards are more flexible and
go beyond just contaminant assessment and allow for corrective
action to be directly incorporated; whereas under interim status,
corrective action has to be achieved via another mechanism such
as from an enforcement order (e.g., a 3008(h)).
Instead of testing for specific parameters as in part 265, part
264 requires the Regional Administrator to specify parameters and
hazardous waste constituents to be monitored on a site-by-site
basis. In each phase of the groundwater monitoring program under
part 264, the number, depth, and location of wells must yield
representative samples of groundwater. In addition, under part
264, a groundwater protection standard is set up for each
constituent found in the groundwater, and if exceeded, corrective
action is initiated. Figure 7 summarizes the various options for
groundwater monitoring for land disposal facilities.

REFERENCES

Code of Regulations, Protection of Environment, 40, parts 190 to 399, revised July 1, 1990.

Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976, as amended by the Hazardous and Solid Waste Amendments of 1984, (42 U.S.C. 6905, 6912(a), 6921, 6924, 6925, and 6935).

U.S. Environmental Protection Agency. 1986. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document. OSWER-9950.1

Basic Groundwater Monitoring Requirements

Groundwater monitoring requirements include:

- Interim status requirements
  (40 CFR Part 265 Subpart F)

- Permit application requirements for groundwater monitoring
  (40 CFR Part 270.14 (c) Part B)

- Operating permit requirements
  (40 CFR Part 264 Subpart F)

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Interim Status Groundwater Monitoring

Groundwater monitoring program includes:

- **Monitoring wells**
  - **1 hydraulically upgradient**
  - **3 downgradient**
- **Sampling/analysis plan**
- **Statistical comparison test**
- **Outline of groundwater quality assessment program**

(Based on regulations at 40 CFR 265.91)

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Interim Status
Groundwater Monitoring (cont'd)

Is Contamination Present During Interim Status?

YES

Implement groundwater assessment program as stipulated by submitted outline.

Continue to make assessment quarterly until closure or permit issuance.
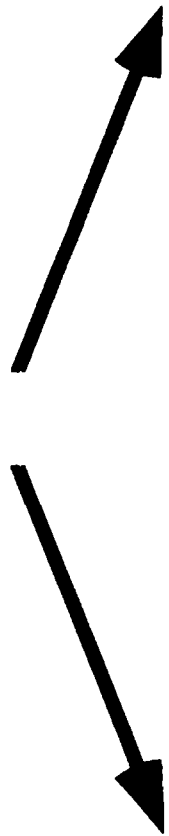
NO

Continue monitoring program until closure or permit application issuance.

(Based on regulations at 40 CFR 265.90 through 265.94)

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Monitoring Over Time

Quarterly monitoring for:

- Drinking water standards
- Groundwater quality parameters
- Indicator parameters
- Water elevations

Semiannual monitoring for:

- Indicator parameters
- Water elevations

Annual monitoring for:

- Groundwater quality parameters

(Based on regulations at 40 CFR 265.90 through 265.94)

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Groundwater Monitoring During Permit

Groundwater monitoring program requirements:

- Specify the point of compliance

- Sufficient wells properly located to yield both
  - background groundwater quality and
  - water quality passing the point of compliance

- Consistent sampling/analysis procedures

- Determination of groundwater elevations during all sampling periods

- Background groundwater quality

- Statistical comparison procedure

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Potential Results of Monitoring

Groundwater monitoring program requirements

No contamination

Detection monitoring (40 CFR 264.98)

Hazardous constituents detected at point of compliance

Compliance monitoring (40 CFR 264.99)

Hazardous constituents detected at point of compliance and downgradient of facility boundary -- exceeding the groundwater protection standard.

Corrective Action (40 CFR 264.100)

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Options for LDFs

INTERIM STATUS FACILITY

GROUND-WATER MONITORING

Closure

Operating Permit

Assessment monitoring (i.e., with groundwater contamination)

Closure With Waste In Place: Post-Closure Requirements

30 YEARS OF MONITORING

Post-Closure Permit

Detection monitoring (i.e., with no groundwater contamination)

Clean Closure

NO MONITORING

Release in excess of the groundwater protection standard at or beyond the point of compliance

Corrective Action Monitoring

Release in excess of background at the point of compliance

Compliance Monitoring

No release to groundwater

Detection Monitoring

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ABSTRACT

The Paperless Environmental Laboratory: A Plan for Realization

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Many laboratories are buying, installing, or modifying their current Laboratory Information Management Systems (LIMS) to produce all the documents necessary to effect the smooth flow of samples through the laboratory. Laboratory managers and analysts most comfortable with keyboards hope to make all paper disappear on the work bench by using direct data entry.

Users of data from environmental laboratories often include attorneys who may need to demonstrate sample custody and integrity of the sample data in order to admit the information into court. These data users are less than comfortable seeing hand-written documents disappear from the laboratory to be replaced by electronic records.

The author presents guidelines for the development of a paperless laboratory system. The guidelines include consideration for laboratory management issues and litigation related issues.

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DATA MANAGEMENT ISSUES
IN THE
HAZARDOUS WASTE INDUSTRY

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ABSTRACT

One of the most direct and yet unaddressed consequences of increased Federal, State, and Local Government regulation of U.S. Industry in the later half of the twentieth century has been the added responsibility of creating those documents and data necessary to verify compliance with these regulations. For an industry such as hazardous waste management, the responsibilities of mandatory records creation have proven to be especially great.

What has not necessarily followed, however, is the development of records and data management systems proportional to the importance that information serves in the operation of a hazardous waste facility. In today's business climate, however, the opposite is equally true--the lack of management attention to the records and data that is routinely produced by the organization can cost plenty, both in terms of dollars and in reduced productivity.

This paper will address the data management issues facing every company in the hazardous waste industry and outline a records management strategy that such companies must consider not only to avoid costly fines/penalties, but to turn their records and data into a positive asset.

INTRODUCTION

As one of the most heavily-regulated sectors of the world economy, the hazardous waste industry has many specific and long-term records/data--management requirements which must be met in order to be allowed to continue to conduct business in its operating jurisdiction. The ability to create those documents and data required for waste profiling, analyses of waste samples, and facility operation has been greatly enhanced by sophisticated laboratory equipment and the computerization of manual recordkeeping practices in general. This development has not, however, resulted in an equal ability to provide long-term protection and

retrievability of this information. To the contrary, the burden to keep analytical records and data for the time periods required by facility permits and government rules has become even more challenging and elevates the task of records management to a higher management priority that it may have been raised to in the past.

RETENTION REQUIREMENTS

All hazardous waste facilities are subject to a number of Federal and State Regulations which impact recordkeeping and data management. Some of the most important recordkeeping regulations are:

RCRA

40CFR, Parts 264.16 and 265.16
- Requires that Training Records on current personnel must be kept until 264.16&265.16 closure of the facility.

40CFR, Parts 164.73 and 165.73
- Requires the owner or operator to keep the written operating record at his facility until closure. Monitoring data at disposal facilities must be kept throughout the post-closure period.

40CFR, Part 265.94
- The owner or operator (for ground water monitoring purposes) must keep records of required analyses throughout the active life of the facility, and, for disposal facilities, throughout the post-closure care period as well.

TSCA

40CFR, Part 761.180 (Subpart J)
- Documents that include the; dates, ID of facility & owner of Facility from whom whom PCBs were received, Dates of PCB disposal or transfer, summary of total weight of PCBs, and total number of PCB articles received or transferred for 5 years after the facility is no longer used for the storage or disposal of PCBs (Chemical landfills must keep this documentation at least 20 years after the landfill is no longer used for the disposal of PCBs. Incineration facilities must collect and maintain data on PCB incineration rates & quantities, combustion temperatures, stack emissions, monitoring data for 5 years from the date of collection.

40CFR, Part 761.180(a)
- Requires that owners or operators of chemical waste landfills collect and maintain water analyses & operating records for at least 20 years after the landfill is no longer used for the disposal of PCBs.

OSHA

29CFR, Part 1904.6
- Requires that "...logs and summaries of occupational injuries, supplemental records of each occupational injury, and annual summaries of injuries ... be maintained for 5 years following the end of the year to which they relate." Failure to maintain these records shall be punished by a fine of not more than $10,000, or by imprisonment, for not more than 6 months, or both. (29 CFR Part 1904.9)

ACCOUNTABILITY

For the hazardous waste facility, recordkeeping and data management is clearly a long-term responsibility that, if neglected, will result in substantial fines. An analysis of administrative actions initiated against regulated facilities by the U.S. Environmental Protection Agency reveals that from the period 1972-1989 there were 12,250 actions which resulted in over $105 million in penalties where inadequate recordkeeping was cited as one of the major violations.[1]

To illustrate the degree to which the recordkeeping practices of a hazardous waste facility can be held accountable by Federal Regulators, consider the activities of the National Enforcement Investigations Center (NEIC) which provides the U.S. Environmental Protection Agency's Office of Legal and Enforcement Council with technical information and evidence in support of potential enforcement actions on a site's violations of permit conditions or federal regulation.

The scope of an NEIC investigation will generally involve the request to have access to all records maintained at the facility. The NEIC project team will gain consent to enter the facility from the owner or operator and schedule a date for the

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[1] **FY 1989 Enforcement Accomplishments Report**, U.S. Environmental Protection Agency, Office of Enforcement, Compliance Evaluation Branch.

investigation to begin. NEIC actions can be of 2-3 weeks in duration and usually require the assistance of facility management staff to obtain requested records and provide additional information. Records/data requested generally originate with randomly selected Waste Manifest Files. The NEIC team will request all related paperwork and data associated with select Manifests. Objectives of this request are to:

1) Track the movement of waste streams through the facility
2) Verify that all documentation is traceable to original manifest, and is logically filed and retrievable.

Related paperwork that must be produced for the NEIC investigators includes the operational records (weight tickets, time & date stamps, logbook pages, records which detail the movement of the waste, charts from emission monitoring for incinerators, location of drums), the laboratory data (analytical raw data, instrument readouts, result summaries, log books, QA/QC checks, and QC tests), and residue management records (for incinerators).

In order for a facility to successfully met the demands of an NEIC investigation and provide timely retrieval of requested records, the facility's recordkeeping system must be in order to demonstrate to regulators that it is in compliance with the recordkeeping requirements of the Code of Federal Regulations and their operating permit. It would be extremely damaging for the facility to be unable to produce a complete tracking record for a Waste Manifest- with the result being additional fines and disruption of normal activities. Beyond this specific example, try to imagine the impacts to a company's operation if a body of records and data were lost due to fire, flood, theft, or slow deterioration in poor storage conditions. It is for these reasons that a systematic- proactive approach has been developed by many companies to provide protection to critical records and data. The need for such an approach for a hazardous waste TSD facility is no less important.

DATA MANAGEMENT ISSUES FOR HAZARDOUS WASTE FACILITIES

The objectives of a records/data management program are simply stated to:

1) Furnish accurate and complete information when it is required

to manage and operate the organization efficiently.

2) Process recorded information as efficiently as possible.

3) Render maximum service to the customer(user of the records)[2]

In addition to these goals, the organization must also ensure that the records and data they have on hand will be admissible in court to defend their actions/decisions which may have occurred much earlier in time. The existence of a record management program satisfies the Uniform Rules of Evidence requirement that a process be in place to produce an accurate result and that the records created by the organization are trustworthy.[3] The organization's records management program must have written procedures, training, and regular audits in order to demonstrate that the organization carefully developed its records program, that staff was fully aware of the recordkeeping requirements, and that the procedures were actually followed by organization's staff.

The components of a records management program for a hazardous waste facility must take into account the following requirements:

1) Long term retention of data (over 30 years),

2) Ability to retrieve analytical records and data based on waste manifest numbers, customer profile IDs, Dates of tests,

3) Timely responses for customer requests for information to decision waste streams, and to recertify wastes for final disposition.

The requirement to maintain facility operating records and analytical data for such long periods of time makes it difficult to rely exclusively on a paper-based system of recordkeeping to stay in compliance with federal regulation. First, paper simply will not last as long as the law requires. Secondly, paper-based recordkeeping

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[2] **Information and Records Management, Robek, Brown,and Maedke, Glencoe Publishing Co. 1987**

[3] **Donald S. Skupsky, Legal Requirements For Microfilm, Computer and Optical Disk Records, Information Requirements Clearinghouse 1991.**

systems take up a large amount of space--space that is limited or unavailable in a laboratory environment. Lastly, paper-based systems provide no information protection to the organization in instances of fires, floods or misfiling of data. It is for these reasons that a forward-thinking records management program should plan and provide for the long-term preservation and security of analytical data by replacing (or reducing) the organization's dependance on paper-based systems with other media.

In those instances where it is impossible to incorporate microfilm or image scanning technology, the organization must provide for controlled climate, secure storage that meets federal guidelines for fire protection.

LABORATORIES

Records management responsibilities for any organization presents a significant challenge to management. In the hazardous waste industry, however, the presence of laboratories dictates an even higher degree of data complexity that the program must address. The sophistication of modern-day laboratory instruments and their ability to produce data means that the records program will have to take into account many forms of output that become part of the analytical record of the waste disposal decision. Examples of different media produced by laboratories are:

1) Perkin Elmer 5000 writes data on 5 1/4" floppy disks

2) Jarell Ash ICAP writes data on RLO1K-DC disk packs or 158 mb tape cassettes

3) Leeman ICAP writes data on paper tapes

4) Hg CV Instrument produces data compilations on thermal paper.

5) INCOS Mass Spectrometry Instruments backup data onto 45 mb tape cassettes w/ IDOS as the system's operating system.

6) Parr Bomb Calorimeter Instrument produces data in the form of 3 and 1/2" paper rolls.

7) Logbooks which provide indexes to the computer media noted above.

The presence of such varied forms of information media dictates two key components of data management strategy for a laboratory environment. One, the nature of electronic media enables the creator to routinely back-up or duplicate data from the instrument's hard disk onto a portable media such as floppy disks and transfer the back-up media to an off-site storage facility or on-site vault designed for computer media. Secondly, although it is relatively easy to create back-ups, the media itself has never been considered an archival storage media and is subject to data loss over a period of time. It is for this reason that a sound data management policy must provide for periodic conversions of data from old media to new media to arrest any possible loss of information due to the age of the original magnetic storage device. The greatest threat to the retrievability of electronic data, however, is neither a physical calamity or human error. The greatest challenge to maintaining control of electronic media is the continual hardware/software technology migration that the computer industry is subject to. New hardware means different size tape drives and new operating systems. New software releases are not automatically compatible with earlier versions. For information that must be maintained and made available for periods in excess of 30 years, the organization can certainly expect to have a significantly different computer hardware configuration and new software requirements than originally where put into place.

In order to ensure that data remains accessible to the organization, the persons responsible for data management must rigorously review the impacts of new hardware and software purchases on data recovery and make necessary conversions before the old equipment leaves the site.

Another major issue facing any organization which desires to develop a data management program is in the selection of media to provide long-term protection for their information. Storage space reductions, time to access files, admissability of media in legal actions, cost, longevity of media, and the type of information being recorded are all factors with varying degrees of priority for different organizations. For the hazardous waste industry, however, primary consideration should be given to the media type which satisfies its need to keep information secure for the required periods of retention. As previously noted, paper-based systems are vulnerable to natural disasters, take an increasingly larger amount of space away from staff and equipment, are subject to misfiles, and, perhaps worst of all, as soon as the file leaves the desk of the user, represents a loss of staff time to retrieve the file for reference purposes.

A comparative analysis of information media types follows:

Media Type Disadvantages	Advantages	
Paper	-Traditionally preferred in legal actions -Requires no special viewing device -Comfort level of users is high	-Requires large storage area -Deteriorates over time -Easy to misfile -Can only be indexed one way
Microfilm	-All courts & governmental agencies will accept as evidence -Recognized by ANSI as an archival media (silver based film will last 200 years) -Reduces storage space by 95%	-The equipment needed to read film is bulky and must be in a common access area -Film (without computer aided computer aided software) is slow to load and retrieve the the desired image. -The hard copy record must be sent off site to be photographed and processed before the film is available. Information is not available for this period of time.
Optical Disk Imaging Technology	-Provides the fastest, most flexible access to documents (files can be indexed numerous ways) -With the existence of a PC or terminal on a desk the information is sent to the user in seconds. -As with traditional computer media, optical disks can be easily duplicated for offsite security -If indexed properly, it is impossible to misfile or lose a file	-Admissibility in court not established -No industry standards

-One 12" Optical Disk can hold up to
260,000 documents (118 cu. ft. or
15 legal sized file cabinets)

The media that the organization selects to establish a records management program will have to be evaluated against these characteristics-with the ultimate decision based upon its own particular concerns. The rate at which companies that are currently receiving and maintaining great amount of information are installing imaging systems, however, demonstrates that its ability to send information
directly to users in very short periods of time establishes it as the office technology of the future. The U.S. Environmental Protection Agency has issued a position relative to this technology-stating that it is permissible to maintain compliance information on electronic imaging systems, but due to the lack of industry standards on optical disk technology, recommends that the original paper records also be maintained. The legal admissibility and industry standards concerns are being addressed at the present time and will soon not be obstacles in evaluating the suitability of this technology for an organization in the hazardous waste field.

ESTABLISHING THE RECORDS MANAGEMENT PROGRAM

A records & data management program for an organization in the hazardous waste industry must have as its principle objectives the following:

1) The protection and security of analytical data created in support of waste treatment and disposal decisions.

2) The maintenance of the facility operating record and the ability to track waste streams & verify that all permit requirements have been satisfied in treatment and final disposition.

3) The ability for staff to quickly access records and data to respond to customer or regulator inquiries.

The facility must establish a written procedure or program for the management of its official records and data. The first place to start is by conducting a records survey (inventory of facility records). The survey will identify the number of different record groups, the volume(# of file drawers or storage boxes), the current

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media(paper, magnetic tape, etc.), the present location(s) of records/data, the interrelationships between different facility groups in creating records, and how the records and data are used by the facility. After completion of the initial survey, the person responsible must research and establish the legal retention requirements and any existing company policies which will determine how long the records must be maintained.

The survey when in final form should be reviewed by the company's upper management for approval and designation as official company policy in regard to recordkeeping requirements. The survey is now the facility's official records retention schedule and is a key component of the requirement to have a written plan or program in place to insure that the facility's records are deemed "trustworthy." The facility's recordkeeping program will also require the development of a corporate-wide directive or procedure which establishes the standards that must be followed in maintaining those records related to disposal decisions, waste receiving, processing, disbursement of waste product, supporting analytical data, and quality assurance.

The recordkeeping policy should address the following topics:

1) Permit Requirements-the policy must include a statement that all record and data will be maintained in accordance with facility permit conditions.

2) Retrieval Requirements-the policy must make clear the requirement to keep records in sufficient detail in order to be able to retrieve analytical data and quality assurance records for individual waste samples and manifests for the duration of the records retention period.

3) Records Storage Area-the policy should state that all records be maintained in secure storage under conditions that will prevent deterioration of the information for the duration of the retention period[4]. The conditions for storage could be those established by the

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[4] Good Automated Laboratory Practices. Office of Information Resource Management, U.S. Environmental Protection Agency.

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National Archives and Records Service[5], for electronic media the storage facility standards outlined by the National Bureau of Standards in Special Publication 500-101 "Care and Handling of Computer Magnetic Storage Media," and the standards set by the National Fire Protection Association publications NFPA 232AM "Archives and Records Centers" and NFPA 232 "Protection of Records."
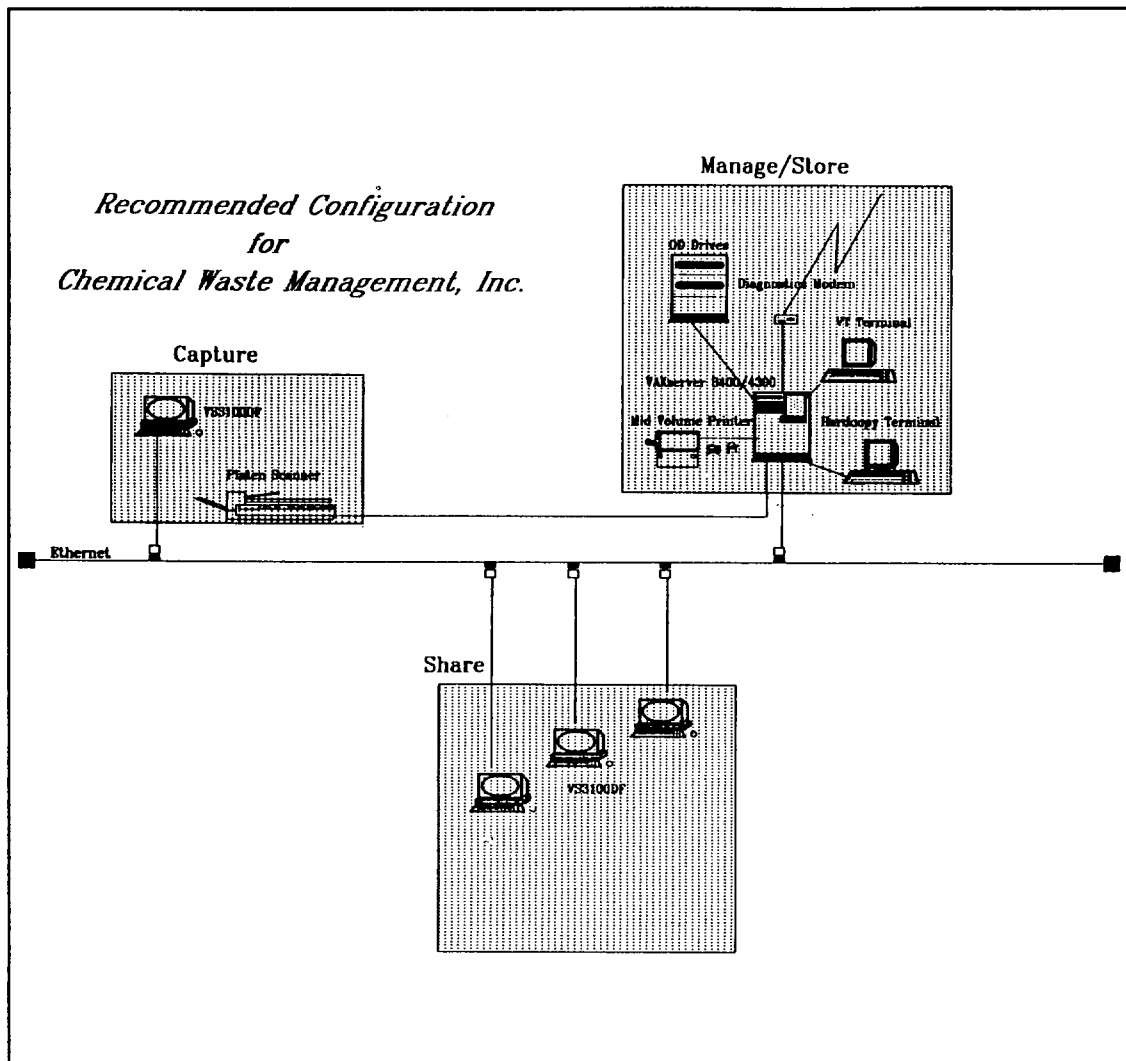
4) Analytical Records-the policy must state that analytical data must be logically filed, manual entries be made in permanent, reproducible ink, must be dated and signed or initialed by the technician. Any changes to the data must be crossed out with a single line, dated and initialed, with no obscuring of the corrected data.

5) Logbooks-must be used whenever information cannot be recorded on the analytical data, loose paper must be permanently affixed to the logbook & dated/initiated.

6) QA Records-must be retained as outlined by the facility operating permit and company policy.

Once the records survey and the Standard Operating Procedure have been completed, the person responsible for the program must investigate the use of microfilm or optical disk technologies and the suitability of each for converting the facility's data/records into a media that will provide for longevity and security of analytical information. Either technology will reduce storage space requirements, allow the duplication and off-site storage of back-up documentation, and insure the integrity of information for the terms of the retention periods. The ability of optical disk technology to provide rapid access to detailed inquiries, however, has established this information media as the preferred method of managing large amounts of data for those organizations which wish to remain responsive to their clients and have a significant recordkeeping burden.

A model of a typical imaging system follows:

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[5] Center Operations Division, Office of Federal Records Centers, National Archives and Records Service, General Services Administration(August 1976)

Recommended Configuration
for
Chemical Waste Management, Inc.

Manage/Store

Capture

Share

Ethernet

For a waste disposal decision process, an organization could electronically scan the Generator's Waste Profile Sheet, all analytical test results, and the Disposal Decision. An electronic folder would be created and indexed by; Customer Profile Number, Customer Name, Laboratory Sample ID Number, and storage box # for the original paper documents. The electronic file could now be retrieved by any of the index keys in a matter of seconds. The original paper file could be transferred to archival storage as the electronic data should satisfy all subsequent information needs. The data written on the imaging system's optical disk is routinely duplicated on a separate disk for security purposes and stored in an off-site location. Customer service is enhanced when a customer requests a copy of an entire file or only a specific document, the imaging system has the capability to transmit a facsimile directly from the provider's PC to the requestor's facsimile transmission device. If Waste Decision Files are indexed by date of decision, the user group would have the ability to retrieve all files prior to the expiration of the original decision in order to recertify waste streams for disposal.

The effect of changes in governmental regulation might dictate the reconsideration of a number of Waste Decision Files and imaging technology has the capability to retrieve electronic files by "key word" searches. For disposal sites, having imaging technology would enable the facility to index all required documents to the original waste manifest number. Raw Data if it is maintained separately from the rest of the Decision File could be indexed to the Customer's name and the Testing Laboratory's sample control number system. With this technology, an organization could truly have control of their files and put their information to work for them.

CONCLUSION

Proper data management techniques for a hazardous waste facility must be based on the realization that required recordkeeping is not only the obligation to create certain forms and data, but that this information must be retrievable for the duration of legal periods of retention. This requirement dictates that the facility apply a systematic approach to record/data creation, active use, and long-term storage. The belief that the filing of a record in a file cabinet or storage box has provided adequate protection to the company's interests has been the source of much later grief and unnecessary expense. As is the case with any regulated industry, the data that is maintained for compliance purposes is (and will be for long periods of time) an extremely valuable asset to a company and requires the

implementation of a program to guarantee the longevity of the records/data not only for compliance reasons, but also to become a positive asset in company operations.

AIR/GROUNDWATER

NEW DIRECTIONS IN RCRA GROUND-WATER MONITORING REGULATIONS

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ABSTRACT

EPA soon expects to issue a Notice of Proposed Rulemaking (NPRM) in the Federal Register concerning amendments to the ground-water monitoring requirements for land-based hazardous waste treatment, storage, and disposal facilities (TSDFs) that are regulated under Subtitle C of the Resource Conservation and Recovery Act (RCRA). The notice will propose amendments to the list of ground-water monitoring constituents for TSDFs, Appendix IX to Title 40, Code of Federal Regulations, Part 264, ("Appendix IX"), and require that certain procedures be used in the design, installation, and operation of ground-water monitoring systems at TSDFs. The proposed changes to Appendix IX include the addition of a required list of detection monitoring analytes (Appendix IX-A), the deletion or addition of several Appendix IX compounds due to analytical considerations, and a site-specific variance from the annual Appendix IX analysis requirement during compliance monitoring. The proposed standards for ground-water monitoring procedures will be specified in revisions to Chapter Eleven of the U.S. EPA document SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," (Third Edition), or more generally referred to as "Chapter Eleven of SW-846." Chapter Eleven of SW-846 specifies requirements concerning the characterization of site hydrogeology, placement of detection monitoring wells, monitoring well design and construction, and ground-water sampling and analysis programs. All hydrogeologic investigations and monitoring activities must comply with the methods and procedures required in Chapter Eleven of SW-846.

The proposed requirements in Chapter Eleven of SW-846 represent EPA's establishment of qualitative data quality objectives (DQOs) for the RCRA ground-water monitoring program. At the same time, EPA's Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV) is in the process of evaluating the efficacy of establishing quantitative DQOs for ground-water monitoring system performance. If appropriate, quantitative DQOs would allow EPA to determine the minimum number and location of monitoring wells required to achieve a specified probability of leak detection. This paper will summarize some of the methods that have been investigated to establish quantitative DQOs for RCRA ground-water monitoring.

INTRODUCTION

Subtitle C of RCRA creates a comprehensive program for the safe management of hazardous waste. Owners and operators of facilities that treat, store or dispose of hazardous waste must comply with standards established by EPA that are "necessary to protect human health and the environment." Implementation of these standards occurs through permits issued to owners and operators by EPA or authorized States.

Standards for protecting ground water from releases of hazardous wastes from permitted TSDFs were promulgated by EPA in 1982 (47 FR 32274; July 26, 1982), and are codified

at 40 CFR Part 264, Subpart F ("Subpart F"). Subpart F requires TSDF owners and operators to characterize their site's hydrogeology, install and maintain a ground-water monitoring system, and to sample and analyze ground water at specific intervals to determine whether hazardous wastes or hazardous waste constituents from the facility are contaminating ground water.

The Subpart F requirements consist of a three-phase ground-water monitoring program: detection monitoring, compliance monitoring, and corrective action. The first phase, detection monitoring, involves at least semi-annual monitoring of "indicator" parameters, waste constituents, or reaction products specified in the facility permit that provide a reliable indication of the presence of hazardous constituents in ground water. Owners and operators employ detection monitoring at new land disposal facilities and at land disposal facilities not believed to be releasing contaminants to ground water. If monitoring indicates that the concentration of a monitored constituent has shown a statistically significant increase over background concentrations, then EPA requires analysis for all Appendix IX constituents and the facility enters compliance monitoring.

Compliance monitoring, the second phase of ground-water monitoring, requires at least semi-annual monitoring for constituents identified in the facility permit, including those constituents detected in ground-water during the detection monitoring program. A facility in compliance monitoring must also monitor ground water for all Appendix IX constituents at least annually and report the concentration of any new constituent detected to the Regional Administrator. All detected Appendix IX constituents are then monitored at least semi-annually during compliance monitoring. The concentrations of all compliance monitoring constituents are compared to concentration limits specified in the facility's permit. Concentration limits are an element of the facility's ground-water protection standard used to determine if ground-water contamination has occurred.

If any compliance monitoring constituent shows a statistically significant increase in concentration above the concentration limits set forth in the facility's ground-water protection standard, the facility enters the third phase of ground-water monitoring, corrective action. In corrective action, the facility owner or operator is required to "remove or treat in place" all constituents that exceed the allowed concentration limits specified in the facility permit. The monitoring associated with corrective action must demonstrate the effectiveness of the clean-up and must be able to determine whether any other constituents are entering the ground water at concentrations above the concentration limits.

The 1982 regulations required that contaminated ground water be analyzed for all constituents contained in Appendix VIII to Part 261 ("Appendix VIII"). While appropriate for hazardous waste listing purposes, the Appendix VIII list presents a number of difficulties when used for purposes of ground-water monitoring (RMAL, 1984; U.S. EPA, 1987c). These difficulties include practical and analytical problems such as monitoring for large categories of chemicals, lack of availability of some analytical standards, and the lack of reliable analytical methods for many constituents. Other problems relate to the dissociation

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or actual decomposition of many Appendix VIII constituents in water, rendering monitoring for these constituents impractical. To address these analytical problems, EPA proposed on July 24, 1986 to replace the requirement to monitor for all Appendix VIII constituents with a requirement to monitor for a new series of ground-water monitoring analytes listed in Appendix IX. Appendix IX was promulgated as a final rule on July 9, 1987 (52 FR 25942), and included those constituents in Appendix VIII that had available analytical methods for the ground-water matrix, plus 17 constituents routinely monitored in the Superfund program.

DISCUSSION OF PROPOSED CHANGES TO SUBPART F

Detection Monitoring Analytes (Appendix IX-A)

The Agency expects to propose amendments to the Subpart F regulations to change the provisions governing the selection of detection monitoring analytes. The regulations currently require an owner or operator of a facility in detection monitoring to monitor for indicator parameters, waste constituents, or reaction products that provide a reliable indication of the presence of hazardous constituents in ground water. Studies have shown that volatile organic compounds (VOCs) serve as reliable leak indicators at hazardous waste TSDFs because they frequently occur in leachate and contaminated ground water (Eckel et al., 1985; Plumb, 1987; Lawless, 1987; Rosenfeld, 1990). Inorganic constituents (e.g., metals) have also been reported to occur in leachate from hazardous waste TSDFs (Bramlett et al., 1987; WMI, 1990 and 1991), and in ground water in the vicinity of TSDFs (Lawless, 1987). In consideration of these data, the Agency expects to propose a list of detection monitoring constituents known as Appendix IX-A.

The Appendix IX-A constituents are a subset of the Appendix IX constituents, and consist of 48 VOCs and 16 metals that the Agency believes would serve as good "release indicators" for hazardous waste disposal sites that receive a variety of wastes. The specific VOCs contained in Appendix IX-A were chosen primarily by determining which VOCs could be identified by gas chromatography/mass spectroscopy (GC/MS) with a reasonable degree of precision and accuracy (Lawless, 1990). Other considerations regarding the selection of VOCs was their reported frequency of occurrence in leachate and ground water (discussed above). The GC/MS method recommended minimizes the number of separate analyses required to determine the concentration of many VOCs in a ground-water sample (e.g., all VOCs in Appendix IX-A can be determined in a single GC/MS analysis). Thus, the use of GC/MS procedures for ground-water analyses provides reliable results and conserves analytical resources. Because of these advantages, EPA assumed that the newly proposed SW-846 GC/MS Method 8260, a modification of Method 8240 (54 FR 3213; January 1989) in SW-846 would be the standard method used for this analysis. All but two (i.e., barium and vanadium) of the 16 metals on Appendix IX-A have been on EPA's Priority Pollutant List since 1979 (U.S. EPA, 1979), and can be analyzed by inductively coupled plasma emission spectroscopy (ICP) or atomic absorption spectroscopy (AA). The analytes that comprise Appendix IX-A are listed in Table 1.

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Although Appendix IX-A may be appropriate for the majority of TSDFs, situations may arise that would warrant further tailoring of the list to meet site-specific concerns. For example, a facility that manages only smelter ash may not normally need to monitor for VOCs, because VOCs would not likely be present in the ash, and therefore, would not provide a reliable indication that the regulated unit was releasing hazardous wastes to ground water. In order to retain flexibility in the current regulations, alternative provisions will allow the Regional Administrator to add or delete constituents from Appendix IX-A after considering the waste managed in the regulated unit.

Proposed Revisions to Appendix IX

Under the Subpart F ground-water monitoring program, Appendix IX is the "master" list of ground-water monitoring analytes. Appendix IX constituents are monitored at facilities that are in compliance monitoring or corrective action. Appendix IX contains 222 constituents that in 1987 had analytical methods that were verified to a sufficient degree, and that were amenable to ground water monitoring on a routine basis (U.S. EPA, 1987c). The 222 constituents on Appendix IX consist of 17 metals and metalloids, 2 inorganic ions, 6 classes of organic compounds (i.e., chlordanes, toxaphenes, PCBs, PCDDs, PCDFs, and xylenes), and 197 specific organic chemicals.

EPA expects to propose removing eleven analytes from the current Appendix IX. The eleven constituents proposed for deletion were chosen on the basis of new analytical data that EPA has generated or received since the Appendix IX rule was first promulgated in 1987. These new data indicate that, for the eleven compounds proposed for deletion, the analytical procedures described in SW-846 do not provide consistently acceptable results in terms of method performance for determining their concentration in ground water (Lawless, 1990). In addition, 4-nitroquinoline 1-oxide is being proposed for deletion from Appendix IX because SW-846 does not provide QC criteria or accuracy and precision data for its analysis. Further, since 4-nitroquinoline 1- oxide is an experimental pharmaceutical, it was not produced in commercial chemical quantities and therefore has a low frequency of occurrence in ground water near TSDFs (Plumb, 1991). The chemical compounds proposed for deletion from Appendix IX are listed in Table 2.

The Agency expects to propose the addition of six constituents to Appendix IX. All six constituents are members of the volatile organic class of compounds, and, as discussed earlier, VOCs have been shown to serve as good release indicators. In addition, all six VOCs are amenable to analysis by GC/MS (Method 8260 in SW-846), and are included in Appendix VIII to Part 261 as part of small classes of hazardous constituents. Furthermore, five of the six compounds are halogenated alkanes, many of which are suspected carcinogens. The six constituents suggested for addition to Appendix IX are listed in Table 3.

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TABLE 1
LIST OF CONSTITUENTS FOR DETECTION MONITORING (APPENDIX IX-A)

Common Name[1]	CAS RN[2]	Common Name[1]	CAS RN[2]
1. Acetone	67-64-1	35. Styrene	100-42-5
2. Acrylonitrile	107-13-1	36. 1,1,1,2-Tetrachloroethane	630-20-6
3. Benzene	71-43-2	37. 1,1,2,2-Tetrachloroethane	79-34-5
4. Bromochloromethane	74-97-5	38. Tetrachloroethylene;	127-18-45
5. Bromodichloromethane	75-27-4	Tetrachloroethene;	
6. Bromoform; Tribromomethane	75-25-2	Perchloroethylene	
7. Carbon disulfide	75-15-0	39. Toluene	108-88-3
8. Carbon tetrachloride	56-23-5	40. 1,2,3-Trichlorobenzene	87-61-6
9. Chlorobenzene	108-90-7	41. 1,1,1-Trichloroethane;	71-55-6
		Methylchloroform	
10. Chloroethane; Ethyl chloride	75-00-3	42. 1,1,2-Trichloroethane	79-00-5
11. Chloroform; Trichloromethane	67-66-3	43. Trichloroethylene;	79-01-6
		Trichloroethene	
12. Dibromochloromethane	124-48-1	44. Trichlorofluoromethane;	75-69-4
Chlorodibromomethane		CFC-11	
13. 1,2-Dibromo-3-chloropropane	96-12-8	45. 1,2,3-Trichloropropane	96-18-4
14. 1,2-Dibromoethane;	106-93-4	46. Vinyl Acetate	108-05-4
Ethylene dibromide		47. Vinyl Chloride	75-01-4
15. 1,2-Dichlorobenzene	95-50-1	48. Xylene (Total)	1330-20-7
16. 1,4-Dichlorobenzene	106-46-7	49. Antimony	(Total)
17. trans-1,4-Dichloro-2-butene	110-57-6	50. Arsenic	(Total)
18. 1,1-Dichloroethane; Ethyldidene	75-34-3	51. Barium	(Total)
chloride		52. Beryllium	(Total)
19. 1,2-Dichloroethane;	107-06-2	53. Cadmium	(Total)
Ethylene dichloride		54. Chromium	(Total)
20. 1,1-Dichloroethylene;	75-35-4	55. Cobalt	(Total)
1,1-Dichloroethene;		56. Copper	(Total)
Vinylidene chloride		57. Lead	(Total)
21. cis-1,2-Dichloroethylene;	156-59-2	58. Mercury	(Total)
cis-1,2-Dichloroethene		59. Nickel	(Total)
22. trans-1,2-Dichloroethylene;	156-60-5	60. Selenium	(Total)
trans-1,2-Dichloroethene		61. Silver	(Total)
23. 1,2-Dichloropropane;	78-87-5	62. Thallium	(Total)
Propylene dichloride		63. Vanadium	(Total)
24. cis-1,3-Dichloropropene	10061-01-5	64. Zinc	(Total)
25. trans-1,3-Dichloropropene	10061-02-6		
26. Ethylbenzene	100-41-4		
27. 2-Hexanone; Methyl butyl ketone	591-78-6		
28. Methyl bromide; Bromomethane	74-83-9		
29. Methyl chloride; Chloromethane	74-87-3		
30. Methylene bromide;	74-95-3		
Dibromomethane			
31. Methylene chloride;	75-09-2		
Dichloromethane			
32. Methyl ethyl ketone; MEK;	78-93-3		
2-Butanone			
33. Methyl iodide; Iodomethane	74-88-4		
34. 4-Methyl-2-pentanone	108-10-1		
Methyl isobutyl ketone			

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TABLE 2
Chemical Compounds Proposed for Deletion from Appendix IX

Common Name[1]	CAS RN[2]
1. Aniline	62-53-3
2. Aramite	140-57-8
3. alpha, alpha-Dimethylphenethylamine	122-09-8
4. 1,4-Dioxane	123-91-1
5. Hexachlorophene	70-30-4
6. 4-Nitroquinoline 1-oxide	56-57-5
7. N-Nitrosomorpholine	59-89-2
8. Pentachloroethane	76-01-7
9. 2-Picoline	109-06-8
10. Pyridine	110-86-1
11. Tetraethyl dithiopyrophosphate	3689-24-5

TABLE 3
Chemical Compounds Proposed for Addition to Appendix IX

Common Name[1]	CAS RN[2]	APPENDIX VIII REFERENCE
1. Bromochloromethane	74-97-5	Halomethane, N.O.S.
2. cis-1,2-Dichloroethylene	156-59-2	1,2-Dichoroethylene
3. 1,3-Dichloropropane	142-28-9	Dichloropropane, N.O.S.
4. 2,2-Dichloropropane	594-20-7	Dichloropropane, N.O.S.
5. 1,1-Dichloropropene	563-58-6	Dichloropropene, N.O.S.
6. 1,2,3-Trichlorobenzene	87-61-6	Chlorobenzene, N.O.S.

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[1] Common names are those widely used in government regulations, scientific publications, and commerce; synonyms exist for many chemicals.

[2] Chemical Abstracts Service registry number. Where "Total" is entered, all analytes in the ground water that contain this constituent are included.

Variance From the Annual Appendix IX Analysis During Compliance Monitoring

During compliance monitoring, the owner or operator is required to monitor for parameters identified in the facility permit at specified frequencies. In addition, § 264.99(g) requires the owner or operator to analyze samples from all wells located at the point of compliance for all Appendix IX constituents at least annually. If additional constituents are found, then the owner or operator must report their concentrations and list these constituents in the facility permit. All additional constituents that are subsequently listed in the facility permit as a result of the annual Appendix IX monitoring, also form the basis for compliance monitoring, and are sampled and analyzed at least semiannually.

Experience has shown that for some hazardous waste TSDFs, annual monitoring for all Appendix IX constituents may not be necessary. Certain analytes such as EPA's Priority Pollutants have been shown in studies to have a higher frequency of occurrence in leachate and contaminated ground water than do other constituents in Appendix IX (WMI, 1990 and 1991; Plumb, 1991). Furthermore, in each of these studies, "non-priority pollutant" Appendix IX constituents were not detected in the absence of priority pollutants. This suggests that routine monitoring for non-priority pollutants may not be necessary at every TSDF. In light of this new information, EPA expects to propose a site-specific variance to the annual Appendix IX monitoring requirements under certain circumstances. Such a variance could involve performing an abbreviated Appendix IX analysis on an annual basis. To exclude a constituent from the annual Appendix IX analysis, the owner or operator would be required to demonstrate that the constituent could not be present in the waste managed by the facility (either as a constituent of the waste, or as a reaction product), and is not present in the facility's soil and ground water. The benefits of the variance would be realized primarily for those constituents that require special analytical methods (e.g., TCDD) rather than for those that are amenable to analytical "scan" techniques such as SW-846 method 8260.

EPA expects that any variance from the annual monitoring requirements for Appendix IX constituents would not relieve the owner or operator from ever monitoring for the excluded constituent(s). The initial, full Appendix IX analysis would still be required in detection monitoring. Retention of this requirement is necessary to characterize the nature and extent of a release and could be used to demonstrate that the excluded constituents are not present in ground water at the facility. In addition, if a successful demonstration is made and the Regional Administrator excludes constituents from the annual Appendix IX compliance monitoring requirements, the owner or operator would be required to monitor for all Appendix IX constituents (including the excluded constituents) at least once every five years, when the permit is usually reviewed or renewed. If at any time a facility that has a monitoring exclusion began to receive or generate wastes that contain any excluded Appendix IX constituents, the facility would be required to resume annual monitoring for the appropriate analytes. Likewise, these steps would need to be followed if a treatment process was modified, or a new one begun, that resulted in the production of the excluded constituents.

CHAPTER ELEVEN of SW-846: GROUND-WATER MONITORING

One of the major topics that arose during EPA's recent review of over forty TSDF operating permits (Permit Quality Review) throughout the nation was the importance that each of the numerous steps taken by an owner or operator to comply with RCRA ground-water monitoring requirements has in determining the quality of the data produced by monitoring networks (U.S. EPA, 1991a). One example of this is the value of an adequate characterization of site hydrogeology. Improper site characterization can lead to incorrect placement of monitoring wells, or a failure to recognize ground-water flow paths and contaminant migration pathways.

In addition, inspections conducted by EPA's Hazardous Waste Ground-Water Task Force (HWGWTF) during the years 1984 to 1987 identified deficiencies in existing ground-water monitoring systems and determined that many of the deficiencies resulted from owners and operators collecting poor quality hydrogeologic data, collecting inadequate quantities of hydrogeologic data (or misinterpreting such data), and using improper sampling and analysis techniques (U.S. EPA, 1988). The deficiencies almost always involved technical areas for which the RCRA regulations provided the least specificity, but that were covered extensively in non-binding EPA guidance documents (e.g., subjects such as hydrogeologic characterization, well construction and location, and ground-water sample collection). The HWGWTF and Permit Quality Review experience highlighted the need to develop nationally consistent regulatory requirements addressing the process an owner/operator must follow to characterize site hydrogeology, to design and construct a ground-water monitoring system, and to collect and analyze ground-water samples.

As a result, EPA expects to propose to require owners and operators to use the methods described in proposed revisions to Chapter Eleven of SW-846 when conducting hydrogeologic investigations, designing and constructing monitoring systems, and performing ground-water sampling and analyses. Chapter Eleven of SW-846 embodies the Agency's best judgment and current understanding regarding ground-water monitoring techniques, and addresses a variety of ground-water monitoring techniques and procedures including: hydrogeologic characterization, well placement, well design, well drilling, well completion, well casing materials, well development, well purging, sampling equipment and methods, and sample handling. EPA does not expect that any new burdens will be placed on the vast majority of owners and operators by requiring them to conform to the methods discussed in SW-846 because these techniques and methods are based on widely accepted practices of most geologists and ground-water professionals. Furthermore, for each phase of ground-water monitoring system design and operation, Chapter Eleven of SW-846 generally offers several methods that are acceptable depending on the specific hydrogeologic setting of a facility, the waste management practices, and the waste characteristics. Where specific techniques or procedures are not provided because of the complexity and site-specific nature of ground-water monitoring programs, Chapter Eleven of SW-846 provides discussion and technical guidance on the available alternatives. In these cases, there is a significant amount of flexibility allowed in the choice of methods used for ground-water monitoring system design and operation.

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Data Quality Objectives for Ground-water Monitoring

The Agency has begun using DQOs for evaluating remedial response activities associated with Superfund sites to define the type and quality of data required to support specific regulatory decisions (EPA, 1987a and 1987b). DQOs include both qualitative and quantitative specifications. Many of the current ground-water monitoring requirements that are specified in Subpart F are broad-based performance standards that allow the Regional Administrator, RCRA Part B permit writers, and owners and operators of hazardous waste TSDF's to account for site-specific factors when designing a ground-water monitoring system that meets the requirements of the RCRA regulations. The wide variations in waste management practices coupled with diverse hydrogeologic settings and geochemical environments across the United States make it difficult to promulgate a regulation specifying a minimum number of monitoring wells and their location that would be applicable to all facilities. EPA instead has relied on technical guidance documents (e.g., U.S. EPA 1986; U.S. EPA, 1989) and the experience of permit writers to implement these types of general performance standards on a site-specific scale. Presently, given the current "state-of-the-art" of ground-water monitoring practices, a qualitative approach to defining the adequacy of ground-water monitoring systems is the norm. However, significant efforts are underway at EPA to develop quantitative approaches for designing ground-water monitoring systems.

The Agency continues to focus on efforts that will improve both the type and quality of RCRA ground-water monitoring data. Changes to Appendix IX and the creation of Appendix IX-A will improve the type of data collected, by changing the constituents for which owners/operators must monitor. A variance to the annual Appendix IX compliance monitoring requirement will ensure that meaningful data are collected. The incorporation of Chapter Eleven of SW-846 into the Part 264 and Part 270 ground-water monitoring requirements will offer more prescriptive directions on what methods and procedures should be used in the design and operation of ground-water monitoring systems. These are part of the Agency's efforts to establish qualitative data quality objectives for the RCRA ground-water monitoring program.

Data quality for ground-water sampling and analysis activities is also addressed in Chapter One of SW-846 titled, "Quality Control." Chapter One of SW-846 identifies the minimum quality control (QC) components to be used when performing all RCRA sampling and analysis activities, and includes the QC information which must be documented. Chapter One of SW-846 provides guidance on the development of quality assurance project plans for field and laboratory work that is conducted in support of the RCRA program. Chapter One was part of the first update package to SW-846, third edition, and is mandatory for compliance with RCRA sampling and analysis requirements.

Quantitative Data Quality Objectives for RCRA Ground-Water Monitoring

The Agency is assessing the feasibility of establishing quantitative DQOs for ground-water monitoring under 40 CFR Part 264, Subpart F. Quantitative DQOs would be developed for

each phase of monitoring and would establish numeric standards that specify the level of performance for RCRA ground-water monitoring systems. Thus, quantitative DQOs for detection monitoring could, for example, require that ground-water monitoring networks achieve a specified probability of detecting contamination. Quantitative DQOs for compliance monitoring could require that ground-water monitoring networks achieve a specified probability of characterizing the extent of ground-water contamination. Quantitative DQOs for corrective action could require that ground-water remediation efforts achieve clean-up standards within a specified probability. A similar approach has been used to support decisions concerning the design of remedial actions for contaminated soils at Superfund sites (Neptune, et al., 1990). In all phases of RCRA ground-water monitoring, quantitative DQOs would allow the Agency to specify the exact number and location of monitoring wells, and number of ground-water samples, required to achieve a desired level of performance.

The Agency's Office of Research and Development is investigating the efficacy of establishing quantitatively-based DQOs for ground-water monitoring (U.S. EPA, 1991b). Research plans are oriented toward developing a process aimed at defining, with a specified probability, that a monitoring well system will detect a release from a TSDF. This process will still involve the collection of detailed site-specific hydrogeologic data to support the development of a conceptual model. This data may then be integrated with a conditional simulation model and/or a contaminant fate and transport model that would predict preferential flow paths of contaminant migration and estimate the probability of leak detection based on monitoring well network configuration.

Relatively early research performed by *Massmann and Freeze* (1987), calculated the probability of contaminant plume detection by monitoring networks. As noted by *Meyer and Brill* (1988), however, these investigations stopped short of optimizing ground-water monitoring network performance (in terms of the probability of detecting a contaminant plume) by failing to generate alternative networks that are more efficient with respect to contaminant plume detection. *Meyer and Brill* utilized Monte Carlo simulations of plume releases to develop a method for optimizing the location of monitoring wells.

Quantitative monitoring network design methods offer intriguing advantages over their qualitative alternatives, and are beginning to find applications at hazardous waste sites. A two-dimensional deterministic model based on the work of *Meyer and Brill* has been used to predict low density, aqueous-phase contaminant plume detection in unconfined aquifers (Wilson, et al., 1991). This model offers a quantitative yet user-friendly approach to monitoring network design. Other applications of quantitative monitoring network design will likely continue to surface in the literature.
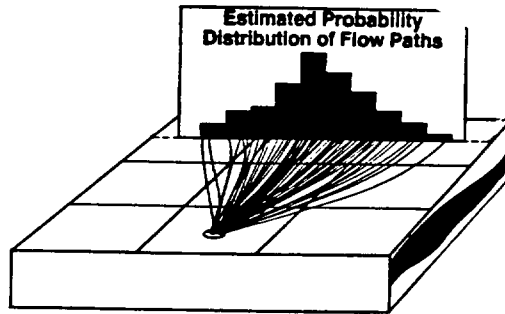
A more recent development of a procedure to estimate the probability of contaminant plume detection uses geostatistical conditional simulation and parameter estimation sequentially to generate contaminant migration pathways (Weber, et al., 1991). Recognizing that aquifer heterogeneities and the high cost of hydraulic conductivity measurements often inhibit adequate site characterization, these researchers utilized hydraulic head and available

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hydraulic conductivity measurements to estimate the distribution of flow paths (Figure 1), and developed a relationship between the probability of plume detection and monitoring system cost (Figure 2). The procedure is also amenable to conditional simulation of hydraulic conductivity if sufficient measurements are available to perform geostatistical analysis (Weber, et at., 1991).
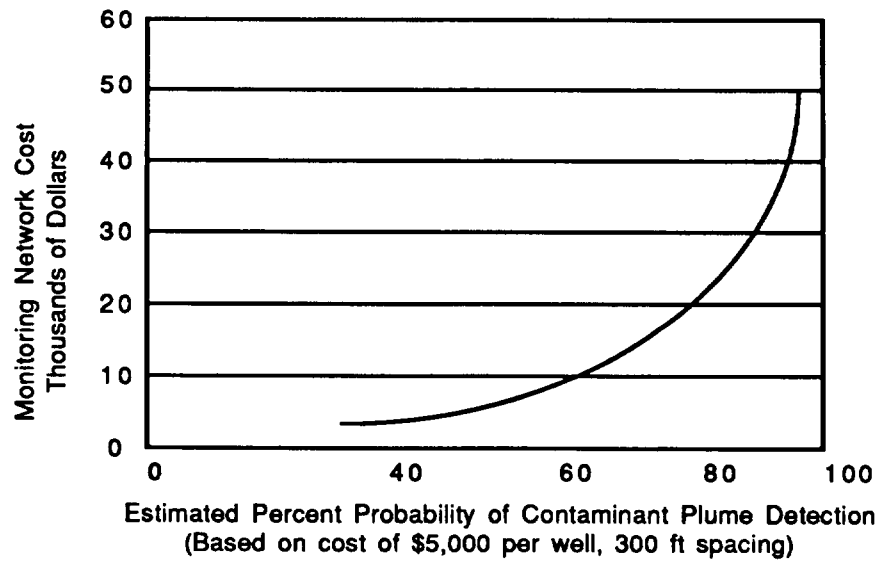
The results of research efforts like those described above could provide EPA with a quantitative means for specifying DQOs for Subpart F ground-water monitoring networks. Current limitations of ground-water monitoring, subsurface characterization, and modeling techniques, however, make it difficult to develop quantitative DQOs (most of the current applications utilize two-dimensional models). For example, it may not be possible or practical to design a monitoring system that will detect releases at a desired probability of contaminant plume detection. Before a probability statement can be made, population characteristics should be known (or assumed to be known). In the context of ground-water monitoring at TSDFs, the population consists of all possible contaminant migration pathways in the subsurface. To characterize this population, very detailed site characterization methods and analyses are required. Consequently, a central issue involves the level of detail that a site characterization must include to define all of the population characteristics. As discussed above however, surrogate parameters (i.e., hydraulic head measurements) for hydraulic conductivity have been used successfully to define the spatial distribution of contaminant migration pathways and evaluate monitoring well performance where data is sparse and collection methods are expensive (Weber, et al. 1991).

EPA will continue to support the development of quantitative DQOs for ground-water monitoring under Subpart F as technical advances allow. EPA will use such information to assess the feasibility of developing quantitative DQOs for ground-water monitoring. If an acceptable procedure is developed for establishing quantitative DQOs, it will be proposed in the Federal Register and formally opened to public comment.

FIGURES

Figure 1 (After Weber, et al., 1991)

Estimated Percent Probability of Contaminant Plume Detection
(Based on cost of $5,000 per well, 300 ft spacing)

Figure 2 (After Weber, et al., 1991)

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SUMMARY

EPA expects to propose amendments to the Subpart F requirements for ground-water monitoring at TSDFs. The proposal will amend the list of ground-water monitoring constituents (Appendix IX) based on analytical considerations; create a subset Detection Monitoring list of constituents that have been shown to provide a reliable indication of releases from TSDFs; issue an exclusion variance from the annual Appendix IX Compliance Monitoring requirement; and require owners and operators of TSDFs to comply with ground-water monitoring methods and procedures contained in a revision to Chapter Eleven of SW-846.

EPA is also conducting research on quantifying ground-water monitoring network design efficiency. Research efforts are investigating the efficacy of optimizing the probability of contaminant plume detection for a given monitoring well configuration. The desired outcome of this research would allow for the establishment of quantitative DQOs for ground-water monitoring.

ACKNOWLEDGEMENTS

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97   DE-MYSTIFYING THE PROBLEM OF FILTERED VS UNFILTERED SAMPLES

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ABSTRACT

A controversy has persisted for at least a decade concerning the filtration versus non-filtration of ground water samples, particularly with respect to samples used for metals analyses. Renewed emphasis on the collection of data of high quality and an ever increasing need to better understand the subsurface environment have resulted in a resurgence of attention on the representativeness of ground water samples to adequately reflect the level of threat to public health and the environment. Often, it is difficult to differentiate the contribution of metals from natural sources, incomplete purging or disturbance of sediments during sampling, or releases from an abandoned or uncontrolled hazardous waste site. This paper examines the various facets of the problem, discusses options for filtration versus non-filtration when collecting samples for different purposes, and clarifies the relative importance of various fractions of a sample (i.e., suspended solids, colloids, dissolved solids, and colloids and dissolved solids adsorbed on suspended solids) in understanding the subsurface environment. The paper also discusses the benefits and drawbacks associated with the related issues of acidification, transport and storage temperatures, use of filters of varying porosity, field versus laboratory filtration, and the development of a well to a turbidity standard. The above issues also are discussed within the context of comparing the sample data to health and environmental benchmarks, both for ground water and for surface water samples. Possible solutions to the problem are suggested.

INTRODUCTION

A topic of fervent debate when discussing ground water sampling plans often focuses on whether "to filter or not to filter" collected samples. One viewpoint is that filtration results in a substantial physical and chemical modification of the sample. Another perspective is that filtration allows data users to concentrate only on those contaminants which are actually dissolved, excluding any substances which may be adsorbed on, or conveyed by, particulate matter in suspension. Both positions have merits and the collection of filtered or unfiltered samples (or both) may be suitable dependent on the questions which need to be resolved (Nielsen 1991).

The reasons for filtration of ground water samples include:

- Removal of suspended solids to permit analyses only of the dissolved fraction of substances in the sample, reflecting drinking water quality as delivered

- Removal of any interference caused by suspended particles (e.g., when ultraviolet spectrophotometric screening techniques are used

- Analysis of "clear" samples, required when using delicate instrumentation easily clogged by sediment-laden samples

- Separate analyses of constituents associated with suspended solids

- Determination of the percent of suspended solids

The disadvantages associated with filtration include:

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- Chemical changes in the sample due to changes in partial pressure of dissolved gases during filtration under positive pressure or a vacuum

- Volatile organic substances may be lost to the atmosphere during filtration

- Aeration of sample during filtration can cause precipitation of metals

- Possible inadvertent removal of substances, both organic and inorganic, that tend to adsorb on suspended particles

- Increased opportunities for sample contamination, especially if filtration is conducted in the field

- Practical difficulties in the field when filtering during sub-zero temperatures and when filtering sediment-laden water

Generally, the problem of deciding "to filter or not to filter" is associated with the analysis of metals. Most ground water samples collected for the analysis of organic compounds are not filtered because:

- Many organic hazardous substances are not natural components of ground water, therefore, the analyst is interested in the total sample concentration

- Most volatile organic compounds can easily be lost during filtration

- Since water solubility and partition coefficients vary among most organic substances, there is no compelling reason to differentiate between the suspended solid and dissolved particulate fractions of a sample collected for the routine analysis of organic substances.

- Except for variations for some pesticides and PCBs, concentrations of organic hazardous substances in ground water do not vary as markedly as metals in proportion to the amount of sediment in a sample.

Thus, the problem of "to filter or not to filter" relates primarily to a perceived need to filter samples of ground water to be used for the analysis of metals. The problem manifests itself in the form of artifacts in ground water monitoring data which cannot easily be explained within the context of having intentionally collected representative samples. For example, very high metal concentrations have been observed in samples collected to determine contamination from a waste site when the metals could not be attributable to that specific source. Sometimes, background concentrations would be highly elevated, but levels near a source would be at trace levels. Very high concentrations (e.g., 640,000 ug/l aluminum, 1,000 ug/l nickel, 500 ug/l chromium) of metals commonly found in soil have been observed in ground water, when normally such concentrations are low (e.g., 200 ug/l, 40 ug/l, and 10 ug/l, respectively) in clear ground water.

Generally, there appears to be a direct relationship between high levels of metals and high levels of suspended solids in the samples, independent of a sample being representative of background or site contamination. High levels of suspended solids are suspected to be the source of the high concentrations of metals. The presence of high levels of suspended solids in ground water samples complicates efforts to establish representativeness of samples and attribution to sources of contamination. In the evaluation of data from such samples, it is

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difficult to differentiate the contribution of metals from natural sources, the incomplete purging or disturbance of sediments during sampling, or releases from a site.

BACKGROUND

There are several terms relevant to a discussion of contaminant particle fractions in water. Under current "Standard Methods" (American Public Health Association, et al. 1989), waterborne solids are divided into two components. One component, "suspended solids," is retained during filtration of water through a 0.45 micron (a micron is one millionth of a meter) filter. The second component, "dissolved solids," passes through the filter. In addition to suspended solids and dissolved solids, there is a fraction of suspended solids termed "colloids."

Suspended Solids

Suspended solids are waterborne particles which do not pass through a filter used to produce a filtrate containing only dissolved solids. In static water, large suspended solids will settle to form sediments. When sediments are disturbed, such as during the purging of a well, they will form suspended solids.

Generally, large-sized suspended solids (e.g., greater than 10 microns in diameter) are not found in ground water. The exception to this norm is the ground water of Karst areas where surface debris and soil particles can enter the system through sink holes. A rapid discharge rate through caverns and crevices can entrain more large particles through erosion of soft limestone.

Naturally occurring solids, such as clay particles and quartz silicates, move as suspensates in ground water. At some locations and at certain times, naturally occurring metallic hazardous substance(s) of concern can be found at relatively high concentrations in ground water. This is particularly true for metals found in surface water and ground waters of mineralized areas. Examples of these areas include locations of ultra-basic rocks rich in nickel and chromium, basaltic and some sedimentary rocks high in zinc and copper, and galena-bearing rocks rich in lead. A major fraction of the metals in the ground water of these areas is the suspended solids present as eroded components of the parent material (rock and overburden). Because eroded particles, in the form of sediments, can become suspended in wells during sampling, they are a major focus of concern.

Colloids

Colloids are extremely small solid particles which will not readily settle out of a solution. Colloids dispersed in water scatter light even though they are too small to be seen by the naked eye. They are intermediate in size between true dissolved solids and large suspended solids which are visible to the naked eye.

Colloids vary in size. They are classified according to size, but there is not a uniform definition with respect to their lower or upper limit. The scale used by the U.S. Department of Agriculture and the Soil Science Society of America defines colloids as clay particles with diameters less than two microns, but which will not pass through a 0.45 micron filter used to extricate dissolved solids from a water sample. This classification is equivalent to particles smaller than fines described by the U.S. Army Corps of Engineers. The Wentworth scale used for sediments, which is a logarithmic scale in that each grade limit is twice as large as the next smaller grade limit, defines clay particles to be smaller than 3.9 microns (Blatt et al. 1972). Since colloids are retained by a 0.45 micron filter, they are considered to be a fraction of suspended solids.

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In surface waters, where water movement inhibits settling, colloids have been considered to be somewhat larger, encompassing small microorganisms such as bacteria, protozoans, and small unicellular diatoms. In this context, colloids are considered to be particles smaller than 10 microns in diameter (Stumm and Morgan 1981).

Where mixtures of pure chemicals are studied under laboratory conditions, colloids may be viewed as particles smaller that one micron in diameter. Such very fine particles may take up to one year to settle from suspension.

Studies have shown that colloids can facilitate the transport of contaminants in ground water. There is evidence that colloids in excess of 1 micron may not only be mobile in ground water but also may move faster than the average ground water flow in porous media as the result of such effects as size exclusion from smaller spaces (Puls 1990).

Colloids have demonstrated strong binding and sorption capacities for inorganic contaminants. As much as 42 percent plutonium in a release has been found to be mobilized as colloids sorbed on suspended solids (Champ et al. 1982). High metal concentrations, as much as 200 parts per billion of copper, lead, and cadmium, were found to be associated with colloidal particles (Tillekeratne et al. 1986). Other studies have shown a strong affinity for metal sorption onto colloidal particles in ground water (Gschwend and Reynolds 1987, Enfield and Bengtsson 1988, Puls and Bohn 1988, Puls 1990).

Dissolved Solids

Dissolved solids are extremely fine particles that pass through a filter with a pore size of 0.45 microns. Such particles will not settle from a water sample, but will remain in a vessel after evaporation of a sample and its subsequent drying in an oven (American Public Health Association, et al. 1989). However, for the purposes of this paper the term dissolved solids will include the "volatile solids" which are ignited and some mineral salts which are volatilized during a dissolved solids determination.

Strictly speaking, dissolved solids include only chemical species in solution. However, the use of a 0.45 micron filter to remove suspended solids means that colloidal particles less than 0.45 microns in diameter are usually characterized as dissolved solids. This convention was adopted as a consensus standard representing a compromise between complete removal of all particulate material and the speed with which filtration may be completed. Thus, some colloidal metal particles have been shown to pass through a 0.45 micron filter, leading to an order of magnitude or more error in using 0.45 micron filtration as an operational definition for "dissolved" (Puls and Barcelona 1989a).

Dissolved solids represent the aqueous phase of transport of substances in ground water. It should be kept in mind that there is a dynamic solid-solution equilibrium in water, wherein elements move from solution to colloids and larger solids and back again depending on physical, chemical, and microbiological factors. Thus, metals may exist at one location in an aquifer in the dissolved state and at another location, or at the same location at a later point in time, as colloidal metal oxides, metal hydroxides, metal carbonates, or chelated metals bound in organic matrices. In fact, they all can be present at the same place and time, all in equilibrium with one another.

Interaction of Fractions

In ground water, the three fractions of particles (suspended solids, colloidal fraction of suspended solids, and dissolved solids) can exist simultaneously. Also, colloids and dissolved

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substances may be found adsorbed on suspended solids. In addition, dissolved substances can be adsorbed on colloidal particles.

The relative states (adsorption, de-sorption, solution) of the metals can change abruptly due to the actions of physical, chemical, and microbiological factors. For example, an acidic environment may lead to the decomposition of metal laden suspended solids (e.g., natural clay and silicate particles), thereby releasing natural metals into solution.

Fractions of Interest in Ground Water Assessment

Current filtration procedures (using a 0.45 micron filter) exclude most colloids and suspended solids from ground water samples, leaving for analysis the aqueous phase containing the dissolved fraction of the hazardous substances of concern. Filtration is useful because some suspended solids, such as well sediments inadvertently collected during sampling, may not be desired and require removal through filtration. However, the removal of colloids may not be desired because of their reported capacity to adsorb and transport contaminants in the subsurface environment.

With respect to colloids, a recent article by Puls (1990) summarized the importance of delimiting their fraction with regard to hazardous waste site assessment activities:

"Inherent in these discussions [concerning colloids] is the concept of 'dissolved' vs. 'particulate' and the rather arbitrary separation technique of using a 0.45 micron filter, commonly used in data collection activities in the laboratory and in the field. If colloids as large as 1 to 2 microns are mobile and capable of transporting contaminants for large distances, then our sampling protocols must make allowances for this component of transport."

Thus, in summary, the desired ground water fractions of primary interest for evaluating contamination of ground water are:

- Natural, large-sized suspended solids such as found in Karst environments

- Dissolved solids and colloids

- Dissolved solids and colloids adsorbed on suspended solids.

Not desired are large suspended sediments artificially introduced into the sample during collection activities.

SAMPLE PROCESSING AND FILTRATION PRACTICES

Ground water samples are collected from active drinking water wells, standby wells, and monitoring wells. Commonly used sampling devices include electrical submersible pumps, positive-displacement bladder pumps, bailers, and suction-lift pumps. The type of sampling device used is based on the rate of well purging possible in view of available well yield, well diameter, limitations in the lift capability of the device, and the sensitivity of selected chemical species to the method of sample collection and delivery to a sampling container (Keith 1988).

Metals samples usually are acidified with nitric acid in the field to pH<2. The purpose of the acidification is to inhibit dissolved and colloidal particles from adsorbing onto solids and the surface of the sample container and forming precipitates (e.g., hydroxides or hydrated oxides).

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Under the Contract Laboratory Program (CLP) of the U.S. Environmental Protection Agency (EPA), metals samples are acid digested in the laboratory prior to analysis. This entails treatment with acid (and also with hydrogen peroxide if analyzed by furnace atomic absorption) and heat (95°C) to oxidize organic materials. The sample is then filtered (or alternatively centrifuged or allowed to settle by gravity) to remove insoluble material (EPA 1987a).

For the initial screening of hazardous waste sites, the EPA has recommended that the Total Recoverable Metals Method, a method performed on an unfiltered sample, be the standard technique in determining metal concentrations in ground water. This technique presumably releases the loosely bound metals from the particulate fraction but does not totally destroy the matrix. This is viewed as preferable to a dissolved metals analysis on filtered samples, which, by contrast, does not account for those metals that are adsorbed to the soil matrix and which may move back and forth in equilibrium with the ground water, resulting in an underestimate of chemical concentrations in ground water from an unfiltered tap (EPA 1989).

However, the Agency has recognized the need for filtering when a sample is highly turbid. For example, if silt persistently appears in a sample because of well construction or design, and the situation cannot be corrected, then it may be worthwhile to perform both the dissolved (filtered) and total metals (unfiltered) analyses. If filtration occurs (i.e., a dissolved metals test is to be performed), the metals samples are to be filtered immediately on-site by the field sampler before adding preservative (EPA 1987a).

Sampling protocols in general practice often recommend that samples from ground water monitoring wells to be used for metals analyses be field-filtered under pressure before preservation and analysis. The filtered samples collected for metals are usually acidified. Acidification of unfiltered samples can lead to dissolution of minerals from suspended clays. The sample should be filtered as soon as possible after it is collected, preferably in the field. Where field filtration is not practical, the sample should be filtered as soon as it is received in the laboratory (American Public Health Association, et al. 1989, EPA 1976).

POTENTIAL SOURCES OF PROBLEMS

This section contains a brief discussion of the predominant mechanisms wherein undesirable suspended solids, in the form of fine particles, become entrained in well water. The predominant mechanisms are through inadequate well construction, development, and maintenance and well purging and sampling.

Well Construction, Development, and Maintenance

The proper construction and development of monitoring wells is essential to the collection of representative water samples. Improperly developed monitoring wells will produce samples containing suspended sediments that may both bias chemical analyses of collected samples and cause clogging of field filtering mechanisms (EPA 1987b).

When constructing monitoring wells, the drilling process may cross contaminate aquifers with loosened fine particles of topsoil, possibly laden with agricultural or industrial chemicals (Keith 1990). Installation of a screen with oversized slots, a poorly designed filter pack, improper screen placement, and removal of cement holding the sand grains together around the well screen also contribute to the movement of fine-grained materials into a well.

Monitoring wells must be developed to provide water free of suspended solids. There are many ways to develop wells. The first step in a common method of well development involves the movement of water at alternatively high and low velocity into and out of the well screen and

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gravel pack to break down the mud cake on the well bore and loosen fine particles in the borehole. This step is followed by pumping to remove these materials from the well and the immediate area outside of the well screen. If the flushing procedure is too harsh, the gravel pack may be dislodged leading to possible screen damage or creation of a conduit for small fines to enter the screen. Inadequate pumping will leave sediments in the well. These sediments can become entrained as suspended solids in samples.

Improper maintenance can lead to the incrustation of carbonates, metal hydroxides, and biofilms of iron bacteria which can slough off as suspended solids (Driscoll 1989). These incrustations can markedly affect the chemistry of the well water.

Purging and Sampling

Because biochemical and geochemical reactions and other factors alter the quality of water stored in a well casing, the stored water must be removed before obtaining a sample representative of the quality of water in the aquifer. The amount of water to be purged from a well prior to sample collection varies from well to well. If a sample is collected too early before complete purging, it may not reflect the quality of water in the aquifer. If collected too late, water or contaminants from areas removed from the well can be drawn into the sample, possibly resulting in a sample which is not representative of aquifer quality at the well location. Often, samples are collected after a standard number of well volumes are purged (e.g., 2 to 10) or when the purged water appears to become "stabilized", determined by the presence of water that appears to be unclouded (Brown and Egan 1989, EPA 1983).

Well water that appears to be clear may contain particulate matter in suspension, particularly if the water is from new or little used wells, such as ground water monitoring wells or standby municipal supply wells. The amount of sediment discharged from a well is affected by the type of pump, well construction, size and type of screen, the purging rate, and other factors. Often, fine grained materials near a well intake erode due to water pressure and well construction. These pass through a well screen and accumulate as sediments in the bottom or on the sides of the well casing. When a bailer or pump intake is activated for sampling, the sediments can be disturbed and entrained as suspended sediments in the water sample (Brown and Egan 1989, Bloese 1983).

Bailers are commonly used for both purging and sampling water from small diameter, shallow wells because of their relatively low cost and portability. However, without very careful control, the movement of a bailer often mixes well water, resulting in a potential for aeration and degassing of the sample. The aeration is the result of repeated submergence and removal of the bailer during sampling, which may result in turbulent flow of water in the wellbore. Further aeration can occur as a result of pouring the collected sample from the top of the bailer into the sample bottle (Keith 1988). Such aeration and degassing causes physical and chemical changes in water quality, creating suspended solids in the form of hydroxides and other precipitates.

Bottom-draw bailers, and suction-lift, gas-displacement, and other types of pumps have been used to minimize the problems of aeration and turbidity. All of these devices have drawbacks (e.g., slow withdrawal rate, degassing), compared to the simplicity of the bailer (Keith 1988, EPA 1983).

Water samples containing suspended sediments derived from well disturbance do not represent true ground water quality. The results of analyses of metals from such samples (if unfiltered) would be biased high relative to true levels in ground water, due to metal release from the disturbed sediments.

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Laboratory Storage and Pre-treatment

The accepted time limit for the storage of metals samples is 180 days (EPA 1987a, EPA 1976). During this period of time, the acidic environment of the sample may cause decomposition of the suspended solids, thereby releasing metals into solution. Also, heat and acid of the laboratory pre-treatment procedure may release metals through decomposition of the suspended solids. These processes do not affect determination of a "total metals" concentration in a sample. However, the effects (i.e., release of metals into solution) of these two processes negate the ability to obtain representative differentiation of the colloidal and dissolved fractions.

Variable Practices

The difficulty of obtaining a representative ground water sample in light of the suspended solids problem is complicated by the lack of consistency in sample filtration and sample acidification. Delays in filtration and preservation and the sequencing of each process result in additional complications. Currently, there is no commonly followed practice for the filtering of ground water samples (Puls and Barcelona 1989b).

Quality control is not implemented uniformly with respect to the preservation of a ground water sample with acid. Often, it is standard practice to preserve a sample by adding a standard amount of acid (e.g., 5 drops), with the intent of creating a pH<2 in the sample. However, due to variation in the buffering capacity of ground waters in different parts of the country, the pH of the a sample may vary from <2 to >5 following addition of the acid. The pH is seldom verified with a pH meter and corrected to <2.

In an examination of field quality control methods in general practice, Keith (1988) found a number of procedures and areas of disparity at the time of sampling and sample preservation that contribute to variances in the quality of the collected water. These practices include:

- aeration and degassing of sample during field filtration

- delaying acidification

- delaying filtration or filtering after acidification

- lack of necessary temperature reduction for successful stabilization of certain samples (e.g., mercury, chromium, cyanide) during transport.

Delay in the preservation of metals samples can lead to substantial variation in the reported concentration. For example, an experiment has shown that the concentration of iron in a sample acidified immediately after collection was 11.6 mg/l; whereas, the concentration of a duplicate sample acidified seven hours after collection was 0.33 mg/l. Replicate samples from another site, acidified in the same manner showed similar results (5.74 to less than 0.08 mg/l). Significant changes were also observed for other metals (Keith 1988).

A major concern related to the timing of acidification of a metals sample relates to aeration of the sample. When ground water is in a reduced state, the addition of oxygen can cause metal precipitation. Aeration of the sample can occur during transfer from the sampling device to a sampling bottle, transfer to a holding container prior to filtration, or during filtration. If fixation of the metals in the sample by addition of acid occurs after filtration, metal precipitates (e.g., metal hydroxides and metals adsorbed to the hydroxides) could be removed by the initial field filtering and not be available for laboratory analysis. The turbulence and associated aeration

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of a metals sample during filtering affects sample quality much more than simply holding a sample which has not been acidified. In fact, studies indicate that aeration of the sample during filtration can have as much affect on sample quality as the sampling activity itself. Acidification immediately after sample collection and prior to filtering minimizes precipitate formation after sampling (Brown and Egan 1989, Keith 1988).

POSSIBLE SOLUTIONS TO THE PROBLEM

Attainment of Turbidity Standard Prior to Sampling

It may be possible to restrict the entrainment of suspended solids into a sample. A monitoring well can be developed in such a way that it is basically free of sediments from construction activities. Although not always possible and only if it has been properly designed and developed, a monitoring well can be maintained in such a way that the screen does not become clogged and the incrustation of carbonates, metal hydroxides, and biofilms of iron bacteria are controlled. However, such chemical and physical maintenance techniques are difficult to perform without destroying the representativeness of samples. Excepting severe damage during well development, a monitoring well can be purged and sampled in such a way that its clarity is equal to that of drinking water (e.g., maximum contaminant level turbidity standard of 5 nephelometric turbidity units).

There are precedents relating to the establishment of clarity in well water before sampling. The goal of several Federal ground water sampling programs (e.g., EPA monitoring program objectives under the Resource Conservation and Recovery Act, the Air Force Installation Restoration Program, and the Superfund remedial program) is to develop, purge, and sample monitoring wells in such a way as to assure clarity in the collected samples of water (Puls and Barcelona 1989b, EPA 1989).

Due to time and resource constraints, there are several problems inherent in the attainment of a turbidity standard of clarity before sampling during a site inspection. These problems include:

- Duration of sampling. Some monitoring wells are so laden with fine sediments that purging rates need to be as low as two liters per hour. Some monitoring wells may require up to seven hours (Keith 1988) to complete an adequate purging and sampling effort, a time and resource requirement which may not be achievable under the conditions of an initial ground water screening.

- Verification. A frequent nephelometric measurement would be required to confirm attainment of a turbidity standard. Although relatively easy to perform, this would be a burdensome task for site inspection personnel, given limited time and resources. The additional sample handling could increase the probability of sample contamination and alteration of the chemical characteristics of the sample.

- Well Development. The development of a well for the purposes of producing water of potable quality is very time consuming and relatively costly compared to the time and resource constraints associated with the installation of a monitoring well for screening purposes.

- Well Maintenance. Monitoring wells installed for site inspections may be sampled once after installation and never again. They may remain unattended for many months or even years between sampling events. Without periodic screen and gravel pack cleaning, treatment for incrustation and biofouling, and other maintenance activities, clarity of samples cannot be assured.

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These problems can be overcome in a long-term monitoring program where wells are sampled periodically (e.g., every quarter). Drawdown rates for such wells are known and the proper well-specific optimal purge volumes determined through records of periodic sampling. The routine, repetitious sampling regimen of such long-term monitoring programs allows for the provision of adequate time for sampling and well maintenance activities. The time and resource constraints of a screening process does not allow such extensive quality control procedures.

Field Filtration

Field filtration of ground water samples to separate colloidal and dissolved solids from suspended sediments is desirable, preferably with vacuum filtration to expedite the filtering process. The disadvantage of field filtration relates to quality control. Under field conditions it would be difficult to avoid sample contamination while coping with several procedures inherent in the filtering process. The filter disks need to be washed with successive volumes of distilled water (American Public Health Association, et al. 1989) and then prewashed with sample water to equilibrate the filter disks with sample water (disk will initially sorb certain metals). However, this problem could be overcome through use of pre-washed disposable filtration devices. Problems also arise with control over the build up of a "filter cake" and resultant clogging of filters associated with high concentrations of suspended solids. During sampling, handling, and filtration, aeration could result in unintentional metal precipitation.

Field filtration has become a routine practice in some monitoring programs, but an exacting expectation for sample representativeness and quantitation may preclude field filtering due to the above mentioned quality control problems. The additional resource burden associated with the filtration of ground water samples in the field may be excessive, given the limited resources available for site inspections.

Laboratory Filtration

Filtration in a fixed laboratory, such as a laboratory under the CLP, is an attractive alternative compared with field filtration. Conditions are conducive for controlled analytical measurement and sample handling.

The disadvantage to filtration in the laboratory relates to the time lag from sample collection to analysis, the greater this time lag, the more the entrained sediments become dissolved by the acidic preservative. Filtration in the laboratory would involve immediate analysis vs. the current practice of metals sample storage for a prolonged period of time, bringing about a new concept in metals analysis. However, the analysis of metals samples upon receipt by the laboratory is logistically feasible, because the CLP requires a rapid turn around for the analysis of other types of hazardous substances.

Preservation and Storage

The filtration of colloids and dissolved solids from large suspended solids requires special care in sample preservation and storage in order to minimize degradation of the large suspended solids by acid. If filtration is conducted in the field, dissolution of the suspended solids fraction is minimal. However, if laboratory filtration is performed, special care must be taken to minimize chemical reactions after acidification (which "fixes" dissolved solids already in solution).

One apparently ideal method of minimizing the chemical reactions which can breakdown the suspended solids in acidified metals samples is to lower the temperature of the samples. This

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is a standard technique for the preservation and storage of many types of samples. Water reaches its maximum density at 4°C. For many decades, it is at this temperature that samples of waterborne coliform bacteria, pathogens, and organisms were stored for immediate transfer to a laboratory for culturing, plating, and analysis. Field samples easily are maintained at a temperature of 4°C by means of an ice slurry (or wet ice) in an ice chest. Maintaining chemical samples in an ice slurry is common practice for certain metals affected by biotic activity (e.g., mercury, chromium, colorimetric analysis of copper, cyanides) and for volatile substances. When metals samples at ambient temperature are placed in an ice slurry (or wet ice), the samples attain a temperature of 4°C within three hours (Keith 1988). This cooling process could aid in stabilizing the various metal fractions until receipt at the laboratory for analysis.

There are a few disadvantages associated with the cooling of metals samples. One disadvantage is that a decrease in temperature of a sample will increase its oxygen saturation level, contributing to aeration of the sample and possible hydroxide formation. However, acidification of the sample should mitigate problems associated with such aeration. The cooling of a ground water sample from a 20°C temperature of a warm, shallow aquifer to 4°C can raise its pH by as much as one-half of a pH unit (Diehl 1970). However, if the sample is acidified properly to a pH<2, any change in the pH due to cooling should have insignificant effects on precipitate formation.

Freezing metal samples is another alternative. Freezing samples will minimize chemical reactions and inhibit breakdown of suspended solids, but presents several problems. The freezing action (unless flash frozen; e.g., with liquid nitrogen) can create a phase separation wherein water free of acid becomes frozen first leaving the remaining liquid more acidified, possibly creating problems in metals recovery in the laboratory (e.g., during the CLP pre-treatment analysis. The field logistical requirements for freezing involve special transport and handling of the freezing agent (e.g., dry ice), extra cost of materials and equipment, and special training of field personnel. The receipt, storage, handling, and thawing of frozen samples in the laboratory may present added logistical and analytical problems.

SUGGESTED FILTRATION PRACTICES

It is recommended that ground water metals samples be acidified immediately upon collection in the field and cooled to a temperature of 4°C for transport to a fixed laboratory for analysis. The acidification to pH<2 should be verified in the field prior to cooling the samples.

The metals samples should be filtered for the separation and analysis of colloidal and dissolved solids immediately upon receipt at the fixed laboratory. After filtration, the filtrate should be acid and heat pre-treated using the current CLP procedure for the pre-treatment of metals samples.

The filter pore size used for filtration should be large enough to allow the bulk of the colloidal particles to be recovered, but small enough as to exclude larger suspended sediments. A commercially available, acid resistent, 5 micron pore size filter is available in standard sizes (e.g., 2.2 cm to 4.7 cm) and is recommended. A larger pore size (10 micron) filter is available, but is not recommended for the size range of colloids associated with ground water. It may be possible that a more preferable 2 micron pore size, acid resistent, filter is commercially available, but its availability needs to be confirmed.

Field filtration is not recommended for ground water metals samples. Should a decision be made to filter ground water metals samples in the field, the following procedure is recommended. Immediately upon collection, the samples should be subjected to mild acid

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treatment (e.g., nitric acid pH 3 to 4) for 10 minutes to free sorbed dissolved and colloidal contaminants from large suspended solids. Then, filtration should be preformed using a 5 micron (or 2 micron if available) pore size filter. The filtrate should be acidified immediately upon collection in the field and cooled to a temperature of 4°C for transport to a fixed laboratory for analysis. The acidification of the filtrate to pH<2 should be verified in the field prior to cooling the samples.

Coupled with the above, relevant site inspection guidance should be developed, focusing on the use of various techniques to minimize the entrainment of suspended sediments in ground water metals samples.

The problem of sediments entrained in ground water samples is associated with an overestimate of the concentration of metals in ground water. Samples collected for organic compounds analyses should not be filtered. This is consistent with common practice to not filter samples collected for the analysis of organic compounds (Keith 1991).

Ground water samples in Karst areas should not be filtered. The presence of suspended solids larger than colloids is an intrinsic feature of these systems and is indicative of natural background levels.

Both filtered and unfiltered surface water samples (split samples) should be used for metals analyses. Data from unfiltered samples should be used for comparison with benchmarks such as Ambient Water Quality Criteria (AWQC) which represent unfiltered concentrations. Data from filtered samples should be used for comparison with benchmarks such as Maximum Contaminant Levels (MCLs) which represent water delivered to a user of a public water supply. Large suspended solids have been removed from such delivered water by various means including sand filters, flocculation, and gravity settling in storage facilities. Even in private, rural water supplies, particulate matter is removed by settling in household compression tanks, gravity and pressure filters, zeolite softeners, and other ion-exchange units for the removal of unwanted hardness.

SUGGESTED CONFIRMING STUDIES

A number of studies need to be conducted to confirm that the recommended sample preservation and filtration procedures are appropriate. The studies should be conducted by a laboratory familiar with the filtration of colloids and dissolved solids from ground water samples containing high concentrations of suspended solids. The following are some of a number of questions which should be addressed by such studies.

- What is the most appropriate type of filter and filter pore size in terms of availability and applicability, given acidified conditions and the need to extricate colloidal and dissolved metal particles from ground water samples?

- What portion of the total metals concentration of a sample is associated with suspended solids greater than 5 microns and greater than 2 microns in diameter?

- Do colloids represent a significant amount of the metals concentration of a sample (excluding dissolved solids)?

- Does the cooling of acidified metals samples significantly reduce the breakdown of suspended solids?

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- Are the quality control problems associated with field filtration too great to warrant field filtration in lieu of laboratory filtration?

- Do the metal concentrations degrade significantly during transport between the field and the laboratory and during temporary storage prior to filtration?

- If samples are not analyzed immediately in a fixed laboratory, will the suspended solids be significantly degraded, given acidification and cold (4°C) storage?

RAMIFICATIONS OF SUGGESTIONS

The use of filtration to separate the colloidal and dissolved metal fractions for analysis, thereby removing large suspended solids from the sample, represents a "forced" control over a sampling problem which may not be controllable in the field. The resultant data, derived from analysis of the filtrate, would be more representative of conditions representing background and site contamination.

Requiring filtration would eliminate the occurrence (though infrequent) when samples were collected to represent background and site contamination, where one of the samples was filtered and the other sample was not filtered.

Data from filtered ground water samples are more appropriate for comparison against drinking water benchmarks. This comparability of sample comparisons applies to both surface water as well as ground water.

The use of filtration recognizes the fact that under the screening conditions of a site inspection, the problem of the entrainment of suspended sediments in ground water metals samples is not easily solved by quality control procedures. The time and resource constraints of a site inspection also may preclude field filtration in lieu of filtration in a fixed laboratory.

Filtration will increase the number of and types of metals samples to be collected and tracked. For example, in surface water, filtered and unfiltered metals samples will need to be collected at each sampling point through the use of split samples. In Karst aquifers, metals samples would not be filtered. For surface water, the data user must be assured that filtered samples are compared with filtered samples and vice versa. All reported water data will need to be flagged with respect to whether the samples were filtered or unfiltered.

The requirements for site inspection personnel would be increased through the implementation of a filtration policy. Field acidification would require verification. Samples will need to be cooled and maintained at a temperature of 4°C and rapid transport to the laboratory assured. Improved quality assurance and quality control requirements relating to purging and sampling may be required.

Contracts with fixed laboratories may need to specify a new pre-treatment protocol in the statement of work for inorganic analyses. The new laboratory procedure would shorten the holding time for metals samples from 180 days to less than 48 hours, resulting in a marked change in routine laboratory procedures.

The removal of colloidal particles represents a new filtration practice involving more extensive quality control procedures. Although the precedent of filtration is firmly established, the separation of colloidal particles would represent a new way of thinking in contrast with the traditional viewpoint of "dissolved" versus "suspended" solids.

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SUMMARY

A new approach to ground water sampling and analysis of metals is proposed. The approach involves the separation of colloids and dissolved solids from ground water samples by means of filtration within a fixed laboratory. This approach will not eliminate all uncertainties, but represents a "forced" control over a sampling problem which may not be controllable in the field during initial screening investigations of an uncontrolled hazardous waste site.

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DETERMINATION OF TARGET ORGANICS
IN AIR USING LONG PATH SPECTROSCOPY

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The EPA Region II, Environmental Services Division (ESD), Surveillance and Monitoring Branch (SMB) has recently acquired a transportable system to perform long path remote sensing of air contaminants. This remote sensing system consists of spectrometers which identify and quantify target organic chemicals in ambient air Pathlengths, up to 500 meters, are defined by use of a retroreflector, a specially constructed mirror assembly which reflects and collimates the signals generated by the spectrometers. The spectrometers used are: a Fourier transform infrared (FTIR); with a resolution of 0.5 cm-[1] and a liquid nitrogen cooled mercury-cadmium-telluride (MCT) photodetector and a long path ultraviolet (LPUV) with a prism monochromator and a photo diode array detector. With meteorological monitoring, this system can be used to monitor the air for many environmental applications: site investigations for Hazardous Ranking System (HRS); fenceline monitoring of industrial sites; off-site health and safety monitoring during remediation or removal projects; monitoring of lagoons for potential air release; and in emergency response to community complaints on air quality. This paper will present the design, application and interpretation of data for the EPA Region II, ESD/SMB, LPUV/FTIR.

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99   MEASUREMENT OF TOXIC ORGANIC COMPOUNDS IN LANDFILL GAS SAMPLES USING CRYOGENIC TRAPPING AND FULL SCAN GC/MS

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A Nutech automated cryogenic concentrator with adjustable sample volume loops is used for analyzing landfill gas samples using full scan GC/MS and selected ion monitoring (SIM). This method is able to quantitate VOC compounds over concentration ranges of 0.5 ppbv to 1000 ppbv. Landfill samples can be effectively collected in evacuated SUMMA passivated canisters and most VOC compounds have a holding time of 14 days. A 0.5 to 500 ml landfill gas sample is loaded into the Nutech Automatic Concentrator and then analyzed with an HP 5890 GC using a 30 meter DB-5 fused silica capillary column connected directly to the source of an HP 5790 MSD. The capillary column is temperature programmed from -40 to 150 C to analyze compounds from F-12 to trichlorobenzene. The relative standard deviation for the method is less than 10% for most compounds and the MDL is about 0.5 ppbv depending on sample size and the carbon dioxide content of the sample. The sampling methods, instrument modifications for analyzing landfill gases will be discussed along with the examples of data, and the limitations of the method.

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THE DETERMINATION OF THE HEAT OF COMBUSTION AND WATER CONTENT OF INCINERATOR FEEDS USING NEAR INFRARED SPECTROSCOPY

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ABSTRACT

Near Infrared Spectroscopy (NIR) allows the simultaneous determination of the heat of combustion and moisture content of a broad range of heterogeneous incinerator feeds, with no sample preparation.

RCRA regulations require the determination of the heat of combustion on all incinerator feeds to determine if they are above the 5000 BTU/lb level. Water content is necessary for proper operating conditions of the incinerator. To satisfy these requirements, a large number of samples are currently analyzed using both bomb calorimetry and Karl Fischer titration, which are labor intensive and time consuming methods. The NIR procedure utilizing selected absorption bands eliminates all sample preparation, while simultaneously determining both parameters.

NIR technology was used to generate heat of combustion and moisture data on 73% of 564 incinerator feeds at a 90% success level, subsequent to software screening to classify the incinerator feeds into physico-chemically unique types. The 73% can be increased to 95% and the success level increased, by consolidating feed type calibration curves and by improving the prescreening software. Additional parameters may be added as the database is expanded. The runtime of two minutes per sample entails an 80% analytical cost savings.

INTRODUCTION

RCRA regulations require the determination of the heat of combustion on all incinerator feeds to determine if they are above the 5000 BTU/lb level. Chemical Waste Management Inc. incineration facilities receive a broad range of liquid hydrocarbon-based wastes requiring incineration. Incinerator feed type compositions cover very wide ranges of constituents with heats of combustion ranging from 1,000 to 20,000 BTU/lb, water contents from 0.1% to 100% and halogen contents from 0.1% to 70%. Heat of combustion and water content are critical sample composition parameters that affect incinerator performance and blend feeds before incineration. Because these analytical parameters critically affect incinerator performance and efficiency, each feed requires chemical analysis using conventional bomb calorimetry and Karl Fischer titration methods, which are both labor intensive and time consuming.

Near infrared reflectance (NIR) spectroscopy is a rapid and sensitive measurement technique that has found many applications in analyzing agricultural and pharmaceutical materials [1,2]. The near infrared spectral region, which spans from 1100 to 2500 nm, has high information content in the form of many overlapped bands arising from overtones and combinations of X-H stretching modes of vibration. The widespread use of NIR spectroscopy can be greatly attributed to the introduction of powerful computerized data processing techniques for interpretation of complicated NIR spectra. The development of this technique for quantitation is primarily due to the availability and use of multilinear regression analysis; however, quantitation is limited to samples of controlled composition. The qualitative information available in the NIR spectral region is used by pattern recognition techniques for the identification and classification of samples of unknown origin.

This paper reports a classic example of using near infrared spectroscopy and chemometrics methods for analyzing hazardous wastes. Because of the nature and spectroscopic complexity of hazardous wastes, a two-step chemometrics approach must be used to successfully extract useful information from the near infrared spectra. The first step is to extract qualitative spectroscopic features from the near infrared spectra for pattern recognition analysis. The second step, then, is quantitation of heat of combustion and water content for multivariate calibrations. Mahalanobis distance pattern recognition analysis is used to develop the classification models from near infrared spectra. Multivariate calibration models are developed by multilinear regression analysis for each of the defined classes. A reasonable degree of accuracy is obtained in predicting the heat of combustion and water content of liquid incinerator feeds provided appropriate calibration is used.

THEORY

Symbols and Notations

The following discussion explains the symbols and notations used in this paper to describe the theory of Mahalanobis distance pattern recognition analysis and Multilinear regression analysis. Bold letters are used to denote matrices and lower-case letters to denote scalars (italic) and vectors (bold). A vector is always a column vector if no transpose is attached. Transposed vectors are denoted by single quote ('). The symbol x is for a NIR spectrum and c is the concentration of the chemical constituent of interest. In addition, i is the number of training set samples (observations) and k is the number of spectral values (wavelengths). With this notation, the model consists of i observations of k dimensions and the two sets of data are denoted by c and X.

The training set is defined as the samples that are used to develop the classification and calibration models. The test set is defined as the samples that are used to evaluate the classification and calibration models and are samples that are not used in the training set.

Mahalanobis distance pattern recognition analysis

The Mahalanobis distance technique assumes a multivariate normal distribution $N(\mu, \Sigma)$ for the class population. The class model consists of a single point in multidimensional space, the class centroid μ. The distance between an ith sample, x_i, to the centroid is given by the generalized squared distance:

$$MD_i^2 = (x_i - \mu)' \Sigma^{-1} (x_i - \mu) \dotfill 1$$

where Σ is the training set's variance-covariance matrix which explains the dispersion of data around the centroid. In practice, the true centroid μ and the variance-covariance matrix Σ of the class population are unknown and, therefore, must be estimated by the mean vector $\bar{x}$ and the variance-covariance matrix S from a sample training set of n. The sample Mahalanobis distance can then be calculated from equation 2:

$$MD_i^2 = (x_i - \bar{x})' S^{-1} (x_i - \bar{x}) \dotfill 2$$

and

$$S = \frac{1}{(n-1)} \sum_{i=1}^{n} (x_i - \bar{x})'(x_i - \bar{x}) \dotfill 3$$

Geometrically, the Mahalanobis distance class model is an ellipsoid-shaped cluster with the population mean at its centroid. A spectrum is classified as a member of a group if the Mahalanobis distance is less than 6 as compared to the Mahalanobis distance for that sample with other groups. An excellent review of the theory of Mahalanobis distances is given by Mark and Tunnell [3].

Multilinear Regression Analysis

Regression analysis is used for predicting BTU values from a collection of independent variables such as wavelengths. The procedure consists of two phases: calibration and prediction [4]. A data matrix is constructed from the NIR instrument response X (absorbance) at selected wavelengths for a given set of calibration samples. A vector of heat of combustion values c is then formed using an independent method such as bomb calorimetry method.

One of the objectives of the calibration phase is to develop a model that relates the NIR spectra to the heat of combustion values obtained by the bomb calorimetry method. In regression analysis, a linear combination of the variables in X is calculated such that the model's estimates of the heat of combustion values of the $\hat{c}$ in the calibration set are as close to the known values of c as possible (minimizes the errors in reproducing c). Mathematically, the linear regression model with a single response (BTU value) can be explained by equation 4:

$$c = X\beta + \epsilon \dotfill 4$$

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where β is a vector of regression coefficients and ϵ is a vector of errors or residuals associated with the regression model. To "fit" the model given in equation 4 to the known values of c, we must determine the values for the regression coefficients β and the residual ϵ consistent with the available data.

The method of least squares selects regression coefficients estimates, $\hat{\beta}$, using equation 5:

$$\hat{\beta} = (X'X)^{-1} X'c \dotfill 5$$

and the estimated response $\hat{c}$ using equation 6:

$$\hat{c} = X\hat{\beta} \dotfill 6$$

The regression estimates $\hat{\beta}$ are consistent with data whose sum of squared differences ($\hat{\epsilon}$) from the observed c is as small as possible.

$$\hat{\epsilon}_i = \sum_{i=1}^{n} (c_i - \hat{c}_i)^2 \dotfill 7$$

where deviations $\hat{\epsilon}$ are the residuals estimate, $\hat{c}_i$ is the multilinear regression estimate of the BTU value and c_i is the actual BTU value for the ith sample.

EXPERIMENTAL

564 samples received from various Chemical Waste Management sites were analyzed by a Bran+Luebbe (Technicon) NIR 400 filter instrument in the dispersive reflectance mode. About half of the samples were also analyzed by a scanning Bomem MB155 FTIR/NIR instrument in transmission mode. Most of the samples contain some amount of solid material, which settles after a period of standing. A few also had two liquid phases. When necessary the samples were shaken or sonicated to minimize phase separation. A QA/QC program has also been developed for the Bran+Luebbe NIR spectrometer during the method development process.

A Bomem MB155 FTIR/NIR connected to a Compaq 386 20 Mhz personal computer was used to acquire NIR spectra. The absorbance data were collected in the NIR spectral range from 10,000 to 4,000 cms^{-1} (or 1100 to 2500 nm). Sixteen scans at 8 cms^{-1} resolution were averaged for Fourier data processing. Using the complete NIR spectrum range provided visual information for identifying spectral patterns responsible for C-H and O-H overtone bands.

The data for pattern recognition and the calibration models were acquired using a Bran+Luebbe NIR 400 filter instrument and a Compaq 386 20 Mhz computer. The

Bran+Luebbe 400 instrument consists of 19 filters mounted on a filter wheel which were configured with different wavelengths. The NIR spectral region selected for the present work ranged from 1600 to 2450 nm since most of the useful spectral information was present in this region. The samples were analyzed using a stainless steel cell covered with a quartz plate to obtain a thin layer of film which was measured in reflectance mode by the filter instrument.

Customized software written in Microsoft Quick Basic program was used for the Technicon 400 instrument data acquisition. The data were then imported to Bran+Luebbe IDAS software for developing Mahalanobis distance pattern recognition and multilinear regression calibration models. Two separate equation files, written in ASCII format, were read by a custom software to predict samples of unknown origin. The custom software first classified the "spectroscopic type" of the sample based on the Mahalanobis distance pattern recognition analysis and then used the appropriate calibration to obtain a quantitative results for heat of combustion and water content.

RESULTS AND DISCUSSION

Conventional Methods Overview

The standard technique for determining the heat of combustion of liquid incinerator feeds is the bomb calorimetric method. The heat of combustion, measured in British Thermal Units per pound (BTU/lb), is determined by burning a previously weighed sample in an oxygen calorimeter under controlled conditions. The energy required to raise the temperature of a given volume of water is measured by observing the temperature before firing the bomb and after a stable temperature is reached. These observations are made and recorded by the calorimetry apparatus which also reports the heat of combustion (BTU/lb).

The standard technique for determining the water content of liquid incinerator feeds is the Karl Fischer titration method. The percent water content is determined by titrating a known amount of sample with standardized Karl Fischer Reagent (KFR) to its endpoint. When there is an excess of KFR, the solution color changes to a dark brown due to presence of free iodine. The Karl Fischer reagent is standardized by titrating KFR with a known amount of water. Using an automatic titrator, the endpoint of the reaction can also be electrometrically determined.

NIR Spectroscopy

Near infrared spectroscopy is based upon molecular heteroatom vibrations producing a charge distribution, which interacts with electromagnetic radiation. The interaction intensity is directly proportional to the dipole moment of the molecular bond, and produces the characteristic absorption patterns representative of the chemical composition of the sample. The mid-infrared region (25.0 to 2.5 μm or 400 to 4000 cms^{-1}) is the most well known range of analysis of organic materials. The sharp spectral bands produced by the fundamental vibrational frequency of the heteroatom bonds are directly related to skeletal and functional structures of organic compounds. Near infrared absorption bands are produced by vibrational overtones, and for each mid-infrared band there are four to seven near infrared

overtones. This crowding produces broad plateaus arising from superimposed harmonics. The loss of structural information is offset by a gain in signal to noise ratio. This makes NIR spectroscopy especially suited for the analysis of hazardous waste liquid incinerator feeds.

The near infrared region (1100 to 2500 nm) is attractive for heat of combustion and water analysis because most of the absorption bands observed in this region arise from overtones and combinations of C-H and O-H stretching vibrations. Near infrared spectra of three types of liquid incinerator feeds are shown in Figure 1. The spectra show prominent bands for each type of incinerator feeds. For example, type 6 feeds have a broad band at 1940 nm that is characteristics of O-H stretching and second overtone vibration. Absorption bands are particularly strong above 2300 nm due to presence of two or more types of hydrogen bonded molecular complexes. Type 1 feeds are primarily fuel oil (hydrocarbon) types of hazardous waste and, therefore, the NIR spectra of such type materials contain a broad C-H overtone band around 1720 nm. PCB type of materials are responsible for peaks at 1650 and 2175 nm in type 2 feeds. The absorptivity of these bands is largely independent of the remainder of the molecule, but does depend on the concentration of the absorbing functional group and, therefore, can be used for predicting the heat of combustion and water content of the liquid incinerator feeds.
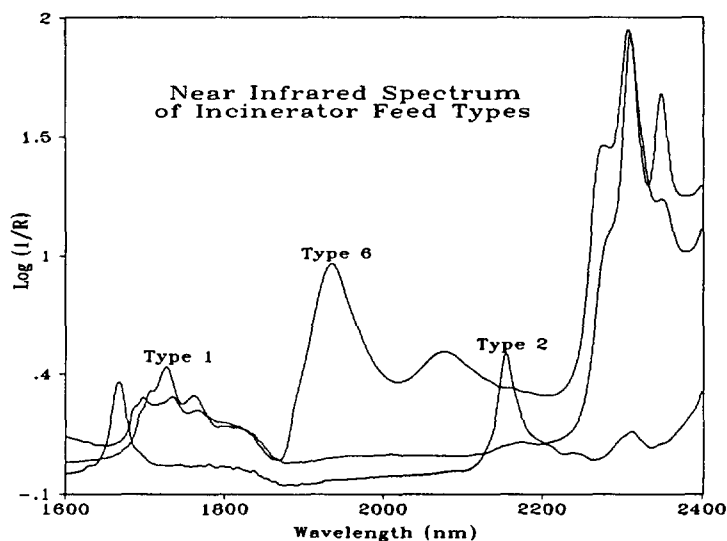

Figure 1: Near Infrared Spectra of Incinerator Feeds

Incinerator feeds have been identified into seven types based upon their NIR spectral patterns. Table I is a summary of matrix types responsible for the seven groups of incinerator feed types. The distribution of the seven groups of incinerator feeds analyzed by the NIR spectroscopy is shown in Figure 2.

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Table I: Summary of matrix types for pattern recognition analysis

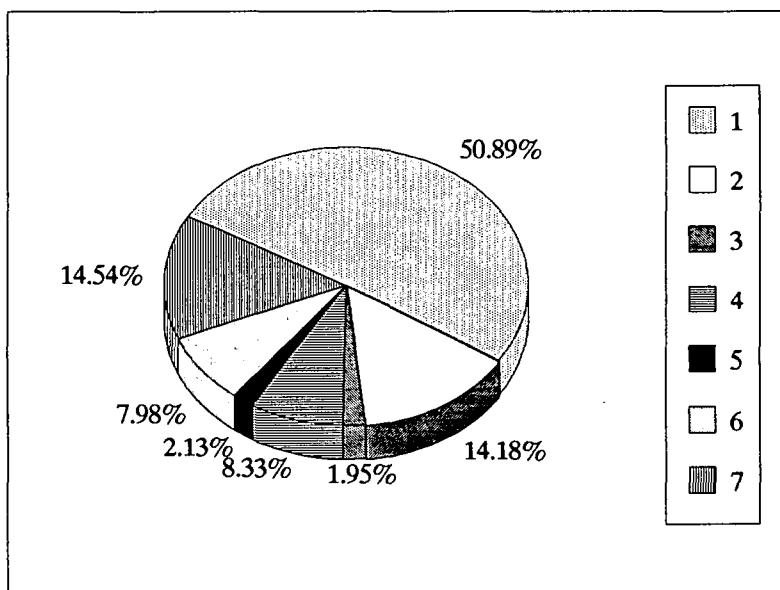| Feed Type	Matrix Type
1	Fuel Oils
2	Halogenated solvents (e.g., PCB)
3	Unknown
4	Aromatic solvents
5	Unknown
6	Polar solvents (e.g., methanol) ??
7	Aqueous solution (e.g., water)

Figure 2: Distribution of seven feed types analyzed by NIR spectroscopy

Near infrared analysis depends on the development of an empirical linear equation, in which the constituent concentration is related to some combination of optical measurements, usually expressed in absorbance or reflectance. To use this empirical approach, the analyst must have a set of samples having known values generated by another method (training set samples). From this set of knowns, the system is trained through an iterative process. Using regressive and correlative data processing, the analyst generates a multiterm linear expression making suitable use of the analytical data. With sufficient experimentation and statistical treatment of the data, this produces a final working calibration curve.

Mahalanobis Distance Pattern Recognition Analysis

In the Mahalanobis distance classification technique, two or more wavelengths are used for classification of samples. The classification of spectra was based on the generalized square distance of an observation from the centroid of a cluster. In addition, only one mathematical model was constructed for all incinerator feed types. In our present work, four wavelengths gave adequate discrimination to identify seven groups of incinerator feeds based on their NIR spectral patterns and Mahalanobis distance pattern recognition analysis. In Figure 3, a three dimensional

plot of wavelength 2100, wavelength 2139 and wavelength 2348 shows good discrimination between various classes. Adding a fourth wavelength 2310, the pattern recognition model was able to classify various feed types more accurately. The legends 1 . . . 7 used in Figure 3 are explained in Table I.
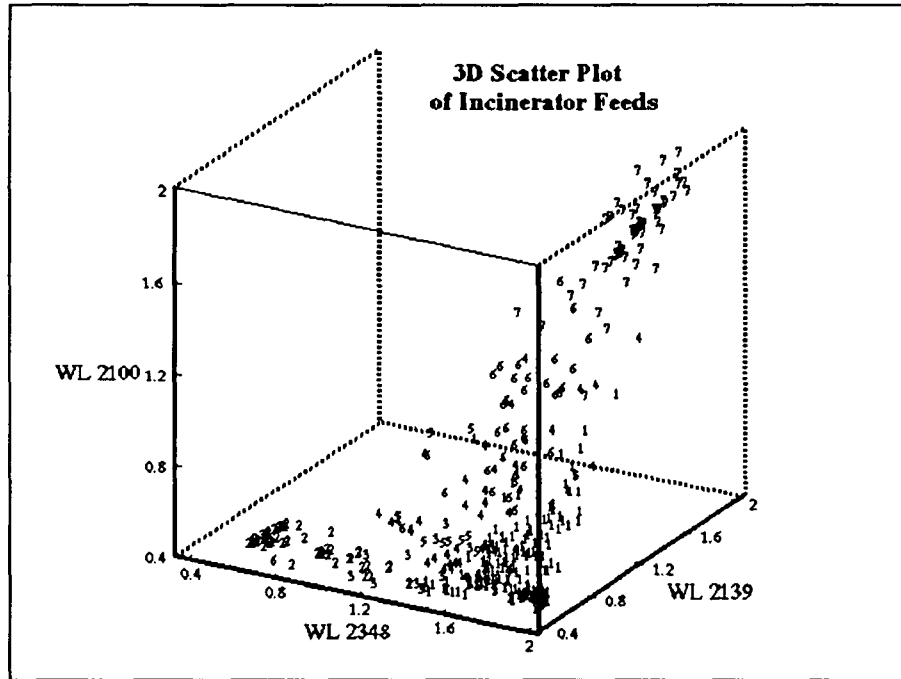

Figure 3: 3-Dimensional scatter plot of wavelength 2100 vs wavelength 2348 and wavelength 2139. See Table I for explanation of legends

The mathematical model for the Mahalanobis distance pattern recognition consists of two matrices: the group-mean matrix and the inversed pooled variance-covariance matrix. Using the model, the Mahalanobis distances between groups were calculated for the training set data from which the model was developed. In addition, greater the Mahalanobis distance between groups, the greater the difference in their patterns. The results for Mahalanobis distances between groups are summarized in Table II. According to Table II, only group 1 and group 4 are close to each other, suggesting a similarity in spectral patterns between them.

Table II: Mahalanobis distances between groups used in the training set

		Group 2	Group 3	Group 4	Group 5	Group 6	Group 7
	Group 1	5.2952	7.1974	3.2439	6.2445	6.1238	7.3523
	Group 2		5.8535	4.9845	5.4749	7.7708	8.4692
from	Group 3			9.0612	7.5224	11.6443	9.7214
	Group 4				5.5473	5.0761	7.6695
	Group 5					10.2863	10.2894
	Group 6						6.1324

Multilinear Regression Analysis

Regressions were performed on the absorbance data (log 1/R) without any prior data pretreatment. Individual models, and the corresponding regression coefficients, were developed and evaluated to achieve maximum inference from the regression analysis. Three types of calibration curves for three groups of liquid incinerator feeds; type 1, type 2 and type 4, have been developed for heat of combustion and water content determination. These three groups comprise about 73% of liquid incinerator feeds analyzed by this technique. Table III summarizes the regression statistics on each constituent for the three incinerator feed types.

Table III: Regression statistics for heat of combustion and water content equations

	F ratio	Corr Coef	SEE (%)	SEP (%)	Range*
Type 1 BTU	295.479	0.968	0.645	0.730	11,000-20,000
H_2O	40.517	0.821	2.229	2.301	0.1-10.0
Type 2 BTU	162.045	0.950	0.575	0.589	5,000-11,000
H_2O	25.431	0.768	0.345	0.398	0.1-1.0
Type 4 BTU	23.735	0.861	1.421	1.436	9,000-18,000
H_2O	31.462	0.890	0.916	0.932	0.1-10

* Range for BTU is BTU/lb and % moisture for water content

In general, the regression statistics given in Table III are used to evaluate the validity of the regression model. The F-ratio for regression is a quality measure for the regression that puts an overall goodness of the regression into one number. A high value of "F" is indicative of a good fit obtained from many samples with a small number of wavelengths. These kinds of calibrations will be more robust against small variations and time. The multiple correlation coefficient is a measure of error versus total variation and should tend to unity. For a given range, the standard of error of estimate (SEE) and standard error of prediction (SEP) evaluates the calibration and the prediction model and should be as small as possible.

Besides evaluating the regression statistics given in Table III, the residuals must also be examined to evaluate the adequacy of the regression model. Figure 4 is a plot of NIR predicted heat of combustion (BTU/lb) values against the actual heat of combustion values obtained using bomb calorimetry procedure for type 1 incinerator feeds. All sample informations on lack of fit is contained in the residuals.
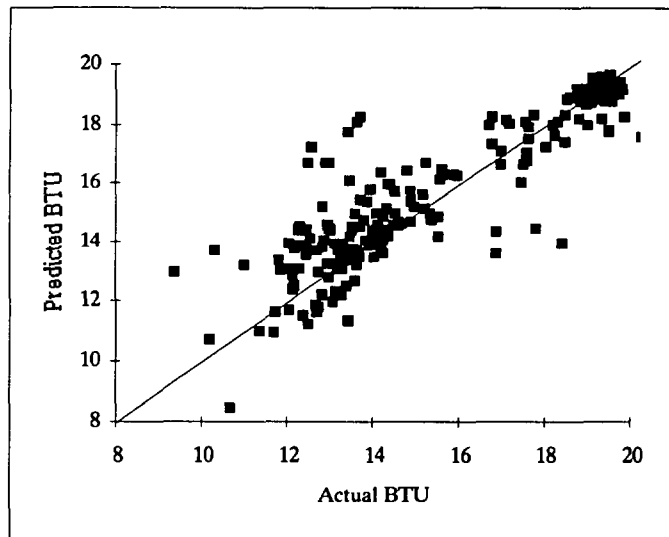
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Figure 4: Plot of NIR predicted BTU versus actual BTU from Bomb Calorimetry

If the regression model is valid, the residuals are the estimates of the model error, which are assumed to have a normal distribution around the mean (μ = 0) and constant variance. Figure 5 is a plot of residuals against the predicted BTU values for type 1 feeds. According to Figure 5, the residual plot for type 1 feeds has a mean equal to zero and a constant variance, suggesting the robust nature of the calibration curve. Residual plots were also evaluated for type 2 and type 4 feeds before using the calibration models to predict the heat of combustion and the water contents of incinerator feeds.
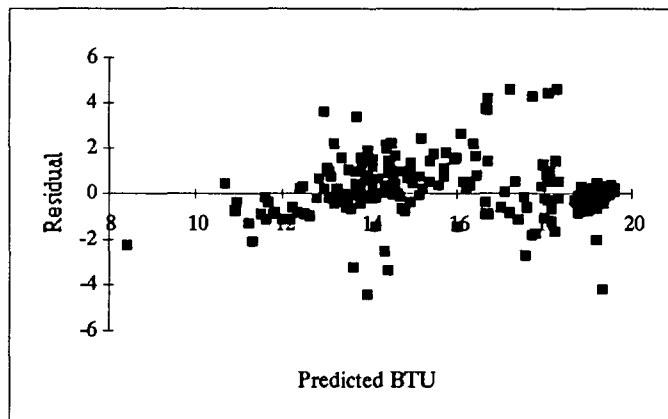

Figure 5: Plot of residuals versus predicted BTU for type 1 incinerator feed

QA/QC Procedure

Instrument performance parameters must be evaluated on a daily basis to demonstrate that the instrument is performing properly. Two instrument diagnostic checks and one instrument performance standard were developed for QA/QC procedure. The two instrument diagnostic checks are checking for the front end board of the instrument and the amount of light energy passing through the filters.

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Kerosene was chosen as the instrument performance standard because of its consistency and wide use in bomb calorimetry procedure.

In addition to the instrument reliability, the method must also be proved reliable. Method performance is monitored throughout the day by using a quality control (QC) check sample. A QC check sample is a material which represents the sample matrix being analyzed. Sample duplicate and fortified samples are used to measure the precision and accuracy of the method.

CONCLUSIONS

NIR technology can be used for analyzing incinerator feeds for heat of combustion and water content. About 73% of the incinerator feeds have been successfully analyzed by the NIR technology. Additional calibration curves will increase the percent of samples analyzed as the database is expanded. The elimination of conventional bomb calorimeter and Karl Fischer titration for sample preparation drastically reduces the analytical costs by streamlining sample analyses. The runtime of two minutes per analysis entails an 80% cost savings.

REFERENCES

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2. Shah, N.K.; Gemperline, P.J.; *Anal Chem.*, **1990**, 62, 465-470.
3. Mark, H.L.; Tunnell, D.; *Anal. Chem.*, **1985**, 57, 1449-1456.
4. Johnson, R.A.; Wichern, D.W.; *Applied Multivariate Statistical Analysis*, Prentice Hall: NJ, **1988**, pp 300-314.

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SOURCE SAMPLING AND ANALYSIS GUIDANCE
A METHODS DIRECTORY[1]

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ABSTRACT

Sampling and analytical methodologies are needed by EPA and industry for testing stationary sources for specific organic compounds such as those listed under the Resource Conservation and Recovery Act (RCRA) Appendix VIII and Appendix IX and the Clean Air Act of 1990.

A computerized directory, Problem POHC Reference Directory, has been developed that supplies information on available field sampling and analytical methodology for each compound in those lists. Existing EPA methods are referenced if applicable, along with their validation status. At the present, the data base is strongly oriented toward combustion sources. The base may be searched on the basis of several parameters including name, Chemical Abstracts Service (CAS) number, physical properties, thermal stability, combustion rank, or general problem areas in sampling or analysis. The methods directory is menu driven and requires no programming ability; however, some familiarity wit dBASE III+ would be helpful.

INTRODUCTION

There are a large number of chemical compounds listed under Appendix VIII[1] and Appendix IX[2] of RCRA and the Clean Air Act of 1990[3], that are regulated by the U.S. Environmental Protection Agency (EPA). EPA has several sampling and analytical methods which are validated for many of these compounds. Other of the listed compounds may be analyzed by these methods but they have not been validated. EPA or State permit writers and industry personnel may not be familiar with each compound and its status; therefore, a data base of each compound listed along with its methodology, has been prepared. If the methodology has been validated for a compound, a reference is given; however, if no method has been validated,

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1. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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the best method to try is indicated. Since the data base was originally developed for use with incinerators, it has an orientation towards combustion methodology.

COMPUTER AND SOFTWARE REQUIREMENTS

An IBM PC or compatible system with a hard disk using DOS 2.0 or higher is required. Version 1.0 of our program requires have dBASE III+ in order to run and is available from the National Technical Information Service (NTIS) under the name "Problem POHC Reference Directory"[6]. This version contains only the compounds listed under RCRA in Appendix VIII. Version 2.0 will also include the compounds listed under Appendix IX and the Clean Air Act of 1990, and it is scheduled to be released shortly. It will be titled "Source Sampling and Analysis Guidance, Version 2.0" and will be available from NTIS. We plan to have Version 2.0 in the compiled format; therefore, this version of our program will not need a data base program such as dBASE III+ or IV in order to run.

DATA BASE CONTENTS

The following information for each compound is given if available: (1) name of compound (The Appendix VIII name is given first with either the Appendix IX or the Clean Air Act name given next. If a common name that had not been used is known, then it is given also.),(2) the CAS registry number, (3) chemical formula, (4) molecular weight, (5) compound class, (6) University of Dayton Research Institute (UDRI) thermal stability class and ranking[4], (7) heat of combustion, (8) combustion ranking[5], (9) boiling, melting and flash points and water solubility, (10) information on toxicity, (11) sampling and analysis methods, (12) validation status of the compound in the methods, (13) general and specific problems, (14) a description of the problems, and (15) solutions (if known). The data in the base is not complete by any means and is constantly being revised. Yearly updates are planned.

RUNNING THE PROGRAM

The first screen seen after opening the program is the main menu shown in Figure 1.

Selection of an option will start a new sequence. Selection of option 1 will print the entire data base (warning: This will take about 1.5 - 2 hours.). This option will probably be used only once to provide a complete hardcopy of everything in the data base; additional copies can be photocopied. Selection of option 4 will print a list of all the compounds with their CAS numbers and data base record number. This is a very useful tool to have available since the data base record number is

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needed when using option number 2.

Figure 1. Opening Screen

MAIN MENU

    1. PRINT ALL RECORDS IN DATABASE
    2. PRINT A SPECIFIC DATABASE RECORD
    3. LIST COMPOUNDS BY PHYSICAL PROPERTY,
       THERMAL STABILITY, OR COMBUSTION RANK
    4. LIST COMPOUNDS BY NAME AND/OR CAS REGISTRY NUMBER
    5. LIST COMPOUNDS BY PROBLEM AREAS
    6. EXIT

ENTER YOUR CHOICE (1-6) FOR THE ABOVE:

Using selection number 2 will bring up the Records Menu
(Figure 2).

Figure 2. Records Menu

    PRINT A SPECIFIED DATABASE RECORD.
    SPECIFY THE RECORD TO BE PRINTED BY:

    1. RECORD NUMBER
    2. COMPOUND NAME
    3. CAS REGISTRY NUMBER
         OR
    4. EXIT TO MAIN MENU

ENTER YOUR CHOICE (1-4) FOR THE ABOVE:

Upon the entry of choice 1, 2, or 3, the question "DO YOU WANT
A HARD COPY OF THE DATA? (Y/N)" will appear. Selection "yes"
will create a printed copy, whereas a "no" answer will only
bring the data on screen. The search routine is such that the
record number is the fastest way to locate an entry; however,
if you do not know the data base record number, you may search
by either the name of the compound or its CAS Registry Number.
The Records Menu will probably be the most used menu since it
provides the complete information on a given compound.

Selection of the third option on the Main Menu brings up the
Specific Compounds Menu (Figure 3).

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Figure 3. Specific Compounds Menu

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          LIST COMPOUNDS ON THE BASIS OF:

          1.  UDRI THERMAL STABILITY CLASS
          2.  UDRI THERMAL STABILITY RANKING
          3.  MOLECULAR WEIGHT
          4.  BOILING POINT
          5.  MELTING POINT
          6.  COMBUSTION RANK

          7.  COMBINATION OF ANY TWO PROPERTIES.

          8.  RETURN TO MAIN MENU

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```

After selecting any of options 1-6, the user will be prompted to input a range for that option before again asking if he wants a hard copy. Selection of number 7 will result in a request for the two properties and the range for each property. This search and listing option can be particularly helpful in Principal Organic Hazardous Constituent (POHC) selection for trial burns, since compounds can be listed by incinerability category and by physical properties.

The fourth selection on the Main Menu (Figure 1) will provide an alphabetical list of the compounds with the data base number. This provides you with the easiest method of searching with option number 1 of the Records Menu (Figure 2).

The Problem Menu (Figure 4) is selected from option 5 of the Main Menu.

Figure 4. Problem Menu

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          1.  LIST ALL PROBLEM COMPOUNDS
          2.  LIST COMPOUNDS BY GENERAL PROBLEM
          3.  LIST COMPOUNDS BY SPECIFIC PROBLEM

          4.  RETURN TO MAIN MENU

       ENTER YOUR CHOICE (1-4) FOR THE ABOVE:

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The first option will list every compound that is recorded to

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have any problem. The second choice brings up the screen shown in Figure 5.

Figure 5. General Problem Types

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      1. ANALYSIS
      2. HAZARDOUS
      3. SAMPLING

    SPECIFY GENERAL PROBLEM TYPE (1, 2, OR 3):

A selection here will list all problem compounds in the area selected. The third choice on the Problem Menu probably is the most useful one since it allows a more limited selection. The menu which goes with the third choice is shown in Figure 6.

Figure 6. Specific Problem Types

GENERAL PROBLEM   SPECIFIC PROBLEMS

1. ANALYSIS   A. CHROMATOGRAPHY E. SENSITIVITY
                    B. INTERFERENCE   F. RECOVERY
                    C. WATER SOLUBLE   G. DECOMPOSITION
                    D. BLANK

2. HAZARDOUS   A. CORROSIVE
                    B. EXPLOSIVE
                    C. INCOMPATIBILITY
                    D. TOXIC

3. SAMPLING   A. BLANK
                    B. BREAKTHROUGH
                    C. DECOMPOSITION
                    D. REACTIVE

SPECIFIED GENERAL PROBLEM TYPE (1,2, OR 3):

After the user selects the general type from the Specific Problem Types menu, then the program prompts the user to select a specific problem type from the selections on the right.

Samples of printouts of individual compounds showing the actual information available are presented in Figures 7 and 8. On Figure 7, points of interest are that hexachlorobenzene is listed on both Appendix VIII and the Clean Air act of 1990 but not on Appendix IX. It has a UDRI class and ranking. Only compounds listed on Appendix VIII have UDRI ratings at the present time. The record also indicates that we have several areas not filled in yet. The data base is not complete, and data will be added as we become aware of it. The sampling and analytical methods for this compound are listed as suggestions since they have not been validated. The heat of combustion is listed for help in determining which compounds in a waste mixture should be selected as POHCs. Figure 8 shows a fully documented compound, benzene. The sampling and analytical methods have been validated, and the references are given. The specific problem type is a blank problem, and suggestions are given on how to overcome this problem.

SUMMARY

A data base program listing sampling and analysis methods along with several characteristics of each compound listed under RCRA Appendix VIII, is available for use with dBASE III+. The data base permits those personnel who need field sampling and analytical procedures for regulation purposes to have a single reference for this information. A second version covering RCRA Appendix VIII, Appendix IX, and Clean Air Act 1990 compounds will be available in late 1991. The second version will be a compiled program, which will not require any additional software (ie dBASE III+ or IV) to operate.

REFERENCES

1.   Code of Federal Regulations, 40, Part 261, Appendix VIII, p 90-98, July 1, 1990.

2.   Code of Federal Regulations, 40, Part 261, Appendix IX, p 98-117, July 1, 1990.

3.   Clean Air Act, Title III, Public Law 101-549, 1990.

4.   Guidance on Setting Permit Conditions and Reporting Trial Burn Results. Volume II of the Hazardous Waste Incineration Guidance Series p 105-123, EPA-625/6-89/019, January 1989.

5.   Guidance Manual for Hazardous Waste Incinerator Permits, Mitre Corp., NTIS PB84-100577, July 1983.

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6.   Baughman, K.W., R.H. James, R.B. Spafford and C.H. Duffey, Problem POHC Reference Directory, EPA-600/3-90/094, January 1991.

Figure 7. Data Output for Hexachlorobenzene

RECORD NUMBER: 361   DATE OF LATEST ENTRY: 04/10/91

COMPOUND: Hexachlorobenzene

CAS REGISTRY NO: 118-74-1
FORMULA: C6-(Cl)6
MOLECULAR WEIGHT: 284.80
COMPOUND CLASS: Chlorinated aromatic
APPENDIX 8? Y   APPENDIX 9?   N   CLEAN AIR ACT OF 1990?   Y

UDRI THERMAL STABILITY CLASS: 1
UDRI THERMAL STABILITY RANKING: 31

BOILING POINT, CELSIUS: 323
MELTING POINT, CELSIUS: 231
FLASH POINT, CELSIUS:
SOLUBILITY, IN WATER: Insol 0.035 ppm

HEAT OF COMBUSTION, KCAL/MOLE: 567.70
COMBUSTION RANKING: 65

TOXICITY DATA:

SAMPLING METHOD: SW-846 No. 0010 (MM5)

ANALYSIS METHOD:
SW-846 No. 8270 (Extraction, GC/MS)

VALIDATION STATUS:

GENERAL PROBLEM TYPE(S):

SPECIFIC PROBLEM TYPE(S):

DESCRIPTION OF PROBLEMS:

SOLUTIONS:

Figure 8.   Data Output for Benzene

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RECORD NUMBER:          77          DATE OF LATEST ENTRY:    12/13/90

COMPOUND:   Benzene


CAS REGISTRY NO:    71-43-2
FORMULA:    C6-H6
MOLECULAR WEIGHT:       78.11
COMPOUND CLASS:     Aromatic hydrocarbon
APPENDIX 8?  Y          APPENDIX 9?    Y       CLEAN AIR ACT OF 1990?    Y

UDRI THERMAL STABILITY CLASS:    1
UDRI THERMAL STABILITY RANKING:       3

BOILING POINT, CELSIUS:    80.1
MELTING POINT, CELSIUS:    5.5
FLASH POINT, CELSIUS:      -11.00
SOLUBILITY, IN WATER:    Sol

HEAT OF COMBUSTION, KCAL/MOLE:         780.96
COMBUSTION RANKING:       47

TOXICITY DATA:   Cancer suspect agent; flammable liquid

SAMPLING METHOD:    SW-846 No. 0030 (VOST)

ANALYSIS METHOD:
SW-846 No. 5040 or Draft No. 5041(Therm. Desorb./P and Trap-GC\MS)

VALIDATION STATUS:
The VOST method has been validated for this compound (See "Validation
Studies of the Protocol for the VOST" JAPCA Vol. 37 No. 4 388-394, 1987).
(Also see "Recovery of POHCs and PICs from a VOST" EPA-600/7-86-025.)

GENERAL PROBLEM TYPE(S):    Sampling

SPECIFIC PROBLEM TYPE(S):   Blank

DESCRIPTION OF PROBLEMS:
Cancer suspect.
Blank problem with Tenax
Benzene is a common PIC.  This may complicate interpretation of results,
and make it difficult to achieve acceptable DRE with low waste feed
concentrations.

SOLUTIONS:
Level of lab blank should be determined in advance.  Calculations should
be based on waste feed concentration to determine if blank level will be
a significant problem.  Benzene should not be chosen as a POHC at very low
waste feed levels because it is likely to make blank or PIC problem
significant.

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A FIELD INVESTIGATION OF GROUNDWATER MONITORING WELL PURGING TECHNIQUES

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ABSTRACT

A field investigation of commonly used monitoring well purging techniques was conducted under different conditions including type of pump, pump inlet location, and the use of packers. Tracers including deionized water, fluorescent dye, and lithium chloride were used to define the amount of stagnant water at any given time in the pump discharge. Tests were conducted in shallow 5 cm (2 in) diameter wells. The effects of drawdown were examined.

All runs conducted in the absence of drawdown with the pump inlet in a fixed position at or above the screen showed a highly variable and unpredictable inclusion of stagnant water. The use of packers did not completely prevent the inclusion of stagnant water into the pump inlet. The inclusion of stagnant water into a sample was minimized by purging from some distance above the screen followed by relocation of the pump inlet into the screen for sample collection. In wells where drawdown occurred during purging, stagnant water inclusion was minimized by reduced pumping rates to allow for sample collection during periods of well recharge. Real time monitoring of indicator parameters such as pH, temperature and specific conductance was not generally successful in indicating when purging was complete.

MONITORING WELL PURGING

It is generally recognized that the composition of the stagnant water within a monitoring well above the screened section is probably not representative of the overall groundwater quality at the sampling site. The water standing in the well casing is commonly referred to as being stagnant, that is, the water has been isolated from the aquifer at least since the last time the well was sampled. During that time, the chemical quality of the stagnant water may have changed by (a) direct introduction of foreign material into the well, (b) interactions with the well casing or at the interface with the atmosphere, or (c) biological activity. Even without such alterations, the stagnant water would not reflect any changes in the groundwater quality that may have occurred since the last time the well was sampled. Because the investigator cannot be certain which, if any, of these influences has occurred or whether inclusion of some of the stagnant water in a sample from the well would significantly change the conclu-

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sions that might be drawn from the data, the safe thing to do is to prevent or minimize such inclusion.

One presently used purging technique presented as a cooperative agreement by the Illinois States Water Survey (ISWS) and Illinois State Geological Survey (ISGS) (1) is to pump the well and calculate the percentage of water at any given time in a pump discharge that can be attributed to drawdown. This approach is based on the knowledge of time-drawdown characteristics of a well and does not account for contributions of stagnant water from any source other than drawdown. Another commonly used purging technique presented by the U.S. Geological Survey (USGS) (2) is to pump a well until indicator parameters such as pH, temperature, and conductivity stabilize. This approach ignores the possibility that a near constant contribution of stagnant water into the sample may result in stabilized readings for the observed parameters. It also fails to account for contributions of stagnant water that are too small to notably affect the measured parameters, but which may significantly alter the outcome of an analysis. Probably, the most commonly used purging practice is to purge an arbitrary number of bore volumes (well casing) with little or no regard to drawdown or indicator parameters.

This research reflects the need for documentary evidence regarding the hydraulic behavior of a monitoring well during purging. By examining truly trace concentrations, the fraction of stagnant water entering a pump inlet can be better defined as a function of bore volumes pumped (or time) and inlet position.

CRITICAL REVIEW OF EXISTING INFORMATION ON MONITORING WELL PURGING

Illinois State Water Survey and Illinois State Geological Survey

ISWS and ISGS have published "Procedures for the Collection of Representative Water Quality Data From Monitoring Wells" (1) which describes in detail guidelines for monitoring well purging. The basic assumption made in this research was that during the initial pumping of a small diameter monitoring well, a significant fraction of the pump discharge comes from stagnant water within the well casing. This effect is due to drawdown. The procedure uses an equation which develops time-drawdown data based on individual monitoring well hydrologic data obtained during pump tests. The resulting theoretical drawdown curve is used to predict the time at which the effects of casing storage due to drawdown become negligible. This curve is intended to be used as a guideline, in conjunction with the observation of indicator parameters for the selection of an appropriate pumping rate and number of bore volumes to be pumped prior to sample

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collection.

Six monitoring wells at different locations within the State
of Illinois were used for the development of this purging
protocol. NCASI encountered several difficulties while
reviewing the results of the study on these six wells. These
difficulties included (a) reproduction of the theoretical
drawdown curves presented, and (b) interpretation and conclu-
sions drawn from the monitored indicator parameters. NCASI
and others have been unable to reproduce any of the published
theoretical drawdown curves for six wells examined by ISWS and
ISGS. For each well, ISWS and ISGS have provided theoretical
drawdown curves derived from the Papadopulos and Cooper
equations which generally show good agreement with the actual
drawdown curves presented. NCASI has used these equations in
the manner described by ISWS and ISGS to produce theoretical
drawdown curves which bear little resemblance to those
published. A careful examination by NCASI has not revealed
the reason for these discrepancies.

The cooperative agreement examined the effects of well purging
on the chemical composition for six monitoring wells. Five of
the six wells were described as having site specific limita-
tions which hindered interpretation of the results. The
single well (Site 5), in which a clearly indicated effect of
purging on indicator parameters was noted, directly contra-
dicted information from the pump test portion of the study.
In spite of limitations described for each of the six sites
examined, ISWS and ISGS concluded that "the chemical data from
this portion of the study have verified the theoretical ratios
of aquifer to stored water predicted during the pump tests".
A subsequent publication by the ISWS "Practical Guide For
Ground-Water Sampling (3) has endorsed the above mentioned
purging protocol.

United States Geological Survey The United States Geological
Survey (USGS) (2) states that in order to obtain a representa-
tive sample from an aquifer at a given location, a well must
be pumped until indicator parameters such as pH, temperature,
and conductivity are constant. Measurement of drawdown during
the purging period is recommended because changes in the indi-
cator parameters may reflect water from different zones of the
aquifer being drawn into the well. This procedure is stated
as the minimum required precaution for insuring that a sample
adequately represents the water quality in the aquifer.

Guidelines for indicator parameter stability have been
presented by Gibs and Imbrigiotta (4). Research by Slawson
et al. (5) examined the variability of indicator parameters
and other constituents in well discharges during continuous
pumping. Appreciable changes were observed in several of the

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parameters, most notably conductivity. These changes were attributed to naturally occurring vertical and horizontal variability within the aquifer from natural influences. Such a situation would not allow for the universal use of indicator parameters to determine when a groundwater sample should be collected.

Consideration should also be given to the general nature of the specified indicator parameters. Conductivity and pH are may be affected by changes in temperature and pressure during sampling. Pressure changes can cause rapid degassing of carbon dioxide and other gases that could affect sample pH and specific conductance.

<u>NCASI Laboratory Purging Investigations</u> NCASI conducted a laboratory investigation to examine factors other than drawdown that could cause stagnant water to enter a pump inlet (6). All tests were conducted at constant head, thereby disregarding the effects of drawdown. In the research, stagnant water in a well column was spiked with a fluorescent dye. Care was taken to minimize density differences induced by either temperature gradients between stagnant and aquifer water or concentration induced density gradients. The well was then sampled with the pump inlet in various positions while the tracer concentration in the pump effluent was continuously monitored. Results demonstrated that an average of about 2 to 4 percent of the water pumped from locations above the screen and an average of about 1 percent of the water pumped from within the screen of the monitoring well came from the stagnant water located above the pump inlet. The mechanism that caused the overlying stagnant water to reach the pump inlet was not investigated, though mixing caused by turbulence around the pump inlet was hypothesized.

<u>University of Waterloo</u> Robin and Gillham (7) conducted a study using non-reactive tracers to judge the effectiveness of various purging procedures. The results suggest a sharp interface and little mixing between fresh water in the screen or below a pump inlet and the stagnant water in the casing. For wells not completely evacuated, pumping from immediately beneath the air/water interface for 2 or 3 bore volumes was deemed sufficient to collect a representative sample. Three tracers were used for the study: deionized water, NaCl (conductivity), and bromide. Of these, NaCl was demonstrated to be an inappropriate tracer due to mixing caused by density differences between the tracer and the fresh water. While deionized water was determined to be an appropriate tracer (verified with bromide) an even greater density difference existed between deionized water and the natural groundwater at the site. Although the deionized water was less dense than the groundwater, the effect of this density difference may

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have acted to discourage mixing around the pump inlet.

EXPERIMENTAL PROCEDURE

Wells

Two shallow monitoring wells were selected for this research. Both wells were constructed of 5-cm ID PVC (2-in) with commercially available PVC screened sections (Timco 0.010 slot). Both wells are situated in a shallow glacial unconfined aquifer composed of sand and clay. Each well is approximately 9.2 m (30 ft) deep and has a standing water level within 1.5 m (5 ft) of the ground surface. Although these wells were only approximately 62 m (200 ft) apart, local variability within the aquifer accounted for marked difference in the hydraulic performance of each well. At the purging rates used in this research, one well experienced very minimal drawdown (less than 0.6 cm, 0.25 in), and the other well experienced extreme drawdown and could easily be pumped dry.

Equipment

Two pumps were used for purging in this research. The majority of the purging runs were conducted using an above ground peristaltic pump (Masterflex, #70-15 head) with a maximum flow rate of approximately 800 ml/min. Several runs were conducted with a submersible pump (Keck #84) with a flow rate of approximately 4.5 L/min.

The fluorescent tracer concentration in the purging pump discharge was detected with a fluorometer (Turner #111) with a flow-through cell for continuous measurement. Conductivity, drawdown, temperature, and pH were monitored continuously using methods described elsewhere (7). Drawdown was monitored with a submersible pressure transducer. All data from the instruments with the exception of pH were recorded on a portable computer. Values for pH were recorded manually due to pH signal recording difficulties. A portable electric generator provided electrical power where needed.

The amount of stagnant water in the pump discharge at any given time was measured directly by the use of one or more of the following tracers: Rhodamine WT, lithium (as lithium chloride), or deionized water. Rhodamine WT was used as the tracer of choice during this research. Rhodamine WT is a non-toxic fluorescent xanthene dye commonly used in percolation studies, potable water systems, and surface water systems. Additionally, Rhodamine WT exhibits both low reactivity and sorption tendencies (8) making it well suited for this research. The initial concentration after the dye had been added

to the stagnant water was approximately 200 ppb. At this concentration in water, the dye imparts no color detectable with the naked eye. In several of the purging tests in the well in which drawdown occurred, the presence of turbidity interfered with the detection of the fluorescent dye. In this situation, lithium was used as the tracer. For several of the tests, deionized water was used as a tracer in conjunction with Rhodamine WT.

General Procedures

At the start of each purging test, the static water level was measured. Tracer was added to the stagnant water in the well in a manner that resulted in a homogeneous concentration within the stagnant water column, without migration into the screen area. To accomplish this, an inflatable packer was used to hydraulically isolate the screened portion of the well from the cased portion above. The packer was designed as a flow-through device so that water could be collected from the screen area during the time the packer was inflated and in position.

The stagnant water above the packer was pumped out and collected in a container at the surface. Aquifer water from the screen area was pumped to the surface at the planned purging rate in order to zero the fluorometer and obtain background readings for pH, conductivity and temperature. With the fluorometer zeroed for the aquifer water, the previously collected storage water was pumped through the fluorometer in a closed loop system. Tracer was added to the casing water until the fluorometer readout was 100 percent. This casing water containing the tracer was poured back into the well to a water level slightly below the static water level so that the volume displaced by the packer would be replaced by aquifer water moving into the screened section rather than by spiked water moving down into the screened section when the packer was removed.

The stagnant water containing the tracer was kept isolated from the screened section with the inflated packer for a minimum of 12 hours to ensure that the undisturbed temperature-depth profile of the stagnant water would be re-established. A preliminary investigation of the wells used for this research, revealed that the temperature-depth profile determined after a month of non-pumping, would be re-established approximately 8 hours after having been disturbed.

A run was initiated by slowly deflating the packer and carefully removing it from the well. The pump inlet was placed at a predetermined depth for the run. Pumping and automated data collection were started. Fluorometry readings

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were recorded every two seconds, other readings except pH were recorded every five seconds. Readings for pH were recorded every 105 seconds. The computer and software allowed for real-time observation of data throughout the purging run.

At the end of a test, the pump inlet was raised to the air/water interface while pumping continued until the fluorometer readings returned to background. At this point new tracer could be added for the next run.

For the runs where it was applicable, the number of bore volumes pumped was based on the volume between the pump inlet (bottom of sample line) and the top of the well screen. For the runs where the pump inlet was placed immediately above the screen top, the duration of a run was measured in the number of liters pumped, rather than bore volumes. Because the measured tracer concentration in the aquifer water was zero for all runs, the fraction of the pumped volume that came from the stagnant zone above the pump inlet is simply the ratio of the measured concentration of tracer in the pumped water to the initial concentration in the stagnant zone.

Two packers were investigated to determine their effect on stagnant water concentration during purging and sampling. Such packers form a seal against the inside of the well casing to isolate the stagnant water above from the pump inlet. In effect, the volume of standing water above the pump inlet is reduced. One packer was a commercially available unit attached to the top of the Keck pump. The other packer was laboratory made and designed as a flow through device.

The effect of purging and sampling in a well experiencing a significant degree of drawdown was investigated. During drawdown, the balance of the water in the pump discharge not accounted by flow into the well from the screen comes from the stagnant casing water above the pump inlet. A sample was collected from such a well by purging the well at a rate great enough to produce drawdown and thus reducing the level of stagnant water. Sample collection occurred at a reduced flowrate during water level recovery. Purging and sampling in this manner allows the stagnant water/aquifer water interface to move upward and away from the pump inlet, reducing the chance for stagnant water to become captured by the pump inlet. As noted previously, due to excessive turbidity in this well, lithium chloride at an initial concentration of 62 mg/L was used as the tracer.

The following purging configurations were investigated during this research: (a) fixed pump inlet positions at approximately 5 cm (2 in) below the air/water interface, mid-casing, and at the top of the well screen, (b) a comparison of Rhodamine WT

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and deionized water as tracers with the pump inlet reposi-
tioned between the screen and the air/water interface several
times during the run, (c) purging from above the screen,
followed by sampling within the screen, (d) packers, (e)
drawdown and recover. Details specific to each test are given
in the section below.

RESULTS AND DISCUSSION

Drawdown did not become significant during the following tests
(maximum 0.6 cm, 0.25 in) at the specified purging rates.

Peristaltic Pump, Inlet Near Static Water Level

Figure 1 graphically presents the results of a purging test
with the pump inlet located approximately 5 cm (2 in) below
the static water level in the monitoring well. The purging
rate during this test was 1.01 L/min.

During most of the time required to remove the initial bore
volume of water from the well (14.3 minutes), the concentra-
tion of stagnant water in the pump inlet was 100 percent. As
the column of fresh water moving up the well casing approached
the pump inlet, there was a corresponding rapid decrease in
the stagnant water concentration detected in the pump dis-
charge. During the removal of subsequent bore volumes the
concentration of stagnant water continued to decrease but was
still detectable in the pump discharge for a relatively long
time (9.0 bore volumes, 128 minutes). At this point the
majority of the stagnant water had been removed from below the
pump inlet, however, it may not have been entirely removed
from above the pump inlet. Earlier research (9) using
visible dye concentrations in transparent well casings
provided evidence that the intermittent inclusion of stagnant
water detected in the pump discharge may have been related to
turbulence and subsequent mixing around the pump inlet. The
reason for the relatively small concentrations of stagnant
water detected at the end of the run is probably related to
the fairly small volume of stagnant water above the inlet,
(0.1L). This volume would most likely have been diluted by
mixing during the pumping of 9 bore volumes (130L). At 9 bore
volumes, the pump inlet was lowered into the screen area.
With the pump inlet located in this position, one bore volume
of water (14.4 liters) was collected without the detection of
stagnant water in the pump discharge. Figure 2 presents a
five minute expanded segment of Figure 1 between 4.0 to 4.3
bore volumes. It shows the intermittent nature of the
intrusion of stagnant water into the pump inlet. The bore
volume axis has been converted to time. While the contri-
bution of stagnant water is relatively small at this point, it
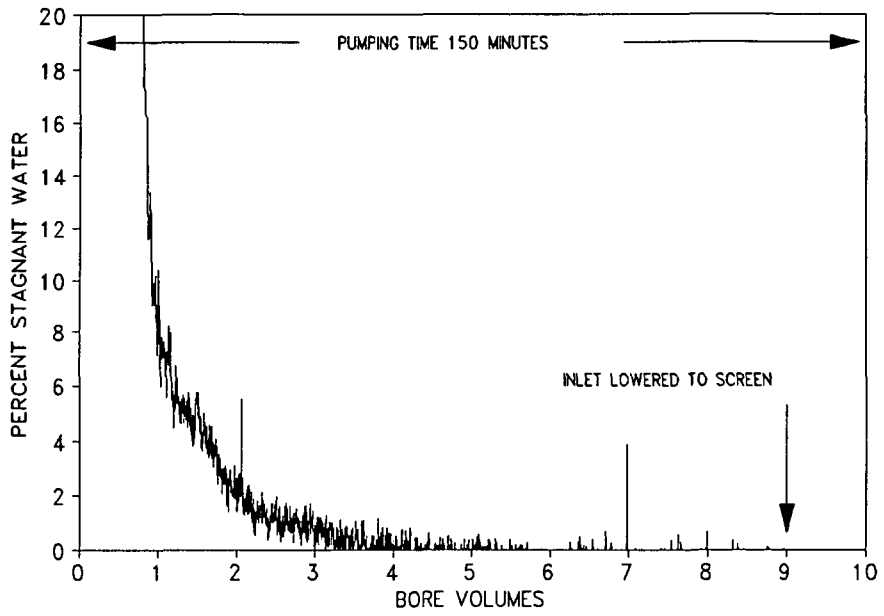is nonetheless measurable, and for intervals up to 30 seconds.
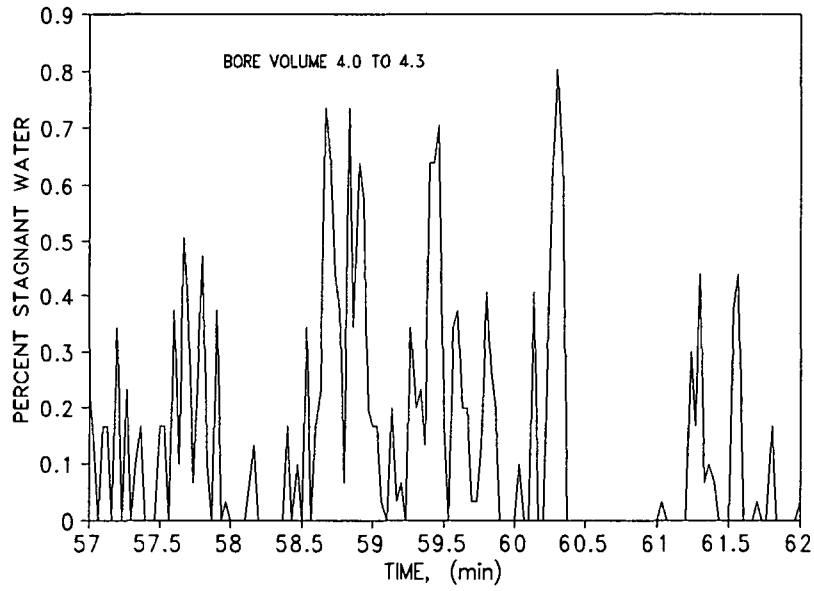
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Fig. 1- Inlet near static water level

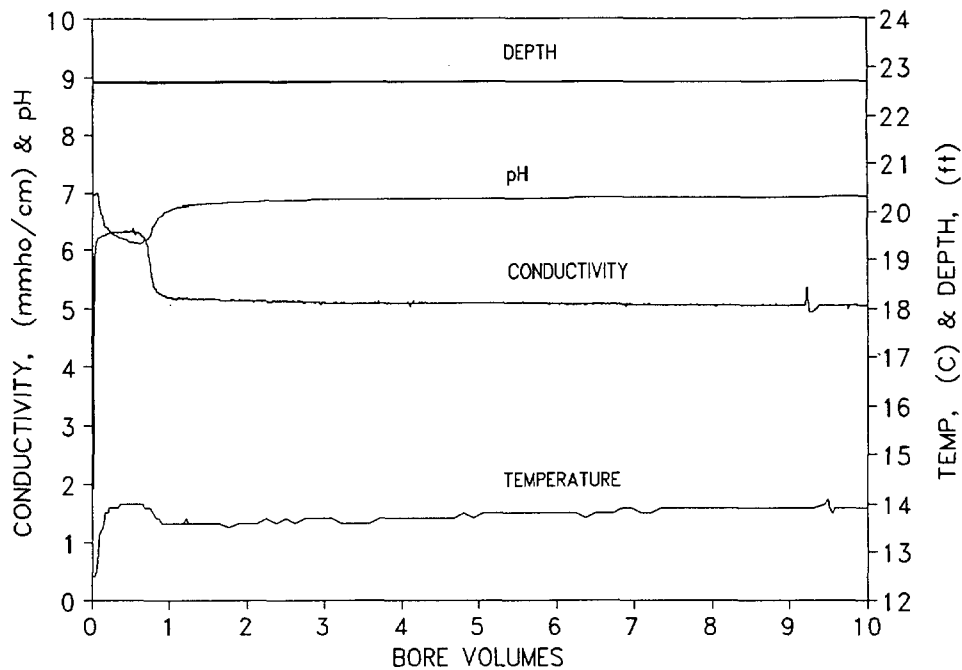**Fig. 2- Expanded view, bore volume 4.0 to 4.3**

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Fig. 3- Indicator parameters

One implication of this is that approximately 500ml of water could be collected as a groundwater sample over a 30 second time interval. Depending on the purpose for which the sample was being collected, inclusion of almost 1 percent stagnant water could be problematic.

As shown in Figure 3, temperature, pH, and conductivity during this run displayed an initial response during the removal of the first bore volume. However, they exhibited little or no change during the pumping of subsequent bore volumes. A visual inspection of these parameters between bore volumes 1 and 2 indicate little if any change, whereas the tracer concentration shown in Figure 1 indicates a stagnant water concentration decreasing between 11 and 2 percent. These parameters were too insensitive for the detection of trace concentrations of stagnant water in this run. An examination of these parameters for all of the other purging runs revealed similar results.

Peristaltic Pump, Inlet at Mid-casing

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Figure 4 displays the results of a purging test with the pump inlet located in the mid-casing position with equal amounts of
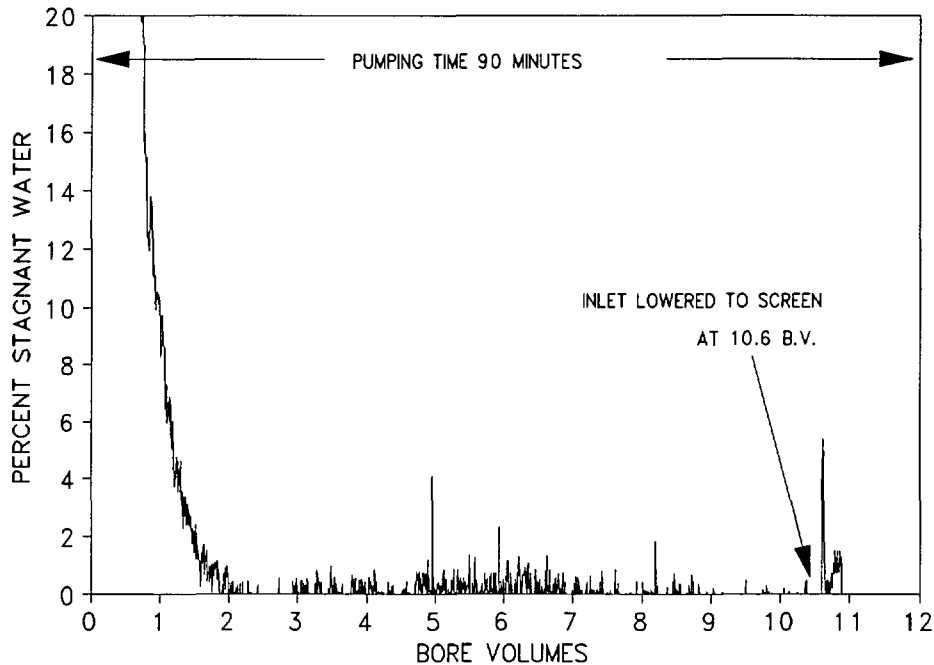

Fig. 4- Inlet at mid-casing

water above and below the inlet.   Examination of Figure 4 reveals results similar to the purging run displayed in Figure 1 in that the majority of the stagnant water below the pump inlet was removed with the initial bore volume of water. While the stagnant water concentration tapered off more slowly between bore volumes 2 and 4 with the inlet position located in the mid-bore position, the subsequent bore volumes pumped after the fourth bore volume appear to have elevated stagnant water concentrations when compared to the run displayed in Figure 1.

Peristaltic Pump, Inlet at Screen Top

Figure 5 displays the results of a purging run with the pump inlet situated immediately above the well screen.
Because there was no volume of storage water below the pump inlet, the lower x-axis in Figure 5 refers to the number of liters pumped.   The absence of storage water below the pump inlet is evidenced by the lack of an initial interval during
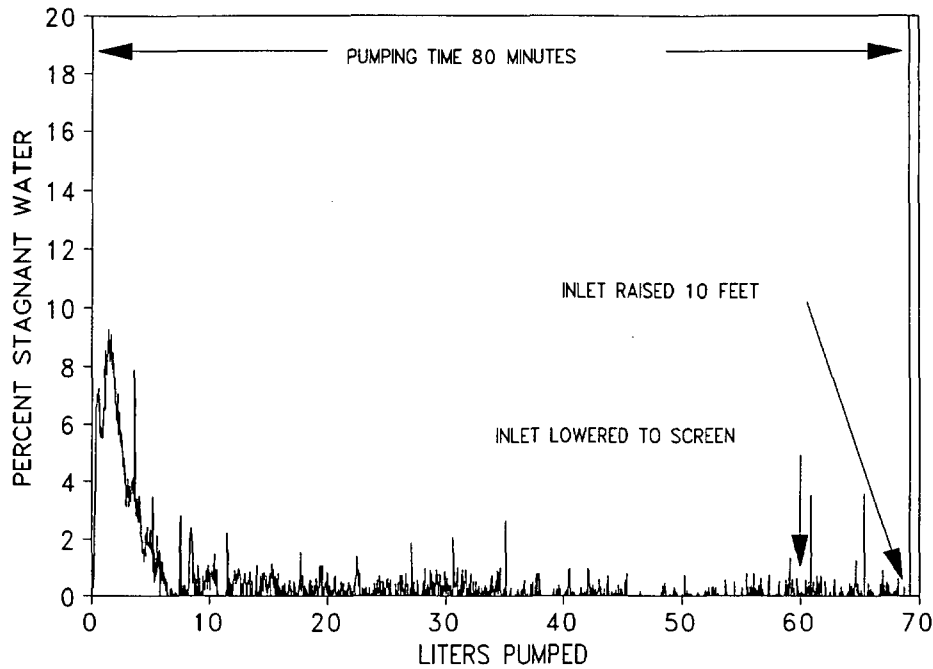
Fig. 5- Inlet at top of screen

which the pump discharge was 100 percent stagnant water. This indicates that the pump inlet was positioned at the stagnant water/fresh water interface. The results suggest that the stagnant water detected in the pump discharge during the 80 minute pumping period was caused by the stagnant water overlying the inlet mixing with the fresh water from the screen. At 60 minutes, the pump inlet was lowered 5 cm (2 in) to the top of the screen with little effect on the stagnant water concentration. At 69 minutes, the inlet was raised 3 m (10 ft) which increased the stagnant water concentration to 100 percent.

Source of Stagnant Water

The results of the preceding three purging trials suggest that the stagnant water detected in the pump discharge was from the dyed water overlying the pump inlet. The reasons are twofold. First, the concentration of stagnant water detected in the pump discharge was apparently affected by the volume of dye overlying the inlet. A mathematical average of the stagnant water concentration detected between the fifth and the sixth

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bore volumes was determined to be 0.026 percent, 0.199 percent, and 0.103 percent for Figures 1, 4, and 5 respectively (Fig.5 concentration determined by examining the data between 38 and 45 minutes, an interval equal to that selected for the concentration determined in Figure 4). One explanation for the average stagnant water concentration in Figure 1 being approximately one order of magnitude smaller than that of Figures 4 and 5 is the smaller volume of stagnant water (0.1L -vs- 7.2L and 14.4L) available for mixing above the pump inlet. The much smaller volume would have been diluted to a greater extent over a given time period, accounting for the smaller percentage of stagnant water in the pump discharge. Second, the results of the run displayed in Figure 5 verify that the pump inlet was positioned at the stagnant water/fresh water interface. The detection of stagnant water for the duration of the 80 minute run indicates that the tracer above the pump inlet was being captured.

Multiple Inlet Positions, Dual Tracers

In an attempt to repeat a purging test conducted by Robin and Gillham (6), deionized water was used as a tracer in addition to Rhodamine WT. During this purging test, varying inlet positions were used starting from the screen top. The purging rate was 1.1 L/min. The water above the screen was replaced with deionized water containing Rhodamine WT using the inflatable packer in the manner described previously. The well was pumped with the inlet immediately above the screen while the fluorescence and conductivity were being monitored. The well was pumped in this manner until the fluorescence approached zero. The inlet was then raised 1.2 m (4 ft) and pumping was continued at the new level until the fluorescence approached zero. This process was repeated several times until the air/water interface was reached.

The results of this test are presented in Figure 6. In general, the shapes of the curves obtained with the fluorescent dye are very similar to the initial portions of curves shown in Figures 1, 4, and 5 in that removal of the majority of the stagnant water below the inlet occurs fairly quickly. The curves from the deionized water conductivity measurements however, contradict those for the fluorescent dye. The deionized water tracer suggests background water quality was reached within a few minutes of each relocation of the pump inlet, whereas the curves from the fluorescent dye tracer still show stagnant water detectable in the percent range several minutes later. The pattern of response for each of the tracers was repeated each time the pump inlet was raised.

Deionized water may be too insensitive a tracer when used to differentiate water sources in a monitoring well. Conclusions

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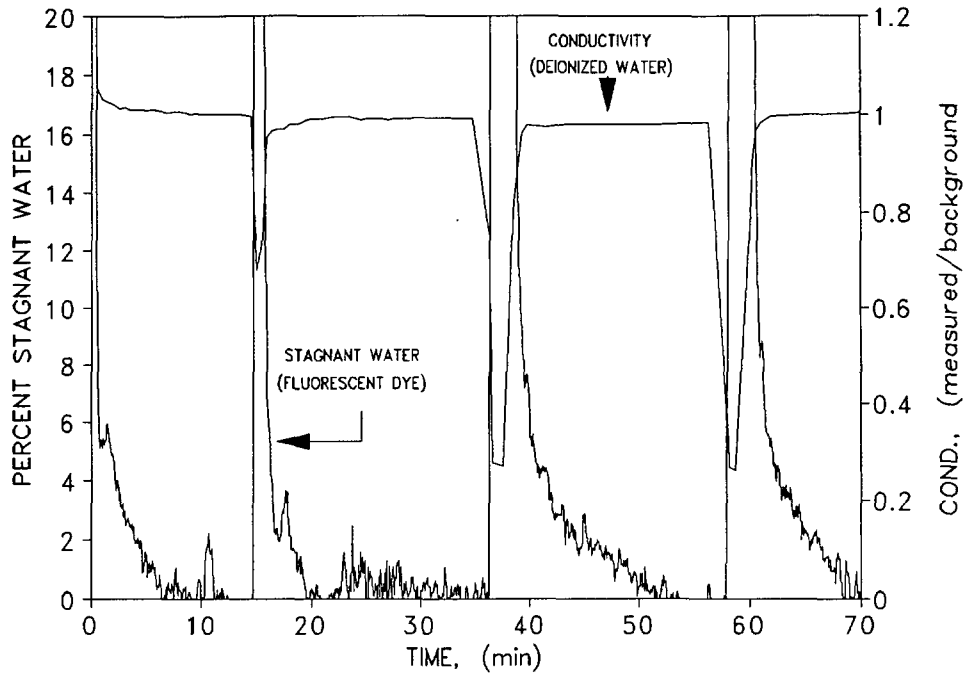
Fig. 6- Comparison of Rhodamine WT and deionized water as tracers

as to required purging volumes based on deionized water tracer tests may, therefore, be inappropriately low for many purposes.

Peristaltic Pump, Pump and Lower

Figure 7 displays the results of a purging test during which the pump inlet was initially positioned five feet above the screen for approximately five bore volumes (18.4L) and then repositioned into the screen for sample collection. The advantage of purging and sampling in this fashion is that the entire column of stagnant water need not be purged in order to collect a representative groundwater sample. This test was conducted in triplicate with similar curves observed for all three runs. During the removal of the initial five bore volumes of water a clean zone generally free of stagnant water was developed below the pump inlet. After apparently lowering the pump inlet, a minimum 40 liter pumping period followed, during which stagnant water was not detected in the discharge.
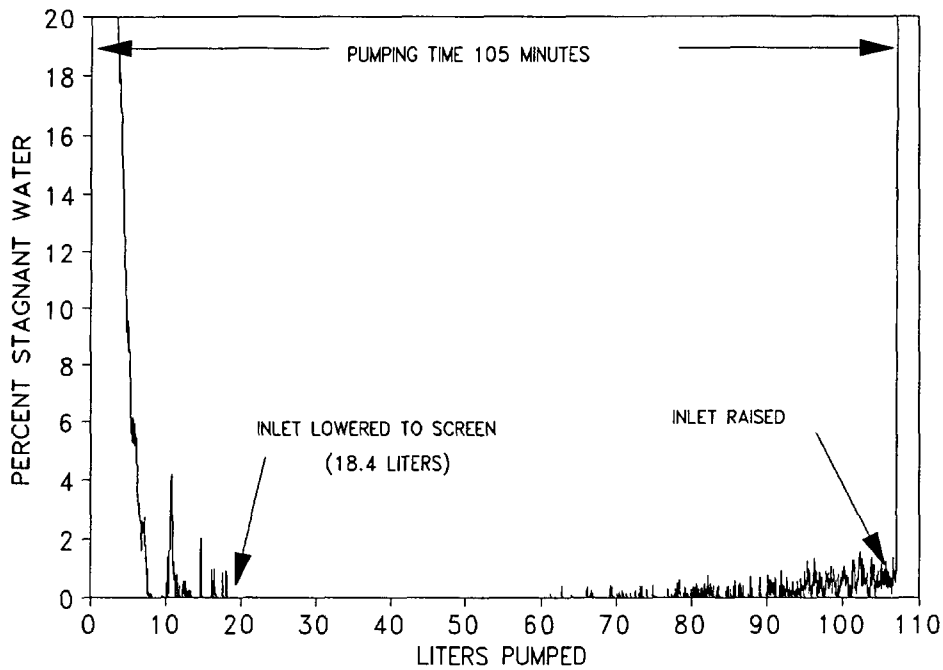
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Fig. 7- Pump and lower

Stagnant water was eventually detected in the pump discharge. This occurred while the pump inlet was still in the screen area meaning that the stagnant water had migrated over the five foot separation between the initial inlet position and the screen. The mechanism for this migration has not been investigated, but is likely due to a combination of diffusion and advection.

PACKERS

Figures 8 (Keck pump) and 9 (laboratory manufactured packer) present the results of purging runs using packers. Tracer was added to the well for each trial in the manner described earlier. At the start of each test the packer used for tracer addition was removed. The packer used for sampling was slowly lowered so that the pump inlet for each trial was positioned immediately above the screen. The packer was inflated and pumping was initiated.

Neither packer functioned as anticipated. This is evidenced by the unexpected contribution of stagnant water to the pump dis-
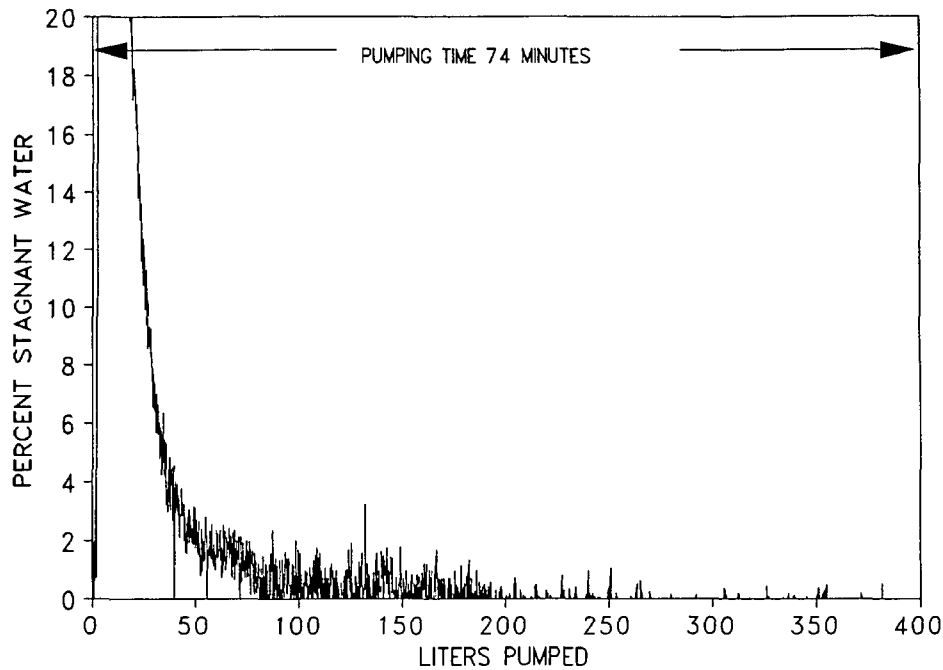
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Fig. 8- Keck Pump with packer

charge. While stagnant water was detected in both runs, there are marked differences between Figures 8 and 9. Both curves exhibit the same general shape. However, the curve for the Keck pump (Figure 8) is dramatically shifted to the right. A portion of the curve from Figure 8 is superimposed onto Figure 9 for comparison. There are three possible causes for the higher than expected contribution of stagnant water in these tests. First, leakage past the packer induced by a decrease in head below the packer during pumping may have caused stagnant casing water to migrate past the packer into the pump inlet. Such a leak could have been caused by an irregularity or crack in the casing wall. Second, in the case of the Keck pump and packer, a significant volume of water is displaced (2.66 L) when the pump is lowered into position. This volume is equivalent to a water level rise of 1.31 m (4.3 ft) in a 5 cm (2 in) well casing. It is assumed therefore, that stagnant water was displaced downward through the screen into the aquifer. This may have caused the dramatic shift to the right of the curve for the Keck pump. Finally, stagnant water held between the packer and the pump inlet may have been drawn in by the same phenomenon observed in other tests were

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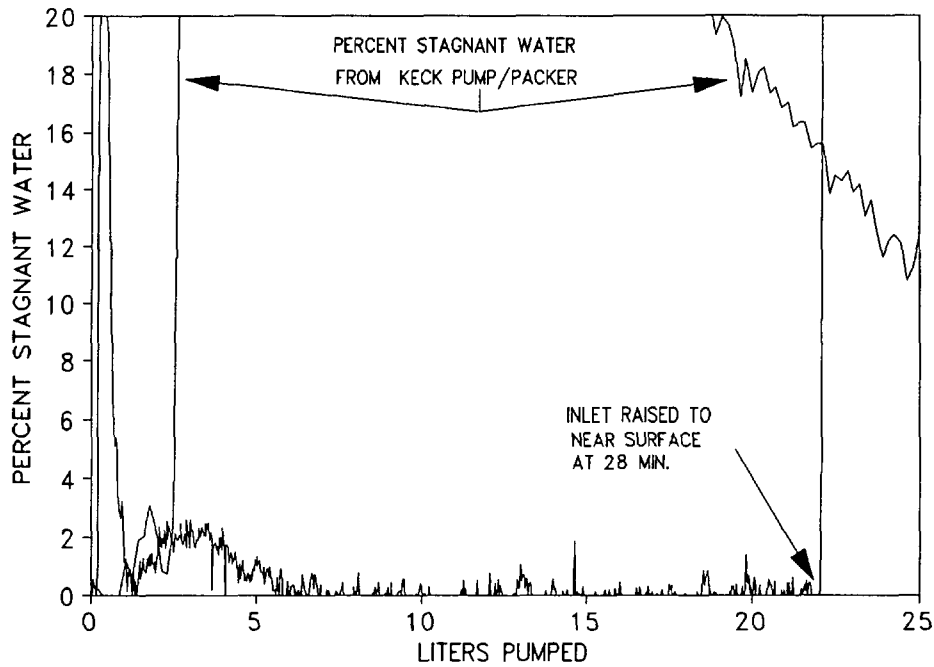
Fig. 9- Peristaltic pump with packer

stagnant water was above the pump inlet. The inlet on the laboratory manufactured flow-through packer was immediately below the packer. However the Keck pump inlet was situated approximately 30 cm (12 in) below the bottom of the packer. This may explain why the test with the Keck pump showed much more frequent and higher spikes of stagnant water than did the flow-through packer.

Purging/Sampling With Drawdown

Figure 10 displays stagnant water concentrations for a well sampled by the drawdown and recover method described earlier. The pump inlet was positioned at the screen top for the duration of the test. The initial pumping rate for the first 25 minutes was approximately 750 ml/min. During the initial portion of this time period when the rate of drawdown was the greatest (as indicated by the slope of the curve marked "depth") a relatively larger portion of the pump discharge would have been from stagnant water. This is confirmed by the larger lithium concentrations. As the rate of drawdown decreases (indicated by decreasing slope of the
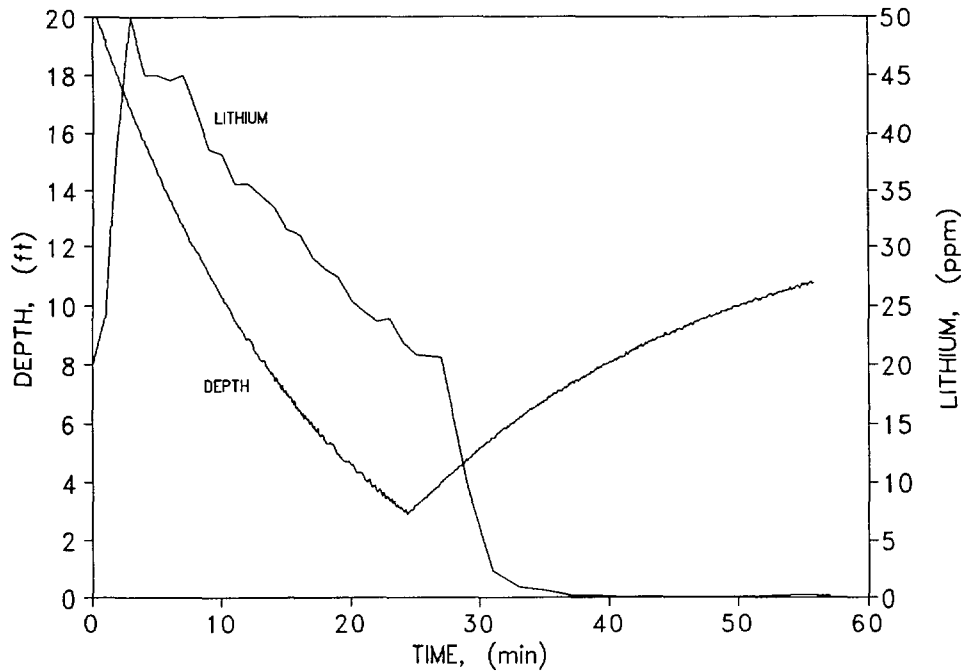
Fig. 10- Purging/sampling with drawdown

"depth" curve) the lithium concentration also decreases, indicating a smaller fraction of stagnant water in the pump discharge. At 25 minutes the pumping rate was decreased to 300 ml/min to allow the well to recharge. Evidence of the stagnant water/fresh water interface moving upward away from the pump inlet is shown by the rapid decrease in lithium concentration. Sample collection during the period of recovery would minimize the inclusion of stagnant water.

The principle illustrated here is related to that used in the ISWS procedure (1). However, since the mathematical methods used there were inadequate to predict the drawdown for this well, it was necessary to measure drawdown directly in order to determine when a sample could be obtained. Direct measurement is not difficult in such a low yielding well, and it could be part of the sampling protocol for such a well.

SUMMARY AND CONCLUSIONS

The results of the research presented here show that the procedures used to sample a well can have an effect on the

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amount of stagnant water in a groundwater sample. All runs conducted in the absence of drawdown with the pump inlet in a fixed position at or above the screen showed a highly variable and unpredictable inclusion of stagnant water. This inclusion of stagnant water may have been caused by turbulence around the pump inlet. Packers were not generally effective in preventing the inclusion of stagnant water into the pump inlet. Deionized water as a tracer in this study was generally ineffective and possibly misleading when compared to Rhodamine WT. The results of tests conducted with deionized water as a tracer which suggest pumping 2 to 3 bore volumes from near the air/water interface may be inappropriately low. Real time monitoring of indicator parameters such as pH, temperature and conductivity was not successful in indicating when purging was complete. Research by Gibs and Imbrigiotta (4) resulted in a similar conclusion.

The inclusion of stagnant water into a sample was minimized by purging from some distance above the screen followed by relocation of the pump inlet into the screen for sample collection. In wells where drawdown occurred during purging, stagnant water inclusion was minimized by reduced pumping rates to allow for sample collection during well recharge. The Illinois State Water Survey procedure for calculating the effect of drawdown was found not to be usable for the wells in this research.

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103 ANALYSIS OF POLYCHLORINATED BIPHENYLS IN WATER AND STACK EMISSIONS BY HIGH RESOLUTION GAS CHROMATOGRAPHY/ HIGH RESOLUTION MASS SPECTROMETRY.

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ABSTRACT

Polychlorinated biphenyls (PCBs) in environmental samples are generally analyzed by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) or high resolution gas chromatography with electron capture detection (HRGC/ECD). Detection limits reported using these techniques for water samples are on the order of 50-500 ppt for the mono-deca PCBs (HRGC/LRMS) or 50-100 ppt for Aroclor characterization by GC/ECD. HRGC/LRMS analysis of air samples (collected on XAD-2) typically show detection levels of 50 to 500 ng for the mono-deca PCBs.

High resolution GC/high resolution MS (HRGC/HRMS) is used routinely for the analysis of polychlorinated dioxins and furans (PCDDs/PCDFs) in water and air samples, with detection limits as low as 10 parts per quadrillion (ppq) for water and 50 picograms (pg) for air.

This HRGC/HRMS technique has recently been utilized for the analysis of PCBs in water and air samples and the sample results indicate that the detection limits of these species are at least two orders of magnitude lower than achieved using the low resolution mass spectrometric technique. Using this technique, PCBs are reported as totals for each congener group (mono-deca) as well as congener specific analysis for 11 congeners, seven of which are quantified by isotope dilution mass spectrometry.

INTRODUCTION

The past few years have witnessed an increasing need for new methodologies that are capable of measuring very small quantities of toxic substances in various matrices, i.e., low parts per trillion (ppt) for soils, parts per quadrillion (ppq) for water and picograms (pg) for air samples collected on solid absorbents.

The proposed method determines polychlorinated biphenyls in

sample extracts representing one liter of water or stack emission (air) samples collected on XAD-2. The method of analysis utilizes high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) operated at a re solving power of 8,000 to 10,000 in the selected ion monitoring (SIM) mode. This method was based on isotope dilution mass spectrometry during which nine $^{13}C_{12}$ - labeled internal standards were used to characterize and quantify all 209 PCB congeners. By using published retention times of the 209 congeners [1], five retention windows bracketing the ten congener groups could be monitored to determine total PCBs by isomer groups (mono through deca) as well as specifically quantify eleven PCB congeners.

EXPERIMENTAL METHOD

For stack emission sampling of stationary sources, the XAD-2 resin was spiked with 10 ng of surrogate standards prior to sampling (Table 1). Following the sampling session, the samples (XAD-2, glass-fiber filter, front half and back half solvent rinses, impinger water and impinger rinses) were returned to the laboratory. The front half and back half rinses were concentrated, then placed inside a Soxhlet extractor along with the rest of the solid fractions of the sampling train. The sample was spiked with 10 ng of PCB internal standards (Table 1), then Soxhlet extracted with 750 mL of methylene chloride. The impinger water was spiked with 10 ng of alternate surrogate standards (Table 1). The water was then liquid-liquid extracted in a separatory funnel using 3 X 60 mL methylene chloride. Both the impinger water extract and the Soxhlet extract were concentrated then combined. The extract was split 50:50, with one-half being archived and the other half subjected to an acid/base wash cleanup. The sample extract was then concentrated to a final volume of 50 microliters.

For water samples, one liter of sample was spiked with the nine internal standards (in acetone) at 10 ng. The sample was allowed to equilibrate for one hour. The sample was then extracted with 3 X 60 mL portions of methylene chloride in a separatory funnel. The extract was concentrated using a K-D apparatus and put through an acid/base wash cleanup. The extract was then concentrated to a final volume of 100 microliters. Before analysis of the PCB extracts, 5 ng of recovery standards (Table 1) are added to the extracts.

CALIBRATION

The mass spectrometer response was calibrated by using the

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set of five initial calibration solutions shown in Table 1. Each solution was analyzed once and the analyte relative response factors (RRF) were calculated.

An acceptable calibration must meet the following criteria:

1) The percent relative standard deviations (RSD) for the mean response factors from each of the unlabeled analytes must be less than 25 or 30 percent depending on the analyte (Table 2).

2) The signal-to-noise ratio (S/N) for the GC signals present in every selected ion current profile must be $\geq$ 10:1.

3) The ion abundance ratios must be within the specified control limits (Table 3).

A continuing calibration was demonstrated every 12 hours by injecting one uL of solution number 2 from Table 1. The RRFs are calculated and compared to the mean RRFs obtained during the initial calibration procedure. An acceptable continuing calibration run must meet the following criteria:

1) The measured RRFs (for the unlabeled PCBs) obtained during the continuing calibration run must be within 25 or 30 percent depending on the analyte (Table 2) of the mean values established during the initial calibration.

2) The ion-abundance ratios must be within the allowed control limits listed in Table 3.

3) The signal-to-noise ratio (S/N) for the GC signal present in every selected ion current profile must be $\geq$ 10:1.

At the beginning of every 12-hour shift during which samples are analyzed the fused-silica capillary GC column performance was verified by injecting a 1-uL aliquot of the PCB window defining mixture (Table 4). This was necessary to identify the various retention time windows for each group of analytes, which are grouped in five mass descriptors. Figure 1 shows the tetra-PCB first and last eluter chromatogram with the corresponding tetra-PCB internal standard.

RESULTS AND DISCUSSION

In order to evaluate the analytical method's ability to

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detect and quantify small quantities of analyte present in water, three sets of five samples at 0.5, 5.0 and 25 ppt were analyzed. The results for the 0.5 ppt matrix spike are given in Table 5 and on Figures 2 and 3. The MDL and LOD values were calculated for the lowest point (0.5 ng/L) samples. The mean %Accuracy for the most congeners were approximately equal to 100%. The mean %Accuracy ranged from 75.6% for 2255-T-PCB to 100% for 2234455-Hp-PCB. The %Recovery of the internal standards range from 44.62% for 22455-Pe-PCB to 280.0% for 334455-Hx-PCB. The high recovery of the carbon labeled 334455-Hx-PCB was due to an interference problem. The %RPD range from 0.0% for 2234455-Hp-PCB to -13.6% for 223344556-Nona-PCB. The results of 5.0 ng/L and 25.0 ng/L were also similar to 0.5 ng/L samples. For both 5.0 ng/L and 25.0 ng/L the internal standards recoveries of 22455-Pe-PCB were the lowest and highest for 334455-Hx-PCB. For 5.0 ng/L mean %Accuracy range from 66.60% for 2255-T-PCB to 119.20% for 244-Tr-PCB. For 25.0 ng/L the mean %Accuracy range from 2255-T-PCB for 111.12% for 3344-T-PCB. The %RPD ranged from -0.80% for 44-Di-PCB to -33.40% for 2255-T-PCB for 5.0 ng/L samples. The %RPD range from 2.56% for 244-Tr-PCB to -28.20% for 2255-T-PCB of 25.0 ng/L samples.

In all three points, the $^{13}C_{12}$-22455-Pe-PCB gave the lowest recovery. One possible explanation for the low recovery might be the compound was not in the same mass descriptor as the recovery standard. Another explanation is that the concentration of carbon-labeled standards are not measured using isotope dilution method. When the corresponding analyte, 22455-Pe-PCB was measured using the isotope dilution method, the mean %Accuracies were 103.6%, 110.20%, and 93.84% for 0.5 ng/L, 5.0 ng/L, and 25.0 ng/L samples, respectively. The concentrations of 224455-Hx-PCB were computed using $^{13}C_{12}$-(245)3-Hp-PCB with mean %Accuracies of 86.80%, 87.02%, and 78.79% for 0.5 ng/L, 5.0 ng/L, and 25.0 ng/L, respectively. This was done because when $^{13}C_{12}$-334455-Hx-PCB was used to compute the analyte concentration, the results were erratic due to the high percent recovery of the internal standard caused by an interference. The $^{13}C_{12}$-224455-Hx-PCB was not used to compute the corresponding analyte concentration because carbon-labeled standard was used as the recovery standard. In the future, the analyte, 224455-Hx-PCB, will be computed using the corresponding internal standard ($^{13}C_{12}$-224455-Hx-PCB) and the $^{13}C_{12}$-334455-Hx-PCB will be used as the recovery standard.

The MDL values for 0.5 ng/L samples were calculated using

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the formula:

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

where S = Standard Deviation
t = Student t.

For the present study, the MDL value for the 0.5 ppt spike was 0.072 ppt. A more rigorous determination of the MDL can be determined spiking seven replicate samples at 0.05 ppt. In lieu of this, the Limit of Detection (LOD) can still be calculated with this data set. Using So (the value of the standard deviation as concentration approaches zero), the LOD (Limit of Detection) was computed using the formula:

$$LOD = 3 * S_o.$$

The LOD for the mono-PCB isomer was 0.036 ng/L.

The matrix spike evaluation for the stack emission samples is currently in progress. The preliminary results show recoveries between 80 and 140% for the eleven PCB target analytes with %RPDs ranging from 5 to 40% for three matrix spikes.

CONCLUSIONS

The extraction, cleanup and analysis procedures described in this method for the trace analysis of mono through deca polychlorinated biphenyls in water are adequate for the isolation and measurement of individual PCBs to detection limits in the low ppq range.

The Limit of Detection (LOD) was calculated to be 36 ppq (parts per quadrillion) for the mono-PCB isomer.

The overall accuracy of the method, as determined by a series of five matrix spikes at three different concentration levels (33 total measurements), was 94.5% [ranging from 66.6% for the 2255-tetrachlorobiphenyl to 120% for the 3344-tetrachlorobiphenyl both at the 5 ppt spike level].

The precision of the method, as calculated from the mean of the 33 analyses, was 6.4% relative standard deviation [ranging from 2.49% for the 3344-tetrachlorobiphenyl to 19.7% for 2255-tetrachlorobiphenyl both at the 5 ppt spike level].

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Table 1. Composition of the Initial Calibration Solutions

Compound	Concentrations (pg/uL)				
Solution Number	1	2	3	4	5

Unlabeled Analytes

Compound	1	2	3	4	5
2-Chlorobiphenyl	0.5	5	10	50	100
44'-Dichlorobiphenyl	0.5	5	10	50	100
244'-Trichlorobiphenyl	0.5	5	10	50	100
22'55'-Tetrachlorobiphenyl	1.0	10	20	100	200
33'44'-Tetrachlorobiphenyl	1.0	10	20	100	200
22'455'-Pentachlorobiphenyl	1.0	10	20	100	200
22'44'55'-Hexachlorobiphenyl	1.0	10	20	100	200
22'344'55'-Heptachlorobiphenyl	1.5	15	30	150	300
22'33'44'55'-Octachlorobiphenyl	1.5	15	30	150	300
22'33'44'55'6-Nonachlorobiphenyl	2.5	25	50	250	500
Decachlorobiphenyl	2.5	25	50	250	500

Internal Standards ($^{13}C_{12}$)

Compound	1	2	3	4	5
4-Chlorobiphenyl[3]	100	100	100	100	100
44'-Dichlorobiphenyl	100	100	100	100	100
244'-Trichlorobiphenyl	100	100	100	100	100
33'4,4'-Tetrachlorobiphenyl	100	100	100	100	100
22'455'-Pentachlorobiphenyl	100	100	100	100	100
22'44'55'-Hexachlorobiphenyl[4]	100	100	100	100	100
22'344'55'-Heptachlorobiphenyl	100	100	100	100	100
22'33'44'55'-Octachlorobiphenyl[2]	100	100	100	100	100
Decachlorobiphenyl	100	100	100	100	100

Surrogate Standard ($^{13}C_{12}$)

Compound	1	2	3	4	5
33'55'-Tetrachlorobiphenyl	100	100	100	100	100
33'44'5-Pentachlorobiphenyl	100	100	100	100	100
22'344'5'-Hexachlorobiphenyl	100	100	100	100	100
22'33'55'66'-Octachlorobiphenyl	100	100	100	100	100

Alternate Standard ($^{13}C_{12}$)

Compound	1	2	3	4	5
22'33'44'-Hexachlorobiphenyl	100	100	100	100	100

Recovery Standards ($^{13}C_{12}$)

Compound	1	2	3	4	5
22'55'-Tetrachlorobiphenyl	200	200	200	200	200
33'44'55'-Hexachlorobiphenyl[4]	200	200	200	200	200

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The method evaluation of stack emission samples is current-
ly in progress with results expected at the time of publi-
cation of this paper.

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Table 1 (continued):

Notes:

1) Based on 100 uL final extract volume,this corresponds to a calibration Range from 50 pg to 10 ng for mono-PCB).

2) The labeled octa-PCB (Internal standard) is used to compute response factors of unlabeled nona-PCBs.

3) The Mono-chloro-Biphenyl internal standard is a $^{13}C_6$ and not a $^{13}C_{12}$.

4) The 22'44'55'-hexa-PCB (internal standard) and 33'44'55'-hexa-PCB (recovery standard) reflect the current method. The original method validation had them switched.

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Table 2. Initial and Continuing Calibrations Response Factors Minimum Requirements

Compound	Relative Response Factors	
	I-Cal %RSD	Con-Cal %Delta
2-chlorobiphenyl	30	30
44'-dichlorobiphenyl	25	25
244'-trichlorobiphenyl	25	25
22'55'-tetrachlorobiphenyl	30	30
33'44'-tetrachlorobiphenyl	25	25
22'455'-pentachlorobiphenyl	30	30
22'44'55'-hexachlorobiphenyl	30	30
22'344'55'-heptachlorobiphenyl	25	25
22'33'44'55'-octachlorobiphenyl	25	25
22'33'44'55'6-nonachlorobiphenyl	30	30
decachlorobiphenyl	25	25
$^{13}C_6$-4-Chlorobiphenyl	30	30
$^{13}C_{12}$-44'-Dichlorobiphenyl	30	30
$^{13}C_{12}$-244'-Trichlorobiphenyl	30	30
$^{13}C_{12}$-33'44'-Tetrachlorobiphenyl	25	25
$^{13}C_{12}$-22'455'-Pentachlorobiphenyl	30	30
$^{13}C_{12}$-22'44'55'-Hexachlorobiphenyl	30	30
$^{13}C_{12}$-22'344'55'-Heptachlorobiphenyl	30	30
$^{13}C_{12}$-22'33'44'55'-Octachlorobiphenyl	25	25
$^{13}C_{12}$-Decachlorobiphenyl	30	30
$^{13}C_{12}$-33'55'-Tetrachlorobiphenyl	25	25
$^{13}C_{12}$-33'44'5-Pentachlorobiphenyl	25	25
$^{13}C_{12}$-22'344'5'-Hexachlorobiphenyl	25	25
$^{13}C_{12}$-22'33'55'66'-Octachlorobiphenyl	25	25
$^{13}C_{12}$-22'33'44'-Hexachlorobiphenyl	25	25

Notes:

1) Isomers that have 25% criteria are those with corresponding $^{13}C_{12}$-labeled standards.

2) The labeled tetra-PCB (IS) will be in a different mass descriptor than the unlabeled tetra-PCB analyte.

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Table 3. Ion-Abundance Ratio Acceptable Ranges

Number of Halogen Atoms	Ion Type	Theoretical Ratio	Control Limits Lower	Upper
1 Cl	M/M+2	3.08	2.62	3.54
2 Cl	M/M+2	1.54	1.31	1.77
3 Cl	M/M+2	1.03	0.87	1.18
4 Cl	M/M+2	0.77	0.65	0.89
5 Cl	M/M+2	0.61	0.52	0.70
6 Cl	M+2/M+4	1.24	1.05	1.43
7 Cl	M+2/M+4	1.04	0.88	1.20
8 Cl	M+2/M+4	0.89	0.76	1.02
9 Cl	M+2/M+4	0.78	0.66	0.90
10 Cl	M+4/M+6	1.18	1.00	1.36

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Table 4. PCB Window Defining Mix

PCB isomer	Group Number
2-chloro (F)	1
4-Chloro (L)	1
2,6-dichloro (F)	2
4,4'-dichloro (L)	2
2,4,6-trichloro (F)	2
2,3,5-trichloro	2
2,2',6,6'-tetrachloro (F)	2
3,4,4'-trichloro (L)	3
2,3,3',4-tetrachloro	3
3,3'4,4'-tetrachloro (L)	3
2,2',4,6,6'-pentachloro (F)	3
2,2',4,4',6,6'-hexachloro (F)	3
3,3',4,4',5-pentachloro (L)	4
2,2',3,4,4',6-hexachloro	4
2,2',3,4,5,6'-hexachloro	4
3,3',4,4',5,5'-hexachloro (L)	4
2,2',3,4',5,6,6'-heptachloro (F)	4
2,2',3,3',4,4',5-heptachloro	4
2,2',3,3',5,5',6,6'-octachloro (F)	4
2,3,3',4,4',5,5'-heptachloro (L)	5
2,2',3,3',4,4',5,5'-octachloro (L)	5
2,2',3,3',4,5,5',6,6'-nonachloro (F)	5
2,2',3,3',4,4',5,5',6-nonachloro (L)	5
decachloro	5

Note: The table contains the order of elution for specific isomers.

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Table 5   Matrix Spike Replicate Analytical Results
(0.50 ppt Spike)

	MS1	MS2	MS3	MS4	MS5	Mean
Analytes		(Concentration in ppt)				
2-Mo	0.46	0.44	0.45	0.48	0.49	0.46
44-Di	0.54	0.53	0.57	0.59	0.57	0.56
244-Tr	0.55	0.53	0.53	0.53	0.59	0.55
2255-T	0.72	0.77	0.73	0.77	0.79	0.76
3344-T	1.20	1.00	1.00	1.20	1.20	1.12
22455-Pe	1.10	1.00	0.98	1.00	1.10	1.04
224455-Hx*	0.86	0.88	0.88	0.89	0.83	0.87
2234455-Hp	1.50	1.40	1.50	1.60	1.50	1.50
22334455-Oc	1.70	1.50	1.60	1.70	1.70	1.64
223344556-No	2.10	2.20	2.10	2.20	2.20	2.16
Deca	2.60	2.50	2.60	2.80	2.70	2.64
$^{13}C_{12}$ Internal Standards		%Recoveries				
4-Mo	68.5	78.0	78.1	73.2	85.3	76.6
44-Di	140.0	149.0	174.0	161.0	157.0	156.2
244-Tr	90.1	105.0	112.0	105.0	107.0	103.8
3344-T	116.0	125.0	123.0	115.0	124.0	120.6
22455-Pe	56.6	52.8	42.8	34.3	36.6	44.6
224455-Hx	301.0	211.0	228.0	246.0	414.0	280.0
2234455-Hp	98.4	103.0	100.0	101.0	107.0	101.9
22334455-Oc	122.0	114.0	112.0	116.0	131.0	119.0
Deca	90.3	92.3	88.0	90.0	89.1	89.9

*$^{13}C_{12}$-(245)3-Hp was used as the internal standard.
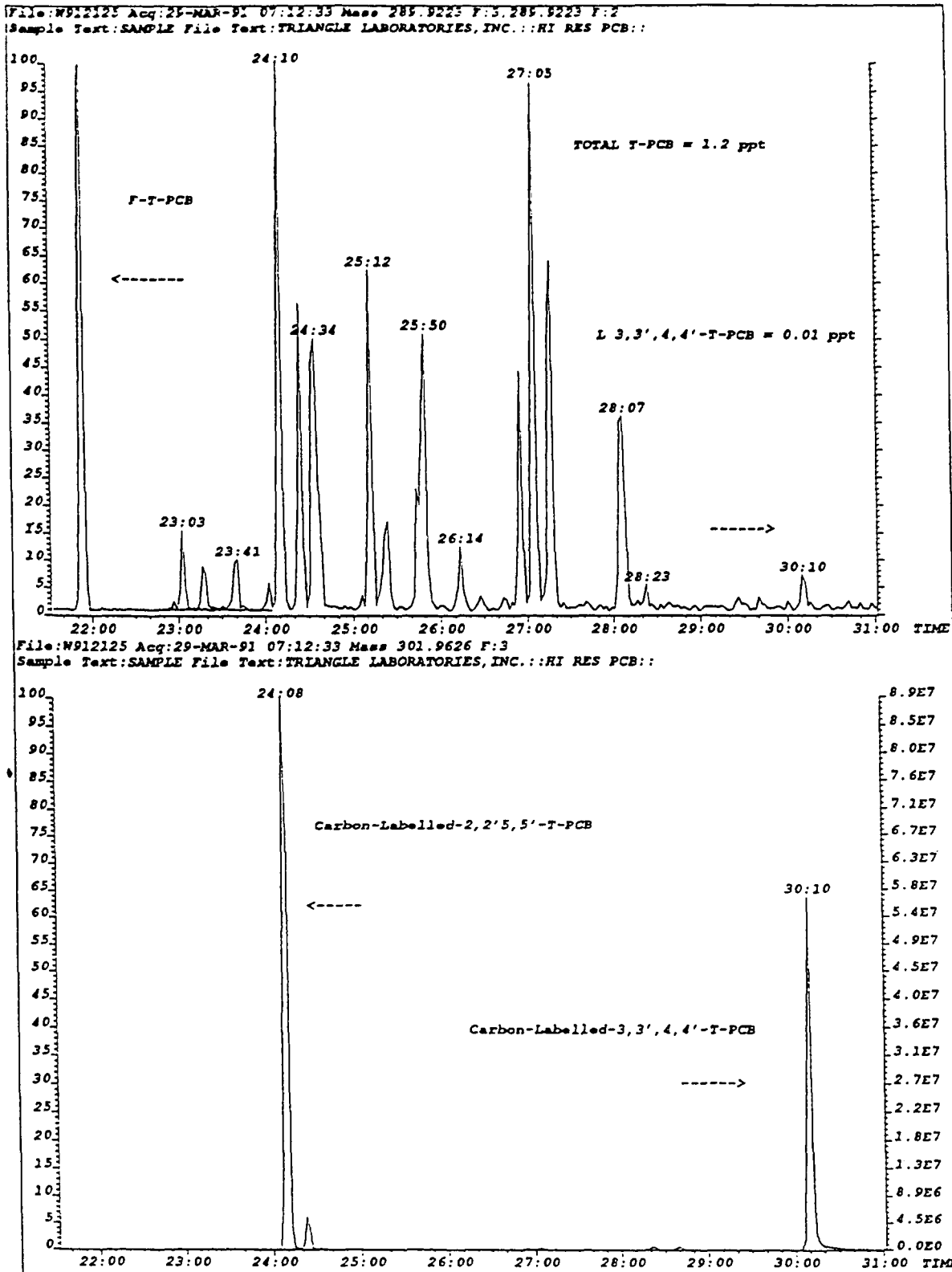
Figure 1

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Figure 2

Figure 3

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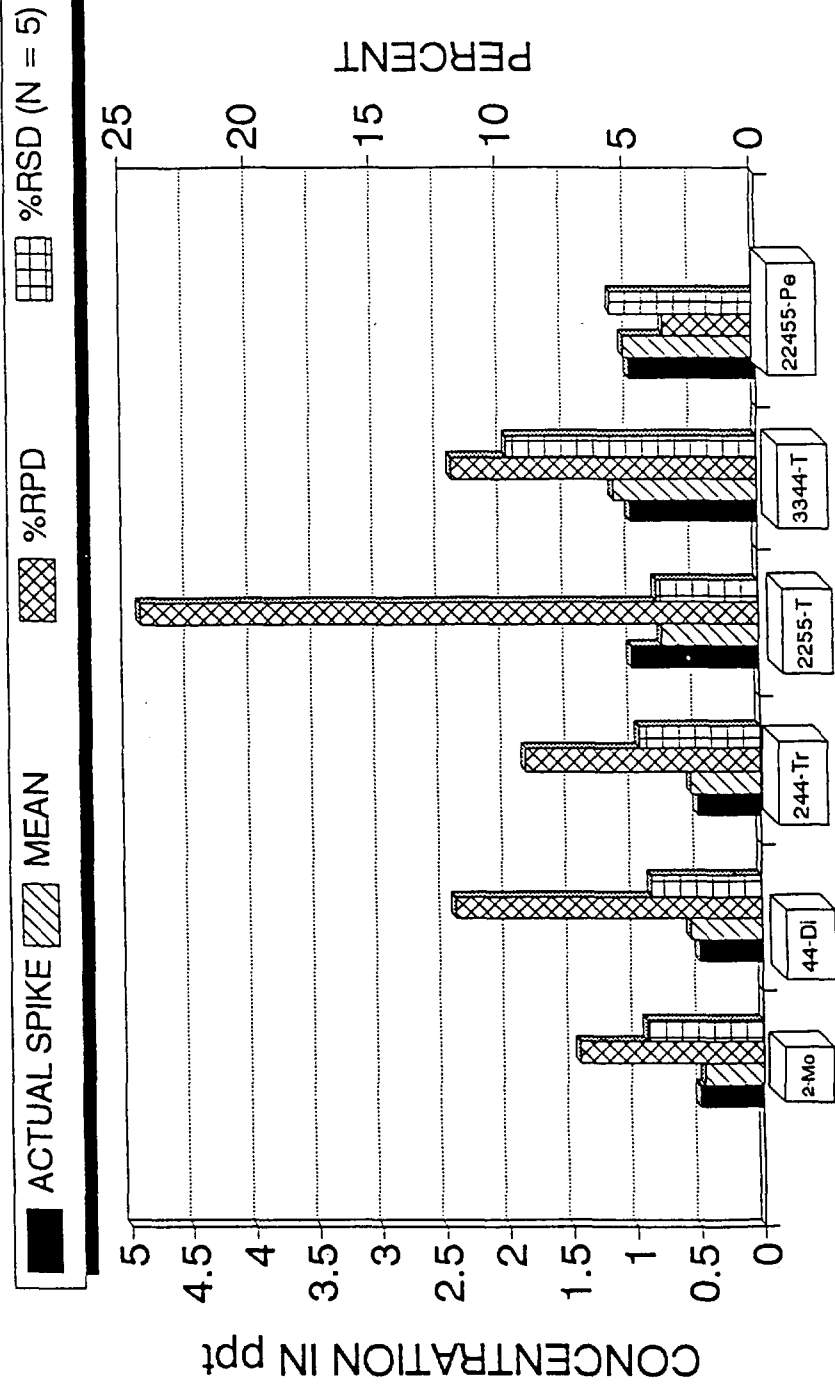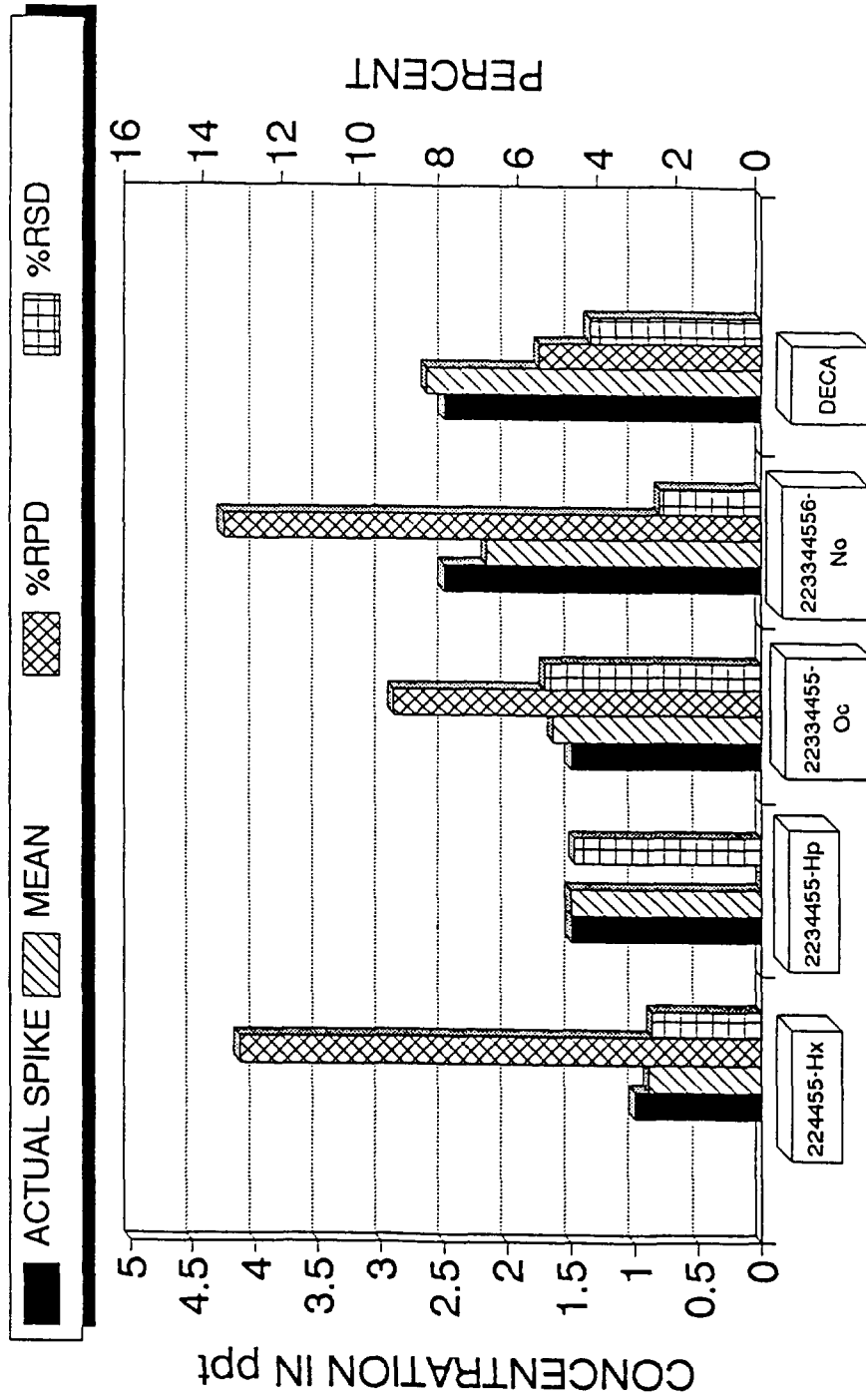
CONTINUOUS ANALYSIS OF VOCs IN AIR USING A NEW, PHENYL-METHYL SILICONE STATIONARY PHASE FOR HIGH-RESOLUTION CAPILLARY GC

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INTRODUCTION

Monitoring (very) volatile organic compounds in outdoor air becomes more and more important, as these compounds are involved in smog formation and are known ozone precursors. Also the US 1990 Clean air Act clearly indicates the need for accurate data. In air, volatile organic components are numerous and often very similar to each other. In most cases they occur in the gaseous phase at ambient temperature at the (sub) part-per-billion level. For these reasons, chromatography is the most suitable method. These considerations and the specifications for a monitoring system have formed the basis for the design of a monitoring system for volatile organic compounds in air, described in this paper—the VOC Air Analyzer (Chrompack International, Middelburg, The Netherlands).

INSTRUMENTAL

The VOC Air Analyzer is a system for **unattended continuous automatic analysis of air** containing (very) low levels of organic components. The VOC Air Analyzer takes samples at regular intervals over a selected time. The volatile organic components are concentrated on an adsorbent tube. When sampling has been completed the adsorbent tube is heated to release the components and transport these to a liquid nitrogen-cooled fused silica trap. Here the sample components are refocussed in a narrow band. The trap is then flash heated by which the sample is introduced into the capillary column for analysis.

A schematical presentation of the VOC Air Analyzer is given in figure 1. It has been designed to simultaneously sample and analyze air using (cryo) adsorption and thermal desorption techniques. Control of the heating and cooling devices, valves, and sampling pump, as well as the synchronization with the gas chromatograph and the integrator-data processor, is performed by the VOCAA-controller.

In the sample collection mode, air is drawn through the valve and the adsorption trap by means of a sample pump with a flow ranging from 10 to 70 mL/min. The adsorption trap filled with appropriate trapping materials such as Tenax, Carbosieve, or Carbotrap, or a composition of these materials, is cooled using liquid nitrogen to a temperature ranging from -20°C to ambient.

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Just before the end of a sampling period, the capillary trap is cooled to a temperature with the range of -180°C to subambient (cooling rate 100°C/min).

In the sample transfer mode, the trapped compounds are transferred from the adsorption trap to the capillary trap using a reversed carrier gas flow. The capillary trap consists of a wide bore fused silica capillary coated with liquid phase and/or filled with adsorbent. The transfer is induced by heating the adsorption trap (heating rate 190°C/min) and switching of the valve. Only in this mode are the sampler and the injector connected. While in this mode, the temperature of the capillary trap is maintained at low temperature set during the precool. To minimize discrimination of the higher boiling compounds and sample transfer time, the transfer flow is higher than the flow defined in the restriction of the capillary column. This is achieved by opening the desorption vent. After the completion of the transfer, the valve is switched again.

To remove any remaining compounds the adsorption trap is heated for a short period to a temperature higher than the one in the sample transfer mode and again using a reversed carrier gas flow. Before sampling is restarted, the adsorption trap is cooled to the desired temperature. Analysis time is optimized to allow separation of the components of interest, cool down to, and equilibration at the initial temperature setting before the sampling period is over. In this way a continuous, unattended operation is possible, based on a one hour cycle time.

It is necessary for most air samplers to remove the moisture in the sample stream, as it might block the adsorption tube or the cold trap with ice. Moisture can be selectively removed on-line by passing the sample stream through a two-stage dryer [Nafion tubes, DuPont Corp. (Wilmington, Delaware), see the right part of Figure 1] reducing the dew point to -55°C. This two-stage dryer is self-regenerating. The drying force is the moisture gradient generated by the underpressure (0.1 atm absolute) in the first stage. The dry air stream is used in the second stage to dry the sample stream. If dry air is available, then a single Perma-Pure (Nafion tube) dryer system can be used, which also removes the water from the sample stream through the semi-permeable wall of the dryer tube. The dry air stream is typically 4-5 times higher than the air sample stream to get the desired drying effect. The complete set of dryers, pump, valves, and Nafion tubes is built in a new dryer/pump unit, which is controlled by the control unit of the VOCAA. A disadvantage of the Nafion dryer is that it partially eliminate polar components which might be present in the air samples. If these types of compounds have to be analyzed, an option is built in to collect the samples without the dryer in line in the sample stream, after which the adsorption tube is heated from -20°C up to +10°C and

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pre-flushed with carrier gas (helium) to remove the water. In this way, however, a substantial part of the C_2-C_4 hydrocarbons in also flushed of the adsorption tube and lost for analysis. For the separation both thick film, apolar phases capillary columns (such as CP-Sil 5 CB, 50 m x 0.32 mm i.d. df = 5.0 μm) and Al_2O_3/KCl PLOT columns can be used. Dual detection (FID and ECD) should be used by splitting the effluent from the analytical column to the two detectors. In order to cover the whole range from C_2-C_{12} hydrocarbons, the apolar column must start at -20°C and programmed up to 210°C. Monitoring compounds in relation to the biospheric ozone formation, such as aliphatic and olefinic hydrocarbons as well as the alkyl aromatics, required a chromatographic column with a high resolution of the very volatile organic compounds, such a ethene and ethane. For this purpose, the Al_2O_3/KCl PLOT column is selected. Temperature program then can start at 40°C, which eliminates the use of a cryogenic unit in the gas chromatograph. On this column, however, it is difficult to analyze some of the halogenated hydrocarbons, such as unsaturated freons.

The above-described analyzer is used by the Dutch National Air Quality Monitoring Network and by the EPA during the Summer 1990 ozone precursor study in Atlanta, Georgia. The VOC Air Analyzer can be used where (very) low concentrations of volatile organic components in air have to be monitored continuously without operators present.

Th range of components that can be analyzed is:
1. Hydrocarbons C_2-C_{18}
2. Halogenated hydrocarbons up to trichlorobenzene
3. Aromatic hydrocarbons up to trimethyl benzene

The application field is air pollution control and in some cases industrial hygiene (especially where levels to control are in the ppb range).

Table 1. shows the composition of an EPA calibration mixture, which can be separated on a 5 μm CP-Sil 5 CB column under the above described conditions. For reasons of sensitivity and identity-conformation dual detection should be used.

RESULTS AND DISCUSSION

Figures 2A and 2B show the results of a 200 mL outdoor air sample at Raritan, New Jersey, being the FID and the ECD signals. Here the apolar column program was started at 40°C and programmed up to 200°C. In Figure 3 the increase in retention and separation is shown, using an Al_2O_3/KCl PLOT column under the same conditions. Typical concentrations of the components are in the 0.1-10 ppb range. Under the conditions described in Figure 3, a continuous monitoring of air was realized during several months. Part of the quantitative results are plotted in

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Figure 4. Similar plots are made for C_4, C_5, C_6, C_7-$_8$ and aromatic components.

A new method for the analysis of C_2-C_6 hydrocarbons and halogenated compounds, including C_5-C_{12} hydrocarbons, is to inject and separate the collected air samples on two capillary columns simultaneously. Such a combination could be an Al_2O_3/KCl PLOT column and an apolar liquid phase, such as CP-Sil 5 CB (thick film). In this way the analysis can start at 40°C-45°C, so cryogenic cooling of the GC oven is avoided, which gives a substantial reduction in the liquid nitrogen consumption. In order to optimize the separation of the chlorinated compounds a new, slightly more polar liquid stationary phase was developed, CP-Sil 13 CB. This is also a polysiloxane phase, containing an average of 14% phenyl/86% methyl groups in the polymer. CP-Sil 13 CB has an excellent selectivity for the halogenated hydrocarbons, as mentioned in EPA 624 and 502-2. By combining FID and ECD detection, some co-eluting peaks can be quantified independently. The stationary phase does not contain electro-negative groups. Combined with the low bleeding of the column this results in a very stable baseline on the ECD trade.

CONCLUSION

The most significant characteristic of the VOC Air Analyzer is the simultaneous sampling and analysis of (very) volatile organic compounds at a frequency of 1 hour or less. Using thick film WCOT or porous PLOT columns, the compounds that can be monitored range from the unsaturated and saturated alkanes, benzene, and the substituted aromatics and various halogenated compounds. The high resolution power of capillary columns allows high quality identification and quantitation and produces information concerning individual compounds relevant in atmospheric processes.

FIGURE CAPTURES.

Figure 1.   Schematic diagram of the Chrompack VOC Air Analyzer, including the new pump-dryer unit.

Figure 2A.   FID signal of a 200 mL outdoor air sample, collected at Raritan, New Jersey. Column: CP-Sil 5 CB. Temperature: 40°C (4 min) to 200°C. Sample collection: -20°C. Desorption: 220°C. Peak identification:
1 = benzene; 2 = toluene; 3 = ethylbenzene;
4 = p.m-xylene; 5 = O-xylene.

Figure 2B.   ECD signal of a 200 mL outdoor air sample. Conditions as in Figure 2A. Peak identification:
1 = trichlorofluoromethane; 2 = methylbromide;
3 = trichloroethane; 4 = carbontetrachloride;
5 = trichloroethene; 6 = tetrachloroethene;
7 = tetrachloroethane; 8 = hexachlorobutadiene

Figure 3.   (see original)

Figure 4.   Plot of the C_2-C_3 concentration fluctuation during a continuous monitoring of outdoor air at Bilthoven, The Netherlands. Sample cycle time was one hour, sample volume: 333 mL.

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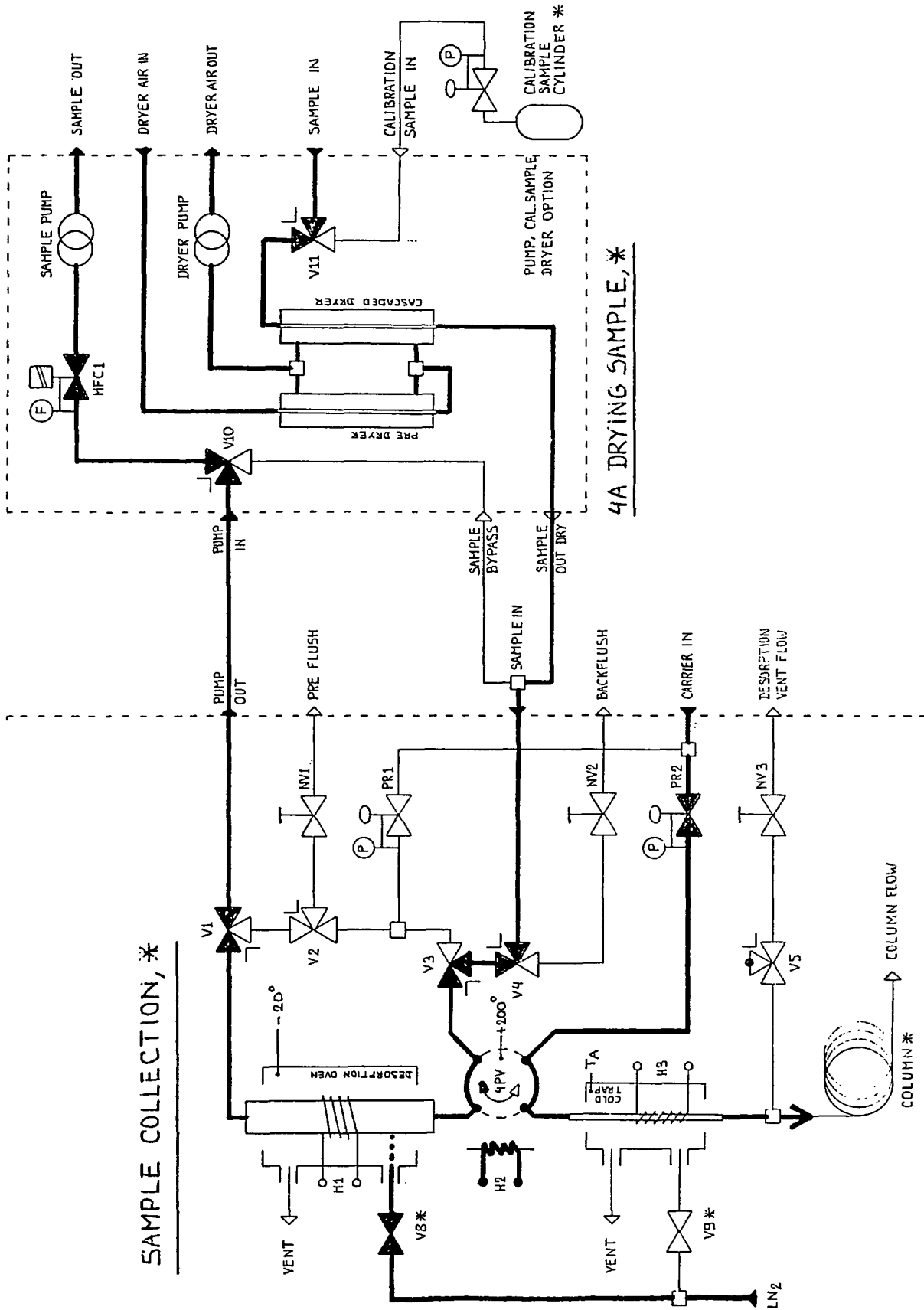
60 COMPONENT CALIBRATION MIXTURE

(1)	Acetylene	(31)	Methylcyclopentane
(2)	Ethylene	(32)	2,4-Dimethylpentane
(3)	Ethane	(33)	1,1,1-Trichloroethane
(4)	Propylene	(34)	Benzene
(5)	Propane	(35)	Carbon tetrachloride
(6)	Isobutane	(36)	Cyclohexane
(7)	1-Butene	(37)	2-Methylhexane
(8)	n-Butane	(38)	2,3-Dimethylpentane
(9)	trans-2-Butene	(39)	3-Methylhexane
(10)	cis-2-Butene	(40)	Trichloroethylene
(11)	3-Methyl-1-Butene	(41)	2,2,4-Trimethylpentane
(12)	Isopentane	(42)	n-Heptane
(13)	1-Pentene	(43)	Methylcyclohexane
(14)	n-Pentane	(44)	2,3,4-Trimethylpentane
(15)	Isoprene	(45)	Toluene
(16)	trans-2-Pentene	(46)	2-Methylheptane
(17)	cis-2-Pentene	(47)	3-Methylheptane
(18)	2-Methyl-2-butene	(48)	n-Octane
(19)	2,2-Dimethylbutane	(49)	Perchloroethylene
(20)	Cyclopentene	(50)	Ethylbenzene
(21)	4-Methyl-1-Pentene	(51)	p-Xylene
(22)	Cyclopentane	(52)	Styrene
(23)	2,3-Dimethylbutane	(53)	o-Xylene
(24)	2-Methylpentane	(54)	n-Nonane
(25)	3-Methylpentane	(55)	Isopropylbenzene
(26)	2-Methyl-1-pentene	(56)	n-Propylbenzene
(27)	n-Hexane	(57)	α-Pinene
(28)	Chloroform	(58)	1,3,5-Trimethylbenzene
(29)	trans-2-Hexene	(59)	1,2,4-Trimethylbenzene
(30)	cis-2-Hexene	(60)	β-Pinene

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VERY VOLATILE ORGANIC COMPOUNDS
C2-C3

1 —— ethane   2 —— ethene   3 —— propene   4 —— propadiene

◇ —— propane

HOURS PAST 00:00 MAY 29 1990

CONCENTRATION (ug/m3)
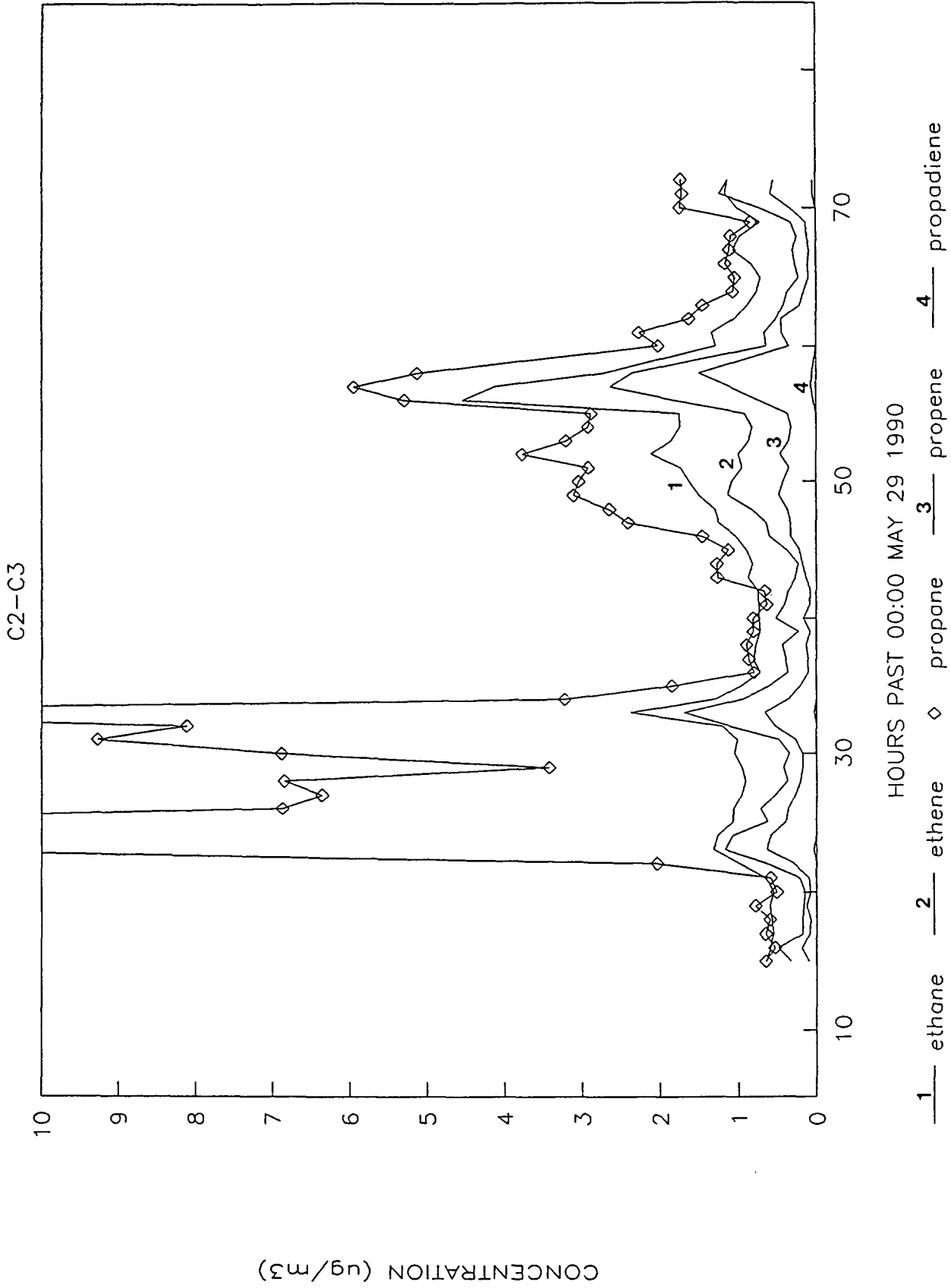
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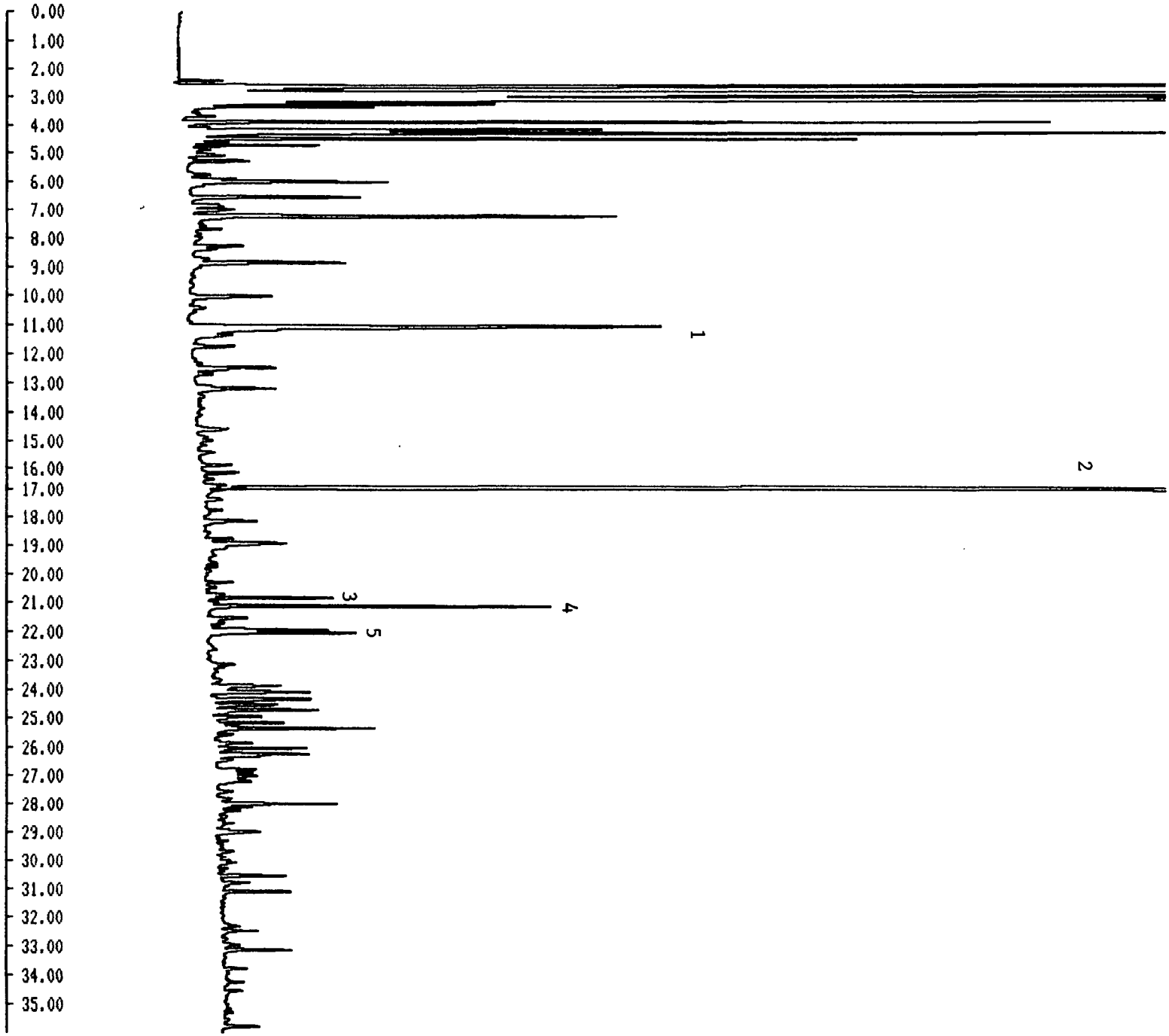
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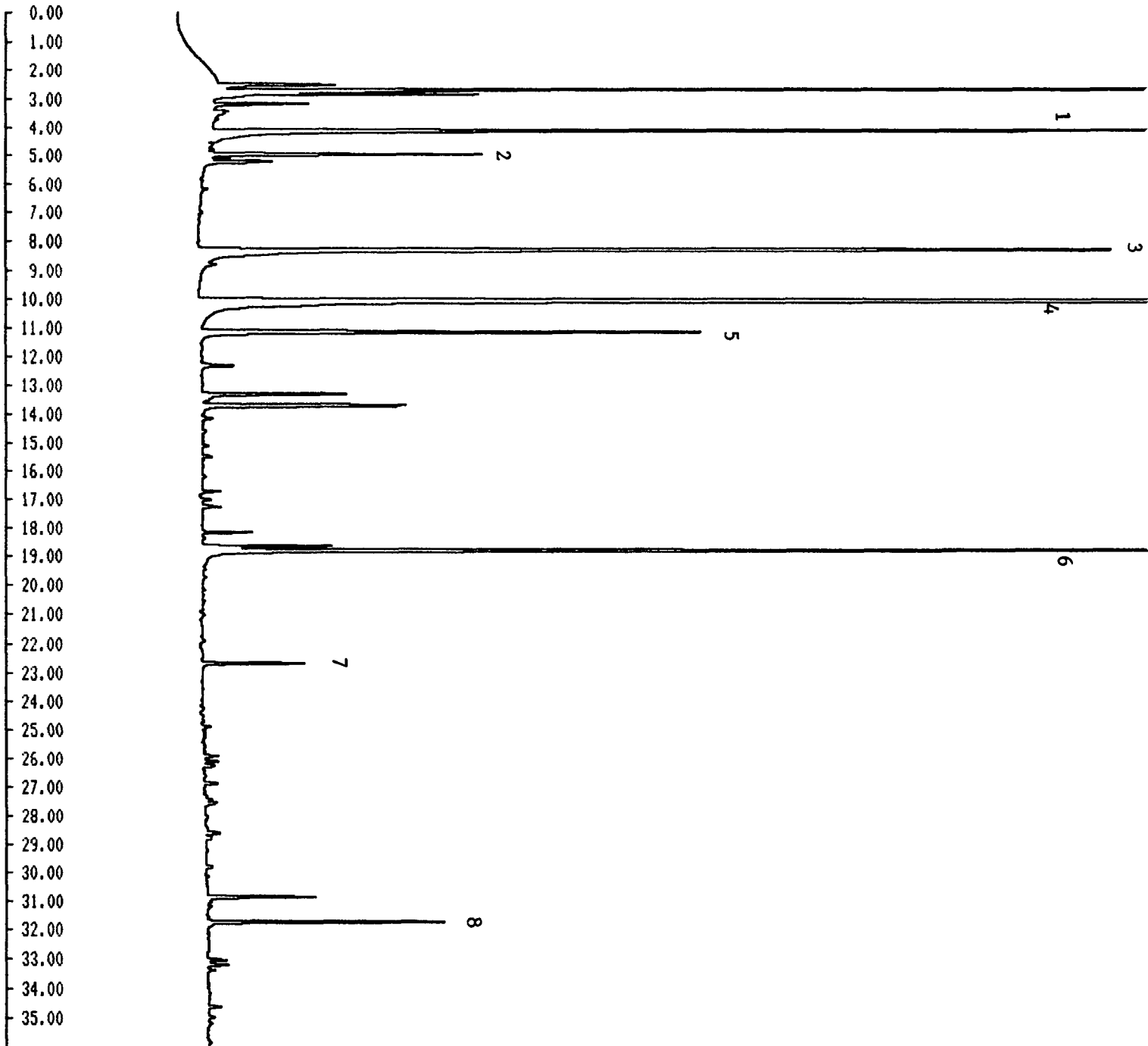
Figure 3 Chromatogram of an air sample. Sample: Outdoor air at Bilthoven Station, June 22, 1990, at 15.00 hr. Column: fused silica 25 m × 0.53 mm i.d. Al_2O_3/KCl, df = 10 μm. Temperature: 40 °C, isothermal 1 min, programmed to 200 °C at 10 °C/min, 200 °C, isothermal 30 min. Carrier: He 0.4 bar. Detector: FID 1, 10E-12 A, 2 mV full scale, 275 °C. Adsorption trap: Carbosieve SIII, Carbotrap, Carbotrap, Carbotrap C (7.5 × 0.29 cm). Capillary trap: Poraplot U fused silica 0.53 mm i.d., 20 μm. Sample coll.: −20 °C 35 min. Sample flow: 9.5 mL/min. Sample vol: 333 mL. Sample desor.: 250 °C, 5 min, desorption vent flow 2.5 mL/min. Cryofocusing: −150 °C 5 min. Injection: 125 °C, 10 min. Back flushing: 270 °C, 10 min, flow: 20 mL/min. Valve: 200 °C. Injection block: 200 °C. Peak identification: 1 = ethane; 2 = ethene; 3 = propane; 4 = propene; 5 = 1-butane; 6 = prodadiene; 7 = n-butane; 8 = trans-2-butene; 9 = 1-butene; 10 = 1-butene; 11 = cis-2-butene; 12 = cyclopentane; 13 = 1-pentene; 14 = n-pentane; 15A = 3-methyl-1-butene; 15B = trans-2-pentene; 15C = 2-methyl-2-butene; 15D = 1-pentene; 15E = 2-methyl-1-butene; 15F = cis-2-pentene; 21A = methylcyclopentane; 21B = cyclohexane; 21C = 2-methylpentane; 21D = 3-methylpentane; 25 = n-hexane; 26 = n-heptane; 27 = benzene; 28 = n-octane; 29 = toluene.
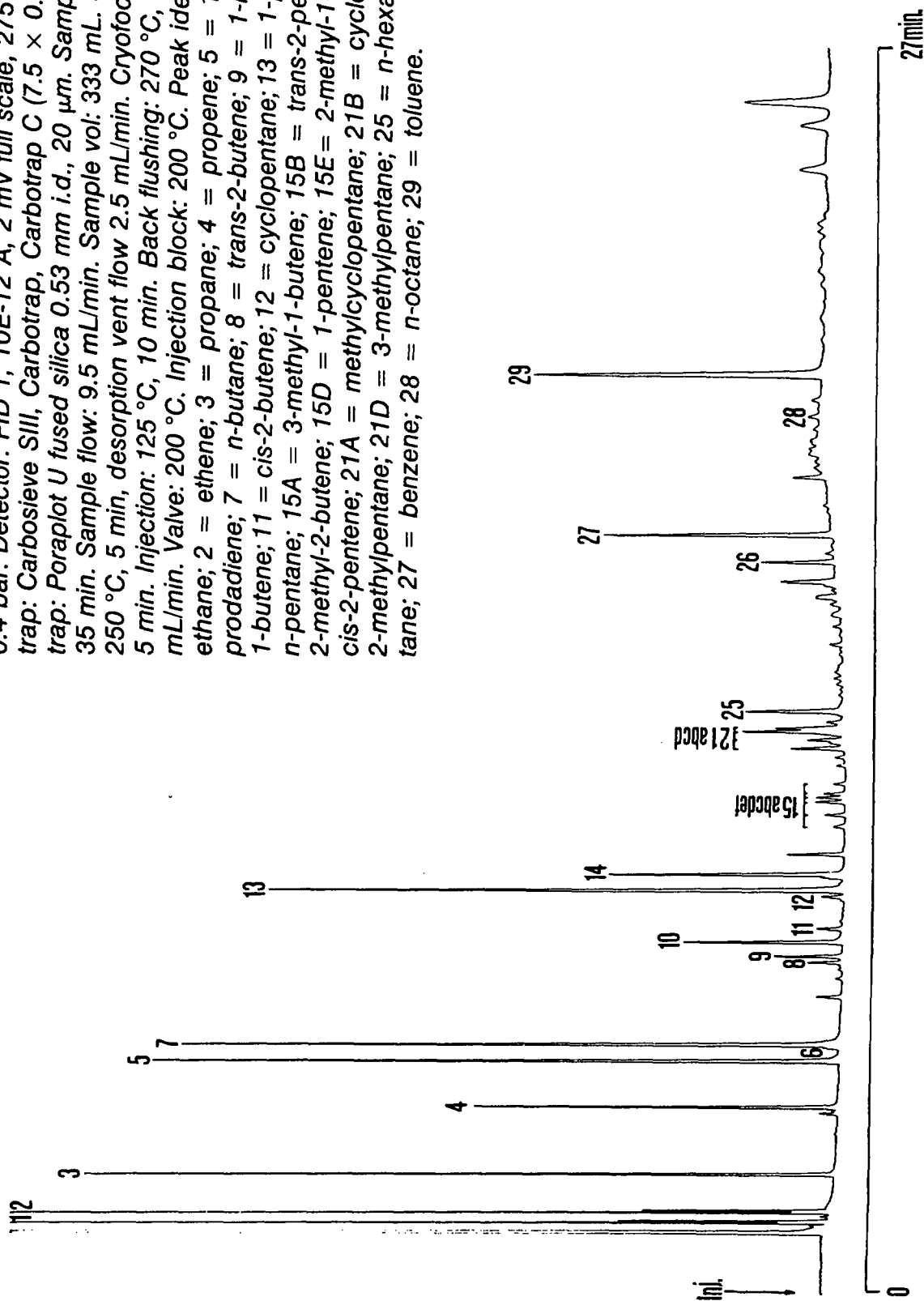
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GENERAL

105 DEVELOPING A UNIFORM APPROACH FOR COMPLYING WITH EPA METHODS

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ABSTRACT

Since the late 1970's, EPA has developed methods using GC and GC/MS technology to support regulatory initiatives. These methods have been promulgated, distributed, and used as contract mechanisms. Commercial laboratories have faced a bewildering array of "approved" methods, generally utilizing identical technology but varying in detail.

As stated in a recent EPA report to the U.S. Congress "Improved coordination is needed in the Agency's methods development program", Enseco supports the activities of the Environmental Methods Management Committee, created to respond to EPA's recommendation and has drafted an approach which results in regulatory control combined with analytical flexibility. The approach controls critical method elements such as the procedural details, calibration, and quality control requirements but eliminates superficial differences that currently exist in EPA methods.

Using as a model the methods available to analyze volatile organics by purge and trap GC/MS (624, 524.2, 8240, 8260, etc.), information is presented comparing and contrasting the differences between EPA methods from various sources. Data will be presented discussing the impact of varying the method details. Finally, an approach will be presented which discusses how laboratories can balance productivity, technical enhancement and method compliance issues.

INTRODUCTION

Since the late 1970's, EPA has developed methods using GC and GC/MS technology to support regulatory initiatives. These methods have been promulgated, distributed, and used as contract mechanisms. Commercial laboratories have faced a bewildering array of "approved" methods, generally utilizing identical technology but varying in detail.

In response to a recent EPA report to the U.S. Congress (Adequacy, Availability and Comparability of Testing Procedures for the Analysis of Pollutants Established under section 304(h) of the Federal Water Pollution Control Act, also referred to as the 518 Report), EPA has formulated the Environmental Methods Management Committee (EMMC) to address the issue of methods consolidation. The Committee's efforts have been described to reduce the number of method variations labs must integrate and to allow more methods to be developed. The methods integration group has stipulated that quality control is an intrinsic part of the methods (1). The approach to consolidation must eliminate superficial differences which result in laboratories needing to run duplicative methods with differing requirements

which do not impact the quality of the data. Since these methods are performed in response to regulatory requirements, it is incumbent upon laboratories to meet the specific requirements of each method, irregardless of the technical merit. This results in redundancy of effort and increased analytical costs to ensure that specific method details are met.

As a solution to this dilemma, EPA has indicated that the various methods utilizing the same technological approach will be combined into one master method by using the "best practices" from each method. We are concerned that this approach will result in methods which have such stringent criteria as to be virtually unusable. Furthermore, the methods will not have the flexibility to meet the Agency's various regulatory needs.

This "best practices" approach is also contrary to an earlier statement by EPA in Environmental Lab. As stated by David Friedman:

> "The approach we have been taking when promulgating analytical methods often has been counter productive. It has stifled creativity; it has led to poor analytical results; and it has, in some cases raised the cost of testing . . . We have to move toward performance standards, not design standards. We must specify what needs to be done, including data quality objectives, not how to do it." (2)

We are presenting here an alternative approach to EPAs recommendation to use the "best practice" from each method to get one method. We propose a minimum acceptable practice (MAP) to be used in concert with Data Quality Objectives (DQOs) to define the analytical requirements for each project. The DQOs and analytical requirements must be documented in a project specific QAPjP which is agreed to as part of the project planning process.

In addressing this problem we have evaluated what aspects of a method are critical to the execution of the method. Minimum QC criteria should be specified outside of the method as proposed for SW-846 (55 Federal Register 4440). The ASTM document "Standard Practice for Generation of Environmental Data Related to Waste Management Activities: QA/QC Planning and Implementation" addresses the minimum acceptable practices to assure the quality of field and analytical activities. Types of control samples that are used to monitor method performance are described externally to the methods and apply universally to all techniques amenable to such external controls. Additional use of matrix-specific QC must be related to the project needs based on the DQOs and not be mandated as a laboratory exercise. The analyte list and QC sample elements are therefore not mandatory elements of the method. Calibration criteria, sample size and preparation procedures are, however, inherent method elements. The specifics of these method elements may be variable and subject to validation.

Supporting information with respect to analytes which may be determined by a method, in addition to any performance criteria obtained under specific conditions should be included as appendices to the method.

Such an approach will improve the quality and usability of data while providing a cost-effective means to generate environmental data. It will also allow for technical enhancements to a method to allow for innovation and improvement. Under the current system you can follow the method exactly and obtain poor quality, unusable data. If you deviate from the method to improve the quality and usability of the data you may be guilty of non-compliance. We must ensure data integrity by requiring those elements that are critical for integrity, while recognizing those elements that are not critical.

Each laboratory must be required to demonstrate method proficiency based on the specifics of the method as performed in that laboratory. This will allow for differences in GC columns, temperature programs, and target analytes to suit the project requirements, and assure the performance of quality control as applied to that method. Each time a change is made to how the method is executed or if additional analytes are to be included a rigorous validation procedure must be performed. A proposal for initial demonstration of proficiency and validation is described in this paper.

In this paper we address the applicability of this approach to the methods for the analysis of volatiles by GC/MS, specifically Methods 624, 524.2, 8240 and 8260. The procedural differences in these methods have been adequately described elsewhere and were not the focus of our efforts (3).

MINIMUM ACCEPTABLE PRACTICES

An analytical procedure should provide enough detail to allow an experienced laboratory unfamiliar with the procedure to generate equivalent data. Thus, extensive procedural details are required to be written into the method. Examples of this level of detail include concentration of calibration standards, mass range, extraction solvent, sample size, internal standards, usable method performance data, etc. However, very few, if any of these details should be mandatory. Rather, as discussed in more detail later, this descriptive information provides the basis for the performance data presented in the method. Other techniques can be used provided they result in equivalent or better performance.

This section presents two examples of the problems with the current approach and presents a proposed solution.

The first example relates to the retention time window used for identifying compounds by GC/MS. The following "requirements" were found:

Method 524: (1983)   "11.2.1 The GC retention time of the sample component must be within t s of the time observed for that same compound when a calibration solution was analyzed. Calculate the value of t with the equation:

$$t = (RT)^{1/3}$$

where RT = observed retention time (in seconds) of the compound when a calibration solution was analyzed." (4)

Method 524.2: (Rev. 2.0, 1986)* "11.1.1 The GC retention time of the sample component must be within 10 s of the time observed for that for that same compound when a calibration solution was analyzed." (5)

* Note: As a comment on the current disarray of methods, we found four versions of Method 524.2, two of which on the surface were stated to be the same (Revision 2.0) and are required in the regulations, but are substantially different. Currently both the 1986 and 1988 versions are promulgated (40CFR141.24). However, the 1988 revision is required for compounds 9 through 18 and the 1986 version required for the remaining compounds (56 Federal Register 3526). Thus, the entire volatile analyte list for drinking water must be performed using two distinct versions of the method with different requirements. Furthermore, Revision 3.0, available in the public domain, is not an approved method.

Method 524.2: (Rev. 2.0, 1988) "11.6 The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture." (6)

Method 624: "12.1.2 The retention time must fall within $\pm$ 30s of the retention time of the authentic compound." (7)

Method 8240: "7.5.1.1.1 The sample component RRT must compare within $\pm$ 0.06RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample." (8)

As shown above, our review found five different "requirements" for establishing this retention time window. Complete and full method compliance would require that laboratories assure that the "correct" approach was used based on the method purportedly used. Since the retention time window is a minor component of identification in GC/MS, we believe that these "requirements" are generally ignored. As an interesting exercise, we evaluated the data from a volatile calibration standard processed using current GC/MS target compound software. We believe that the system would correctly identify the compounds using any of the definitions.

A more appropriate wording of this section would be:

Identification of target compounds is based upon both retention time and mass spectral agreement. The data contained in this method were based on a $\pm$ 0.06 RRT window. Other approaches may be used if they provide equivalent performance.

As another example, consider the language in Section 7.2.3 of Method 8240 which states "Prior to use, condition the trap daily for 10 minutes while

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backflushing at 180°C with the column at 220°C." In this one sentence, there are six requirements, "Prior to use", "daily", "10 minutes", "backflushing", "180°C", and "220°C". Accordingly, if someone was to develop a different trap which could be conditioned at 170°C for 8 minutes, it could not be used. Again, we would rewrite this sentence to read:

> The trap must be conditioned to maintain performance.
> It is recommended that the trap be backflushed at 180°C
> for 10 minutes. Other approaches can be used provided
> the trap maintains performance as measured by analyses
> of QC samples.

In summary, there are many imperatives contained in methods. We should always be questioning the intent of the imperative and verifying that it is a requirement. Is there no alternative? Do we really mean "must"? Or, would we allow a deviation? If the "requirement" is merely a description of what was done during method development/implementation, then it should not be a requirement. We do believe that the imperative writing style adds clarity. For example, "Purge 5 mLs" is much clearer than "5 mLs is purged". However, these imperative statements should be followed by language that indicates other approaches could be performed.

A review of EPA methods for measuring volatile organics by purge and trap GC/MS indicate that there are thousands of requirements. For example, we found 28 requirements in Section 7.3 of Method 8240 relating to daily calibration. This is in addition to the other 50 or so calibration requirements in Method 8000 and the requirement for initial calibration in section 7.2. We believe these requirements could be reduced to a few critical elements, minimum acceptable practices, and all others reworded to indicate the conditions used. For example, for calibration by GC/MS we believe the key requirements are:

1. The mass spectrometer must generate reliable mass spectra, as demonstrated by the measurement of a reference mass marker compound such as bromofluorobenzene.

2. A predictable relationship between response and concentration must be established. This calibration response must be used to define the upper and lower limits of quantitation.

3. The calibration must be shown to be in control during instrument operation.

How then do we assure data quality and comparability? Two ways. First, data quality objectives, established for each and every analysis, are used to specify the requirements expected of the method. For example, if my objective is to measure vinyl chloride in groundwater at 10 ppb with a precision of less than 25%, I would establish the procedural details around this objective. I might for example analyze a larger sample, use vinyl chloride as my matrix spike and specify a 15% RSD for initial calibration.

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If my objective was to survey groundwater for the Appendix IX list of volatiles, I might use representative compounds as matrix spikes and have a larger %RSD for initial calibration, i.e., use the default conditions in the method.

If the method is written to allow for the most general objective, then requirements can be superimposed for more specific objectives.

The second process to assure data quality and comparability is to establish a rigorous method validation process. This process, described later, will allow virtually any change to the method, as long as the change is validated. Otherwise, the information contained in the method become the requirement. The two processes, DQOs and method validation, must be used in tandem.

This approach is not significantly different from the approach in EPA-600/8-83-020, "Guidelines and Format for EMSL-Cincinnati Methods". (4) In fact, the original Method 524, appended to EPA's report, was the closest example to our approach of the methods surveyed. Unfortunately, many of the niceties of this method were eliminated in subsequent revisions. For example, the original method allowed for alternate traps if "it has been evaluated and found to perform satisfactorily". This language was eliminated from the revisions.

DATA QUALITY OBJECTIVES

In 1984, the Quality Assurance Management Staff (QAMS) at EPA proposed that the design of environmental data collection programs be based on the development of Data Quality Objectives (DQOs). DQOs are statements of the level of uncertainty that a decision maker is willing to accept in results derived from environmental data, when used in a regulatory or programmatic decision (9). The DQO process is designed to ensure that the quality of data is compatible with the requirements of the decision making process. By utilizing this process, the participating parties can design an environmental data collection program and its associated QA/QC program which results in data which satisfies the needs of decision makers in a cost effective manner.

In the DQO process, the decision maker must describe the decision, why data are needed and background on the problem. The type of information needed for the decision is described with respect to the scope and type of data required. The use of the data must be defined, along with the importance of the data for making a decision. The consequences of an incorrect decision resulting from inadequate environmental data are also described. The extent to which false positives and false negatives can be tolerated must be defined. In addition, a description of the available resources to fund the project must be stipulated.

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The second stage of the DQO process impacts the laboratory. It is in this portion that the specific data required are defined with respect to analytes, matrices, spatial and temporal requirements. The results to be derived from the data are stipulated. That is, are the data to be assessed for a particular statistic, for values relative to a regulatory action level, or for determination of baseline or background levels. The desired performance with respect to precision and accuracy, and acceptable levels of false positives or false negatives are detailed. It is this portion of the DQO process which should effect the specific method requirements and the laboratory should have the flexibility to establish and validate method criteria to meet the needs of the project.

Matrix-specific QC should be defined in conjunction with these elements rather than being stipulated as an inherent part of the method. The same method can be used to meet a regulatory limit or provide data to determine baseline levels and therefore the frequency and makeup of matrix-specific QC (spike levels and spike components) should be controlled by the type of information being sought, not specified in the method itself.

Every project should go through this evaluation and specification process in which the DQOs are clearly defined. The consensus of the lab, the data user and the regulator must be forged before the work begins. The process should be formalized in a project-specific Quality Assurance Project Plan (QAPjP).

We therefore believe that the methods should have fewer elements relating to the project objectives and that these elements should be addressed by the DQO process. For example, we believe that analytes should not be listed in the method. Rather, a list of compounds evaluated by the method and their performance (precision, bias, detection limits) should be contained as an Appendix to the method. (As a side benefit, this list could be expanded to include additional analytes and/or additional performance data without rewriting the method.) As another example, the components used as matrix spikes, the spike levels and spike frequency should not be specified in the method, but in the project objectives. For example, we are continually amazed at the number of customers who are interested only in PCBs but who require representative pesticide compounds be spiked, because the compounds are listed in Method 8080.

By segregating project objectives from method requirements, data users will be forced to make decisions based on their objectives, and not on some default condition in the method. For example, the ASTM Standard Practice addresses the issue of matrix spikes by first defining a matrix spike as "an aliquot of sample spiked with a known concentration of target analyte(s)" and then requiring matrix spikes to be analyzed "based on the DQOs of the data collection activity". (10)

Thus, the data user must decide on the compounds and the frequency. Obviously, the laboratory must be more involved in the overall process. However, we believe that this approach will improve the quality and

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usability of the data. As presented by Jim Barron of OERR at the Analytical Methods Caucus in San Diego in March 1991, EPA has focused almost entirely on data authenticity. (11) This approach implies that "quality" is achieved when the method is followed exactly and that "fraud" is committed when the method details are not performed. As stated by Mr. Barron, the method can be followed exactly and unusable data of poor quality can be generated. Conversely, useable data of high quality obtained by a non-approved modification of the method can be rejected. We believe that our approach will not only improve the quality and usability of the data but will also restrict charges of fraud to those instances where actual fraud occurs.

This approach obviously increases the complexity of the laboratory work and could result in bottlenecks which would prevent work from ever being performed. We believe the solution to this dilemma is to establish default conditions which are used in many situations, such as those determined from a general survey. In these situations, the default conditions could be written into the method. For example, the default condition for an Appendix IX volatile analysis could be the analytical conditions in the method, representative target compounds for matrix spikes, matrix spikes every twenty samples per project, a five point calibration for all compounds with a 30% RSD for all compounds with two allowed out. The default conditions for analysis of TCLP leachate for toxicity characteristic compounds might involve modifying the sample size relative to the method, using all target compounds as matrix spikes, spiking every sample and requiring a 25% RSD for every compound with a three point calibration.

This approach requires that the laboratory and the data user agree on the objective, prior to the initiation of the project. We have developed a project initiation checklist which addresses these types of issues. In our process, we seek to obtain consensus from the data users on the following issues:

- o   Sample containers, preservatives, holding times
- o   Operational details - sample size, calibration, etc.
- o   Quality control samples - frequency, spike components, spike levels, control limits
- o   Detection limit requirements
- o   Report format, content

In those situations where the objective are not clearly known, we have established default conditions which relate to these issues. These default conditions are documented in our laboratory QAPP, in method SOP's, and in other reference documents. For example, we have a document which lists the spike components and spike levels for routine methods and another document which lists analytes and reporting limits for every test performed.

METHOD VALIDATION

As discussed in the Section 518 report, a validated method is a method based on sound technical principles that can be used routinely to achieve some base level of performance. (12) We believe that method performance data obtained by the author of the method should be included in an appendix so that potential users can evaluate the usefulness of the method.

We also believe that laboratories who propose to use the method must demonstrate a basic capability to generate comparable data using the method. While we believe that the existing approach in Methods 624 and 8240 adequately address this issue, we would recommend a more rigorous approach. We propose that the method contain performance data for a limited number of analytes, such as those on the priority pollutant or target compound lists. This performance data would be used by laboratories to assess their performance. Laboratories wishing to use the method would be required to analyze seven spiked samples (ideally standard reference materials) at concentrations spanning the working range of the method. Statistical tests (f-test and t-test) would then be performed to demonstrate equivalency.

This process would demonstrate that a laboratory has the basic capability to perform the method for a limited number of analytes. On going quality control activities would then demonstrate the laboratory's performance on a continual basis.

The more important issue relates to expanding the analyte list or to modifying the method. We believe that the methods should be sufficiently flexible to allow for extensive modification. However, to provide a measure of control, we recommend that any change to the method and any addition to the basic analyte list be permitted only if a rigorous validation is performed. While on the surface this recommendation may seem overly stringent, if the proposed change will substantially improve the method (better quality, cheaper, faster, safer, etc.) then the effort will be justified. Otherwise, there is no need to change.

Method validation must address method characteristics such as:

    o   detection limit,
    o   working range,
    o   precision,
    o   ruggedness,
    o   matrix,
    o   analytes,
    o   comparability, and
    o   bias

Adding a new analyte is distinctly different from modifying an existing validated method. In the first case, very little if anything is known about the performance and thus a more extensive validation must be performed. We are developing an internal approach which involves four activities. The initial activity is to establish the working instrumental range. Once the working range is known, spiked samples, spanning the working range are carried through the method. If this process is

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successful, ruggedness testing is performed. Finally, blind spiked samples are analyzed. (13)

From these analyses, sufficient information will be provided to thoroughly document all of the method characteristics for the new analytes.

For an existing analyte in an existing method, the method characteristics should be known. The key when changing the method conditions is to demonstrate that the change did not significantly affect the performance. The process involved would require 14 analyses of a spiked sample, seven analyses under the existing method conditions and seven using the proposed modification. Statistical tests (f-test and t-test) would then be performed to demonstrate equivalency.

The previous section discussed replacing method requirements with method descriptions. These method descriptions would be the default requirements unless an equivalency study was performed. Thus, for many of the method details, a proposed change would not be justified relative to the efforts involved. However, if the change was important, e.g. packed column versus capillary column there would be a system to allow for the change.

No equivalency process will address every sample and every method condition that may be experienced. The purpose of this validation process is to demonstrate that the proposed change is fundamentally sound. Laboratory controls and project specific quality control activities are used on an ongoing basis to assess the quality of the laboratory work.

SUMMARY

As David Friedman discussed in his Environmental Lab article, this approach will give analysts (and laboratories) more freedom. For this approach to work, the laboratories and data users must therefore accept more responsibility to ensure that the work is performed correctly. Freedom to change methods will not result in constantly varying methods. This approach will not meet the laboratory needs any better than the current requirements. The driving force for this approach is the achievement of technically sound, defensible data that does not burden the laboratory with overly restrictive requirements.

We recognize that rewriting all of the existing methods to incorporate this approach is a formidable challenge. In the interim, we would request the EMMC to introduce language into each method which will allow deviations based on DQOs and validation data.

Finally, the establishment of DQOs prior to initiation of the work, must be mandated by EPA. It can no longer be acceptable for data users to request an analysis from a laboratory without specifying the requirements.

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PERFORMING TCLP ANALYSES TO GET MEANINGFUL DATA

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The Hazardous Waste Regulations which were promulgated in March of 1990 have had significant impact on waste generators and the commercial laboratory. The major change in the regulation is the substitution of the Toxicity Characteristic Leaching Procedure (TCLP) for the Extraction Procedure Toxicity test. Upon closer examination of the regulation, IEA Inc. of New Jersey discovered several difficulties for waste generators and many new challenges for the laboratory. Typical problems are:

1.0 The waste generator may not be able to tell how many analyses will be required (and the total cost) until after samples have been submitted to the laboratory and initial testing has been performed.

2.0 With many types of samples, matrix interferences severely affect the analysis of one or more fractions.

3.0 For multi-phase samples, data from up to six complete TCLP analyses has to be combined through defined and complicated formulas to a final set of numbers which is then compared to regulatory levels to make a hazardous/nonhazardous decision.

4.0 The regulatory levels for the individual analytes in a particular fraction, such as semivolatiles, cover a range greater than the linearity of the instrument used to do

the analysis.

5.0 Matrix spike levels and other QC requirements are much different from that of "normal" SW846 methods.

All of the above concerns caused IEA, Inc. of New Jersey to take an integrated approach to TCLP analysis. This approach includes all laboratory staff understanding TCLP data quality objectives, client communication, optimized sample preparation methods, TCLP specific analytical schemes, and an automated computer data handling strategy. The end result is a high quality product which specifically addresses the data quality objectives of TCLP and presents the results in a format that is both easy to read and understand. This paper describes this integrated approach in detail.

107   TOTAL CYANIDE BY PHOTOLYSIS

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ABSTRACT

The purpose of this study was to develop and examine a viable method which could provide better quantification of the total cyanide (both soluble and insoluble organometallic complexes) content in a waste. The methods which have been employed comprise the derivatization and gas chromatographic separation of benzylic nitrile derivatives. The results have shown promise in that the reaction occurs spontaneously and at room temperature. Present studies are currently aimed at reducing the overall detection limit and at determining the degradation efficiency of the cyano-metallic complexes through photolysis. At the conclusion of the study, in-house samples will be prepared to compare the prospective with the current EPA methods SW-846 9010 and 9012.

108   AMMONIA and TOTAL KJELDAHL NITROGEN DETERMINATIONS USING FLOW INJECTION ANALYSIS WITH GAS DIFFUSION

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Abstract

Free ammonia and total Kjeldahl nitrogen (TKN) in wastewater have been determined by flow injection analysis (FIA) using a gas permeable membrane. Final effluent from ten sample sites representing the top five standard industrial code (SIC) classifications for the nitrogen parameters were tested. Results comparing this new method with the established EPA methodologies are presented.

FIA methods introduce an aliquot of sample using an injection valve. The valve generally is capable of delivering 40 to 200 uL of sample into a reaction stream which produces ammonia gas. The gas permeates an in-line membrane to enter into an indicating acceptor stream where a color change takes place.

Data indicate that the gas diffusion methods give results equal to or better than currently approved EPA protocols. Operating ranges were determined to be from 0.02 to 10 mg/L with a method detection limit (MDL) of 0.006 mg/L for ammonia and from 0.2 to 10 mg/L with a MDL of 0.02 mg/L for TKN.

The gas diffusion technique is simpler than other automated nitrogen procedures. It does not require harmful chemicals; is not sensitive to Kjeldahl digest pH; and is capable of producing a result in 70 seconds.

Introduction

The growing concern about the environment and the quality of drinking water have caused a substantial increase in the number and frequency of analyses performed by laboratories. The nitrogen parameters (ammonia and TKN) are a particularly important indicator of the quality of water and soils and are monitored routinely. Traditionally these parameters are measured using distillation techniques, ion selective electrodes and a variety of automated colorimetric procedures.

A number of drawbacks exist using the current EPA approved chemistries. The phenate method for ammonia and TKN (EPA 350.1/351.1) requires the use of a high concentration of phenol. Reagent toxicity and disposal issues certainly need attention when this method is used. Similarly, the salicylate methodology for TKN (EPA 351.2) uses sodium nitroferricyanide which is also classified as a hazardous chemical. In addition to the health risks associated with the phenol reagents used in the EPA methods 350 and 351, the smell of the reagents can be a nuisance.

The automated EPA chemistries can be difficult to operate. Both methods are temperature dependent requiring close control. The salicylate method is prone to precipitation problems which cause clogging of the reagent channels. The most troublesome aspect to using these methods is the influence of pH on method sensitivity. Strong buffers are required to maintain pH control. The TKN analysis is particularly a problem in terms of final sample pH. During sample digestion, the organic matter in a sample will consume acid. Therefore it is possible that the indivdual digestion tubes can contain slight acid variations.
Block digestion as a sample preparation for FIA gas diffusion methods proved to be efficient and in general troublefree during the testing phase of this work.

The FIA gas diffusion technique addresses the automated chemistry method drawbacks. The reagents used are sodium hydroxide, water and a colorimetric indicator. An aliquot of sample is injected into a carrier stream which is merged with sodium hydroxide to raise the pH of the sample. Under alkaline conditions ammonium ion becomes ammonia gas which passes through an in-line gas permeable membrane into an interference free colorimetric indicator. The color change of the indicator is monitored at 590 nm and is proportional to the amount of ammonia that passed through the membrane. Variations in the acid content of samples is overcome by using an excess amount of sodium hydroxide. The cycle time of the method is 70 seconds.

In 1990, Tecator AB (Sweden) field tested and submitted the gas diffusion method to the EPA for nationwide method approval and inclusion in the <u>Federal Register</u>. This process was performed as outlined in the EPA bulletin entitled "Requirements for Alternate Test Procedures for Inorganic Parameters in Non-Continuous National Pollutant Discharge Elimination System Monitoring". The results of this study are summarized in this paper.

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Sample Site Selection

In accordance with the June 20, 1990 protocol, ten (10) industrial sites representing five (5) SIC listings for each parameter supplied by EPA were sampled (2 per SIC site) and are listed in Table 1.

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Table 1 SIC Listings for Nitrogen Parameters

Ammonia   **TKN**

SIC	Industry	SIC	Industry
4952	sewerage	4952	sewerage
2621	paper mills	2621	paper mills
2869	industrial chemicals	2869	indust. chemicals
4911	electrical services	1475	phosphate rock
2911	petroleum refining	2611	pulp mills

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Reference Methods

The methods chosen to compare the automated FIA procedures were the ion selective electrode procedure EPA methods 350.3 and 351.4. These methods were chosen since the EPA had a large data base to compare results generated by the proposed methods. In the case of TKN, the electrode method requires block digestion. This feature was appealing since our procedure of choice is block digestion and not the macro digestion procedure commonly used with the distillation methods. Further, EPA was adamant that no deviations from the referenced methods take place. Since the only other block digestion sample preparation procedure approved used the salicylate chemistry, our choice was to use the electrode procedures.

Experimental

Sample Collection and Preservation

Samples were collected in either glass or polyethylene containers. The samples were acidified by the addition of a sufficient amount of conc H_2SO_4 to lower the pH to <2 followed by refrigeration at 4°C. Using this procedure, the maximum allowable holding time is 28 days.

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Analysis Requirements

ATP submission to the EPA can be undertaken for nationwide use (NW) or limited use (LU) by EPA Regional, State or commerical labs and individual dischargers. Table 2 describes the number and type of required analyses and quality control checks that need to be presented in the ATP submission.

In summary, for nationwide ATP approval a method submittal must include 250 analysis results from the top five (5) SIC classifications for a particular parameter (125 each for the approved and proposed methodologies) and 38 quality control checks for a total of 288 pieces of data.

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Table 2 Effluent Sample and Subsample Analytical Requirements

Type	Applicant	Analyses			Quality Control		
		unspiked	spiked	total	known	unknown	total
NW	Any	10	240	250	25	13	38
LU	EPA Regional State or commerical	5	120	125	13	7	20
LU	Indiv. discharger	5	60	65	7	4	11

****

Digestion Procedure

A block digester was pre-heated to 160°C. 100 mL of sample or an aliquot of sample diluted to 100 mL was placed in each digestion tube. Sulfuric acid-mercuric sulfate-potassium sulfate solution was added to each sample tube. Two boiling rods were placed in each tube. A fume exhaust manifold was placed over the digestion tubes which were then lowered into the preheated block for one hour. The block temperature was then raised to 380°C for one and one half hours. The tubes were removed from the digester; the boiling rods rinsed and the residue diluted to volume.

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Apparatus

FIA System

Tecator FIA System to include:

Injection valve capable of injecting 40 to 200 uL samples
Tecator gas diffusion chemifold
Thermostat
590 nm detection system

Digestion Apparatus

Tecator aluminum block digester (6 or 20 place)
Fume removal manifold
Digestion tubes, 250 mL
Boiling rods

FIA System Operating Information

Injection time	20s
Cycle time	70s
Analysis rate	50/hr
Sample loop	40 - 200 uL
Temperature	30°C
Wavelength	590 nm
Pathlength	10 mm

Flow Diagram Information (See Figure 1)

Mixing coil: 100 cm x 0.7 mm id
                (temperature - 30°C)

Flow rates: Sample   (blk/blk) = 1.4 mL/min
                Reagent 1 (or/or) = 1.8 mL/min
                Reagent 2 (or/wh) = 0.9 mL/min
                Indicator (blk/blk) = 1.4 mL/min

Reagents:

	Ammonia	TKN
Reagent 1	water	5 N NaOH
Reagent 2	0.5 N NaOH	5 N NaOH

Revised 3/91

Figure 1

Ammonia/TKN Flow Injection Gas Diffusion Manifold

FIA SYSTEM OPERATING INFORMATION

Injection time:	20s
Cycle time:	70s
Analysis rate:	50/hr
Sample loop:	200μL
Temperature:	30°C
Wavelength:	590 nm
Pathlength:	10 mm
Evaluation:	peak height
Gain:	1

FLOW DIAGRAM INFORMATION

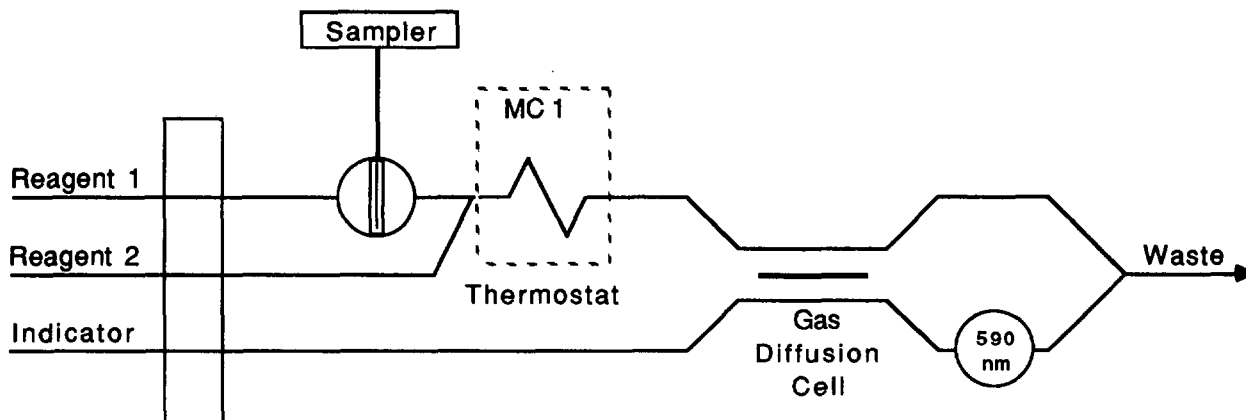Mixing coil 1:   100 cm x 0.7 mm i.d. (temperature = 30°C)

Flow rates: Sample (blk/blk) = 1.4 mL/min
Reagent 1, NaOH (or/or) = 1.8 mL/min *
Reagent 2, NaOH (or/wh) = 0.9 mL/min
Indicator (blk/blk) = 1.4 mL/min

* For Ammonia Reagent 1 = Water

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Quality Assurance

Each laboratory using these methods in regulated environmental monitoring is required to operate a formal quality assurance/control program. The minimum initial requirements of this program consist of the demonstration of the laboratory's capability with these methods. On a continuing basis,the laboratory should check its performance (accuracy and precision) by analyzing reagent blanks and check standards, fortified blanks and/or fortified samples preferably at a minimum frequency of 10% of the total samples analyzed by the methods. The laboratory should maintain the performance records that define the quality of the data generated with the method.

Method Detection Limit (MDL)

The procedure for determining the MDL is outlined in 40 CRF, Part 136, Appendix B, Rev. 1.11. A refined second document in Environmental Science and Technology (1981, 12, 1427) by EPA personnel further explains the MDL calculation. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The MDL for ammonia and TKN was experimentally calcuated to be 0.0064 and 0.023 mg/L respectively (Table 3).

Results

Linear Range

Calibration curves for the ammonia and TKN gas diffusion methods were linear over the concentration ranges tested. Figure 2 is the calibration curve for ammonia in the 0.02 - 2.0 mg/L range (gain setting = 5). It is described by $y = -0.0092 + 0.5578x$ $R = 1.00$. A second calibration for ammonia in the 0.2 - 10 mg/L range (gain setting = 1) was run and is described by $y = -0.0046 + 0.0969x$ $R = 1.00$. The TKN method was linear over the 0.2 - 10 mg/L range. The TKN curve is described as $y = -0.003 + 0.0713x$ $R = 1.00$.

Accuracy and Precision

Data indicate that the gas diffusion methodology is capable of measuring ammonia and TKN levels over the indicated ranges with high accuracy and good precision. Results are presented in Tables 4 and 5. Analysis of EPA unknown samples were carried out over the course of the work (3 months). Results are presented in Tables 6 and 7. EPA has yet to declare the value but the five (5) individual ampules of each unknown is consistent over the three (3) month testing period.

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Figure 2

NH3, T-W-0020-1, High Range (Revised 3/91)

$$y = -0.0046 + 0.0969x \quad R = 1.00$$

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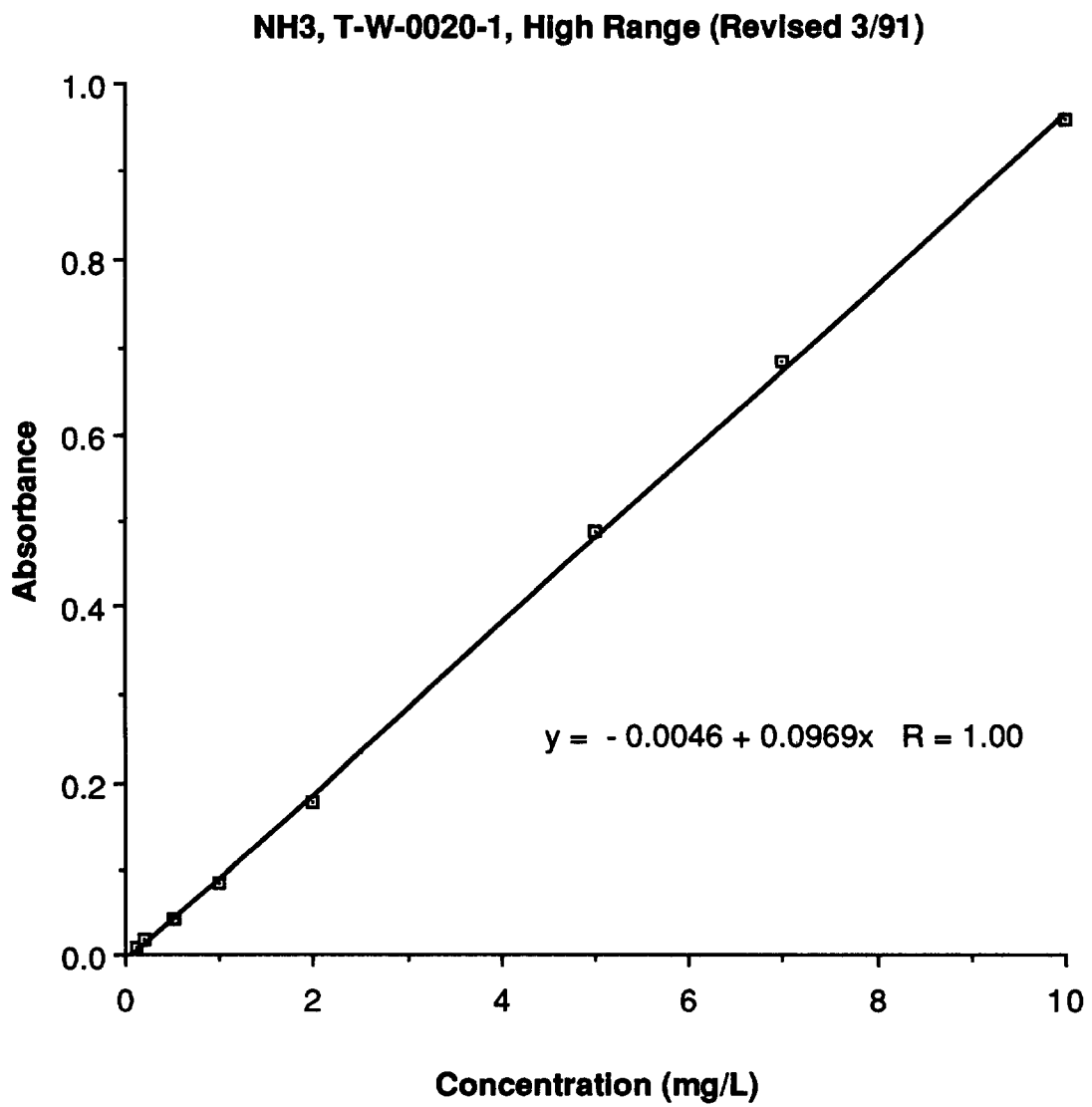
SIC Sample Analysis

A sample data set which compares the EPA accepted methodology (ISE) and the gas diffusion method for ammonia for a SIC sample is presented in Table 8. Table 9 shows similar data for a TKN SIC sample.

Compiled data for the entire data set are shown in Tables 10 and 11.

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Table 3 MDL Information

	TKN	Ammonia
Mean (n = 7)	0.329	0.0175
St Dev	0.0063	0.0023
S_a^2	0.00011	0.000006
S_b^2	0.000039	0.000005
$F_{.95(6.6)}$	4.28	4.28
S_a^2/S_b^2	2.78	1.18
S_{pooled}	0.0087	0.0024
MDL (mg/L)	0.023	0.0064

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Table 4   Ammonia Accuracy and Precision

Known	Mean	St Dev	RSD (%)	Bias	% Recovery
0.04	0.04	0.01	25.00	0.0	100.0
0.25	0.24	0.02	8.33	−0.01	96.0
0.51	0.51	0.01	1.96	0.0	100.0
1.00	0.99	0.02	2.02	−0.01	99.0
4.00	4.08	0.04	0.98	+0.08	101.7
9.05	8.90	0.05	0.56	−0.15	98.3

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Table 5 TKN Accuracy and Precision

Known	Mean	St Dev	RSD (%)	Bias	% Recovery
0.20	0.20	0.02	10.00	0.0	100.0
0.30	0.30	0.03	10.00	0.0	100.0
0.90	0.91	0.01	1.10	+0.01	101.1
2.50	2.53	0.01	0.40	+0.03	101.2
4.00	3.95	0.03	0.76	−0.05	98.8
8.00	7.99	0.25	3.13	−0.01	99.9

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Table 6 Analysis of EPA Ammonia Unknown Samples

	Unknown #1	Unknown #2	Unknown #3
Trial 1	20.66	3.55	0.98
Trial 2	21.13	3.49	1.00
Trial 3	20.69	3.46	1.18
Trial 4	20.35	3.42	0.96
Trial 5	20.91	3.53	0.93
Mean	20.75	3.49	1.01
St Dev	0.26	0.05	0.09

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Table 7 Analysis of EPA TKN Unknown Samples

	Unknown #1	Unknown #2	Unknown #3
Trial 1	0.73	11.37	12.59
Trial 2	0.72	10.30	12.91
Trial 3	0.75	10.60	13.34
Trial 4	0.76	11.00	13.05
Trial 5	0.71	11.00	13.00
Mean	0.73	10.85	12.98
St Dev	0.02	0.37	0.24

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Table 8

Tecator AB Alternate Test Procedure Data

Nitrogen, Ammonia, Method T-W-0020-1

Automated FIA Gas Diffusion Reference No. N90 0018

Technique	Sample A		Sample B		Sample C		Sample D	
	ISE	FIA	ISE	FIA	ISE	FIA	ISE	FIA
Trial 1	0.19	0.20	388	379	809	794	1208	1189
Trial 2	0.17	0.20	388	388	780	802	1194	1183
Trial 3	0.16	0.20	387	381	789	800	1183	1187
Mean	0.17	0.20	388	383	793	799	1195	1186
St Dev	0.01	0.0	< 1	3	10	3	9	2

Source: SIC 4952 Sewerage Plant #1

Note: Ammonia results in mg/L; ISE Method EPA 350.3

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Tecator AB Alternate Test Procedure Data

Nitrogen, TKN, Method T-W-0021-1

Block Digestion, Automated FIA Gas Diffusion EPA Reference No. N90 0015

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Table 9

Technique	Sample A		Sample B		Sample C		Sample D	
	ISE	FIA	ISE	FIA	ISE	FIA	ISE	FIA
Trial 1	0.18	0.14	8.2	8.0	16.1	16.1	24.2	24.2
Trial 2	0.19	0.17	7.9	8.0	16.7	15.8	24.8	24.4
Trial 3	0.18	0.17	8.2	8.1	15.7	16.4	24.6	23.4
Mean	0.18	0.16	8.1	8.0	16.2	16.1	24.5	24.0
St Dev	0.0	0.01	0.1	0.01	0.4	0.2	0.2	0.4

Source: SIC 4952 Sewerage Plant #1

Note: TKN results in mg/L; ISE Method EPA 351.4

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Table 10

Combined Ammonia Data

SIC 4952   Sewerage

		Confidence Intervals	
Technique	Mean	-3s	+3s
FIA	0.16	0.12	0.24
ISE	0.16	0.10	0.22
FIA	393	357	429
ISE	399	361	437
FIA	800	791	809
ISE	782	722	859
FIA	1202	1150	1254
ISE	1182	1148	1226

SIC 2621   Paper Mills

FIA	0.16	0.01	0.31
ISE	0.14	0.01	0.29
FIA	387	355	419
ISE	398	367	429
FIA	771	712	830
ISE	764	676	852
FIA	1209	1160	1258
ISE	1196	1151	1241

SIC 2869   Industrial Chemicals

FIA	0.19	0.13	0.25
ISE	0.17	0.08	0.26
FIA	388	333	443
ISE	398	387	409
FIA	794	768	820
ISE	793	775	811
FIA	1197	1177	1217
ISE	1198	1182	1214

SIC 4911   Electrical Services

FIA	0.18	0.12	0.24
ISE	0.16	0.02	0.34
FIA	403	401	405
ISE	388	373	403
FIA	808	780	836
ISE	794	768	820
FIA	1202	1196	1208
ISE	1191	1160	1222

SIC 2911   Petroleum Refining

FIA	0.20	0.08	0.32
ISE	0.15	0.12	0.18
FIA	392	386	398
ISE	392	371	413
FIA	806	782	830
ISE	799	772	826
FIA	1206	1146	1264
ISE	1200	1156	1244

Note: Ammonia results in mg/L

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Table 11

Combined TKN Data

SIC 4952   Sewerage

Technique	Mean	Confidence Intervals	
		-3s	+3s
FIA	0.14	0.05	0.23
ISE	0.16	0.08	0.24
FIA	8.0	7.1	9.1
ISE	8.1	7.1	9.1
FIA	16.2	15.4	17.0
ISE	16.2	12.2	20.2
FIA	24.1	22.3	25.9
ISE	24.5	22.3	26.7

SIC 2621   Paper Mills

FIA	0.14	0.11	0.17
ISE	0.13	0.01	0.25
FIA	8.0	8.0	8.0
ISE	8.0	7.3	8.7
FIA	16.2	15.6	16.8
ISE	16.1	14.3	17.9
FIA	24.0	23.3	24.7
ISE	23.8	21.5	26.1

SIC 2869   Industrial Chemicals

FIA	0.18	0.15	0.21
ISE	0.17	0.05	0.29
FIA	8.1	7.9	8.3
ISE	8.0	7.6	8.4
FIA	16.0	15.5	16.5
ISE	16.2	14.9	17.5
FIA	24.1	23.6	24.6
ISE	23.9	22.8	25.0

SIC 1475   Phosphate Rock

FIA	0.18	0.15	0.21
ISE	0.14	0.01	0.28
FIA	7.8	6.8	.8
ISE	8.2	6.9	.5
FIA	16.2	15.6	16.8
ISE	16.2	15.7	16.7
FIA	23.8	21.9	25.7
ISE	24.0	22.8	25.2

SIC 2611   Pulp Mills

FIA	0.13	0.02	0.24
ISE	0.18	0.12	0.24
FIA	8.1	7.6	8.6
ISE	8.2	7.0	9.4
FIA	16.4	15.3	17.5
ISE	16.3	14.0	18.6
FIA	24.2	23.7	24.7
ISE	24.0	22.4	25.6

Note: TKN results in mg/L

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Discussion

Precision and accuracy for the FIA gas diffusion methods are shown in Tables 4 and 5. For ammonia samples the standard deviation did not exceed 0.05 and recovery ranged from 96.0 to 101.7 percent. For TKN the standard deviation did not exceed 0.25 and recovery ranged form 98.8 to 101.2 percent. Tables 6 and 7 show analyses of EPA unknowns for ammonia and TKN respectively. Again, very good precision for the FIA gas diffusion technique is exhibited.

Tables 8 and 9 show complete data sets for both the ISE reference methods and the FIA methods from one of the sewerage sites (SIC 4952). Four samples were tested in triplicated by the ISE and FIA procedures for both TKN and ammonia. The equivalency of the FIA gas diffusion technique to the ISE reference method is obvious.

Tables 10 and 11 show the combined data for each of the two sites for each parameter (TKN and ammonia) and each SIC code. In almost all cases the precision of the FIA gas diffusion technique is equivalent or better than the ISE reference technique.

Conclusion

The FIA gas diffusion technique for testing ammonia and TKN in wastewater has been shown to provide equivalent results to the EPA reference ISE methods (350.3 and 351.4). At a rate of 50 samples per hour it offers an automated approach to TKN and ammonia analysis of wastewater additionally it does not have the drawbacks of the phenate and salicylate methods (350.1, 351.1 and 351.2) which were stated in the introduction.

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109   AN OBJECTIVE CRITERION FOR TERMINATING PERMEABILITY TESTS

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ABSTRACT

In present day (1991) geotechnical engineering laboratories, when permeability testing is performed, whether the testing is being performed for research purposes or design purposes, the criteria used to terminate the permeability tests vary from laboratory to laboratory. While an experienced engineer may be able to determine when equilibrium has been reached, his judgment is based solely on his past experience with the type of soil/permeant/permeability test combination he is using: thus it is a subjective judgment.

Subjective judgments are used in engineering every day, especially in the field of geotechnical engineering, with its highly variable soil types and soil conditions. Most laboratory tests used to determine distinct properties of a given soil have an objective criterion associated with the tests. For example, the Proctor test uses a specific energy input; the plastic limit uses a 1/8-inch thread; the liquid limit uses the number of blows to close a given width groove along a 1/2-inch length of the groove; and shear strength tests use a given percent strain depending on the use and type of soil.

In recognition of the uncertainties and inadequacy of a totally subjective test termination criterion, this paper will investigate a new and more generally applicable objective criterion for terminating a permeability test. This approach is applicable to the soil types commonly tested in a geotechnical or materials testing laboratory.

The termination criteria developed are not intended to replace the judgment of the engineer or researcher. The termination criteria are tools to be used as an objective confirmation of the judgment of the engineer or researcher in determining that a test has reached equilibrium. In no case should judgment be overridden if the engineer or researcher feels the test has reached equilibrium.

Background

The use of relatively impervious compacted clays and grouted sands for such purposes as liners in hazardous and toxic waste landfills, as cores in earth and earth-rock dams, and as cutoffs for dams requires a thorough understanding of the capability of the soil to satisfactorily perform its intended function. The major indicator of the ease with which water is able to travel through a soil is referred to as the permeability of the soil.

Permeability and Hydraulic Conductivity

The terms permeability and hydraulic conductivity are often interchanged in the field of geotechnical engineering. From the

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fluid flow aspect, this is only correct if the fluids are held at 20 C. The fundamental difference is that to calculate intrinsic permeability, the temperature (and thus viscosity) of the permeant is taken into account. The use of the term "permeability" throughout this paper is to be taken as hydraulic conductivity, as no effort is usually taken in soil mechanics laboratories to measure fluid temperature.

Definition of Permeability

Permeability can be defined as the discharge velocity through a unit area of soil under a hydraulic gradient of unity (Cedergren, 1989). It is more commonly known as the coefficient 'k' in Darcy's law for laminar flow in a soil media. Darcy's law can be stated by the equation

$$Q = kiAt \qquad\qquad \text{Eq. 1}$$

where Q is the quantity of seepage flowing through a cross section of soil having an area A normal to the direction of flow, under a gradient i, during a period of time t. If the terms in Equation 1 are rearranged, Equation 2 is obtained, which is the basis for the experimental determinations of permeability that measure the amount of seepage over a period of time under a given gradient.

$$k = Q/iAt \qquad\qquad \text{Eq. 2}$$

The coefficient of permeability has units of velocity and is usually expressed in centimeters per second, cm/s, for soils having a low coefficient of permeability. Other commonly used units include ft/day and ft/yr.

The coefficient of permeability is usually assumed to be constant for a given soil type. However, it can vary widely for a given soil type or other material depending on a number of factors, as discussed in detail by Taylor (1948), Daniel (1985), Bodocsi (1988), Bowers (1988), Carson (1988), Cedergren (1989), and Conrad (1991).

Laboratory Methods for Determining Permeability

The two most commonly used methods for determining the coefficient of permeability of a soil sample in a laboratory are the constant head permeability test and the falling-head permeability test, utilizing either a rigid wall or a flexible wall permeameter. A discussion on the constant head and falling-head tests can be found in Cedergren (1989). Daniel, et al., (1985), Carpenter (1986), and Evans (1986) discuss permeameters in detail.

Terminating A Permeability Test

During a permeability test the measured permeability of a soil sample often undergoes a prolonged period of transitional behavior before an equilibrium value of permeability is reached. The decision as to when an equilibrium value has been reached is not straightforward. In general, no concensus criteria exist for terminating the

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permeability test procedure.

The existence of a standardized objective criteria would allow for more reliable comparisons of permeability between independent research laboratories and commercial soil testing laboratories, would aid in the elimination of inconsistencies in permeability test results, and would eliminate unnecessary testing time (Pierce and Witter, 1986).

Review of the Literature

A review of the literature has revealed several termination criteria in use at the present time, with subjective judgment being the most common method used.

Subjective Judgment

The method of subjective judgment can be described as a method in which a subjective decision is made regarding whether the permeability of a test sample has reached equilibrium by examining a plot of permeability vs. time for the test. A horizontal plot is sometimes used as an indicator of equilibrium. However, the soil being tested may result in a permeability on the order of say 10^{-7} cm/s. A horizontal plot on this scale may be interpreted as equilibrium, even when the slope has some small deviation from the horizontal. At this order of magnitude of permeability, a very slight deviation in the permeability plot may in fact be an increase or decrease of several percent. In other words, equilibrium may not have been reached. Conversely, if the soil type were such that a value of permeability on the order of 10^{-3} cm/s resulted, a large deviation from the horizontal may in fact represent only a small percent increase or decrease in permeability. In the latter scenario, equilibrium may have been reached and the engineer may not realize this due to the visual appearance of the plot.

The previous paragraph used percent increase or decrease in permeability as a measure of comparison of the data points from reading to reading during a permeability test to determine if equilibrium has been reached. This is similar to the method used by McCandless (1988). In this termination criterion, if the value of permeability does not vary by more than a predetermined percent for a set number of readings, it is judged that equilibrium has been reached. The difficulties inherent in this method are how to determine an acceptable percent change in permeability over the course of several readings and how to arrive at the number of readings over which the termination analysis is to be made. For soils with a low value of permeability, a relatively small percent change might be selected. The question still remains: "How small of a percent change is acceptable?" Even when combining the percent change over several readings with a visual examination of a plot of the permeability test data, questions arise as to whether equilibrium has been reached. Conversely, for a soil with a higher permeability value, the question becomes: "How large of a percent change is acceptable?"

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Other Methods Used to Terminate a Permeability Test

Pierce and Witter (1986) use a combined criterion, specifying that at least one pore volume of permeant must have passed through the sample and the slope of a plot of log permeability vs. number of cumulative pore volumes cannot be shown, by the use of a regression analysis, to differ significantly from zero. Although this criterion is one of the most promising termination methods to be developed, the use of linear regression for determining the slope of the plot has several statistical shortcomings.

Bryant and Bodocsi (1986) suggest the use of an adaptation of Mann's test for monotone trend and also discuss the use of a Bayesian analysis. Other termination criteria, used individually or in combination with other criteria, include: a predetermined number of pore volumes passing through the sample; a change in permeability by several orders of magnitude; a predetermined concentration of the effluent (if a chemical permeant is used); a plot of log permeability vs. some measure of time becoming horizontal; a value of k greater than 10^{-7} cm/s being reached (for a soil to be used as an approved EPA cover or liner); or the passing of at least two pore volumes of permeant through a soil sample in conjunction with a horizontal plot of log permeability vs. some measure of time. Although several of the criteria used show promise and attempt to overcome some of the shortcomings of subjective judgment, these criteria do in fact also exhibit some disadvantages.

The most promising termination criterion appears to be that suggested by Bryant and Bodocsi (1986). This source has developed the groundwork for a statistically based termination criterion which overcomes the statistical disadvantages of the method developed by Pierce and Witter. The method developed by Bryant and Bodocsi uses Mann's test for monotone trend to determine if equilibrium has been reached within predetermined statistical levels of significance and bounds.

Application of Mann's Test For Monotone Trend

Advantages Over Regression Analysis

Mann's statistic (Bryant and Bodocsi, 1986) is designed to be sensitive to any increasing trend, and by altering the method slightly, the statistic is also sensitive to any decreasing trend. Conversely, linear regression may be relatively insensitive in a case where permeability is increasing at a decreasing rate, such as happens when the permeability test is approaching equilibrium. Mann's statistic is less sensitive to occasional unusual observations, which occur in most permeability tests. These occasional unusual observations might unduly affect a slope computed by least squares regression analysis such as in Pierce and Witter's method. Finally, Mann's statistic does not require the assumption of normally distributed within test errors. Regression analysis requires the latter (Bodocsi and Bryant, 1986).

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General Example

In order to apply Mann's test for monotone trend to a set of permeability test data, Bryant and Bodocsi have heuristically adapted it for use in a sequential manner. For this general example, the procedure will be described as if a permeability test were being run for a soil in which the test results would indicate a general increase in permeability with time as the test approaches a final equilibrium value. The 4 steps involved in the procedure are discussed below.

1. The permeability test is permitted to run over a preliminary period of time to allow at least two pore volumes of flow to pass through the test sample.

2. Following the preliminary testing period, permeability values are measured at n equally spaced points in time (t = 1, 2, ..., n). Mann's test for monotone trend, a nonparametric statistical test, allows for the use of data which is not normally distributed (contains less than approximately 30 data points). The use of too few data points provides insignificant results. Bryant (1986-1987) recommends the use of 15 data points at the start of the procedure.

Equally spaced test readings should be used. This is a generally accepted practice in most laboratories, with readings taken at approximately the same time every day. As long as the time between test readings does not vary drastically, the use of approximately equal time intervals should be adequate. For test samples exhibiting a permeability less than 10^{-10} cm/s, the pore volumes of flow permeating a test sample during a reading interval may be difficult to determine, depending on the experimental apparatus being used and the environment in which the apparatus is being used. Carson (1988) indicates that a value of permeability of 10^{-12} cm/s may be the lowest value of permeability which can be obtained with a conventional permeability testing apparatus. The use of a constant flow permeameter may eliminate this lower bound. The permeability values are converted to $\log_{10}$ permeabilities, denoted as y_t, in this step.

3. Mann's test is used to test a null hypothesis of no trend (i.e., the plot of y_t vs. time is horizontal and equilibrium has been reached) against the alternative hypothesis of an increasing trend in (i.e., the value of y_t continues to increase with time) at a specified level of significance a_1. If the null hypothesis of no trend is rejected, then the oldest test observation is deleted from the data set and a new observation is made. Step 3 is repeated until the null hypothesis of no trend is accepted. Step 4 is then conducted.

a_1 represents the probability of a Type I error occurring. To guard against a Type I error, a_1 is chosen to be small. The actual value of a_1 is selected to be 0.01, approximately representing a 99% confidence level that a Type I error will not occur.

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After the first n data points for analysis are selected, Mann's test statistic is computed by calculating the tied ranks and the bivariate ranks for the 2 x n matrix X representing the row x column matrix of the first n data points of time and permeability. The matrix X is

$$X = \begin{matrix} X_1 & X_2 & X_3 & \cdots & X_n \\ Y_1 & Y_2 & Y_3 & \cdots & Y_n \end{matrix}$$

This results in a 3 x n matrix F. Row 1 of F contains the tied ranks R_{1j} of the first row of X; row 2 of F contains the tied ranks R_{2j} of the second row of X; row 3 of F contains the bivariate ranks Q_{ij} of X.

The tied rank R_{ij} of an element X_i of a vector is defined as

$$R_{ij} = 0.5 + \quad u(X_i - X_j) \qquad \text{Eq. 3}$$

where

$$u(t) = \begin{matrix} 1, & \text{if } t < 0 \\ 0, & \text{if } t = 0 \\ -1, & \text{if } t > 0 \end{matrix}$$

The bivariate rank Q_{ij} of a pair of elements (X_i, Y_i) is defined as

$$Q_{ij} = 0.75 + \quad u(X_i - X_j)u(Y_i - Y_j) \qquad \text{Eq. 4}$$

where u(t) is defined as in Equation 6.

Kendall's Tau for Step 3, T_3, is

$$T_3 = (4 \quad F_{3j} - n^2 - 3n) / (n(n-1)) \qquad \text{Eq. 5}$$

where F_{3j} is the sum of the elements of row 3 of F.

Mann's statistic for Step 3 is found by dividing T_3 by the variance of Kendall's T, S_T, which is

$$S_T = 2(2 \times n + 5) / (9 \times n \times (n - 1)) \qquad \text{Eq. 6}$$

Mann's statistic for Step 3, denoted by Z_3, is now

$$Z_3 = T_3/S_T \qquad \text{Eq. 7}$$

Z_3 is now compared to the critical value of Z, Z_c, for a level of significance a_1. If Z_3 is greater than Z_c, the null hypothesis is rejected. The next step is to add a new data point after the next reading and drop the oldest data point.

4. Step 4 requires that the experimenter specify an upper bound

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on the slope of y_t vs. time plot from horizontal at the termination of the permeability test. This bound is referred to as B^*, which is greater than zero for a general increase in permeability with time.

In Step 4, the data is adjusted by computing a value of y_t^*, which is

$$y_t^* = y_t - B^*t \qquad\qquad \text{Eq. 8}$$

Mann's test is now performed on the adjusted test data, as in Step 3. If the null hypothesis of no trend for the adjusted data is accepted at a level of significance a_2 against an alternative hypothesis of a downward trend in the adjusted upper bound data, then the permeability test is terminated: equilibrium has been reached. If the null hypothesis is rejected, an additional observation is made, but the oldest observation in the data set is not deleted. The sample size is thereby increased by one data point. Return to Step 3 and repeat the procedure until the null hypothesis is accepted in Step 4.

For acceptance of the null hypothesis for Step 4, Z_4 must be less than Z_c at a level if significance a_2. When this occurs, the null hypothesis for Step 4 is accepted. The permeability test can now be terminated and the permeability value for the sample is that determined for the terminating observation.

a_2 represents the probability of a Type II error. To guard against a Type II error, a_2 is chosen to be small. The actual value of a_2 is selected to be 0.05, a level of significance commonly used in engineering statistical applications (Brubaker and McGuen, 1990).

B^* is a measure of the degree of trend the experimenter judges to be practically, as opposed to statistically, significant. B^* represents an upper bound (for tests exhibiting generally increasing permeabilities) of the slope of the permeability plot, below which the experimenter wants the final slope of the permeability plot to be, in order to be considered for hypothesis testing in Step 4. B^* cannot be selected statistically per se; it can however be selected practically, using the results of past tests and appropriate levels of significance a_1 and a_2. A goal of this research is to select practical values of B^* to use in Step 4. B^* is proposed to be dependent on soil type.

A typical statistical hypothesis test would terminate testing immediately upon acceptance of the null hypothesis in Step 3. Acceptance of the null hypothesis in Step 3 does not necessarily provide statistically strong evidence that a trend does not exist. It only implies that such a hypothesis can be maintained.

Step 4 adds a check to determine whether the procedure is sensitive enough to detect trends of a meaningful magnitude. With relatively noisy data, as is the case for permeability tests, the insignificance of a hypothesis test for trend does not provide a reasonable termination criterion. The insignificance of the test must be combined with a mechanism which ensures achievement of an adequate

sensitivity against trends of a meaningful magnitude. To guard against a Type II error, the selection of B^* is critical. Step 4 also increases the sample size to increase the sensitivity of future tests.

In summary, the procedure terminates a permeability test after two statistical criteria have been met:

   1.   A hypothesis that the slope of a plot of y_t vs. time is equal to zero can be maintained, and

   2.   A hypothesis that the slope of a plot of y_t vs. time is equal to or greater than B^* (for tests exhibiting generally increasing permeabilities) or is equal to or less than B^* (for tests exhibiting generally decreasing permeabilities) is almost certainly false.

The Permeability Plot

A typical permeability plot consists of the dependent variable, permeability, plotted on the ordinate scale, usually as $\log_{10}$, vs. the independent variable, time, plotted on the abscissa. The measure of time should be such that an equal interval of time is obtained for each data point. The two most common measures of time used for permeability tests and the associated permeability plot are raw time on test, measured in consistent units of hours, days, etc., and cumulative pore volumes of flow passing through the sample.

The use of cumulative pore volumes of flow was thought to be superior to the use of raw time. At the start of a permeability test, readings are taken at specified periods of time, which are usually dependent on soil type and the judgment of the experimenter. As a test progresses, an increased or decreased number of pore volumes of flow will pass through the sample during the specified time period. If the time interval between readings is maintained, especially for soils with low permeabilities, reading the difference in fluid levels in the standpipes becomes difficult, depending upon the permeability apparatus being used. This introduces errors into the calculated value of permeability for a reading interval. If the time interval is modified, resulting in reading intervals which allow for approximately similar volumes of permeant to pass through the sample between readings, a regular interval measure of time is obtained.

Bodocsi and Bowers (1989) and Carson (1988) indicate that the use of cumulative pore volumes of flow as a measure of time results in a difficult analysis of graphical plots of log permeability vs. time when the material has a low value of permeability. Permeability plots using pore volumes of flow on the abscissa become vertical as the permeability test progresses, indicating a decrease in permeability and the associated reduction of volume of permeant passing through the sample. Raw time is found to be the superior measure of time for materials with extremely low values of permeability. Where equipment restrictions do not apply and readings can be taken at equally spaced time intervals, a time scale using raw time should be used. The final determination of which scale to use

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on the abscissa rests with the experimenter.

Bodocsi and Bryant (1986) state empirical and practical reasons for the use of a $\log_{10}$ scale on the ordinate. This practice is used in this paper.

In summary, a plot of log permeability vs. some measure of time is to be analyzed to determine if the slope of the permeability plot at equilibrium is essentially zero, within practical and statistical means.

Parameter Selection

Several parameters are required to perform the various steps discussed for determining when to terminate a permeability test. The statistical levels of significance a_1 and a_2 and the upper or lower bound on the slope of the permeability plot, B^*, are used to guide the experimenter as to whether or not the permeability test should be terminated. The methodology used to select applicable parameters to use in the algorithm is discussed.

Methodology

Bodocsi and Bryant (1986) recommend a practical selection of B^* based on the results of past permeability tests and appropriate levels of significance. This methodology requires data from many permeability tests and some indication of when the permeability test should have been terminated.

Bodocsi, et al. (1986), Bowers, et al. (1988), and Carson (1988) ran a large number of permeability tests. The test data includes data using water as a permeant to determine the baseline permeability of a sample and using various chemicals as permeants to determine the affects of chemical permeants on various grouts. McCandless (1988) ran several permeability tests to determine the acceptability of various solidification/stabilization mixes. Eighty five data sets were selected for analysis in this work. Most of the permeability plots for the data had an approximate horizontal segment, representing an apparent termination time.

A panel of five experts was assembled to determine when to terminate a permeability test, based on the permeability plot for a given data set. These individuals have a strong experience background in permeability testing. They have struggled with permeability test data in the past in trying to determine if a given permeability test should be stopped.

Each expert reviewed the history of the permeability plot for each of the 85 data sets, eliminating data points which were thought to be non-representative of the history of the test (i.e., bad reading, apparatus problems, sample deterioration, etc.). The expert then determined when he, as an experimenter, would have terminated the permeability test. The expert was asked to consider only the portion

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of the plot which would have been available during the actual test. In other words, "future" readings were not to be considered.

Several panel members were intimately familiar with many of the data sets. The data sets were given generic names, Data Set 1, Data Set 2, and so on, in an attempt to mask the actual identity of the data. Those panel members familiar with the data indicated that several of the plots looked familiar, but an effort was made to use an unbiased judgment in determining the termination point.

The panel members were asked to indicate which method they used to select the termination point. Some form of subjective judgment was used by all panel members.

Final Data Sets and Ranges of Permeability

The data sets supplied to the panel members were modified to eliminate the data points thought to be non-representative of the test history. The data files were then set up for use in computer runs through a FORTRAN computer program which mimics the SAS routine used by Bryant to calculate the required statistical information.

Five ranges of permeability data were used, based on the apparent order of magnitude of the termination points selected by the panel. The panel agreed on the termination point in most cases. In several instances, the data set was broken up into two separate data sets, to reflect the selection of one termination point by two or three of the panel members and the selection of another termination point a large number of readings away from the former point by the remaining two or three panel members. The ranges of permeability for which parameters will be selected are 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9}, and 10^{-10} cm/s.

Initial Runs To Select Parameters

Several data sets were run to test the significance of a_1 and a_2 on the selected termination point. For all computer runs, B^* was allowed to vary for each combination of the levels of significance, resulting in a total of 500 combinations of a_1, a_2, and B^* for each data set. The computer program was modified to print a summary table, listing the combination of the parameters used to indicate the first point at which the procedure would stop the permeability test. For the data sets analyzed, B^* was the more significant parameter, resulting in a change in the selected termination point of several data points for a change in B^* of only 0.0001. Clearly, B^* is the more significant parameter, regardless of the selection of the combination of levels of significance.

Selection of B^*

With a_1 and a_2 set at 0.01 and 0.05 respectively, the determination of B^* proceeded as follows. The computer program was modified to print a summary table indicating the first point at which the null hypothesis for Step 4 was accepted, along with the value of B^* used for that run. B^* was varied from 0.0001 to 0.10. Each data set was

evaluated, with the values of B^* and permeability being tabulated for the termination point selected by each panel member.

Several data sets gave an indication that the value of B^* used in the analysis is not significant or the values used for B^* were not small enough or large enough to be sensitive to the data set. In other words, the test was shown to terminate at the same data point for every value of B^* used, or the test was shown to terminate prior to or long after reaching the termination points selected by the panel. These data sets will have to be reanalyzed using values of B^* less than 0.0001 and greater than 0.10. Therefore, at the time of this writing, the results should be considered preliminary.

Discussion

A plot of log permeability vs. log B^* was generated using the Harvard Graphics software. This plot illustrates apparent relationships of log permeability vs. log B*, depending upon the order of magnitude of permeability. The relationships appear to be more sensitive for the higher orders of magnitude of permeability.

The apparent relationships between B^* and Permeability were analyzed using simple linear regression with $\log_{10}$ transformations on the data for three orders of magnitude of permeability: 10^{-7}; 10^{-9}; and 10^{-10} cm/s. The relationships using the data transformations indicate correlations of 0.528, 0.725, and 0.117, respectively for these orders of magnitude of permeability. Obviously, other data transformations will need to used to determine the most significant relationship.

At this time, there does not appear to be a general relationship between B^* and permeability. The relationship appears to be limited to distinct ranges of permeability. Future analyses will clarify the extent and significance of these relationships and develop mathematical equations to use in the termination procedure to select an appropriate value of B^*. These equations will then be programmed into the computer routine to intrinsically select B^* during the analyses, while allowing override by the user.

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Notation

a_1 = statistical level of significance for Step 3
a_2 = statistical level of significance for Step 4
A = cross-sectional area of soil sample
B^* = bound on slope of permeability plot used in Step 4
i = hydraulic gradient
k = coefficient of permeability
n = number of data points used in the test
Q = flow rate of permeant through a soil sample
Q_i = bivariate rank of a pair of elements X_i, Y_i
R_i = tied rank of an element X_i
S_T = variance of Kendall's Tau
T = Kendall's Tau
T_3 = Kendall's Tau for Step 3
T_4 = Kendall's Tau for Step 4
t = time
Y_t = $\log_{10}$ permeability for a time t
Y_t^* = adjusted $\log_{10}$ permeability for use in Step 4
Z = Mann's Test Statistic
Z_3 = Mann's test statistic for Step 3
Z_4 = Mann's test statistic for Step 4
Z_C = critical value of Z for use in hypothesis testing

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SAMPLING AND ANALYSIS PLANS TO EVALUATE THE PERFORMANCE OF LEAD-BASED PAINT ABATEMENT

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Abstract

The U.S. Department of Housing and Urban Development conducted a lead paint abatement demonstration at 169 houses from five metropolitan areas. The U.S. Environmental Protection Agency plans to conduct a follow-up study at these houses to measure levels of lead in dust and soil. Six types of interior locations will be sampled for dust. Three types of exterior locations will be sampled for soil. Dust and soil will be chemically analyzed for lead. In general, soil and dust samples will be digested by nitric acid and hydrogen peroxide, and analyzed by ICP or graphite furnace AA. Soil samples will be sieved and dried before digestion. Dust results will be reported as a loading (μg/square foot) and a concentration (μg/g). Soil results will be reported as a concentration (μg/g).

Introduction

In response to requirements mandated by the Lead-Based Paint Poisoning Prevention Act, as amended by Section 566 of the Housing and Community Development Act of 1987, the U.S. Department of Housing and Urban Development (HUD) carried out a lead paint abatement demonstration project in FHA re-possessed housing. The demonstration was conducted in five metropolitan areas across the country. Single family FHA houses in these cities that were owned by the department were tested for lead-based paint. Homes that met certain criteria were chosen for the lead paint abatement project. This HUD project is now virtually completed.

Under an interagency memorandum of understanding, the U.S. Environmental Protection Agency is providing technical support to HUD on lead-based paint issues. EPA plans to conduct a follow-up study to the HUD abatement demonstration in order to measure the levels of lead in household dust and exterior soil in the years following abatement. The purpose of the study is to assess the long-term efficacy of the

abatement methods used in the HUD demonstration project. This information is needed before the nation embarks on a costly abatement program.

Study Homes

In the HUD Demonstration, 169 houses were abated for lead paint. Both interior and exterior housing components were abated. Six different methods of lead paint abatement were used in the project (encapsulation, enclosure, heat gun stripping, chemical stripping, mechanical stripping, and component replacement). The first two methods cover existing lead paint, the last four remove it. An individual home was likely to be treated by more than one abatement method.

In order to have enough houses for the statistical analysis in the follow-up study, houses have been classified as either encapsulate/enclosure houses or removal houses. Classification was made on the basis of the square footage abated in the interior of the house by the encapsulate/enclosure methods (encapsulation and enclosure) and the removal methods (heat gun stripping, chemical stripping, mechanical stripping, and component replacement). Interior abatement was chosen for classification of houses because of an a *priori* assumption that interior lead paint abatements have the most impact on interior dust levels.

Interior dust and exterior soil will be collected at each house that has been re-sold, re-occupied, and recruited for the study. Six interior locations will be sampled for dust: floors, window sills, window stools, inside entryways, air ducts, and upholstered furniture/rugs/carpets. Three exterior locations will be sampled for soil: outside entryways, along the house foundation, and near the property line. The selection of locations will be discussed in the next section.

Selection Of Sample Locations

For the follow-up study, two rooms in each house will be selected for sampling. Rooms will be selected so that the predominant abatement method used in the room matches the predominant interior abatement method for the house. In each room, a floor section, a window sill, and a window stool will be sampled. An air duct will be sampled in each room, if an air duct is present. In addition, one carpet, rug, or piece of upholstered furniture will be sampled in each room, pending availability. Finally, the interior of two entryways will be sampled.

Table 1 summarizes the environmental sampling planned for the study, including both regular samples (vacuum dust and soil cores) and field quality control samples (wipe dust, field blanks, and side-by-side

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samples) intended to assess sampling variability and potential sample contamination. As shown in this table, a total of 23 samples will be collected from each house during each sampling campaign, with a grand total of over 6,000 samples being collected in all three sampling campaigns.

The objectives of the Abatement Performance Study include both assessing long-term performance of abatement methods and investigating the contribution to interior dust lead levels from other sources. The role of each type of sample listed in Table 5 for meeting these objectives is as follows:

- Vacuum dust from floors -- Provides primary measure of performance for interior abatement;

- Vacuum dust from window sills -- Provides primary measure of performance for interior abatement;

- Vacuum dust from window stools -- Provides measure of performance for interior abatement, possible measure of performance for exterior abatement, and possible transport of exterior soil from outside to inside the house;

- Rugs, upholstery, and air ducts -- Provides measure of source contribution to interior dust lead levels;

- Entryway floor -- Provides measure of possible transport of exterior soil from outside to inside the house;

- Soil cores -- Provides primary measure of performance of exterior abatement, and measure of possible transport of exterior soil lead into the house;

- Wipe dust from floors -- Provides consistency check against earlier results from HUD Demonstration and other studies;

- Field blanks -- Provides assessment of potential sample contamination; and

- Side-by-side samples -- Provides assessment of sampling variability.

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TABLE 1. SUMMARY OF ENVIRONMENTAL SAMPLING PLANNED
FOR THE ABATEMENT PERFORMANCE STUDY

Sample Type	Samples Per House	Total for One Campaign*	Total for Three Campaigns
Regular Samples			
1. Vacuum dust			
a. Perimeter floor	2	180	540
b. Window sill	2	180	540
c. Window stool	2	180	540
d. Rug/Upholstery	2	180	540
e. Air ducts	2	180	540
f. Entryway floor	2	180	540
2. Soil cores			
a. Near foundation	2	180	540
b. Property boundary	2	180	540
c. Entryway	2	180	540
Quality Control Samples			
3. Wipe dust			
a. Floor	1	90	270
4. Field blanks			
a. Vacuum dust	1	90	270
b. Soil cores	1	90	270
5. Side-by-side samples			
a. Vacuum dust floor	1	90	270
b. Soil cores	1	90	270
Total samples	23	2070	6210

*Assuming an average of 90 houses sampled in each campaign (i.e., 105, 90, and 75 houses in the first, second, and third campaigns, respectively).

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Interior Dust

It is anticipated that results from the Abatement Performance Study may be compared with earlier results from the HUD Demonstration and HUD National Survey. For this reason the sampling and analytical methods for the Abatement Performance Study have been selected to match as closely as possible the methods used in these earlier two studies. The sampling and analytical methods planned for interior dust sampling in the Abatement Performance Study are summarized in Tables 2 and 3 respectively. Some important points to note in these tables are the following:

- Sampling will be performed in two different rooms of each house -- for abated houses this will provide a measure of the variability in abatement performance within a house, while for control houses this will provide a measure of the variability in background lead levels within a house. Rooms in abated houses will be selected according to the largest square footage abated and the highest percentage abated by the predominant abatement method for the house.

- Sampling will be performed in each room separately for floors, window sills, and window stools -- for abated houses, this will provide a means to assess differences in the way an abatement method may perform on different structural components, and for control houses this will provide a further measure of the within-house variability of background lead levels.

- Sampling will also be performed in each room separately from one rug or upholstered furniture piece, and one air duct; in cases where more than one such component is available in a room, the specific component for sampling will be randomly selected from those available.

- Vacuum sampling, rather than wipe sampling, is the primary method planned for interior dust -- as noted earlier, this method allows for measurement of lead on a concentration basis so that comparisons among abatement methods, houses, and across time can be made, controlling for potentially biasing effects due to variations in the total amount of dust present; vacuum sampling also allows rugs and upholstered furniture to be sampled.

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TABLE 2. SAMPLING METHODS FOR INTERIOR DUST

	OTS Abatement Performance Study	HUD Demonstration	HUD National Survey
Sampling device	Vacuum (Gast rotary pump, modified 37-mm mixed cellulose ester filter cassette)	Chubs Thick Baby Wipes with Aloe (5-3/4x8")	Vacuum (Gast rotary pump, modified 37-mm mixed cellulose ester filter cassette)
Sampling Area	4 square feet (floors, rugs/upholstery) Entire area (window sills, stools)	One square foot (floors, window sills, window stools)	Four square feet (floors) Entire area (window stools, sills)
Samples Collected	Total of 12 samples: One window sill (two rooms) One window stool (two rooms) One perimeter floor location (two rooms) One front entryway floor One back entryway floor Two area rug/upholstered furniture Two air ducts	Three samples per abated area: One window sill per abated area One window stool per abated area One floor per abated area	Total of at least 7 samples: One floor at front (or most heavily used) entryway One floor in wet room One floor in dry room Each window stool in wet room Each window stool in dry room Each window sill in wet room Each window sill in dry room
Compositing	Will be determined after review of pilot sampling results	None	None

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TABLE 3. ANALYTICAL METHODS FOR INTERIOR DUST

	OTS Abatement Performance Study	HUD Demonstration	HUD National Survey
Sample preparation summary	Filter digested in HNO_3/H_2O_2 Diluted to 25 mL	Wipe ashed at 550-600 C for 2 hrs. Acid digested in HNO_3/H_2O_2 Diluted to 10 mL	Filter digested in HNO_3/H_2O_2 Diluted to 25 mL
Instrumental Technique	Graphite furnace atomic absorption	Flame atomic absorption	Graphite furnace atomic absorption
Est. LOQ	15 µg/g or 0.15 µg/sample	µg/sample	0.15 µg/sample
Data reporting	µg/g and µg/ft²	µg/ft²	µg/sample
QA/QC Notes:	NIST Buffalo River sediment (SRM 2704) and Estuarine sediment (SRM 1646) used for reference materials.	No reference material used Used side-by-side sampling for duplicates	In-house spiked soil used for reference material

For the exterior, two sides of the house will be selected at random. Foundation samples will be taken one foot from the foundation of the house on the two sides of the house selected. Foundation samples will consist of five equally spaced samples along the side of the house. The five equally spaced samples will be composited into a single soil sample. On the same two sides of the house selected for foundation samples, samples will be collected near the property boundary. Two randomized positions along the property boundary will be chosen. Boundary samples will consist of a composite of three soil samples collected at the vertices of an equilateral triangle with a side length of 20 inches. Finally, soil samples will be collected outside the same entryways for which interior dust samples were collected. Entryway soil samples will consist of three soil samples collected at the vertices of an equilateral triangle with side length of 20 inches.

Exterior Soil

The HUD Demonstration evaluated the abatement of both interior and exterior painted surfaces, and in fact, for many houses exterior abatement was the most significant activity performed. Furthermore, the same abatement method might be expected to perform quite differently on interior and exterior surfaces. Therefore, the Abatement Performance Study will evaluate both interior and exterior abatement.

If an abatement method fails to completely control an exterior lead-based paint hazard, then the resulting effect would most likely be seen as an increase in soil lead concentrations close to the foundation of the house. Therefore, exterior soil sampling will provide the primary means for assessing the performance of exterior abatement. In this assessment, lead concentrations measured in soil samples taken close to the foundation will be compared with those measured in samples taken at the property boundary which are as far as possible from the foundation, and therefore, primarily affected by only background sources of lead, rather than lead-based paint abatement. As with interior dust sampling, results of soil sampling from the Abatement Performance Study will also be compared with earlier results from the HUD Demonstration and National Survey. Therefore, the sampling and analytical methods for soil in the Abatement Performance Study have been selected to closely correspond to those used in these earlier two studies. Those methods are summarized in Tables 4 and 5, where the following important points should be noted:

- Soil samples will be collected both at the foundation of each house and at the property boundary -- for abated houses this will provide a measure of both soil potentially contaminated by abatement (i.e., at the foundation) and soil contaminated mostly by background sources (i.e., at the property boundary); for control houses this will provide a measure of the spatial variations in background soil lead levels.

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TABLE 4. SAMPLING METHODS FOR EXTERIOR SOIL

	OTS Abatement Performance Study	HUD Demonstration	HUD National Survey
Sampling device	1-inch ID soil recovery probe, top 0.5 inch of soil is taken.	0.75 inch ID tube (0.5 square inch surface area), top 0.5 inch of soil is taken.	SPR 24x1-1/8 soil probe, top 2-3 cm of soil is taken.
Samples Collected	Total of 6 samples: One taken 1 ft from foundation (two opposite sides of unit) One at property boundary (two opposite sides of unit) One at front entryway One at back entryway	Total of 4 samples (both before and after abatement): One taken 1 ft from foundation (all 4 sides of the unit)	Total of 3 samples: One taken 1 ft from foundation (where exterior XRF occurred, or if no XRF, then at a wall selected randomly) One taken halfway between XRF-sampled wall and property boundary One at entryway
Compositing	Foundation samples will be a composite of 5 uniformly-spaced cores. Boundary and entryway samples will be a composite of 3 cores spaced 20 inches apart.	All samples are a composite of 5 uniformly-spaced cores along the length of the wall.	All samples are a composite of 3 cores spaced 20 inches apart.

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TABLE 5. ANALYTICAL METHODS FOR EXTERIOR SOIL

	OTS Abatement Performance Study	HUD Demonstration	HUD National Survey
Sample preparation summary	Sample drying and homogenization Digest 0.5 g using $HNO_3H_2O_2$ Dilute to 50 mL	Oven dry, sieve Oven dry at 105 c for 24 hrs. 1 gram digested in HNO_3 Dilute to 100 mL	0.5 gram digested in HNO_3/H_2O_2 Diluted to 50 mL
Instrumental Technique	Inductively coupled plasma atomic emission spectrometry	Flame atomic absorption	Inductively coupled plasma atomic emission spectrometry
EST. LOQ	6 µg/g	6 µg/g	6 µg/g
Data reporting	µg/gram dry wt	µg/gram dry wt	µg/gram
QA/QC Notes:	NIST Buffalo River sediment (SRM 2704) and Estuarine sediment (SRW 1646) used for reference materials	Reference material not specified	In-house spiked soil used for reference material.

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- **Samples will be collected from two opposite sides of the house -- for abated houses this will provide a measure of the variability in abatement performance, while for control houses this will provide another measure of the spatial variations in background soil lead levels. In selecting sides of the house for sampling, priority will be given to sides including the largest square footage abated and the highest percentage abated by the predominant abatement method for the house.**

- **Samples will be collected immediately outside the front and rear entryways -- for both abated and control houses this will provide a means for assessing possible transport of exterior lead into the house.**

Summary

Sampling and analysis methods described in this manuscript are currently being tested in a pilot study. There may be changes to the methods described after the pilot is completed.

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111   FURTHER EVALUATION OF THE CAGE MODIFICATION TO THE TCLP

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ABSTRACT

The purpose of WA 17 was to further evaluate the proposed cage modification to Method 1311. The new proposal incorporates the use of a stainless steel cage for the testing of solidified/stabilized waste without prior particle size reduction. Central to this issue is whether the cage approximates the level of stress that a stabilized waste would undergo if disposed in a landfill.

To evaluate the utility of the cage, wastes were collected from several waste generators, including electroplating operations, secondary lead smelters, and creosote wood preservers. The wastes were stabilized by addition of cement. The stabilized wastes were tested for compaction strength to provide a standard by which to assess the level of stress imparted by the cage. It is though that low strength stabilized wastes should be significantly degraded while high strength formulations should be less degraded. Extractions were conducted with the cage, and hard plastic bottles to directly compare the level of stress imparted by each extraction method.

It was found that the bottle and cage were equivalent with respect to the amount of degradation observed for low strength stabilized wastes i.e. all were degraded completely. High strength wastes showed that the cage was more aggressive than the bottle and that waste stability in the TCLP extraction fluid was equally important in predicting the degree of degradation of the waste. One of the stabilized wastes did show a correlation between high compaction strength and survivability in the cage. As the compaction strength of the formulations decreased, the amount of sample degradation increased.

In general, the proposed cage modification would provide a aggressive challenge to the stability of a stabilized waste without prior size reduction.

112 COMPARATIVE STUDY OF EPA TCLP AND CALIFORNIA W.E.T FOR METALS IN DIFFERENT MATRICES.

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ABSTRACT :

EPA implemented the Toxicity Characteristic Leaching Procedure (TCLP) to simulate leaching of hazardous waste and to identify additional characteristics of waste, primarily organic constituents in RCRA waste in September, 1990. But for hazardous waste characterization particularly for metals, California has a Waste Extraction Test (WET) which covers seventeen metals including eight regulated by EPA under TCLP.

Comparative studies were carried out to evaluate the TCLP procedure against California W.E.T for leaching of EPA regulated metals (Ag, As, Ba, Cd, Cr, Pb, Hg, Se). Originally, EPA incinerator ash sample (EPA Interlaboratory Study XX sample) was used for comparison, and it was found that california WET gave higher results than the TCLP for the regulated metals extracted.

Later some of the actual hazardous waste soil, sludge and liquid samples received at HML (Hazardous Materials Laboratory), Berkeley, Ca. from different contaminated sites around California were extracted using both TCLP and Calif. WET procedures and were analyzed by ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy).

California WET gave consistently higher results for all eight EPA regulated metals in all the matrices tested. Also California WET seems to be a more aggressive test than TCLP, even if the TCLP results are doubled to account for the different extraction ratio which is 1-20 for TCLP and 1-10 for California WET. There was no apparent relationship between soluble metals in TCLP extract as a percentage of W.E.T or as a percentage of total metals in different samples.

California Waste Extraction Test is also applicable to other metals (Be, Co, Cu, Mo, Ni, Sb, Tl, V, Zn) which are regulated under Title 22 , California Administrative Code, but not under EPA RCRA regulations. When results for these metals by the two extraction protocols were compared, Calif. WET came out superior than TCLP.

In addition, California WET also has advantages over EPA-TCLP procedure because it is simpler in that it does not require sample digestion after extraction, no pH measurement before extraction and no pre-selection of extraction solution.

INTRODUCTION :

The most significant risk from the hazardous waste results from the leaching of toxic constituents into groundwater. The EPA designed Extraction Procedure Toxicity Test (EP Tox.) to simulate the leaching of solid hazardous waste co-disposed with municipal waste in a sanitary landfill and to asses the potential impact of the leachate on ground water contamination. But since EP Toxicity test has a limited applicability due to short list of constituents , EPA proposed a "second generation" extraction procedure TCLP as a replacement to address the shortcomings of EP Toxicity. The TCLP protocol includes the expanded list of regulated contaminants from the fourteen listed in the EP Toxicity protocol to a total of fifty-two which includes eight metals. California has a equivalent extraction test (WET) for soluble metals under its code of regulation "Title 22" which includes seventeen metals. There are many contrasts among these three procedures, which are listed in the figure 2. Maximum contaminants levels for seventeen metals are listed in figure 3.

This study was designed to compare the extraction efficiencies of tclp and Calif. wet test. This comparison was accomplished in two ways. In the first, the metal extraction effectiveness of the two extraction procedures was evaluated on a EPA incinerator ash for some metallic contaminants (listed in Table 3) and

some additional metals. The second phase included evaluating the efficiency of the extraction on actual soil and sludge samples received at HML, Berkeley, Ca. The effect of sample digestion was also investigated on extracts from both methods using EPA 3010 digestion procedure (as recommended in tclp protocol).

METHODS :

SAMPLE PREPARATION:

Incinerator ash sample was very homogeneous, so no sample preparation was done. HML soil samples were grinded and passed through 10 mesh sieve to get a homogeneous sample before extraction. The liquid samples (containing <0.5% nonfilterable solids) were filtered through appropriate filter papers (0.45 um for wet & 0.6 um for tclp) while sludge samples were filtered through appropriate filters; filtrate was saved and solid part was extracted with proper extraction fluid, filtered and combined with original filtrate before analysis.

TCLP Procedure :

Incinerator ash sample received as a part of EPA Interlaboratory study xx was used in the preliminary investigation. TCLP protocol was followed as outlined in tclp flowchart (Figure 1). In order to select the proper extraction fluid for tclp , sample pH was determined . The sample pH in reagent water was 5.69, but after adding 3.5 ml of 1.0 N Hcl to the sample solution, heating to 50 C for 10 minutes and cooling, the pH came down to < 5.0 (pH 4.70), so extraction fluid #1 was used. Extraction fluid #1 is a acetate buffer which is prepared by adding 5.7 ml of glacial acetic acid to about 900 ml deionized water, then adding 64.3 ml of 1.0 N NaoH, and diluting to a volume of 1 liter. The pH of fluid was 4.93.

25 gm of ash sample was extracted in triplicate for 18 hrs. over a rotary extractor at 30 r.p.m. with 500ml of extraction fluid. The samples were filtered through 0.6 um glass microfiber filters (14.2 cm) under pressure with nitrogen (in Millipore Hazardous Waste Filtration System OM 100). The filtrate for each replicate was divided in to two portions; one portion was analyzed as such , while the other portion was digested using EPA 3010 digestion procedure (SW 846, 3rd edition ,1986). Both the extracts were analyzed for soluble metals with ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy).
25-50 gms of HML soil and sludge samples, and 100 ml of liquid sample were used for TCLP extraction. The above TCLP protocol was followed.

CALIFORNIA WASTE EXTRACTION TEST (WET) :

California wet does not need pH test of the sample before extraction. Wet extraction fluid (citrate buffer) was prepared by adding 42.0 gm of monohydrate citric acid in 950 ml of deionized water and then adjusting the pH to 5.0 by adding 50 % NaoH and making the volume to 1 liter. Prior to use in the extraction step, buffer was deoxygenated by purging with nitrogen gas. 25-50 gms of incinerator ash and HML samples were extracted with 250-500 ml of citrate buffer on a regular mechanical shaker for 48 hrs. After extraction the fluid was filtered through 0.45 um filter paper . The filtrate was divided into two portions; one part was analyzed as such while other part was digested using EPA 3010 digestion procedure. Both these extracts were analyzed for soluble metals by ICPAES.

TOTAL METALS :

Incinerator ash and all other samples were also digested using EPA 3050 digestion procedure (SW 846, 3rd edition, 1986) and analyzed for total metals for comparison purposes. Yttrium was used as internal standard in all samples and standards to compensate for viscosity differences in different matrices before analysis. Icp was used for analysis of all the samples except Hg.

Hg ANALYSIS :

Hg analysis on soil and sludge (total Hg) and undigested portions of TCLP and WET extracts (soluble Hg) was done by Cold Vapor technique (EPA 7470, SW 846, 3rd edition, 1986).

QUALITY CONTROL :

Method blank, method spike , matrix spike duplicates, qc check sample, and EPA reference standards (ICAP-19, ICAP-7, WP-287) were analyzed with each set of samples as a quality control check on analysis . Percent rsd, rpd, and % recovery were calculated as a means of determining the precision and accuracy of the data.

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RESULTS :

The results of Incinerator ash sample for total, and soluble metals in wet and tclp extracts are summarized in figure 4. The mean and % rsd of three replicates are listed . The concentration of total metals in ash sample varies widely from less than detection limit for selenium to 55000 mg/kg for Calcium. Although there is 10 mg/kg of Ag in ash sample, but none is extracted in tclp or wet extract. Arsenic and Chromium are present at about the same level (69.4 and 62.6 mg/kg respectively) as total metals in the ash sample, but As is not extracted at all and Cr is only 0.2% in TCLP extract, as compared to 5.2% As and 1.3% Cr in wet extract as a %age of total metal content. In general, soluble metals extracted by TCLP as a percentage of total metals varied from non-detected (As, Se, Ag) to maximum of 4.8% for Cd (Figure.7a), where as wet extracted quite a higher concentration of As (5.2%), Pb (6.5%) and Cd (7.3%). This data indicates that WET extracted consistently higher amounts of soluble metals as compared to tclp for all the metals analyzed in this experiment. Of particular interest are As and Pb which were extracted in significantly higher amounts by wet method as compared to tclp. Using soil and sludge matrices besides Incinerator ash gave similar results. Results of HML#1542 (sludge) and HML# 1543 (soil) samples are discussed here. Both these samples came from Empire Mine , Grass Valley, Ca. and were high in total As and Pb, and also had Ba and Cd above STLC (soluble threshold limit concentration). The pH of the samples was between 5-6. Both these samples were digested for total metals as well as extracted by tclp and wet methods for soluble metals. The data has been graphically presented (Figures 8,9). In order to fit the data to scale, bars for total metal represents only 10% of total metals concentration (Figure 8) while 5% for As and Pb , and 1% for Ba and Cd (Figure 9). Interpretation of this data showed the same trend that wet test gave quite higher results than tclp for both soil and sludge samples for As, Ba, Cd, and Pb. Total Ag, Cr, and Se were less than detection limit and consequently none was extracted in tclp and wet extracts. Both these samples were high in total as well as soluble Hg than threshold limits (figure 3). Total, wet, and tclp concentrations of Hg in sludge sample was 32.9, 2.65, and 0.53 mg/kg while in soil 95.0, 3.21, and 0.39 mg/kg respectively (Figure 8a). In addition, studies were carried out to find out if digestion after extraction makes any differences in the recovery of metals. A set of soil samples received at HML from a contaminated shipyard in San Francisco, and another set of sludge samples from metal recycler, Short Scrap Iron and Metal Inc, Redding were used. These samples were analyzed for total and soluble metals. A portion of the extracts from both the TCLP and wet extracts was taken and digested with EPA 3010 (as recommended in tclp protocol) and other half portion was analyzed as such. The results were compared of both digested and undigested extracts for both tclp and wet methods (Figure 10,11).The data indicate that there is no differences in digested and undigested extracts for recovery of any of these metals tested. Although digestion step for the extract is only a part of tclp protocol, but was tried in the wet method too for these samples . Out of four soil and two sludge samples tested in this experiment , none of the metals showed a significant difference in digested and undigested recoveries.

TCLP results when multiplied with a factor of two in order to take into account the dilution factor of(1-20) compared to WET (which is 1-10) in a soil sample from Orange County Steel and Salvage, Anaheim, Ca. were still lower than wet (Figure7b). Similarly some of the soil and sludge samples received at HML from Empire Mine, Grass Valley, Ca. were high in total Pb and As (Figure 8,9), but soluble Pb (wet) extracted in sludge sample was about 8.3 % of total where as in soil it was about 5% , although total Pb was about 6000 mg/kg in both the sample matrices. Higher conc. of soluble Pb (wet) in sludge sample may be due to the fact that part of sludge sample was liquid which had more soluble Pb and was recombined with the extract after the solid portion was extracted with appropriate extraction fluid. Arsenic shows the same pattern, since total As ranged from 1630-1750 mg/kg in sludge and soil, respectively (Figure 8a), but soluble As (wet) in sludge was 1.2% and 0.7% in soil as percentage of total As. In essence the data shows that both As and Pb as soluble metals (by wet method) are present in higher concentration in sludge sample than in soil, but percentage wise Pb is extracted more than As by the same method in the same matrices. Although same relationship is true in tclp extraction procedure for sludge and soil i.e Pb is extracted more by tclp in sludge than soil, but As is higher in soil sample than sludge though total As amount is the same in both matrices. There seems to be no consistent relationship of wet and tclp soluble metals extracted as percentage of total metals. The reasons for higher recovery in wet than tclp seems to be associated with type of buffer and extraction time. Citrate buffer used in wet is more aggressive than acetate buffer and also longer extraction time of 48 hrs in wet than 18 hrs. in tclp might be a factor in solubilizing more metals. For liquids (containing <0.5 % nonfilterable solids), a HML sample (F1783) which was high in silver did not show any significant difference between tclp and wet soluble silver (Figure 8a), since the sample was not subjected to extraction and was only filtered through specified filter papers in each method.

QUALITY CONTROL:

A comprehensive QC guidelines were followed to validate the data for precision and accuracy (figure 5,6). All the QC samples show very good precision and accuracy. Method blank results donot show any contamination

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duplicate matrix spikes where each matrix was spiked before digestion or extraction. In method spikes, reagents or extraction fluids were spiked before extraction or digestion. Method spikes recoveries for tclp and wet varies from 80-95 % except for Ag . Relative percent difference (RPD) for duplicate method spikes in both extracts range from 0.2-13 %, except for Ag in tclp which is 24.8 (figure 5). For total metal analysis, RPD for matrix spike duplicates on incinerator ash sample is under 13 % except for Ag and Ba, and % recoveries of matrix spikes are in high eighties. Low Ag recovery may be due to addition of Hcl in method EPA-3050. Same may be the reason for bad precision (high rpd) in matrix spike duplicates (total metals) for Ag. But these deviations do not affect our results because total Ag was below detection limit in all soil and sludge samples and was present at such a low level in ash sample that it was not extracted in tclp and wet extracts. Low matrix spike recovery for Ba in total metal determination may be due to the precipitation of Ba as Baso4 in the ash sample. Inhouse HML soil qc check sample with known values was also digested and analyzed and % recoveries varied from 98-114%. To check the accuracy of instrumental analysis of the samples, EPA reference standards (Icap-19, Icap-7) were analyzed along with the samples and percent recoveries ranged from 99-110% (figure 5). Matrix spikes recoveries of Pb in total and wet extract does not showup due to high concentration of Pb present in these samples, and also conc. beyond the calibration curve (100 ppm) of Icp instrument.

Tclp and wet extracts were also post spiked at 10mg/kg and 4mg/kg level. Percent recoveries for pre-spikes in wet ranged from 42-76% while in post spike varied 74-121%. Tclp pre-spike recoveries ranged from 11-83% while post spikes were 76-107%. In general, post-spikes recoveries were good for both extraction methods, but pre-spikes recoveries were better in wet extracts than tclp. Precision was good in both tclp (under 15%) and wet (under 6%) (figure 6). Both the precision and accuracy were better in Calif. wet than tclp. For Hg analysis, method spike for wet and tclp gave recoveries 71.6 and 128%, respectively, when spiked at 1.0 mg/kg. EPA WP-287 reference standard (T.V. 0.1 mg/kg) gave 108 % recovery when analyzed by cold vapor along with soil and sludge samples (Figure 8a).

CONCLUSION :

Differences exist between tclp and wet methods in terms of solubilizing metals in different matrices of soil ,sludge, and incinerator ash. Wet gave higher results for all EPA regulated metals and some additional metals tested. Wet results for metals were still higher even when tclp results were multiplied with a factor of two to account for difference in dilution factor for both the methods. Also wet procedure is simpler than TCLP, that it does not require no pre-selection of extraction fluid, no pH determination of sample, and also no after digestion of extract and thus saves lots of total analysis time for routine samples. Although digestion of samples after extraction is part of tclp method, but in the samples tested it did not make any significant difference in soluble metals recovered whether extract was digested or not, both in tclp and wet methods. There is no apparent relationship between tclp or wet in soluble metals extracted as a percentage of total metals in different matrices.

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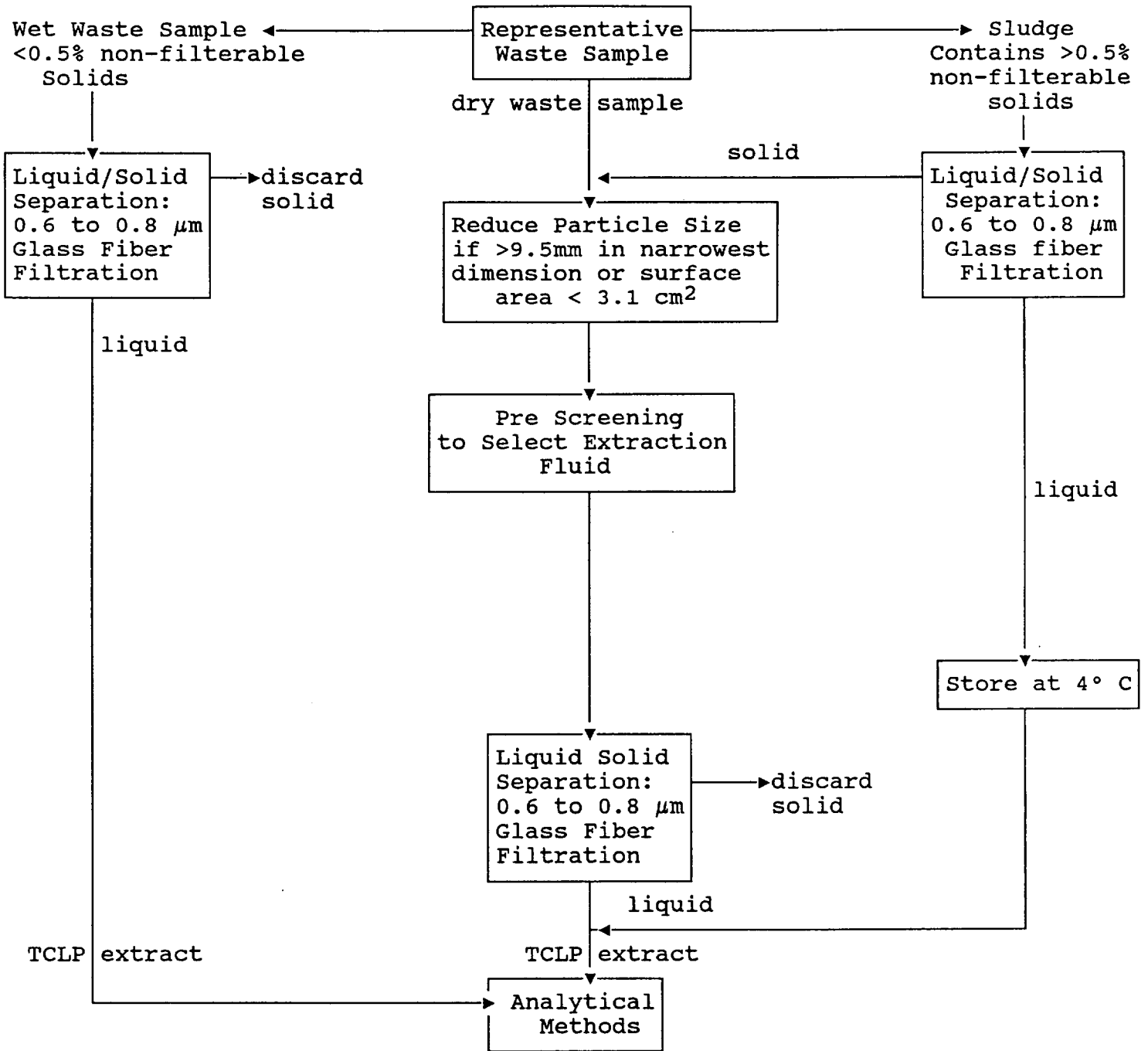
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TCLP Flowchart for Metals

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Wet Waste Sample ◄──────────┌─────────────────┐──────────────►  Sludge
<0.5% non-filterable        │ Representative  │                Contains >0.5%
   Solids                    │  Waste Sample   │                non-filterable
                             └─────────────────┘                   solids
                             dry waste│sample
                                      │              solid
        ┌──────────────┐              │         ┌──────────◄──────────┐
        │Liquid/Solid  │──►discard    ▼         ┌─────────────────┐
        │Separation:   │   solid    ┌───────────────────────┐   │Liquid/Solid  │
        │0.6 to 0.8 μm │            │Reduce Particle Size   │   │Separation:   │
        │Glass Fiber   │            │if >9.5mm in narrowest │   │0.6 to 0.8 μm │
        │Filtration    │            │dimension or surface   │   │Glass fiber   │
        └──────────────┘            │   area < 3.1 cm²      │   │Filtration    │
                                    └───────────────────────┘   └─────────────────┘
          liquid                              │
                                              ▼
                                    ┌───────────────────────┐
                                    │   Pre Screening       │
                                    │to Select Extraction   │          liquid
                                    │       Fluid           │
                                    └───────────────────────┘
                                              │
                                              │                 ┌─────────────────┐
                                              │                 │ Store at 4° C   │
                                              │                 └─────────────────┘
                                              ▼
                                    ┌───────────────────────┐
                                    │Liquid Solid           │──►discard
                                    │Separation:            │   solid
                                    │0.6 to 0.8 μm          │
                                    │Glass Fiber            │
                                    │Filtration             │
                                    └───────────────────────┘
                                              │        liquid
TCLP│extract                       TCLP│extract  ◄──────────────────┘
                                              ▼
                                    ┌──────────────┐
                                    │► Analytical  │
                                    │  Methods     │
                                    └──────────────┘
```

FIGURE 1

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Major Differences Among the three Extraction Procedures

W.E.T.	TCLP	E.P.Tox
1. One set extracting solution. Citrate Buffer pH 5.0	Extraction fluid selection depends on sample pH: a. Acetate buffer pH 4.93 ± 0.05 b. Acetic acid solution pH 2.88 ± 0.05	One extraction solution: distilled deionized H_2O + 0.5 N acetic acid to pH 5.0 ± 0.2
2. Sample to extraction fluid ratio is 1:10	Sample to extraction fluid ratio is 1:20	Sample to extraction fluid ratio is 1:20
3. Does not specify extraction vessel design	TCLP requires extraction bottles made of glass, polypropylene, high density polyethylene for non-volatiles	Protocol does not specify reaction vessel design
4. Requires use of 0.45 μm membrane filter for extract after extraction	TCLP requires use of 0.6 to 0.8 μm glass fiber filter	Requires use of 0.45 μm cellulose triacetate filters
5. Uses mechanical shaker for extraction	Requires rotary agitation in end over end fashion at 30 ± 2 r.p.m.	Allows either a blade/stirred open vessel or a rotary end over end agitator
6. Extraction period of 48 hours	18 ± 2 hours	24 hours
7. No monitoring of pH required during extraction	No monitoring of pH required during extraction	Requires monitoring and adjustment of pH to 5.0 during extraction
8. Does not require acid digestion after extraction for metals	Requires acid digestion after extraction for metals other than mercury	Requires acid digestion of extract for metals other than mercury

FIGURE 2

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Maximum Concentration of Metallic Contaminants for Characteristic of EP Toxicity, TCLP, and California W.E.T.

Contaminant	Maximum Concentration mg/L
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

California Wet Only

Antimony	15.0
Beryllium	0.75
Cobalt	80.0
Copper	25.0
Molybdenum	350.0
Nickel	20.0
Thallium	7.0
Vanadium	24.0
Zinc	250.0

FIGURE 3

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Department of Health Services
Hazardous Materials Laboratory

Inorganic Section

California W.E.T. vs T.C.L.P. Comparison Study
EPA Incinerator Ash
Summary of Results

Total Metals (mg/kg)

	A	B	C	Mean	RSD
Ag	9.03	8.73	13.0	10.3	23.2
As	73.8	69.8	64.6	69.4	6.6
Ba	404	401	316	374	13.4
Ca	54900	55700	54500	55000	1.11
Cd	368	372	392	377	3.4
Cr	58.2	64.0	65.6	62.6	6.22
Mg	6890	7290	7150	7110	2.85
Ni	27.2	31.9	28.6	29.23	8.25
Pb	7290	7390	7320	7330	0.70
Se	<3.0	<3.0	<3.0	<3.0	0.00
Zn	23500	24400	24300	24100	2.05

Soluble Metals by TCLP Extraction (mg/L)

	A	B	C	Mean	RSD
Ag	<0.01	<0.01	<0.01	<0.01	0.00
As	<0.03	<0.03	<0.03	<0.03	0.00
Ba	0.18	0.17	0.19	0.18	5.56
Ca	604	593	597	.598	0.93
Cd	17.8	18.4	18.5	18.2	2.08
Cr	0.14	0.11	0.12	0.12	12.4
Mg	89.8	88.7	90.0	89.5	0.78
Ni	0.17	0.20	0.18	0.18	8.33
Pb	40.0	37.7	37.0	38.2	4.11
Se	<0.06	<0.06	<0.06	<0.06	0.00
Zn	402	407	411	407	1.11

Soluble Metals by California W.E.T. (mg/L)

	A	B	C	Mean	RSD
Ag	<0.01	<0.01	<0.01	<0.01	0.00
As	3.47	3.62	3.69	3.59	3.13
Ba	1.02	0.96	1.03	1.00	3.77
Ca	3000	3010	2973	2990	0.64
Cd	26.3	27.7	28.1	27.4	3.45
Cr	0.80	0.84	0.82	0.82	2.44
Mg	241	241	238	240	0.72
Ni	0.52	0.49	0.49	0.50	3.46
Pb	496	472	457	.475	4.14
Se	<0.06	<0.06	<0.06	<0.06	0.00
Zn	1410	1420	1390	1410	1.09

FIGURE 4

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September, 1990

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Inorganic Section

Quality Control for W.E.T. vs TCLP Study

	Method Blank	EPA ICAP-19			EPA ICAP-7			HML Soil QC		
		found	true	% Recovery	found	true	% Recovery	found	true	% Recovery
Ag-Silver	<0.01	---	---	---	1.00	1.00	100	51.3	50.9	101
As-Arsenic	<0.03	0.99	1.00	99.0	---	---	---	47.1	45.3	104
Ba-Barium	0.01	---	---	---	1.02	1.00	102	41.7	39.8	104
Cd-Cadmium	0.02	1.07	1.00	107	---	---	---	24.1	24.3	99.2
Cr-Chromium	<0.06	1.04	1.00	104	---	---	---	49.5	43.3	114
Ni-Nickel	<0.02	1.02	1.00	102	---	---	---	29.7	30.1	98.7
Pb-Lead	0.08	1.10	1.00	110	---	---	---	49.9	50.7	98.4
Se-Selenium	<0.06	1.06	1.00	106	---	---	---	54.1	52.4	103
Zn-Zinc	0.04	1.10	1.00	110	---	---	---	61.1	55.0	111

Spiked Duplicates for Total Metals determinations

	Unspiked (mean)	Spike A	Spike B	RPD	Spike added	%Recovery Mean
Ag-Silver	0.21	0.53	0.19	94.4	10	1.5
As-Arsenic	1.39	9.64	10.5	8.54	10	86.8
Ba-Barium	7.48	11.4	5.61	68.1	10	10.3
Cd-Cadmium	7.54	15.5	16.4	5.64	10	84.1
Cr-Chromium	1.25	9.46	10.1	6.54	10	85.3
Pb-Lead	147	*	*	*		
Se-Selenium	<0.06	8.33	9.47	12.8	10	89.0

Method Spiked Duplicates

	% Recovery (means of 2)		R.P.D.	
	TCLP	W.E.T	TCLP	W.E.T.
Ag-Silver	18.2	67.8	24.8	7.82
As-Arsenic	95.0	90.8	3.41	0.54
Ba-Barium	92.0	80.0	4.22	2.26
Cd-Cadmium	93.0	80.0	4.86	2.36
Cr-Chromium	88.7	84.1	6.61	0.24
Pb-Lead	82.7	79.1	9.08	6.75
Se-Selenium	88.6	92.4	12.9	1.28

FIGURE 5

Units are mg/L or mg/kg
Sample is EPA Incinerator Ash

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State of California
Department of Health Services
Hazardous Materials Laboratory

Inorganic Section

TCLP vs California W.E.T. Study

Quality Assurance

California W.E.T.

	Method Blank	Unspiked mean	Spike A	Spike B	RPD	Spike added	% Recoveries A	% Recoveries B	mean	Post Spike Spike Result	Post Spike Spike added	Post Spike % Recovery
Ag	0.01	<0.01	<0.01	<0.01	0.00	10	0.00	0.00	0.00	7.40	10	74.0
As	0.04	3.59	10.2	10.7	4.78	10	66.1	71.1	68.6	13.9	10	102
Ba	0.01	1.00	5.02	5.33	5.99	10	40.2	43.3	41.8	11.1	10	101
Cd	0.01	27.4	32.8	33.3	1.51	10	54.0	59.0	56.5	35.9	10	96.0
Cr	0.06	0.82	7.58	7.73	1.96	10	67.6	69.1	68.4	10.3	10	95.2
Pb	0.02	475	470	473	0.63	*	*	*		*		
Se	0.06	<0.06	7.45	7.79	4.46	10	74.5	77.9	76.2	12.1	10	121

* beyond calibration of ICP

TCLP

	Unspiked mean	Spike A	Spike B	RPD	Spike Added	% Recoveries A	% Recoveries B	Mean	Post Spike Spiked	Post Spike Spike Added	Post Spike % Recovery
Ag	<0.01	<0.01	<0.01	0.00	10	0.1	0.1	0.1	3.05	4.00	76.3
As	<0.03	1.12	1.06	5.5	10	11.2	10.6	10.9	4.02	4.00	101
Ba	0.18	1.13	0.97	15.2	10	9.50	7.90	8.70	3.98	4.00	95.2
Cd	18.2	26.8	26.1	2.6	10	86.0	79.0	82.5	21.5	4.00	96.8
Cr	0.12	2.67	2.48	7.4	10	25.5	23.6	24.6	3.95	4.00	95.8
Pb	38.2	43.2	42.8	0.9	10	50.0	46.0	48.0	42.3	4.00	102
Se	<0.06	2.70	2.48	8.5	10	26.4	24.2	25.3	4.29	4.00	107

Units are mg/L or mg/kg
Sample is EPA Incinerator Ash

FIGURE 6

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FIGURE 7

Total, WET, TCLP
Sludge sample F1542
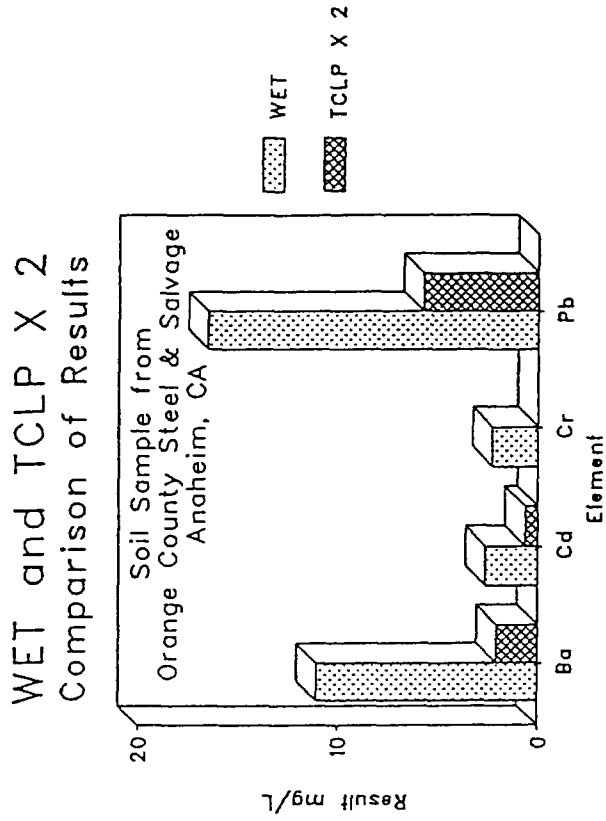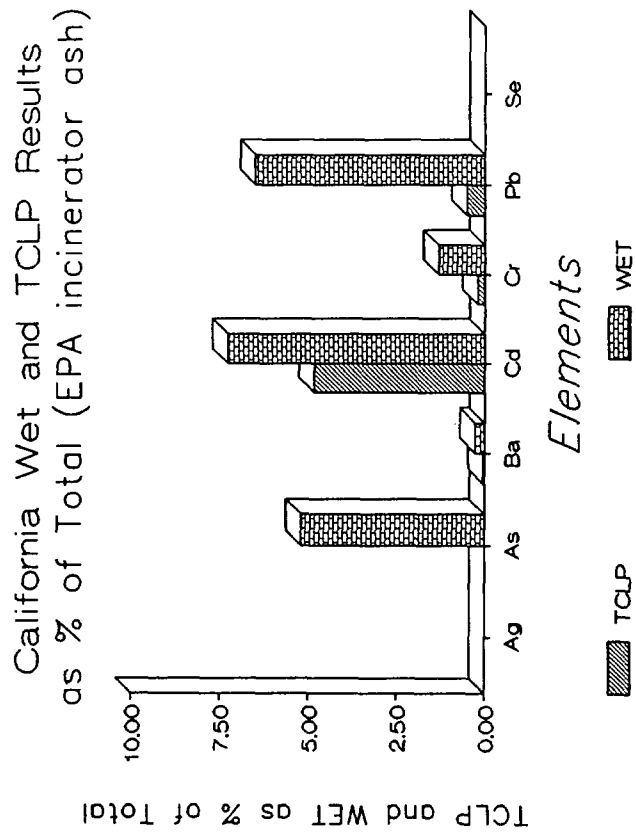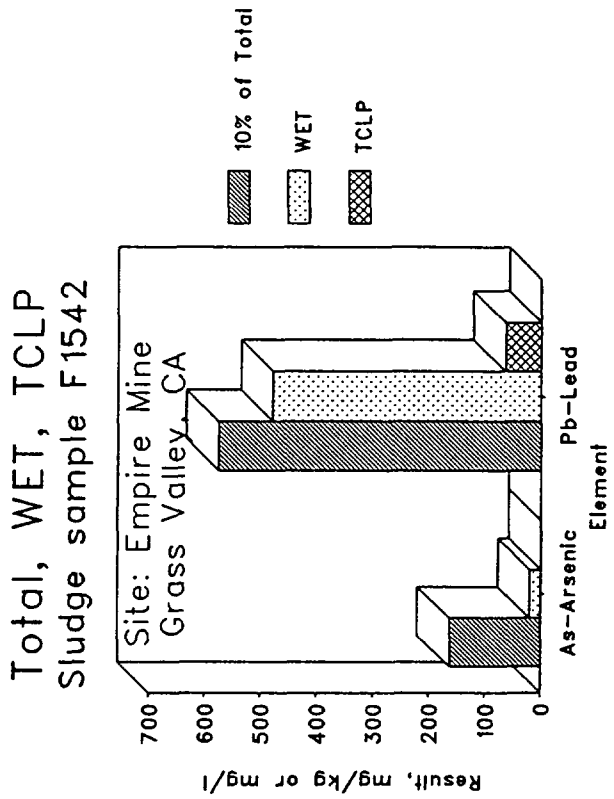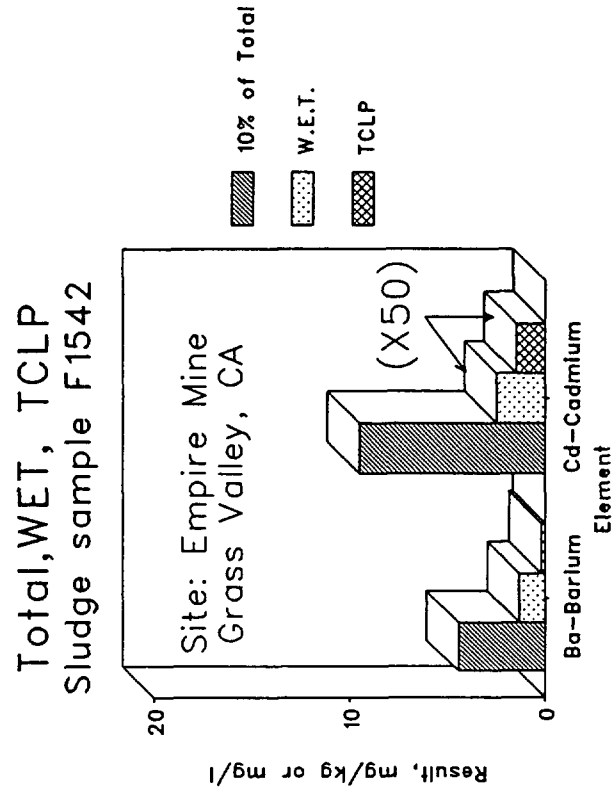
FIGURE 8

Comparison Of Total, Tclp, And California Wet Extracts (mg/kg)

HML NUMBER SAMPLE TYPE	F1542 SLUDGE			F1543 SOIL		
	TOTAL	WET	TCLP	TOTAL	WET	TCLP
AS-ARSENIC	1630	19.6	< 0.19	1750	11.8	0.76
BA-BARIUM	44.4	1.33	0.22	105	0.89	< 0.13
CD-CADMIUM	95.1	0.05	< 0.03	121	0.37	0.18
CR-CHROMIUM	< 9.40	0.19	< 0.19	< 9.40	< 0.19	< 0.19
PB-LEAD	5760	478	64.2	6190	311	25.7
SE-SELENIUM	< 25.5	< 0.51	< 0.51	< 25.5	< 0.51	< 0.51
AG-SILVER	< 3.90	< 0.08	< 0.08	< 3.90	< 0.08	< 0.08
Hg-Mercury	32.9	2.65	0.53	95.0	3.21	0.39

Quality Control (Hg-Analysis)

	True Value	Result	% Recovery
EPA WP-287	0.100	0.108	108
Hg-Standard	0.500	0.470	94
Mtd-Spike(Wet)	Spiked at 1.0 mg/kg		71.6
Mtd-Spike(Tclp)	Spiked at 1.0 mg/kg		128

Soluble Silver by "WET" and "TCLP" (filtered through .45 or .6 – .8 micron)
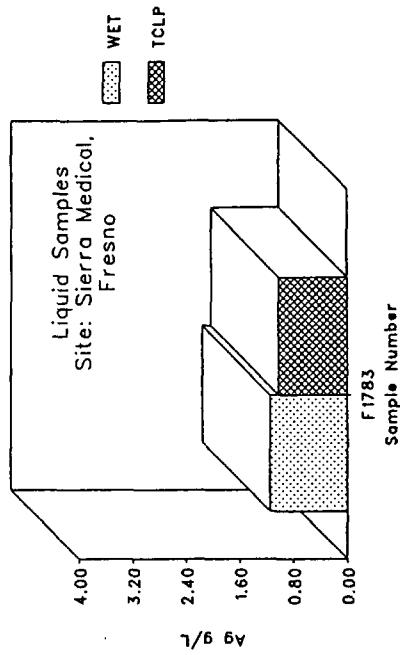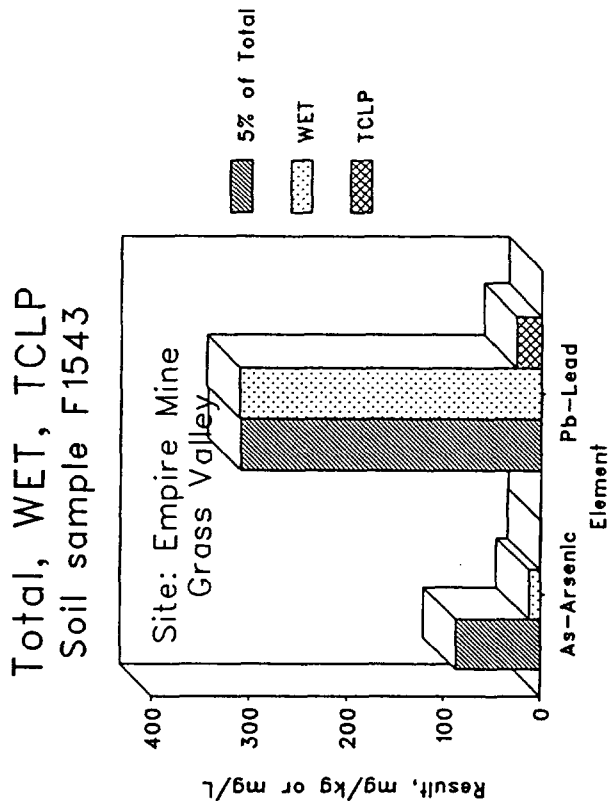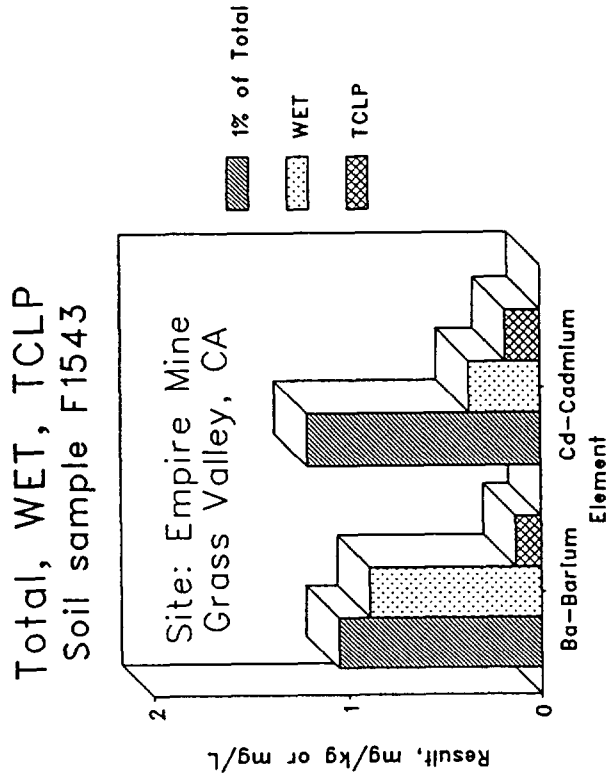
Liquid Samples
Site: Sierra Medical, Fresno

FIGURE 8A

Total, WET, TCLP
Soil sample F1543

Site: Empire Mine
Grass Valley, CA

1% of Total
WET
TCLP

Total, WET, TCLP
Soil sample F1543

Site: Empire Mine
Grass Valley

5% of Total
WET
TCLP

FIGURE 9

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California Department of Health Services
Hazardous Materials Laboratory

Inorganic Section

Comparison Between Digested and Undigested TCLP Extracts

Triple A Hunter's Point, San Francisco (Soil samples)

HML NUMBER	C863 D	C863 UD	C864 D	C864 UD	C866 D	C866 UD	C871 D	C871 UD
As-Arsenic	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19
Ba-Barium	3.88	3.82	1.68	1.66	1.33	1.32	1.07	1.04
Cd-Cadmium	<0.03	<0.03	0.03	0.04	<0.04	<0.03	<0.03	<0.03
Cr-Chromium	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19
Pb-Lead	1.40	1.33	5.37	5.31	2.88	2.82	1.27	1.20
Se-Selenium	<0.51	<0.51	<0.51	<0.51	<0.51	<0.51	<0.51	<0.51
Ag-Silver	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08

Short Scrap Iron & Metal, Inc., Redding (Sludge samples)

HML NUMBER	F2541 D	F2541 UD	F2542 D	F2542 UD
As-Arsenic	<0.19	<0.19	<0.19	<0.19
Ba-Barium	1.67	1.68	4.26	4.26
Cd-Cadmium	0.18	0.18	0.11	0.11
Cr-Chromium	<0.19	<0.19	<0.19	<0.19
Pb-Lead	1.28	1.21	0.56	0.55
Se-Selenium	<0.51	<0.51	<0.51	<0.51
Ag-Silver	<0.08	<0.08	<0.08	<0.08

Notes: D = Digested, UD = Undigested. Mean of two replicates reported.

FIGURE 10

California Department of Health Services
Hazardous Materials Laboratory

Inorganic Section

Comparison Of Digested And Undigested California Wet Extracts

Triple A Hunter's Point, San Francisco (Soil samples)

HML Number :	C863		C864		C866		C871	
	D	UD	D	UD	D	UD	D	UD
As-Arsenic	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	0.20	0.19	< 0.19
Ba-Barium	14.9	14.9	7.87	7.65	3.24	3.22	3.18	3.15
Cd-Cadmium	0.07	0.08	0.08	0.08	0.07	0.07	0.06	0.07
Cr-Chromium	2.88	2.92	3.53	3.40	1.03	1.01	1.04	1.05
Pb-Lead	15.1	15.1	21.07	21.0	26.2	26.5	7.83	7.95
Se-Selenium	< 0.51	< 0.51	< 0.51	< 0.51	< 0.51	0.51	< 0.51	< 0.51
Ag-Silver	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	0.08	< 0.08	0.08

Short Scrap Iron And Metal Inc., Redding (Sludge samples)

HML Number :	F2541		F2542	
	D	UD	D	UD
As-Arsenic	< 0.19	0.19	< 0.19	0.19
Ba-Barium	5.62	5.58	24.7	24.7
Cd-Cadmium	0.70	0.70	0.75	0.78
Cr-Chromium	0.48	0.47	0.55	0.53
Pb-Lead	27.5	27.2	17.3	17.4
Se-Selenium	< 0.51	0.51	< 0.51	0.51
Ag-Silver	< 0.08	0.08	< 0.08	0.08

Notes: D = Digested, UD = Undigested. Mean of three replicates reported.

FIGURE 11

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