FIFTH ANNUAL

WASTE TESTING

AND

QUALITY ASSURANCE

SYMPOSIUM

July 24-28, 1989

OMNI SHOREHAM HOTEL
WASHINGTON, D.C.

PROCEEDINGS

VOLUME II

Fifth Annual Waste Testing And
Quality Assurance Symposium
July 24-28 1989

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ORGANICS

THE USE OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/ MASS SPECTROMETRY FOR THE CHARACTERIZATION OF DYES*

L.D. Betowski, Research Chemist, Quality Assurance and Methods Development Division, T.L. Jones, Chemist, Quality Assurance and Methods Development Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, P.O. Box 93478, Las Vegas, Nevada 89193-3478; J. Yinon, Visiting EPA Scientist and Senior Research Fellow, Head of Applied Mass Spectrometry Group, Department of Isotope Research, Weizmann Institute of Science, Rehovot, ISRAEL

ABSTRACT

The U.S. Environmental Protection Agency is concerned with the detection of and analysis for organic compounds that, for reasons of nonvolatility or thermal lability, are not amenable for gas chromatography (GC) or gas chromatography/mass spectrometric (GC/MS) analysis. It has been estimated that up to 80 percent of the organic compounds in current usage fall into this category.

One group of nonvolatile compounds that spans several organic classes and has been known to be found in the environment, especially in the southeast quadrant of the United States, is dyes. Because of our previous work with these compounds and because dyes include individual compounds that contain many different functional groups, they were chosen as subjects in a comparison of the thermospray-liquid chromatography/mass spectrometry (TSP-LC/MS) and particle beam-liquid chromatography/mass spectrometry (PB-LC/MS) interfaces.

Thermospray-LC/MS is not only an interface, but also an ionization technique. This feature results in both advantages and disadvantages for the technique. The advantages to thermospray over other LC/MS methods are relatively high sensitivities for many (but not all) compounds, the generation of ions without an external ionization source (although one can be provided as an option), and relatively simple spectra which almost always provide molecular weight information. The disadvantages are its selective sensitivity (compounds with low proton affinities will often show low sensitivities) and the absence of much fragmentation which precludes the effective use of libraries and structural interpretation.

***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. No official endorsement should be inferred.

Particle beam-LC/MS is a relatively new technique and has not been well tested, but offers the potential to make LC/MS directly analogous to GC/MS in the fact that both use the electron impact (EI) mode of ionization with the resultant abundant fragmentation pattern and the concomitant use of standardized libraries of EI spectra.

This present work compares TSP-LC/MS with PB-LC/MS for limits of detection, abundance of fragmentation, and practicability by using the dyes as analytes. The results show that TSP-LC/MS with a wire-repeller is more sensitive to the dyes by two to three orders of magnitude than the PB-LC/MS system. The instruments on which the comparison was made were a Vestec thermospray system interfaced to a Finnigan Triple Stage Quadrupole TSQ®45 and an Extrel ThermaBeam™ system also interfaced to the Finnigan TSQ®45. The use of the triple quadrupole mass spectrometer enabled collision activated dissociation (CAD) on the protonated molecules that were generated in the thermospray mode. The PB-LC/MS generated EI spectra for the dyes that were rich in structural information and these were compared with the CAD spectra.

INTRODUCTION

Dyestuffs are of environmental interest because of their widespread use as colorants in a variety of products. Synthetic intermediates, byproducts, and degradation products of these dyes could be potential health hazards due to their toxicity or carcinogenicity or both.

Several analytical methods have been developed for the identification and quantification of these dyes in order to monitor them in the environment. Thermospray-liquid chromatography/mass spectrometry (TSP-LC/MS) has been found to be a suitable technique for the analysis of nonvolatile dyes[1-5]. Recent improvements to the thermospray ion source have improved the sensitivity of the technique for many analytes[6]. However, one of the drawbacks of TSP-LC/MS, especially for environmental monitoring, is that one obtains mainly molecular and adduct ions, and this information may not be sufficient for structural elucidation of compounds of unknown structure. Tandem mass spectrometry (MS/MS) has been used to deconvolute fully the structural information contained in the thermospray mass spectra of dyes[1,3], but there would be great merit to be able to analyze dyes with a single quadrupole LC/MS system and obtain structural information. The new particle beam-liquid chromatography/mass spectrometry (PB-LC/MS) interfaces offer such an advantage[7,8,9] by generating electron impact (EI) spectra of compounds introduced via high performance liquid chromatography (HPLC). In order to assess such a system, we have interfaced an HPLC by means of an Extrel ThermaBeam™ LC/MS interface to a Finnigan TSQ®45 mass spectrometer. Thus, we were able to perform a direct comparison of TSP-LC/MS and PB-LC/MS for the analysis of dyes.

EXPERIMENTAL

Materials

The following dyestuffs, identified by their Colour Index (C.I.) name, were obtained from the sources indicated and were used without further purification: 1-6, 8, 9, 11, and 14 (Aldrich Chemical Company, Milwaukee, Wisconsin); 7, 10, and 13 (Sandoz Colors and Chemicals, Charlotte, North Carolina); 12 (Ciba-Geigy Dyestuffs and Chemicals Division, Greensboro, North Carolina).

Dyes were dissolved in an appropriate solvent prior to analysis; dyes 1, 3-5, 7, 9, and 14 in acetonitrile-water (50/50, v/v), dyes 2, 8, 10, and 11 in methanol, dyes 6 and 12 in acetonitrile, and dye 13 in methylene chloride-acetonitrile (50/50, v/v).

Instrumentation: Thermospray Ionization Mass Spectrometry

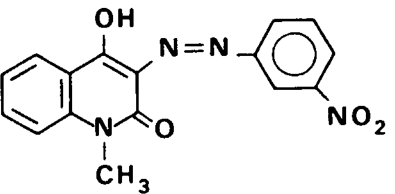
The instrument used was a Finnigan MAT Triple Stage Quadrupole TSQ®45 mass spectrometer equipped with a modified Vestec Corporation ion source and thermospray interface. The modification in the Vestec ion source consisted of the addition of a wire-repeller and is described in detail elsewhere[6]. This repeller was operated at a voltage range of 200-250 V. The system was operated as a single quadrupole mass spectrometer for the detection limit study and was calibrated with polyethylene glycol (Aldrich), average molecular weight 400. The total scan time was 1.5 sec. Collision activated dissociation (CAD) spectra were generated in a daughter ion scan with an Argon pressure of 1 mT and a collision energy of 20 eV.

The HPLC instrumentation consisted of a Rheodyne Model 7125 injector valve fitted with a 10-µL sample loop and a Spectra-Physics SP8700XR solvent delivery system. A syringe pump (ISCO LC-5000) was connected to the system to deliver the buffer - 0.1M ammonium acetate - post-column via the thermospray interface into the source. All samples were introduced by direct injection, bypassing the column. The mobile phase was methanol-water (50:50). Typical operating conditions of the thermospray interface were as follows: T (vaporizer) = 120 to 130°C; T (tip) = 220 - 235°C; T (source) = 250°C; and T (jet) - 200 to 220°C.

Instrumentation: Particle Beam LC/MS

A Finnigan MAT TSQ®45 equipped with a 4510 EI/CI source was used. The PB-LC/MS interface was an Extrel Corporation ThermaBeam™ interface, fitted to the ion source by a machined adaptor. This heatable adaptor, made mainly of Vespel (DuPont Corporation) and partly of brass and approximately 8 cm in length, was heated to 200-250°C. The ion source was operated at 240°C. Filament emission current was 10.3 mA and the electron multiplier voltage was 1600 V. The preamplifier

AZO CLASS



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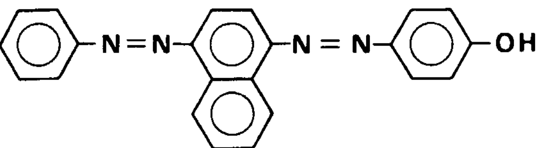

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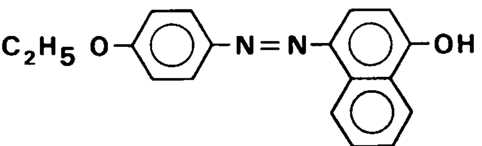

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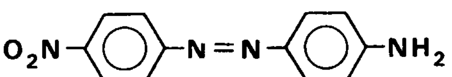

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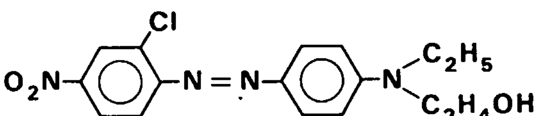

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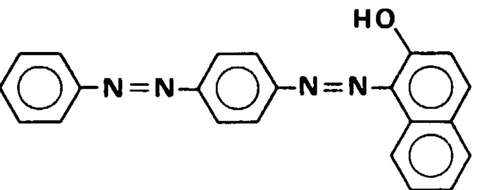

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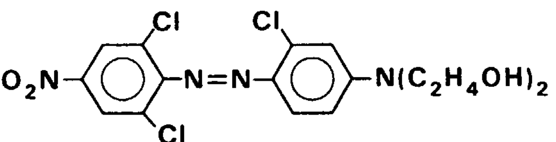

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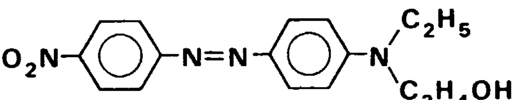

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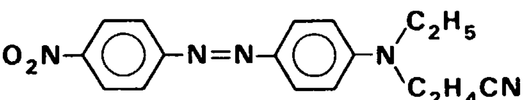

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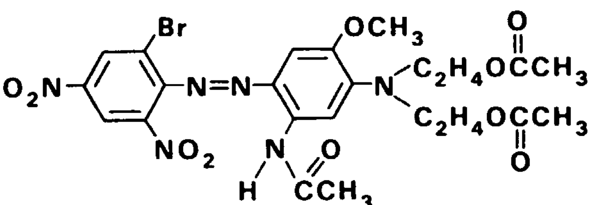

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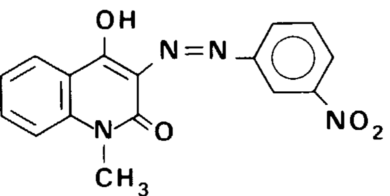

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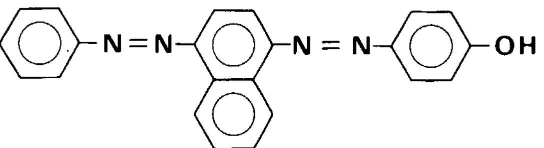

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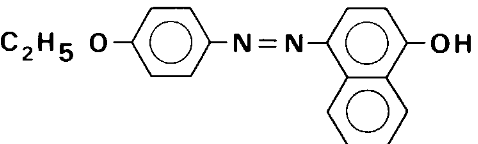

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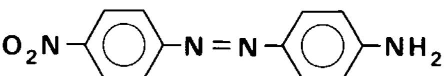

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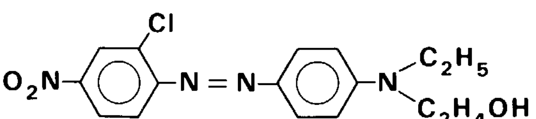

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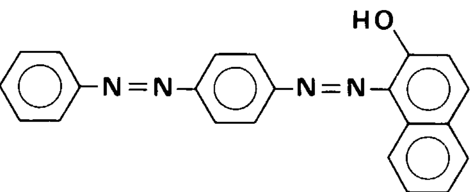

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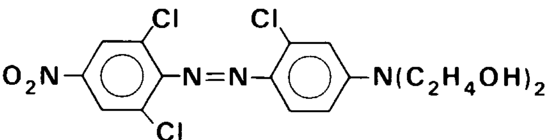

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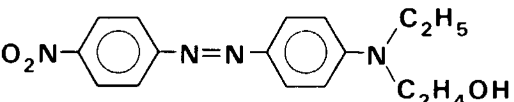

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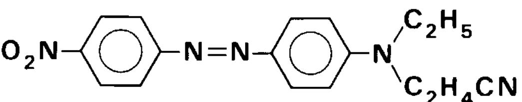

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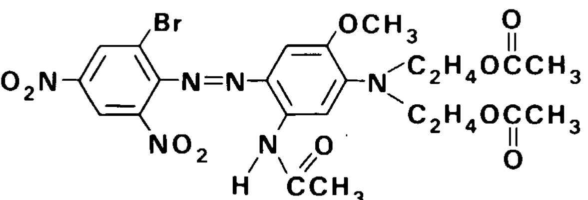

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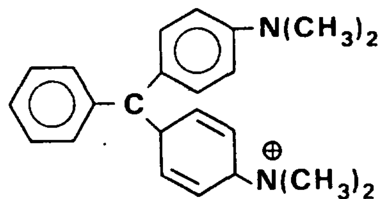
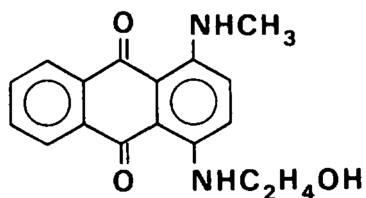


11. Basic Green 4

ANTHRAQUINONE CLASS



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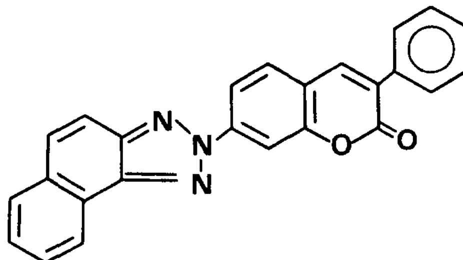
COUMARIN CLASS



13. Fluorescent Brightener 236

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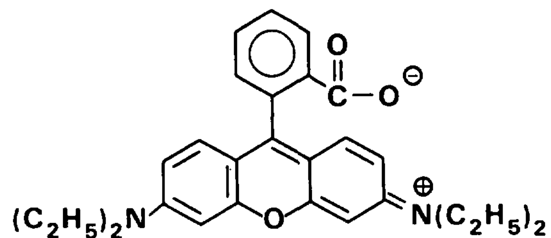

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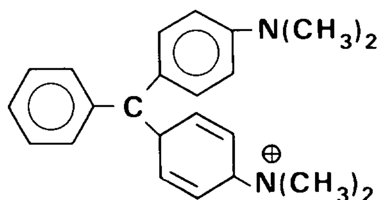

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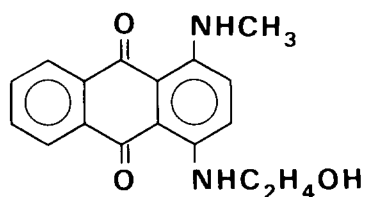

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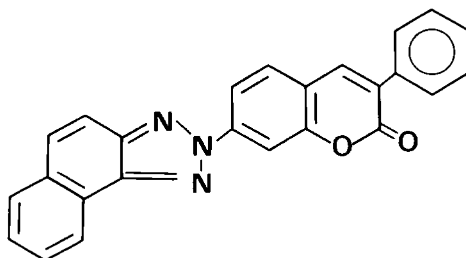

13. Fluorescent Brightener 236

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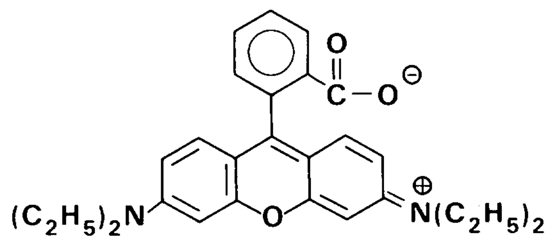

14. Solvent Red 49

sensitivity was set at 10^{-8} Amps/Volt. The ThermaBeam™ nebulizer temperature was 210-240°C. This temperature varied with the composition of the mobile phase gradient. The ThermaBeam™ expansion chamber temperature was 95°C. The HPLC consisted of a Spectra-Physics SP8700XR solvent delivery system with a Rheodyne Model 7125 injector valve fitted with a 10-µL sample loop. The column was a 15 cm x 4 mm internal diameter Varian Micro Pak MCH-5-N-CAP C_{18} column. The HPLC was operated in the gradient mode, starting at a mobile phase of methanol-water (50:50), changing within 5 minutes to 100 percent methanol, and holding at that level for 10 minutes. Flow rate was 0.9 mL/min.

RESULTS AND DISCUSSION

The detection limits of the commercial dyes are reported on Table I. Commercial dyes are formulations and are often not pure. The approximate purity of each dye is listed on this table. The limits of detection were obtained by recording the mass chromatograms of characteristic ions of the dyes under full-mass scan with a signal-to-noise ratio of at least three and were not corrected for purity. Furthermore, the dyes were sampled through direct flow injection analysis, bypassing the column, under thermospray ionization. Each dye was injected separately through the HPLC under PB-LC/MS analysis. Also included in this table are the limits of detection for six of the dyes that were previously obtained under thermospray ionization with an ion source without a repeller[3]. Enhancement factors of between 10 and 400 are observed for the configuration with the wire-repeller. The comparison of the thermospray ionization (with repeller) and the PB-LC/MS shows enhancement factors of between 20 and 16,000 in favor of thermospray ionization. These numbers may reflect the fact that the system was optimized for thermospray ionization while the connection between the ThermaBeam™ PB-LC/MS interface and the Finnigan mass spectrometer was fabricated in our laboratory. For reference, the limit of detection for caffeine with this PB-LC/MS interface was approximately 15 ng. Preliminary results on an optimized PB-LC/MS system indicate better limits of detection by 2 to 10 for these dyes over what was presented here[10]. Nevertheless, the sensitivity of thermospray ionization for these dyes is better than the PB-LC/MS by up to 3 orders of magnitude.

The particle beam EI mass spectra of five azo dyes are compiled in Table II. These should be compared with the CAD spectra of these dyes listed in Table III. The CAD spectra were obtained as daughter ion mass spectra of the protonated molecule from thermospray ionization. These compounds show similar degrees of fragmentation in both the particle beam EI mass spectra and the CAD spectra. Most of the compounds show enough fragmentation under either mode that these dyes can be identified by library searches or structural interpretation.

These compounds generally show diagnostic ions which are characteristic of azo dyes. These ions are associated with cleavage at the azo linkage at the C–N or N–C bond or at the N–N bond, e.g., m/z 92 (aminophenyl ion) and 122 (nitrophenyl ion) for Disperse Orange 3 under the CAD mode and m/z 92 (aminophenyl ion) under the particle beam EI mode.

SUMMARY

The use of HPLC methods to introduce compounds into a mass spectrometer offers the potential to regulate pollutants that were, heretofore, outside the scope of traditional analytical methods. Many dyes are among those compounds that for reason of nonvolatility or intractability do not elute from a GC. Thermospray-LC/MS has been applied to these dyes in the past, but very little structural information was generated by this technique. One solution to this problem had been to use tandem mass spectrometry to effect CAD spectra that could be used for structural identification. The drawback to this scheme has been the cost of tandem mass spectrometers which usually starts at 150 percent of the single quadrupole mass spectrometric system. Thus, the routine analytical laboratory does not have access to this instrumentation.

Particle beam-LC/MS offers the potential for generating useful structural data on a single quadrupole system. The feasibility of using such an instrument for analyzing for environmental pollutants has been shown[9]. This present work has extended the comparison of TSP-LC/MS and PB-LC/MS to organic dyes. The results show that TSP-LC/MS has better detection limits than PB-LC/MS for the dyes that were used. One reason for this difference in limits of detection, which in some cases reached three to four orders of magnitude, can be attributed to a particle beam interface that was not optimized to the mass spectrometer on which it was used. A major contributing factor in these differences was the use of a wire-repeller for TSP-LC/MS. This development has increased the sensitivity of thermospray ionization by a factor of 10 to 400 for the dyes.

Particle beam-LC/MS did generate spectra rich in structural information. CAD daughter ion spectra taken on a triple quadrupole mass spectrometer showed a similar abundance of fragmentation although not identical with the particle beam EI spectra.

The general conclusion of this work is, at the present time, TSP-LC/MS and PB-LC/MS remain complementary techniques, each offering something unique in their application. For work that involves trace analysis of dyes, TSP-LC/MS would be the choice. For structural identification or confirmation on a single quadrupole mass spectrometer, one would use the PB-LC/MS system. Lastly, the triple quadrupole mass spectrometer remains a versatile system for structural identity, especially when used in conjunction with TSP-LC/MS.

Table I. Detection Limits for Commercial Dyes

Dye	Structure	MW	Dye Content (%)	TSP (w/o repeller) Detection Limit (ng)	TSP (with repeller) Detection Limit (ng)	PB LC/MS Detection Limit (ng)
Disperse Yellow 5	1	324	C.30	-	5	500
Disperse Orange 13	2	352	C.15	150-200	20	5500
Solvent Red 3	3	292	100	-	10	200
Disperse Orange 3	4	242	C.20	-	2.5	50
Disperse Red 13	5	348	C.25	-	10	4400
Solvent Red 23	6	352	C.85	50	5	500
Disperse Brown 1	7	432	C.25	-	10	2700
Disperse Red 1	8	314	C.30	-	0.1	250
Disperse Orange 25	9	323	C.20	-	10	500
Disperse Blue 79	10	624	100	250-500	10	300
Basic Green 4	11	329	C.98	20	0.67	700
Disperse Blue 3	12	296	C.20	20	0.05	800
Fluorescent Brightener 236	13	389	100	25-50	4	600
Solvent Red 49	14	442	C.97	-	1	500

Table II. Particle Beam EI Mass Spectra of Azo Dyes

Dye	MW	m/z of ions observed (% relative abundance)
Disperse Yellow 5	324	324(1), 295(1.5), 202(3), 174(7), 138(9), 108(100), 92(17)
Solvent Red 3	292	292(17), 263(3), 235(4), 171(6), 149(9), 143(100), 121(48), 115(36), 108(18)
Disperse Orange 3	242	242(3), 213(4), 212(10), 120(55), 92(100)
Disperse Red 13	348	317(22), 287(20), 154(17), 144(25), 142(28), 134(25), 133(100), 126(40), 120(30), 105(50), 104(50), 99(20), 92(32), 90(40).
Disperse Brown 1	432	432(1.5), 403(15), 402(5), 401(17), 359(5.5), 357(7), 313(5), 214(15), 208(17), 206(36), 185(40), 183(78), 176(39), 167(32), 149(77), 139(100), 124(49), 104(82), 90(48)

Table III. CAD Spectra of $(M+H)^+$ Ions of Azo Dyes Generated by Thermospray Ionization

Dye	$[M+H]^+$	m/z of ions observed (% relative abundance)
Disperse Yellow 5	325	325(34), 279(5.7), 187(100), 138(23), 116(13), 67(8.5)
Solvent Red 3	293	293(6.2), 143(42), 139(5.1), 121(100),115(8.2), 111(6.3), 108(6.6), 103(5.7), 93(5.7), 91(34), 77(44), 65(19)
Disperse Orange 3	243	243(13), 197(11), 140(5.1), 122(100), 93(8.2), 92(32), 76(8.9), 75(27)
Disperse Red 13	349	349(97), 318(14), 303(14), 289(24), 178(37), 156(12), 147(44), 134(10), 120(8.2), 119(6.8), 106(5.4)
Disperse Brown 1	433	433(63), 402(17), 387(8.3), 357(23), 311(9.4), 228(20), 218(12), 197(100), 193(12), 190(37), 185(55), 184(6.9), 183(10), 180(5.5), 170(7.6), 166(15), 163(33), 161(8.3), 158(30), 153(92), 152(6.9), 147(6.2), 145(8.3), 144(14), 143(5.5), 140(6.9), 139(7.9), 131(5.5), 128(5.5), 126(7.9), 122(5.5), 120(12), 119(15), 118(17), 117(5.5), 116(6.2), 114(59), 113(6.2), 107(13), 99(18), 70(25) 45(8.3)

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THE ANALYSIS OF THE CHLORINATED HERBICIDES AND ESTERS BY THERMOSPRAY-LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY (TSP-LC/MS)

Tammy L. Jones, Chemist, Quality Assurance Division, Leon D. Betowski, Research Chemist, Quality Assurance Division, U.S. Environmental Protection Agency, EMSL-Las Vegas, Las Vegas, Nevada 89193-3478[1]

ABSTRACT

The standard method for the analysis of chlorinated acid herbicides and their esters (e.g.,2,4-D, Silvex and Dalapon) is Method 8150. This method requires hydrolysis of the sample extract followed by derivatization (an esterification). Disadvantages of the current procedure are that the esterification reagent (diazomethane) is both toxic and explosive and that hydrolysis is time consuming and may not always be quantitative.

The analysis of the chlorinated herbicides by thermospray-liquid chromatography/mass spectrometry (TSP-LC/MS) allows the direct analysis of both the free acid and esterified herbicides, eliminating the need for hydrolysis and derivatization in the method.

INTRODUCTION

The use of chlorinated phenoxyacetic acids and related compounds as herbicides originated in the 1930's with the work of Kögl and collaborators, who showed that indole 3-acetic acid or auxin promotes cell elongation in plants. Many of the chlorinated phenoxyacetic acid derivatives show an auxin-like activity without being rapidly metabolized in the plants. These herbicides, therefore, act by promoting uncontrolled growth in the plants. These compounds generally have a low mammalian toxicity, but impurities and high dosages may cause teratogenic effects in rodents(1).

The goal of this research was to find a way to detect the chlorinated herbicides (free acid form) and their esters

[1]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. No official endorsement should be inferred.

without the need for hydrolysis and subsequent esterification as now required in RCRA Method 8150. Method 8150 is a gas chromatographic (GC) method that specifies an electron capture detector with the option of a GC/Mass Spectrometer (MS) for confirmation. The usual esterification reagent, diazomethane, is both carcinogenic and explosive; elimination of the esterification step would be advantageous. Sample hydrolysis is a time consuming step and may not always be quantitative.

The use of TSP-LC/MS not only eliminates the need for the hydrolysis and esterification steps in the analysis of the chlorinated herbicides and esters, but provides a method for the direct analysis of these compounds[2], using a compound specific detector, the mass spectrometer. The potential of TSP-LC/MS to analyze for chlorinated phenoxyacetic acids at the ppb level has been shown by Voyksner[3], who operated in the "filament on" mode using negative-ion detection. Without the "filament on" mode the detection limits were only 1 µg for negative-ion detection and 10 µg for positive-ion detection. The application of a wire-repeller[4] in the thermospray source has greatly improved the limits of detection for thermospray positive-ion mode. This present work, therefore, has investigated thermospray introduction and various modes of ionization for the analysis of samples for chlorinated phenoxyacid herbicides.

EXPERIMENTAL

A Finnigan MAT TSQ 45 was interfaced to a Spectra-Physics SP8700XR gradient pump and an ISCO LC-5000 syringe pump for postcolumn flow via a Vestec Thermospray system. A wire-repeller was inserted into the ion source opposite the ion exit orifice[3]. The repeller was operated at 225V in the positive ion mode and at 0V in the negative ion mode. Negative ion spectra were acquired with the discharge on and filament off.

A flow of 0.4 mL/min was used through a 15cm x 2.1mm Supelcosil 5-µm LC-18 analytical column from Supelco (Bellefonte, PA). A linear gradient elution program of 100% water to 100% methanol in ten minutes with a fifteen minute hold was used. The system was then programmed back to 100% water and held there for ten minutes before the next sample was analyzed. A flow of 0.88 mL/min of 0.1M ammonium acetate was added via a postcolumn to the main flow and before the LC/MS interface. A total flow of 1.0 - 1.2 mL/min is necessary for optimum thermospray operation.

Typical operating temperatures of the thermospray interface

were as follows: T(vaporizer) = 123 - 130°C; T(tip) = 190 - 210°C; T(jet) = 205 - 220°C; T(source) = 230 - 240°C.

Standards were prepared from pesticides received from the Pesticide and Industrial Chemicals Repository, U.S. Environmental Protection Agency Repository (Research Triangle Park, NC).

The samples were extracted according to the protocol as outlined in Method 8150, with some modifications. The extraction scheme was followed until the hydrolysis step, at that point the extract was evaporated by K-D and then blown down under nitrogen, with solvent exchange into methanol.

RESULTS AND DISCUSSION

The structures of the herbicides investigated in this study are shown in Figure 1. They are all chlorinated phenoxy acids except dalapon, which is a chlorinated aliphatic acid, and dinoseb which is a nitrated phenol. Four chlorinated phenoxy acid esters and endothall were also

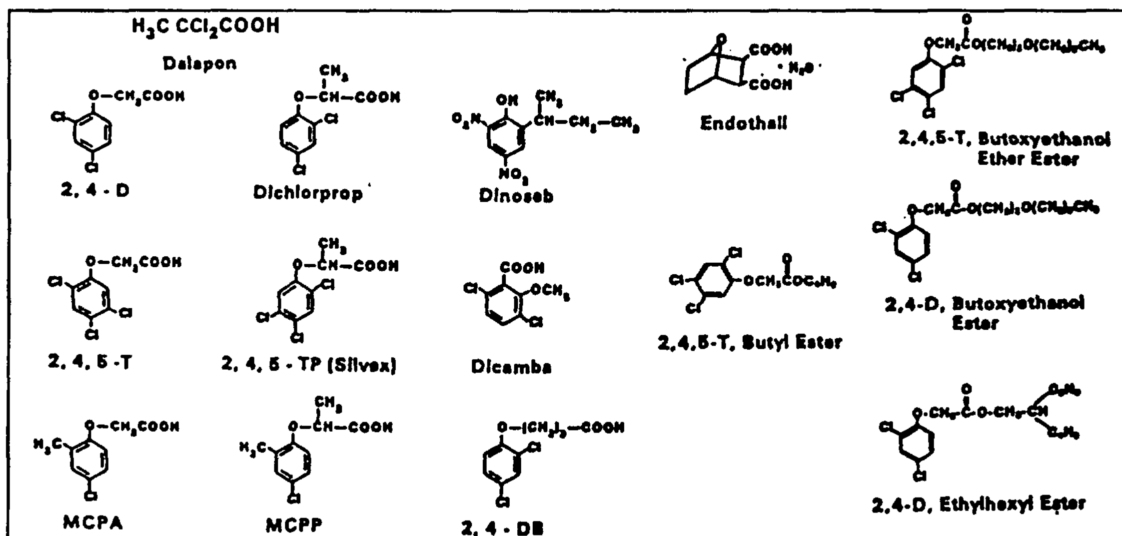

Figure 1 - STRUCTURES OF THE CHLORINATED PHENOXY ACID HERBICIDES AND THEIR ESTERS

examined in order to ascertain whether the chlorinated acid esters would be discernable by this method.
It was established that the chlorinated phenoxy acid esters were easily separated and quantifiable using this procedure. The compounds investigated, their molecular weights, and retention times are listed in Table I.

Table I - CHLORINATED HERBICIDES MOLECULAR WEIGHTS AND RETENTION TIMES

COMPOUND	M.W.	RETENTION TIMES
DALAPON	142	1:34±0:08
DICAMBA	220	1:59±0:07
2,4-D	220	9:40±0:30
MCPA	200	10:17±0:38
DICHLORPROP	234	11:10±0:38
MCPP	214	11:48±0:45
2,4,5-T	254	12:05±0:34
SILVEX	268	13:03±1:12
DINOSEB	240	13:38±0:51
2,4-DB	248	16:11±0:46

Various modes of ionization were examined in order to determine which mode would produce not only the greatest sensitivity but also structural information. The two most common modes of ionization available to the general LC/MS user are the positive and negative (discharge on) ionization modes. Two other ionization modes were examined that are unique to the LC-TSP/MS that was used in this study: the daughter ion collision activated dissociation (CAD) mode and the wire-repeller induced CAD spectra in the positive ion single quadrupole mode.

The results determined that the two general modes of ionization would be best for a general SW-846 method. The positive and negative ion mode spectra and their limits of detection (LOD) are summarized in Table II.

Voyksner reported 10 μg positive ion thermospray detection limits for similar compounds[3]. Due to the increased sensitivity produced by the wire-repeller in the present work, quantities between .002 and .160 μg of the compounds in

Table I could be observed in the positive ion thermospray mode. In the positive ion mode the base peak in almost all cases is the $(M+NH_4)^+$ ion, with the exception being dinoseb in which the $(M+NH_4-NO)^+$ ion is the base peak; for two compounds, 2,4-DB and dinoseb, the $(M+H)^+$ ion is present. No ions were detected in the positive ion mode for dalapon.

Table II - LIMITS OF DETECTION IN THE POSITIVE AND NEGATIVE ION MODES FOR THE CHLORINATED HERBICIDES

COMPOUNDS	POSITIVE MODE QUANT. ION	LOD (ng)	NEGATIVE MODE QUANT. ION	LOD (ng)
DALAPON	*	-	$141(M-1)^-$	11± 4
DICAMBA	$238(M+NH_4)^+$	13± 5	$184(M-HCl)^-$	3.0± 1
2,4-D	$238(M+NH_4)^+$	2.9± 1	$219(M-1)^-$	48±25
MCPA	$218(M+NH_4)^+$	116± 8	$199(M-1)^-$	2.8± 5
DICHLORPROP	$252(M+NH_4)^+$	2.7± 1	$235(M-1)^-$	25 ± 24
MCPP	$232(M+NH_4)^+$	5.0± 2	$213(M-1)^-$	12± 4
2,4,5-T	$272(M+NH_4)^+$	169± 8	$218(M-HCl)^-$	6.5± 5
SILVEX	$286(M+NH_4)^+$	162± 1	$269(M+1)^-$	43±30
DINOSEB	$228(M+NH_4-NO)^+$	24±12	$240(M)^-$	19± 6
2,4-DB	$266(M+NH_4)^+$	3.4± 2	$247(M-1)^-$	114±38

As expected, the $(M-H)^-$ ion is a major species in the negative ion (discharge on, filament off) spectra of the chlorinated phenoxy acids. It forms the base peak in six of the nine chlorinated acids. Losses of chlorine and losses of the acid moieties contribute to the generation of most of the fragment ions that occur in the negative ion spectra of these compounds. In our study six of the ten herbicides show better limits of detection in the negative ion mode with the discharge on than in the positive ion mode. Under negative ion conditions our instrument configuration also produces abundant fragmentation; it is the preferred method of analysis for the herbicides. In fact 2,4-DB and 2,4-D are the only herbicides in this study that show much better detection limits in the positive ion mode.

In order to generate structural data from the positive ion thermospray ionization mode, CAD experiments were performed on a triple stage quadrupole mass spectrometer. This was successful, but an attempt was made to duplicate this type of fragmentation on a single quadrupole mass spectrometer. This would have more general use in the typical analytical laboratory. Therefore to increase the amount of fragmentation

in a single quadrupole the wire-repeller was moved further into the thermospray stream and closer to the sample cone orifice. The voltage on the wire-repeller was also increased to 400 V. This resulted in an increase in the fragmentation of the chlorinated herbicides and spectral patterns that were similar to electron impact (EI) spectra.

SUMMARY

Liquid chromatography-TSP/MS affords a unique technique that allows the analysis of diverse compounds, of widely varying polarity, in an assortment of matrices. The introduction of the wire-repeller to the thermospray source has increased the range of detection of many of these compounds, especially in the case of the chlorinated herbicides. The overall method was successful in being able to determine the chlorinated phenoxy acid herbicides, by LC-TSP/MS, at not only low detection levels but also in the removal of the esterification and hydrolysis steps from the extraction scheme. The best possible ionization method was determined to be the negative ion mode with the "discharge on". This gives sensitive detection limits and some ion fragmentation. Much fragmentation is also generated with the wire-repeller induced ionization technique.

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DEVELOPMENT OF ANALYTICAL METHODS FOR NON-VOLATILES USING PARTICLE BEAM LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY SYSTEMS

THOMAS D. BEHYMER, RESEARCH CHEMIST, THOMAS A. BELLAR, RESEARCH CHEMIST, AND WILLIAM L. BUDDE, DIVISION DIRECTOR, ENVIRONMENTAL MONITORING SYSTEMS LABORATORY, U. S. ENVIRONMENTAL PROTECTION AGENCY, 26 W. MARTIN LUTHER KING DRIVE, CINCINNATI, OHIO 45268

ABSTRACT

Several types of particle beam interfaces for high performance liquid chromatography/mass spectrometry (HPLC/MS) systems have been described. These interfaces permit a new approach to the development of methods for the determination of compounds not amenable to capillary column gas chromatography mass spectrometry (nonvolatiles). Caffeine has been proposed as a test substance for the optimization of particle beam HPLC/MS interface operating parameters. Adjustable operating parameters for particle beam interfaces include the position of the capillary transfer line with respect to the entrance to the desolvation chamber, the temperature and flow rate of the nebulization gas, the temperature of the desolvation chamber, and the composition of the mobile phase. These operating parameters were varied and the integrated signal intensities of ions from a variety of nonvolatile compounds were compared with intensities from caffeine ions. A generally good correlation was established between the intensities of ions from the nonvolatile compounds and the intensities of the caffeine ions. A mixture of compounds was selected to provide a total system performance check of the HPLC column, the particle beam interface, and the capability of the spectrometer to produce a standard electron impact mass spectrum. The components of the test mixture were selected to elute within a reasonable time from a reverse phase C-18 HPLC column using a gradient elution acetonitrile-water solvent system. Two critical requirements for particle beam HPLC/MS are the stabilities of integrated ion intensities over a minimum of an eight hour period, and the relative stabilities and reproducibilities of the electron impact (EI) mass spectra over a similar time period. Ion intensity stability over a minimum of an eight-hour period is required so that concentration calibrations maintain validity for a reasonable number of samples. Similarly, EI spectra must be relatively stable to permit automatic peak identifications via reverse search algorithms and spectra from reference data bases. Stabilities of signal intensities and EI spectra over eight hour periods were studied for a number of compounds not amenable to GC/MS (nonvolatiles). Compounds studied included carbamates, N-substituted amides, N-substituted ureas, phosphoramides, and sulfur containing compounds. Mean relative standard deviations of signal intensities and reproducibilities of EI spectra were in the range of 10-30% for most compounds. Relative sensitivities of compounds were determined by measurements of the integrated ion intensities per nanogram of compound injected into the HPLC/MS system.

Analysis of Unknown Pollutants in Groundwater and Hazardous Waste Using Liquid Chromatography/Particle Beam Mass Spectrometry.

Mark A. Brown, In Suk Kim, Raimund Roehl, Fassil I. Sasinos and Robert D. Stephens. Hazardous Materials Laboratory, California Department of Health Services, Berkeley, California 94704

Abstract: Particle Beam Liquid Chromatography/Mass Spectrometry (LC/PB/MS) is a powerful tool for the analysis of target pollutants but complementary methods are required for nontarget compounds. A method for chlorophenoxy acid herbicides is shown as an alternative to SW-846 method 8150, and for 4-chlorobenzene sulfonic acid, using reversed phase and anion exchange chromatography. Calibration curves and practical quantitation limits for electron impact (EI) and positive and negative chemical ionization mass spectra for 21 compounds, and EI spectra for five azo dyes of environmental concern are described. EI spectra are matched by library search algorithms. Characterizing nontarget pollutants is more difficult. LC/PB/MS is used to look at aqueous leachate samples from Stringfellow, Casmalia and McColl hazardous waste sites, and drinking water in California. LC separation of nontarget compounds *via* anion exchange and reversed phase chromatography, and molecular weight and natural isotope abundance data from EI, positive, and negative chemical ionization PB/MS provides a partial characterization. Identification *via* mass spectrum library matching has not been effective because most unknown compounds are not contained in existing MS libraries. LC inductively coupled plasma (ICP) MS of environmental samples yields qualitative elemental analysis showing the presence or absence of key heteroatoms in organic pollutants including chlorine, other halogens, phosphorus and sulfur. This complementary approach will provide a single method for the characterization of nontarget pollutants in hazardous waste and drinking water.

INTRODUCTION

The characterization of either target or nontarget pollutants involves two discrete steps; 1) the application of appropriate extraction, concentration and separation techniques, and 2) the application of detection and confirmatory methods. Both steps must take into consideration the polarity (or ionic character), volatility, aqueous solubility, thermal lability, and mass spectral fragmentation of the pollutant.

Limitations of Gas Chromatography for Detection and Conformation of Pollutants. Conventional environmental analytical methods rely on gas chromatography (GC) for resolution even though the physical properties of most organic compounds make them unsuitable for GC separation. The physical properties of all organic compounds mapped on a two dimensional "chemical space" with the axis of increasing polarity *versus* increasing molecular weight (Figure I) illustrates that the small space containing compounds suitable for GC analysis is restricted to those with relatively low polarity and molecular weight. As a quantitative indication of this discrepancy, out of currently more than six million chemicals listed in the CAS registry only approximately 123,000 mass spectra (about 2%) have been published (*via* GC inlet or direct inlet probe). Several recent studies indicate that probably most organic environmental pollutants fall into the less accessible (*via* GC) but much larger region of "chemical space".

Analysis of leachates from 13 hazardous waste sites in the U.S.A. shows less than 10% of the total organic content accounted for using conventional analytical methods. The high percentage of unidentified material in this survey is considered to reflect large quantities of nonvolatile or aqueous nonextractable organic compounds, *i.e.* that portion of total organic material in the aqueous sample that is not extractable into an organic solvent under any pH conditions (Bramlett *et al.*, 1987). In a similar study, total organic halocarbon levels in groundwater monitoring well samples at 16 hazardous waste sites are analyzed both by a total pyrolysis method (SW-846 method 9020) and a volatile/semivolatile GC/MS method (SW-846 methods 8240 and 8270). The total pyrolysis method invariably indicates substantially higher total organic halocarbon levels relative to the GC/MS based methods. This discrepancy is attributed to a significant nonvolatile component of the total organic halocarbon content at these sites that is overlooked by a GC based method (Pruskin *et al.*, 1987). Similarly, HPLC Thermo-

spray MS is required to confirm that approximately half the unidentified total organic halocarbon from BKK, a hazardous waste site located in southern California, is the nonconventional pollutant 4-chlorobenzene sulfonic acid. Only 4% of the total organic halocarbons had been previously identified using standard GC methods (Stephens, *et al.*, 1987).

Analysis of Unknown and Known Compounds in Stringfellow Hazardous Waste Site Leachate Samples. The Stringfellow Superfund site in California poses analytical problems that are similar to those encountered with most waste sites across the United States and that may be best addressed *via* LC/MS based methods. Most organic compounds in aqueous leachates from this site cannot be characterized by GC/MS based methods. Analysis of Stringfellow bedrock groundwater shows that only 0.78% of the total dissolved organic materials are identifiable *via* purge and trap analysis (SAIC report, 1987). These are compounds such as acetone, trichloroethylene *etc*, whose physical properties are ideally suited for GC/MS separation and confirmation. Another 33% of the dissolved organic matter is characterized as "unknown", *i.e.*, not extractable from the aqueous samples under any pH conditions and thus not analyzed *via* GC. Another 66% is 4-chlorobenzene sulfonic acid (PCBSA), an extremely polar and water soluble compound that is also not suitable for GC analysis. This compound, a waste product from DDT manufacture, is known to occur at this site because of the history of disposal of "sulfuric acid" waste from industrial DDT synthesis. In another study by the same group, two major waste streams originating from Stringfellow are shown to contain fully 45% and 40% respectively of the total organic carbon as PCBSA (measured by ion chromatography and UV detection).

A conventional analytical procedure using purge-and-trap analysis and acid base/neutral extraction with Stringfellow aqueous leachates shows that the majority of the total organics are not effectively fractionated but rather end up unresolved in the final aqueous remainder fraction (Ellis et al., 1988). This fraction contains the highly polar and water soluble organic materials that are ideally analyzed by an HPLC based method. Although PCBSA had been originally measured prior to the fractionation process its highly polar, water soluble, ionic, nonextractable nature indicate that it rightfully belongs in the aqueous remainder fraction.

ICP/MS as a Complementary Method for the Identification of Nontarget Pollutants. Inductively coupled plasma (ICP) mass spectrometry (MS) is a relatively new elemental analysis technique that was originally developed for the determination of metals. The only elements that cannot be detected by ICP/MS in positive ion mode are helium, neon and fluorine. The potential of ICP/MS as an element-specific detector for liquid chromatography has been described, but only for metallic or semi-metallic elements, *e.g.*, cadmium, cobalt, arsenic and selenium (Thompson and Houk, 1986; Dean *et al.*, 1987; Heitkemper *et al.*, 1988). ICP/MS can also be used to detect phosphorus, bromine, iodine, and even carbon with detection limits in aqueous solution of: chlorine 5 - 800 ug/l; bromine 1 - 2 ug/l; iodine 0.01 - 2.0 ug/l; sulfur 100 ug/l; and phosphorus 20 ug/l (Fulford and Quan, 1988; Koppenal *et al.*, 1988).

Recent work on combining liquid chromatography with ICP/MS performed at the California Department of Health Services Hazardous Materials Laboratory indicates that it also can serve as a sensitive detection method for nonmetals. At present, we focus on the detection of chlorine and sulfur in LC effluents because those two elements frequently occur as heteroelements in nonconventional pollutants.

The Polar and Less Well Characterized Organic Fraction of Environmental Samples must be Considered from the Viewpoint of the Protection of Human Health. In one study, fractionation of mutagenic components of the effluent from water treatment plants reveals that the majority of the mutagenic activity is made up of highly polar compounds that are not amenable to GC based analyses. This fraction includes classes of chemicals such as halogenated organic acids and phenols (Colman *et al.*, 1984). To fully characterize the potential impact of all organic hazardous waste components upon human health we need to develop and validate practical techniques for the extraction, concentration, separation and detection of highly polar compounds in an unaltered form. Liquid chromatography mass spectrometry and inductively coupled plasma mass spectrometry are two analytical methods that are particularly well suited for analysis of this important environmental fraction.

MATERIALS AND METHODS

HPLC/Particle Beam/MS consists of a Hewlett-Packard 5988a mass spectrometer equipped with a Hewlett-Packard Particle Beam HPLC interface and 1090 HPLC. Ionization modes include electron impact, and positive and negative chemical ionization using methane, isobutane or ammonia. LC methods are initially developed on a Hewlett-Packard 1050 HPLC equipped with a 1040 diode array detector and "Chem Station" for data acquisition. Anion exchange chromatography columns are made by SGE (Ringwood, Australia) (Model 250GL-SAX, 25cm X 2mm) eluting with ammonium acetate buffer and acetonitrile. Reversed phase columns (10 cm and 22 cm X 2 mm) are made by Applied Biosystems (Santa Clara, California, USA). Solvents are combinations of methanol/water or acetonitrile/water. Disposable solid phase extraction columns (reversed phase and ion exchange) are obtained from Analytichem International (Harbor City, California, USA).

LC/ICP/MS facilities consist of a Perkin Elmer SCIEX Elan 500 inductively coupled plasma mass spectrometer system equipped with a temperature-controlled spray chamber and multiple nebulizers (concentric, cross-flow, and high solids), a Dionex 4000i quaternary gradient pump with high pressure injection valve, a variety of Dionex ion chromatography columns, a Linear UVIS 203 absorbance detector, a Tracor 560 photoconductivity detector, and a complete Dynamic Solutions Maxima 820 chromatography data station. Software which allows the transfer of data from the Elan 500 computer to the Maxima data station and other PC-based software has been developed in house. The ICP mass spectrometer is set up as an element specific detector for chlorine and sulfur, monitoring chlorine (^{35}Cl) and sulfur (^{34}S) nuclides simultaneously.

Methods Development Considerations. Sensitivity limitations indicate that the direct detection of components in aqueous samples *via* LC/PB/MS or LC/ICP/MS is generally not possible without prior concentration and extraction. Therefore unconventional extraction/concentration procedures to isolate and concentrate nonconventional pollutants are required. The majority of organic materials in a typical aqueous real world sample are not extractable with organic solvents such as methylene chloride. More appropriate concentration and recovery methods include lyophilization (freeze drying), various commercially available solid phase extraction and concentration techniques, as well as conventional liquid/liquid extraction procedures using organic solvents. Organic solvent liquid/solid methods are still clearly the best available technique for extraction and concentration of organic analytes from solid matrices including soil and sludges. Extraction and concentration for aqueous samples uses solid phase extraction (SPE) cartridge with cation and anion exchange, reversed phase, and polar normal phase as dictated by the nature of the matrix and pollutants under analysis. Concentration of an aqueous leachate or drinking water sample by evaporation under reduced pressure or lyophilization is used for producing samples suitable for subsequent HPLC separations. Although the volatile fraction is lost, this process greatly concentrates the nonvolatile components. Solid samples such as soils, sludge or fly ash are conventionally extracted with organic solvents such as ether/aqueous methanol.

Thin Layer Chromatography as a Preliminary Screen for Unknown Samples. An environmental sample may contain organic materials with a wide range of physical characteristics, *e.g.*, from hydrophilic-/strongly anionic or cationic to lipophilic/neutral. Thin layer chromatography (TLC) is routinely used with conventional silica gel plates as a preliminary screening for new samples and as an aid for establishing the most appropriate HPLC columns and conditions for fractionating components of a complex mixture. The three solvent developing systems used are acetone:hexane 1:1 (lipophilic/neutral), 2-propanol:ethyl acetate:ammonium hydroxide:water 25:25:4:1 (basic), and 2-propanol:acetonitrile:glacial acetic acid:water 65:35:1:1 (acid). Organic materials are visualized by UV quenching on the fluorescent plate, iodine staining and by spraying with phosphomolybdic acid solution. Materials with reasonable retention in the neutral solvent system are generally best resolved *via* standard reversed phase LC. Materials with reasonable retention using the acid or base developing solvent systems are generally best resolved *via* ion chromatography methods.

Analysis of target compounds using analytical standards depends upon the combination of matching both HPLC retention times and EI or CI mass spectra with those obtained from analytical standards. Thus the major effort involves the determination of an appropriate HPLC column for any given analyte or analyte class. For example, conventional reversed phase HPLC columns are useless for extremely polar compounds such as sulfonic and certain carboxylic acids; ion exchange based columns are more appropriate.

Analysis of nontarget compounds, "complete unknowns", is somewhat similar in that the retention time and the type of LC column giving the best results also yields clues as to chemical classification, *e.g.*, good retention and separation upon an anion exchange column suggests that the analytes are anionic. Detection and confirmation information that is necessary for unknown identification is also obtained from other instrumentation including LC/ICP/MS, and UV spectrophotometry.

RESULTS AND DISCUSSION

Particle Beam LC/MS is Suitable for Quantitative and Qualitative Analysis of Target Compounds. LC/PB/MS is effective both as a qualitative and quantitative method for a wide range of chemical classes. Complete calibration curves and practical quantitation limits have been produced using analytical standards of 21 compounds, under various modes of ionization, that have been associated with a potential groundwater contamination in the town of Macfarland, California (Table I).

Table I. Practical Quantitation Limits (PQLs, nanograms injected), Correlation Coefficients and Quadratic Regression Parameters (a and b) of 21 Compounds with Electron Impact, and Positive and Negative Chemical Ionization Particle Beam Mass Spectrometry, Direct Flow Injection with Full Scan Mode.

COMPOUND	Electron Impact				Positive Chemical				Negative Chemical			
	PQL	R^2	aX^2	bX	PQL	R^2	aX^2	bX	PQL	R^2	aX^2	bX
2,4-DINITROPHENOL	172	0.984	-0.002	25.3	—	—	—	—	106	0.947	-0.012	196
ACEPHATE	134	0.995	0.099	91.4	93	0.984	1.53	1,350	65.5	0.976	1.53	76.1[b]
ALDICARB	234	0.996	0.010	73.7	83.7	0.994	0.04	172	275	0.990	0.014	-4.7[b]
AZINPHOS METHYL	48.9	0.996	0.215	315	48.9	0.994	0.447	686	9.9	0.996	3.86	3,360
BROMOXYNIL	93.0	0.976	0.067	-59.0	57.2	0.987	0.289	399	10.1	0.989	21.3	8,120
DIMETHOATE	73.1	0.991	0.197	391	40.9	0.998	0.387	511	5.2	0.996	5.61	6,330
DINOSEB	—	—	—	—	712	0.939	0.004	-4.85[a]	582	0.960	0.055	-123[a]
DIQUAT	117	0.994	0.107	257	—	—	—	—	—	—	—	—
DIFENZOQUAT	56.5	0.992	0.173	570	33.1	0.999	0.176	166	—	—	—	—
ENDOSULFAN	171	0.996	0.055	2.25[b]	38.2	0.997	0.106	82.8	13.6	0.998	1.72	3,550
ETHYL PARATHION	—	—	—	—	—	—	—	—	19.8	0.998	1.76	383
FENBUTATIN OXIDE	116	0.995	0.133	336	82.9	0.983	0.059	266	80.2	0.994	0.259	184
GLYPHOSATE	778	0.947	-.0003[a]	9.47	1,040	0.980	0.0002	0.31[b]	—	—	—	—
METHIDATHION	30.6	0.999	1.09	578	28.3	0.995	0.418	1,170	4.1	0.996	3.99	2,600
METHOMYL	124	0.998	0.423	204	34.8	0.983	0.0085	38.2	—	—	—	—
MONOCROTOPHOS	159	0.988	0.095	418	19.6	0.997	0.351	550	—	—	—	—
PARAQUAT DICHLORIDE	61.3	0.994	0.136	180	209	0.998	0.010	23.5	—	—	—	—
PENDIMETHALIN	780	0.979	0.003[a]	3.16	73.4	0.992	0.265	299	16.0	0.986	1.56	-326
PROPARGITE	31.7	0.997	1.16	1,708	42.3	0.998	0.295	158	—	—	—	—
TRIFLURALIN	510	0.992	0.0040	-4.54[a]	413	0.993	0.0256	37.0[a]	—	—	—	—
ZIRAM	92.7	0.990	0.0092[a]	121	132	0.991	0.0091	69.8	—	—	—	—

All regression coefficients are significant at $p < 0.01$ except those marked [a] $p < 0.05$ and [b] $p > 0.05$.

Figure II_{a-c} shows representative mass spectra and calibration curves with correlation coefficients for three compounds, paraquat *via* EI ionization (a); propargite *via* methane positive chemical ionization (b); and ethyl parathion *via* methane negative chemical ionization (c). Particle Beam LC/MS provides

the full spectrum for these representatives of different physical classes of compounds, ranging from organic salts such as paraquat hydrochloride, to extremely lipophilic compounds such as fenbutatin oxide (with a molecular weight of >1,000). Not surprisingly, either positive or negative chemical ionization (CI) almost always gives greater sensitivity when compared to EI ionization. All of the calibration curves show the quadratic second order type of relationships seen in Figure II. A reduction in the response factor (area response per unit injected) for all analytes at lower concentrations produces a loss in sensitivity at lower concentrations and effectively compresses the dynamic range.

PB/MS of Aniline Dyes via Electron Impact Ionization. Aniline dyes are classical nonconventional pollutants and are ideal candidates for a LC/MS based method of detection and quantitation. Their physical properties, including low volatility, thermal lability, moderate to high molecular weight and high polarity (especially the sulfonic acid derivatives) make them extremely difficult to analyze using any conventional GC based method. Figure III shows the EI mass spectra of 2 ug each of four different industrial azo dyes. "Acid orange", also tested, shows essentially no response. For the others the mass spectra generally show something like a parent ion. The samples chromatographed are not pure, so the spectra almost certainly contain ions due to impurities as well as the parent compound.

LC/PB/MS Detection and Quantitation of Chlorophenoxy Acid Herbicides in Soil. An interlaboratory check sample provided by the EPA of soil spiked with the chlorophenoxy acid herbicides Silvex and 2,4-D was obtained. EPA method SW-846 8150 specifies soil extraction and alkaline hydrolysis of any esters present followed by (re) esterification *via* diazomethane and detection and confirmation by GC/MS. The methylation step is required because the free carboxylic acids will not pass through conventional GC analytical columns. Reversed phase chromatography functions equally well to resolve free carboxylic acids or the corresponding esters and thus can eliminate the diazomethylation step. Detection and quantitation is *via* LC/PB/MS with selected ion monitoring (SIM) and EI ionization (using 4-ions each). Figure IV shows the LC/PB/MS chromatogram for the actual soil extract using EI/SIM. Table II compares the reference values from the interlaboratory check to the LC/MS values, which are 13% and 21% low for Silvex and 2,4-D, respectively.

Table II. EPA laboratory evaluation data for soil spiked with the chlorophenoxy herbicides Silvex and 2,4-D comparing results from an LC/PB/MS method to EPA method SW-846 8150. The accuracy of the data is in the top 27% of all labs reporting.

analyte	reference value (ppm)	LC/MS value	% diff.
2,4-D	43.4	34.1	79%
Silvex	32.5	28.4	87%

These results compared very favorably with those reported from 28 other laboratories that had used the conventional GC/MS method. The slightly low values from the LC/PB/MS method may be in part because extraction efficiency was not corrected for. The accuracy of the LC/PB/MS based method is indicated by the fact that our values are in approximately the top 27% of all laboratories reporting in comparison with reference values. Clearly LC/PB/MS methods can yield quantitative results that are comparable with GC/MS methods, and offer very specific advantages in terms of sample preparation and simplicity of analysis. This is currently being expanded to produce a general method for all of the chlorophenoxy acid herbicides that are specified in EPA SW-846 method 8150 in both soil and water.

Analysis of Stringfellow Hazardous Waste Site Groundwater. Preliminary TLC of lyophilizates from Stringfellow aqueous leachate samples indicate that only the acid elution system gives movement from the TLC plate origin, suggesting that the unknowns contained in these samples are highly polar, probably acidic and that fractionation will be best achieved *via* anion exchange chromatography.

The aqueous remainder fractions were subjected to ion chromatography (IC) PB/MS analysis *via* negative CI (NCI). The NCI spectrum of 5 ug technical PCBSA chromatographed on a 25 cm X 2 mm

anion exchange column (retention time 10.2 min) shows a m^- ion at 192, m-1 at 191, and a m-35-1 base ion at 156 corresponding to [m - HCl]. Figure V shows the NCI spectrum of the major peak (retention time 8.2 min.) for an aqueous remainder fraction. Surprisingly, no peak is observed with a retention time corresponding to PCBSA, even in the extracted ion chromatogram (major ion from PCBSA 156 amu). Figure VI shows the TIC of a mixture of the aqueous remainder fraction (5 ul) spiked with 5 ug PCBSA standard. The two components are well separated under these conditions. The NCI spectrum of the major peak observed in ion chromatography (IC) PB/MS appears to have no relation to PCBSA, although its retention in ion chromatography suggests that it is an organic anion, *e.g.*, a carboxylic or sulfonic acid.

ICP/MS Ion Chromatography of the Organic Constituents of Stringfellow Leachates was used to test the latter possibility. For the chromatographic separation, the same conditions (column, eluent, and flow rate) as for the LC/PB/MS experiments described previously were used. Figure VII shows ^{35}Cl and ^{34}S traces for chromatograms obtained with the Stringfellow aqueous remainder fraction and for a 1 ug/ul injection of PCBSA. IC/ICP/MS detects the presence of both chlorine and sulfur in the PCBSA peak and confirms the difference in retention time for PCBSA and the major unknown compound in the aqueous remainder fraction. Most significantly, the unknown compound contains chlorine but not sulfur, thus making it clear that it is not a sulfonic acid. Review of all the results obtained on the aqueous remainder fraction submitted to HML for analysis suggested that the integrity of the sample may have been compromised by shipment in an unsuitable container, *i.e.* a liquid scintillation vial with a cap line by aluminum foil.

In order to resolve this issue, new samples of Stringfellow leachates were collected. Portions were evaporated under reduced pressure at room temperature, and the residue subjected to anion exchange chromatography with UV (Figure VIIIa) and ICP/MS (Figure VIIIb) detection. Reversed phase and other types of commercially available HPLC columns completely fail to provide either retention or resolution of components from this concentrate. IC/PB/MS confirms that the large early eluting peak is indeed PCBSA. Substantial long wavelength adsorption of many of the other, unidentified components seen in this chromatogram suggests that the unknowns have extended conjugation and are quite possibly aromatic. No EI spectra generated from any of these unknowns, including the PCBSA peak, are matched by EI library searches.

Companion Techniques for the Identification of Unknowns in Stringfellow Leachate Extracts: Liquid Chromatography ICP/MS. The failure of IC/PB/MS to provide identification of more of the components in Stringfellow samples separated *via* ion exchange chromatography indicates that additional techniques are required. Ion chromatography ICP/MS using conditions developed for LC/PB/MS provides qualitative and quantitative analysis of chlorine and sulfur in unknowns from Stringfellow leachates shows that in addition to the PCBSA peak containing these elements, several later eluting peaks also contain these elements. The combined information that many of these unknowns are probably aromatic and contain both sulfur and chlorine is an enormous aid in the consideration of tentative structural assignments for these unknown pollutants.

Anion Exchange Chromatography as a General Approach for the Resolution of Unknown Pollutants. Anion exchange chromatography PB/MS is the method of choice for the analysis of the Stringfellow leachate samples as described above, and may be the best method for resolution of components in samples from other sites. Reversed phase liquid chromatography is not useful for this type of sample nor for most actual hazardous waste samples that have been examined in this laboratory. Most of the organic materials in leachate samples appear in general to be so polar that they simply do not interact with the bonded phase of a reversed phase HPLC column.

Figure IX shows a UV chromatogram using a standard reversed phase column of a lyophilized ground water monitoring well sample taken from a hazardous waste site at Casmalia, California. Although there is the appearance of separation and resolution, close examination reveals that all of the peaks are eluting at approximately the void volume of the column. In this case the solvent was 98% water 2% methanol, leaving very little room for modification. Figure X shows the same sample

chromatographed on a strong anion exchange column (SAX) (similar to the one used with the Stringfellow samples), showing resolution of a major peak at 4 minutes and at least four subsequent peaks. In a similar experiment, Figure XI shows a UV chromatogram using a reversed phase column of a lyophilized sample of drinking water from Santa Clara, California. Most of the material is eluted very early with little or no retention. The same sample chromatographed on the SAX column (Figure XII) shows retention and resolution of at least three peaks.

Organic Anions may Predominate in Leachates from Hazardous Waste Sites. Clearly ion chromatography is useful for resolving the organic constituents of both leachate and drinking water samples from Stringfellow, Casmalia and Santa Clara. This suggests that a large proportion of the organic materials in these samples are organic acids. This may be due partially to the fact that many environmental chemical transformations, including microbial metabolism or photolysis, involve oxidation and hydrolysis to yield free carboxylic, sulfonic or phosphorous acids. A second possibility is that the waste materials produced by chemical manufacturing processes that are disposed of at waste sites tend to be the water soluble, anionic compounds such as the PCBSA in "sulfuric acid waste" from the chemical manufacture of DDT.

Figure XIII shows our only successful example of LC/PB/MS reversed phase chromatography of an extract from a leachate sample taken from a waste site located at McColl, California. The effectiveness of reversed phase chromatography in this case is probably due to the selective nature of the isolation/concentration procedure used. Thus, 100 ml of the aqueous sample was passed through a conditioned C18 SPE cartridge which was air dried and the isolates eluted with methanol. The EI spectra of the two major peaks (Figure XIII bottom left and right) look essentially identical and are not recognized by a library search match. The PBM algorithm used for library search typically tends to only consider the low mass ions, and in this case suggests that the compound is SO_2 (mass 64)! Positive CI is more useful in this case (Figure XIV) showing what are probably protonated molecular ions at 211 and 239 respectively for the two peaks, along with m+29 adduct ions which are typical for methane PCI.

Limitations of LC/PB/MS for the Structural Elucidation of Complete Unknowns in Waste Samples. It had been anticipated that EI spectra generated by LC/PB/MS of unknown organic compounds would provide identification *via* library search algorithms. The failure of a computer library match seen with the McColl water sample described above illustrates the actual limitations of this expectation. Another example is shown in Figure XV; a positive CI spectrum of the Santa Clara drinking water lyophilizate that is resolved *via* anion exchange chromatography produces three peaks, one of which has a retention time of approximately 5.2 min. The positive CI mass spectra of this peak shows ions with molecular weights all the way up to 317 amu. An apparent periodicity of peaks separated by 14 amu suggests that the unknown may contain a long chain hydrocarbon moiety (a C_{20} carboxylate mw = 312). The EI spectrum of this peak (not shown) also yields no library match. The UV spectrum (Figure XVI) provides the type of additional analytical data that is required for identification of unknowns; it reveals that the unknown is not aromatic, lacks extended conjugation and is consistent with an alkyl carboxylic acid. The next step with this material is to isolate sufficient material using anion exchange chromatography to obtain an FT-IR spectrum with the aim of identifying any other functional groups and confirming the presence of a free carboxylic acid. Thus although good quality EI spectra have been obtained of individual peaks from the chromatography of numerous hazardous waste and drinking water samples from a wide variety of sites, only a single useful library match has been made (of diisooctyl phthalate isolated *via* reversed phase SPE from a drinking water sample). Consideration of Figure I indicates that this should not be surprising; the vast majority of known organic compounds do not have EI spectra available (and needless to say the infinite number of unknown compounds have no available mass spectra).

"Unnatural Products" Chemistry. The complete identification of unknown compounds that we have successfully resolved using LC/PB/MS will clearly require additional analytical information, such as will be provided *via* liquid chromatography ICP/MS, FT-IR, UV or proton and heteroatom NMR. This situation is analogous to that of a natural products chemist faced with making a complete structural a-

ssignment of an unknown compound isolated from some matrix such as seaweed instead of a leachate from a hazardous waste site. The natural products chemist would exploit the complete array of analytical instrumentation and not attempt identification based solely upon low resolution (quadrupole) mass spectrometry.

CONCLUSIONS

Limitations of obtaining library match identifications with environmental unknowns using LC/PB/MS. Particle Beam liquid chromatography mass spectrometry has proven to be an extremely powerful confirmatory detection tool for the target compounds. Characterization of unknowns in real environmental samples, on the other hand, has proven to be more difficult. Successful concentration, separation, and EI and CI mass spectrometry, has not lead to identification. Experience has shown that rarely are either target or nontarget pollutants present in mass spectral libraries. It has become clear that a single technique such as LC/PB/MS is insufficient for the identification of unknown or nontarget pollutants. For this reason we have begun to explore the use of the use of liquid chromatography ion chromatography/inductively coupled plasma/mass spectrometry as a companion technique. Even without a complete optimization, we found that ICP/MS can yield valuable information on the elemental composition of unknown pollutants separated by liquid chromatography with good sensitivity and excellent selectivity. In this respect LC/ICP/MS is an ideal companion method to LC/PB/MS which is aimed at obtaining molecular information on those compounds. Preliminary results indicate that these two approaches in combination have significantly enhanced our laboratory's ability to characterize unknowns in environmental materials. Further development of these two technologies is proposed as a new and powerful approach to the characterization of nontarget pollutants.

ACKNOWLEDGMENTS

We would like to thank EPA EMSL Las Vegas for their partial financial support for this project.

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Figure I. "Chemical Space" plotted along the axis of increasing polarity *versus* increasing molecular weight.

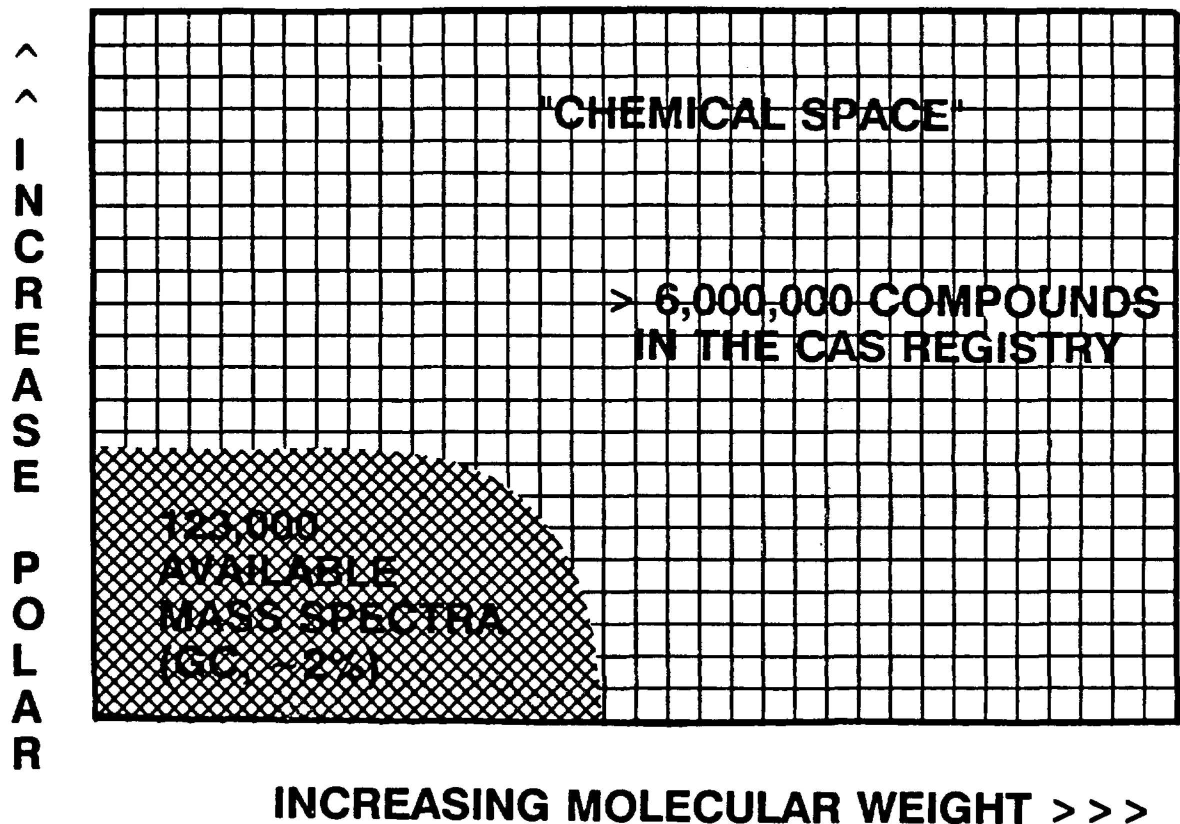
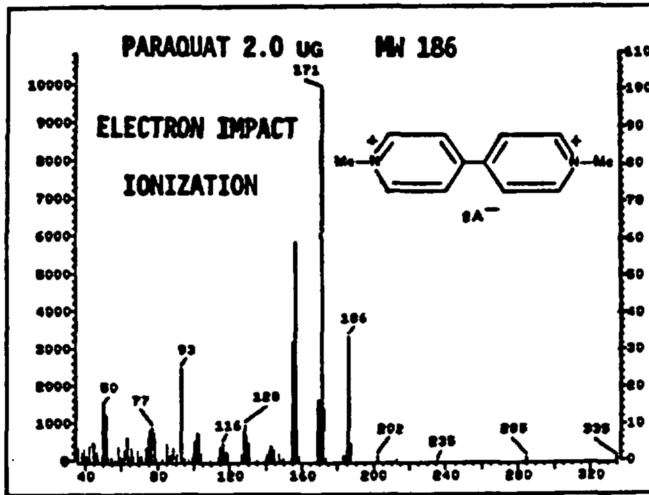
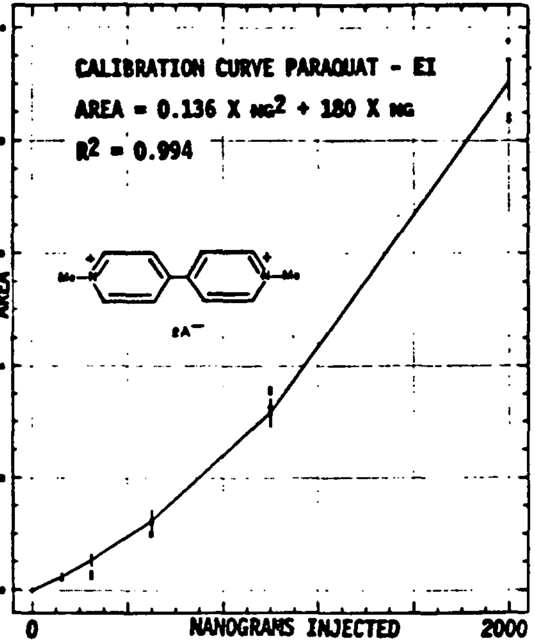
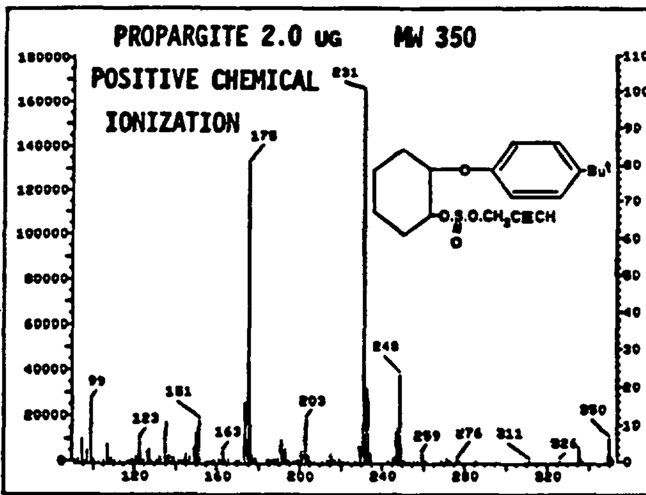
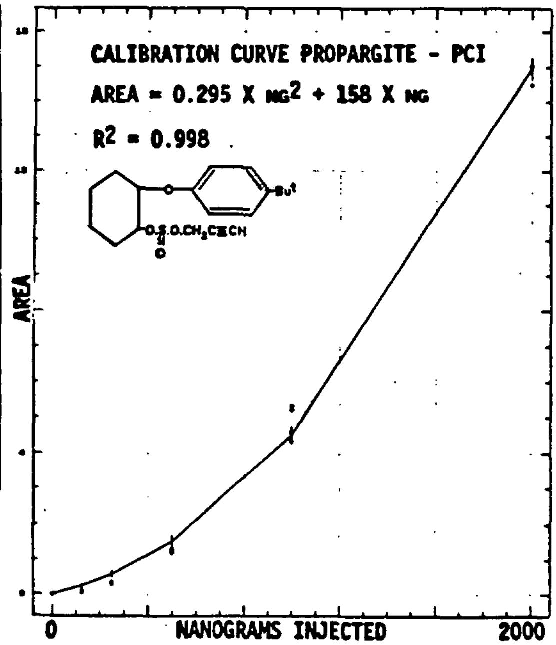


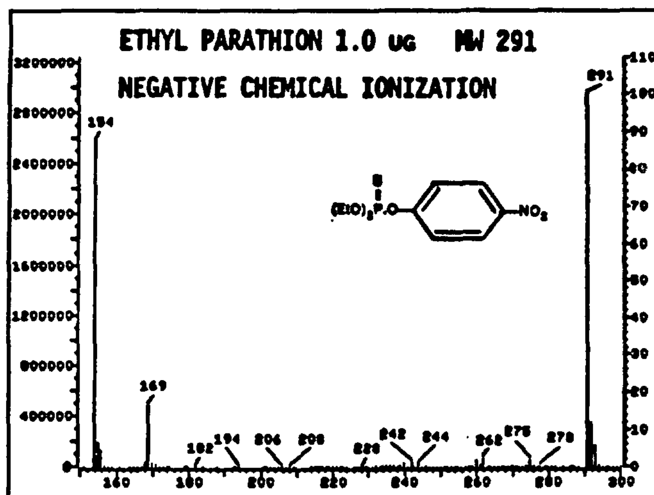
Figure II. Mass spectra and calibration curves for a) Paraquat (EI); b) Propargite (PCI); and c) Ethyl Parathion (NCI).










ETHYL PARATHION 1.0 UG MW 291
NEGATIVE CHEMICAL IONIZATION

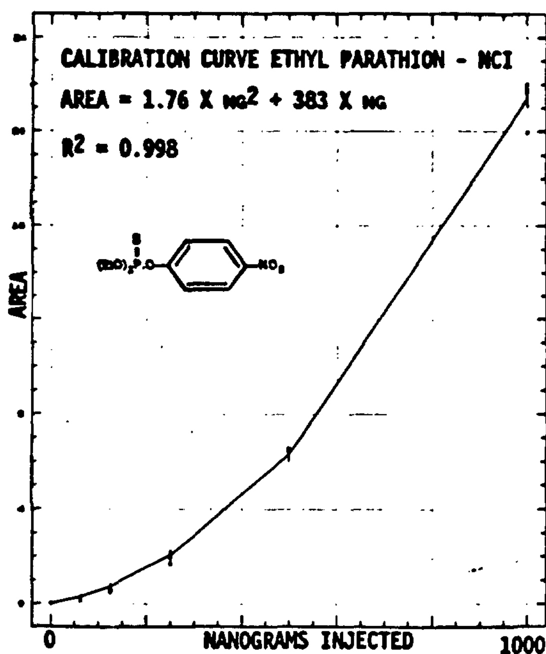
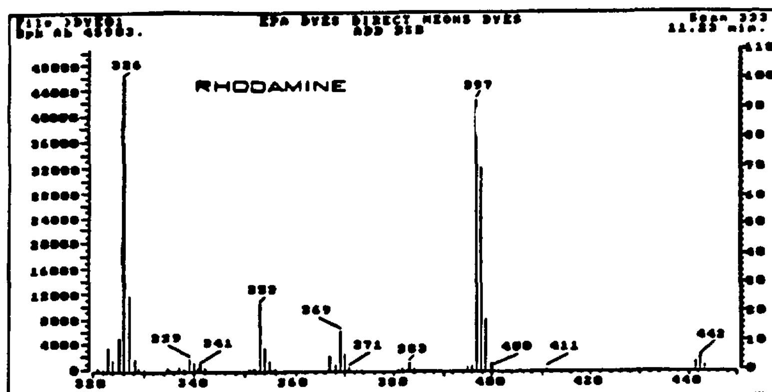
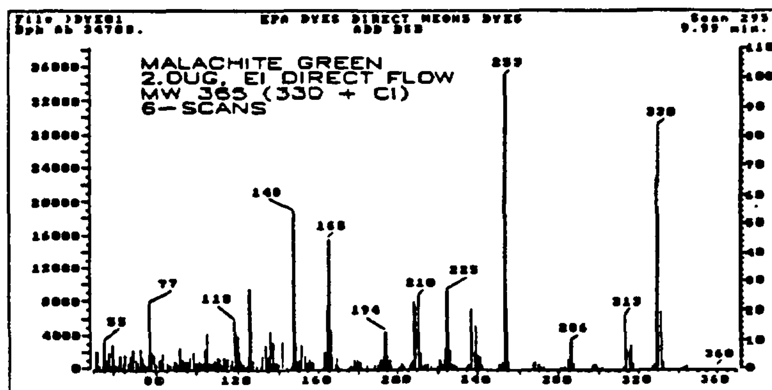
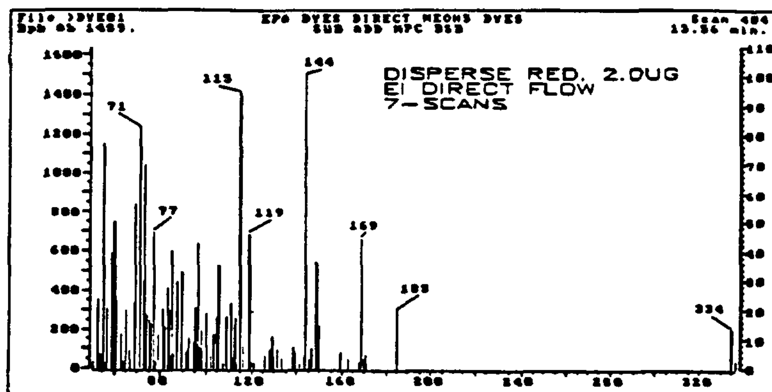

CALIBRATION CURVE ETHYL PARATHION - NCI
AREA = 1.76 X NG2 + 383 X NG
R2 = 0.998
AREA
NANOGRAMS INJECTED
0
1000

Figure III. EI mass spectra of four azo dyes.







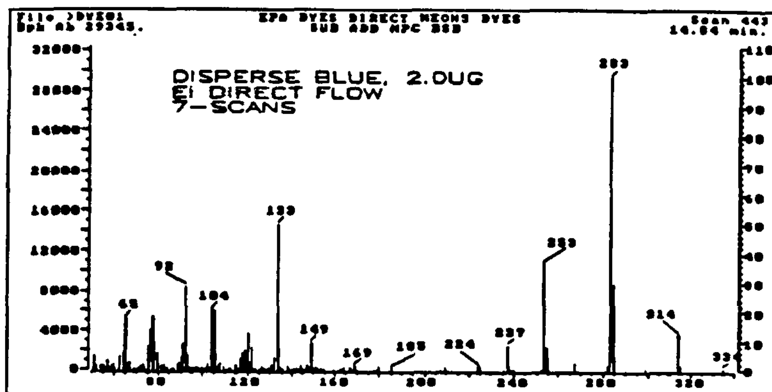


Figure IV. Spiked soil sample extracted by EPA method SW-846 8150 - Reversed phase chromatography, EI - SIM.

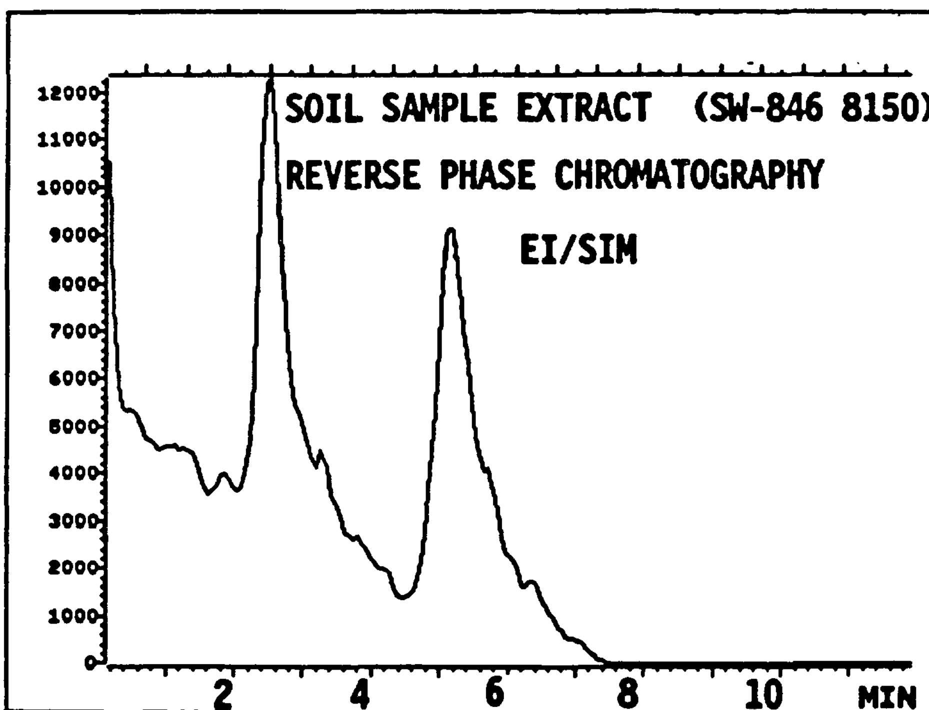


Figure V. Negative CI MS of the major unknown peak in anion exchange chromatography PB/MS of a Stringfellow aqueous remainder fraction.

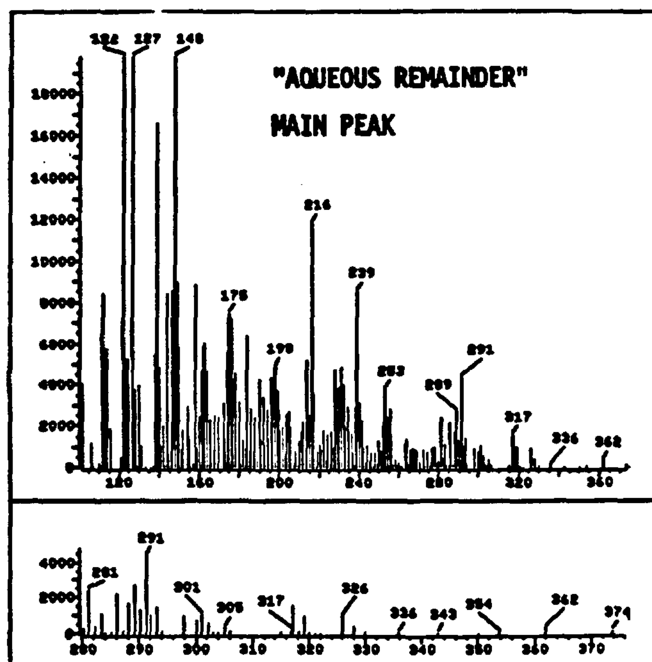


Figure VI. Total ion chromatogram of a mixture of a Stringfellow aqueous remainder fraction (5 ul) spiked with 5 ug PCBSA standard.

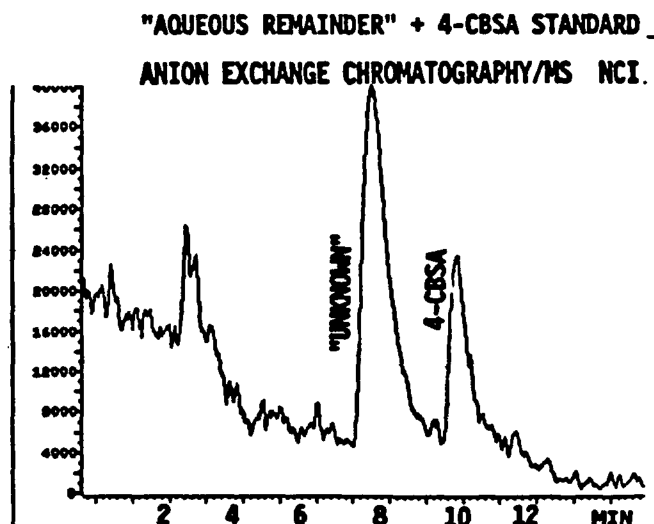
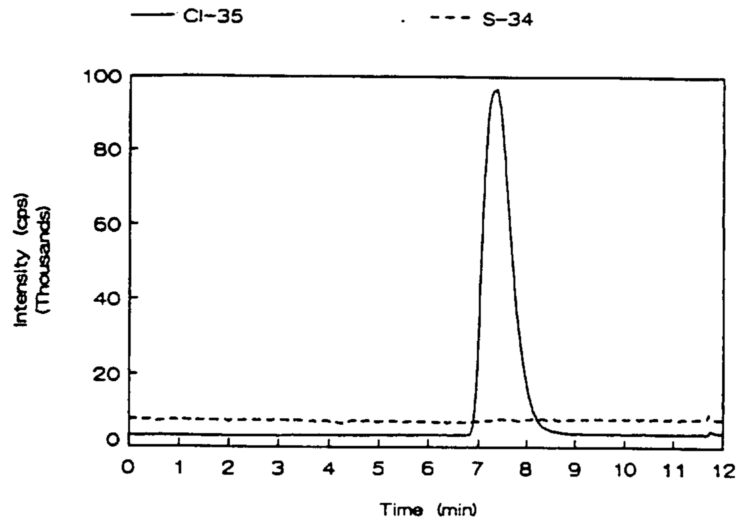


Figure VII. Ion chromatograms of Stringfellow aqueous remainder fraction and 1 ug/u/ standard of PCBSA with simultaneous monitoring of ^{35}Cl and ^{34}S by ICP/MS.



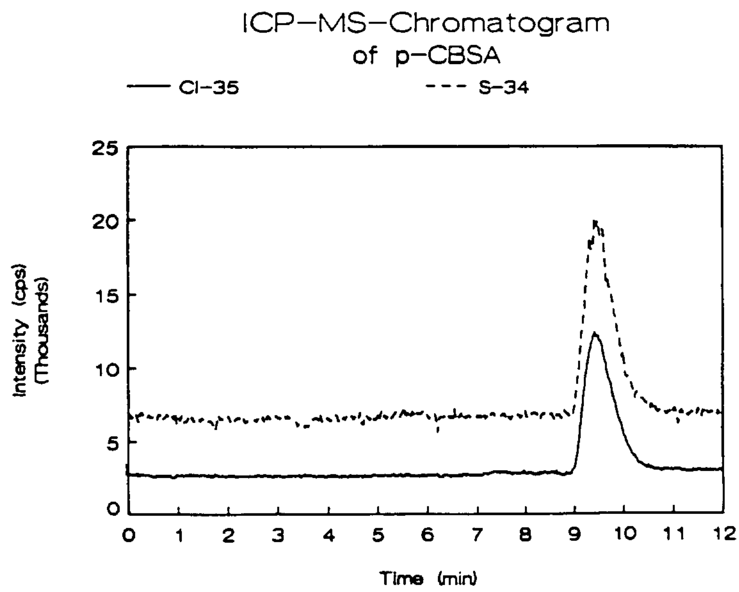
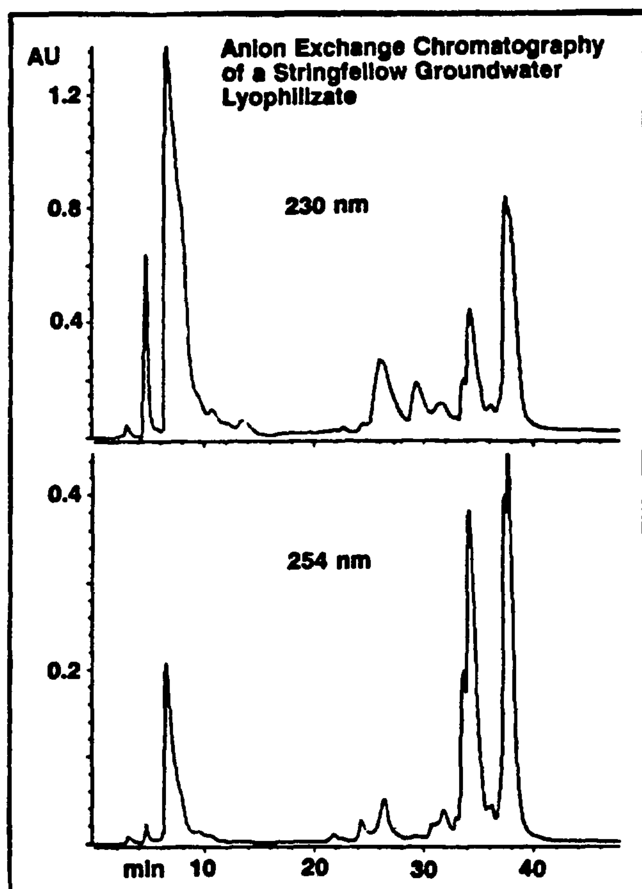


Figure VIII. Stringfellow leachate concentrate Ion chromatography with a) UV and detection.



b) ICP/MS

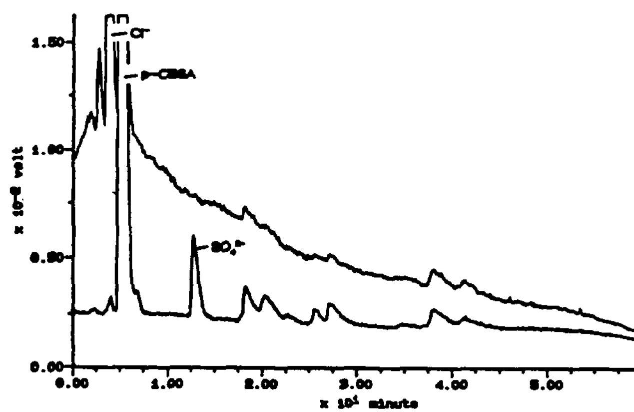


Figure IX. Standard reversed phase column UV chromatogram a of a lyophilized ground water monitor-inn well sample taken from a hazardous waste site at Casmalia, California.

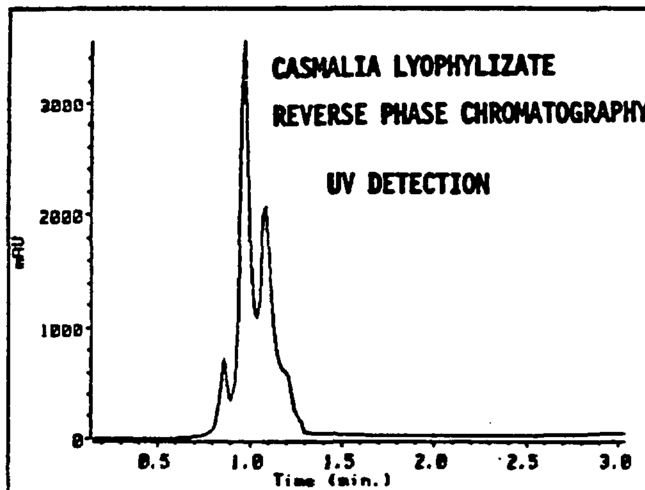


Figure X. Anion exchange column (SAX) UV chromatogram a of a lyophilized ground water monitor-inn well sample taken from a hazardous waste site at Casmalia, California.

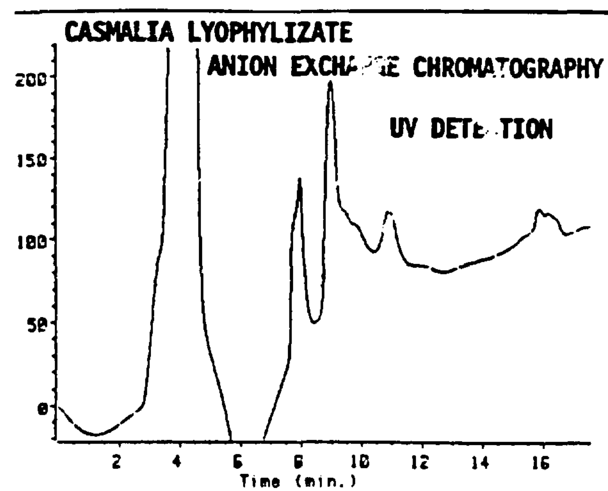


Figure XI. Reversed phase column UV chromatogram a of a lyophilized sample of drinking water from Santa Clara, California.

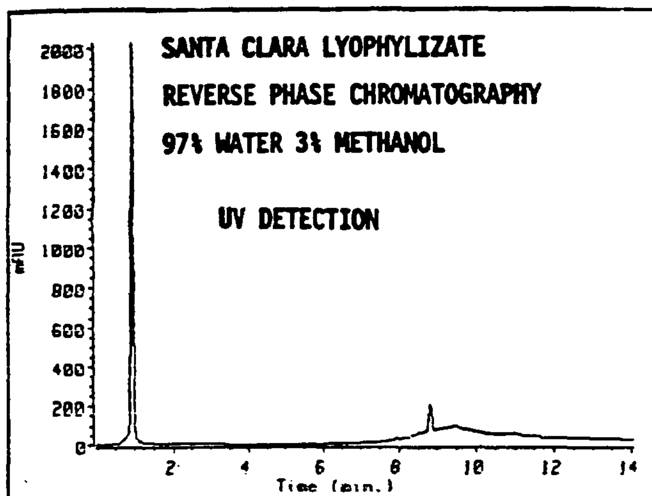


Figure XII. Anion exchange column (SAX) UV chromatogram a of a lyophilized sample of drinking water from Santa Clara, California.

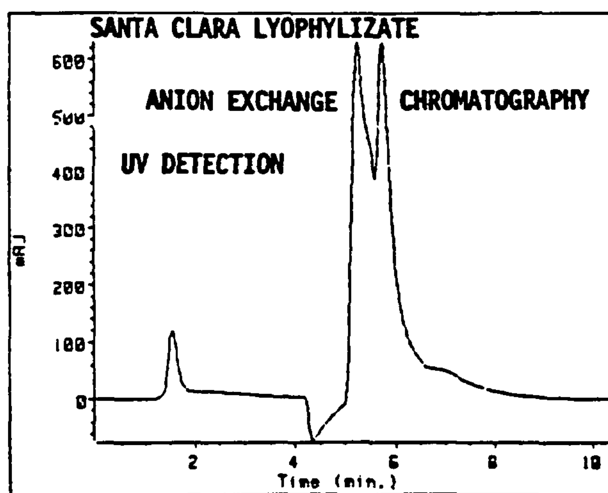


Figure XIII. EI ionization LC/PB/MS reversed phase chromatography of an extract from a leachate sample taken from a waste site located at McColl, California.

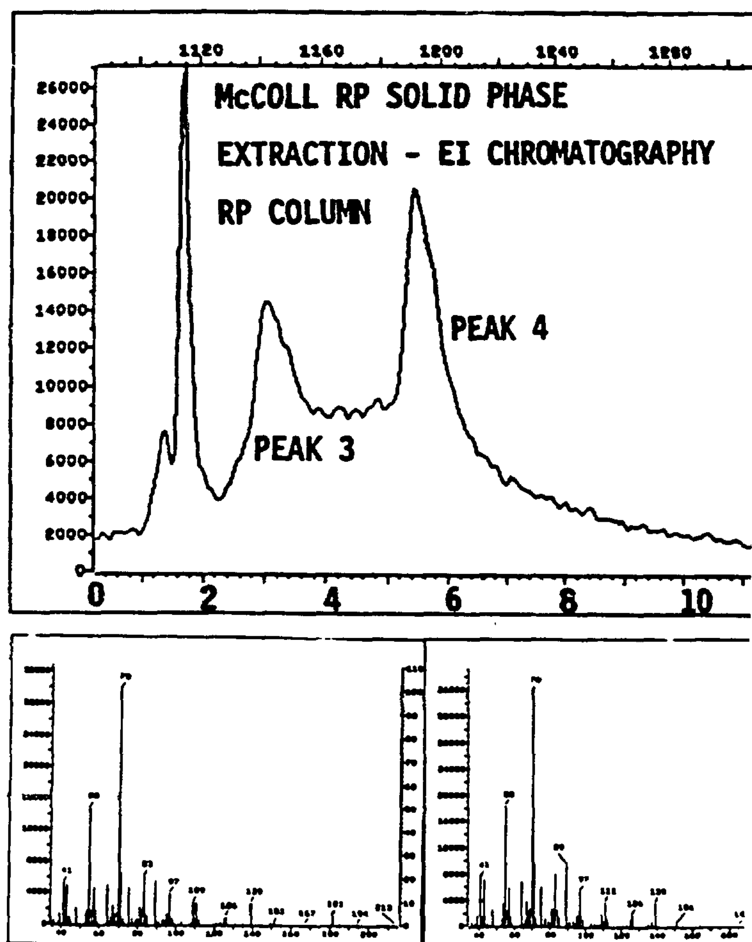


Figure XIV. Positive chemical ionization LC/PB/MS reversed phase chromatography EI ionization of an extract from a leachate sample taken from a waste site located at McColl, California.

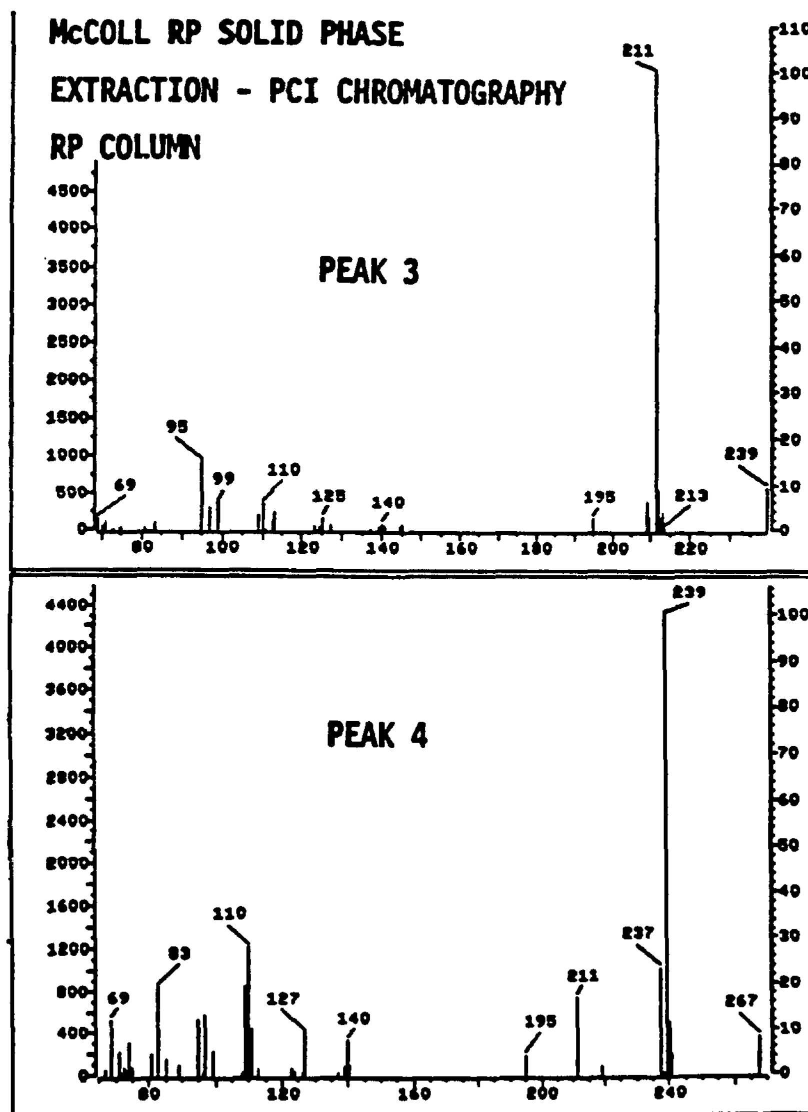


Figure XV. Positive chemical ionization spectrum of the Santa Clara drinking water lyophilizate anion exchange chromatography peak 2 (retention time of approximately 5.2 min.).

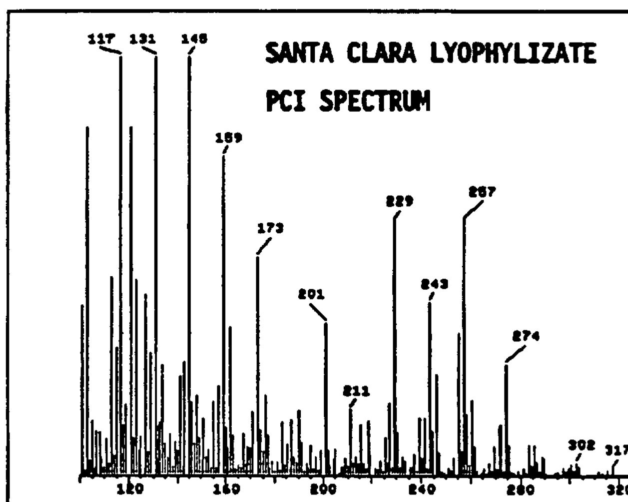
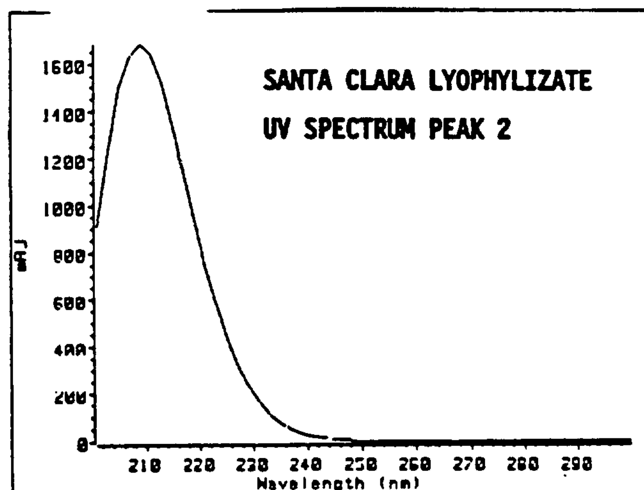


Figure XVI. UV spectrum of the Santa Clara drinking water lyophilizate anion exchange chromatography peak 2 (retention time of approximately 5.2 min.).



PARTICLE BEAM LCMS IN ENVIRONMENTAL ANALYSIS

D.J. Northington, B. Michael Hovanec, and Michael Shelton, West Coast Analytical Service, Inc., 9840 Alburtis Ave., Santa Fe Springs, CA 90670

ABSTRACT

A list of more than 60 compounds was selected as potential target analytes from regulatory lists such as Appendix 8, California Prop. 65, and the Michigan List. The response to particle beam (PB, Extrel Thermabeam) EI-LCMS using flow injection was studied to determine which compounds may be appropriate for further investigation. Of the more than 60 compounds studied, fifty gave adequate response (Response= 1 to .01 relative to caffeine). The applicability of reverse phase liquid chromatography to the LCMS analysis of these compounds was then studied. Of the fifty compounds studied, thirty-eight appear to have adequate reverse phase PB-LCMS behavior. The results of calibration curves, detection limits, sample prepartion, and sample analysis will be reported.

IINTRODUCTION

The advent of particle beam interfaces holes some promise for developing a generalized survey LCMS analysis for non-volatile organic pollutants akin to the GCMS methods 8240 and 8270 used for volatile analytes. The attributes of particle beam interfaces which encouaged further study along these lines are (1) the production of EI mass spectra, (2) the applicability to a wide range of compound types, and (3) the applicability to a variety of LC separations.

RESULTS AND DISCUSSION

Of the more than sixty compounds whose response to PB-LCMS and reverse phase LC was studied, eighteen compounds were chosen for further study which eluted over the reverse phase gradient and gave dependable response during early LCMS experiments. Calibration curves were determined over the range of 25 to 2500 ng injected on column. The chromatogram of a standard is shown in Figure 1 with the LCMS conditions. Table 1 shows the correlation coefficients of linear regression from the calibration curves. The detection limits shown in Table 1 were determined as three times the standard deviation of response from the three replicate 25 ng standard injections. Figures 3 and 4 are examples of the most

linear and least linear calibration curves.

The PB interface parameters of nebulizer gas flow rate, temperature, and LC flow rate and composition were also studied. The applicability of this technique to environmental samples is currently under investigation, and preliminary findings will be reported in this presentation.

Table 1. Detection Limits and Correlation Coefficients.

Compound	Detection Limit (ng)	Correlation Coefficient
Caffeine	30	
Cycloheximide	15	0.997
Cyclophosphamide	64	0.999
Benzidine	11	0.990
4,4'-Diaminodiphenyl ether	13	0.965
Methylene bis(aniline)	12	0.997
Strychnine	26	0.993
3,3'-Dimethoxybenzidene	14	0.989
Thiobis(aniline)	8	0.984
Auroamine O	19	0.953
Warfarin	20	0.9997
3,3'-Dichlorobenzidine	10	0.997
Methylene bis(2-chloro-aniline)	12	0.963
4,4'-Dimerhylamino-benzophenone	4	0.992
Rotenone	14	0.996
Malachite Green	27	0.956
Tetrachlorobisphenol A	118	
Tetrabromobisphenol A	323	

Figure 1.

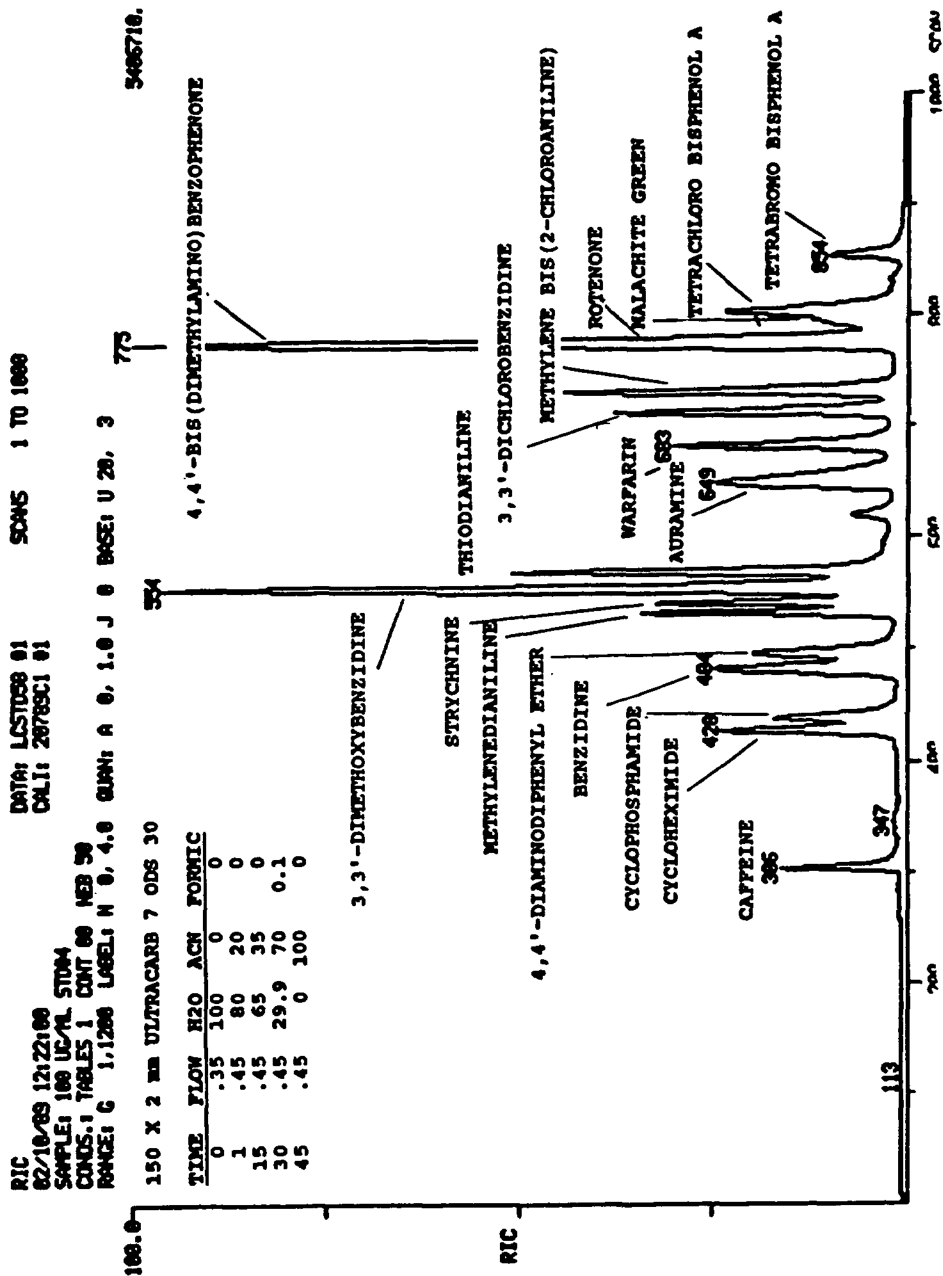


Figure 3.

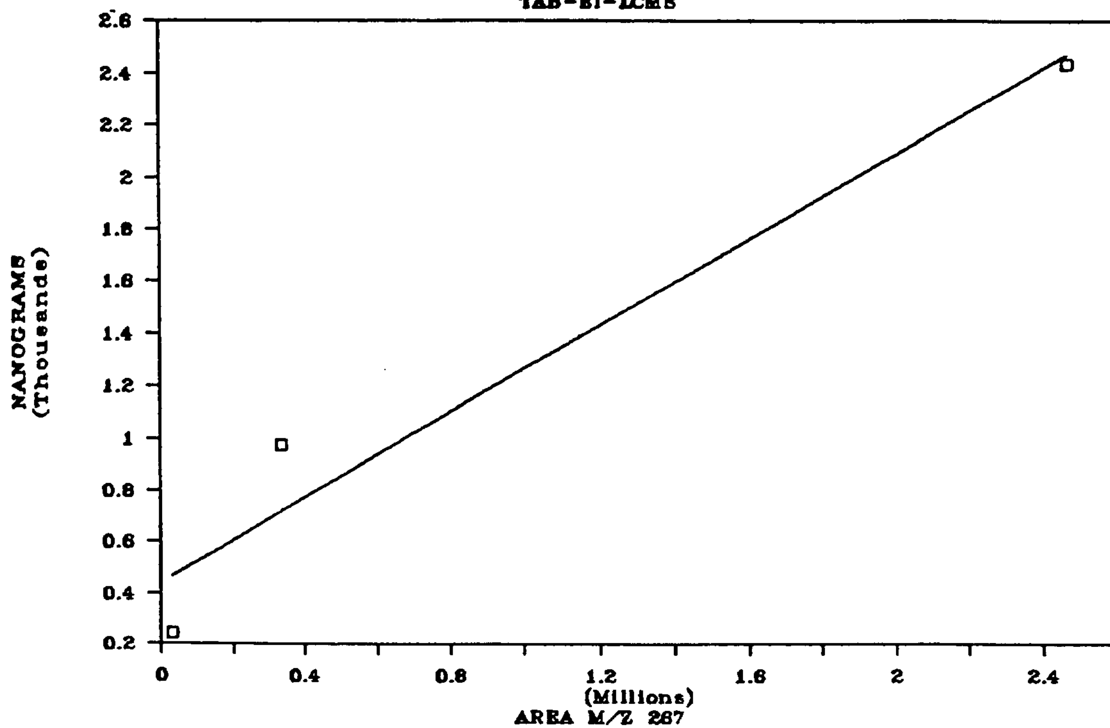
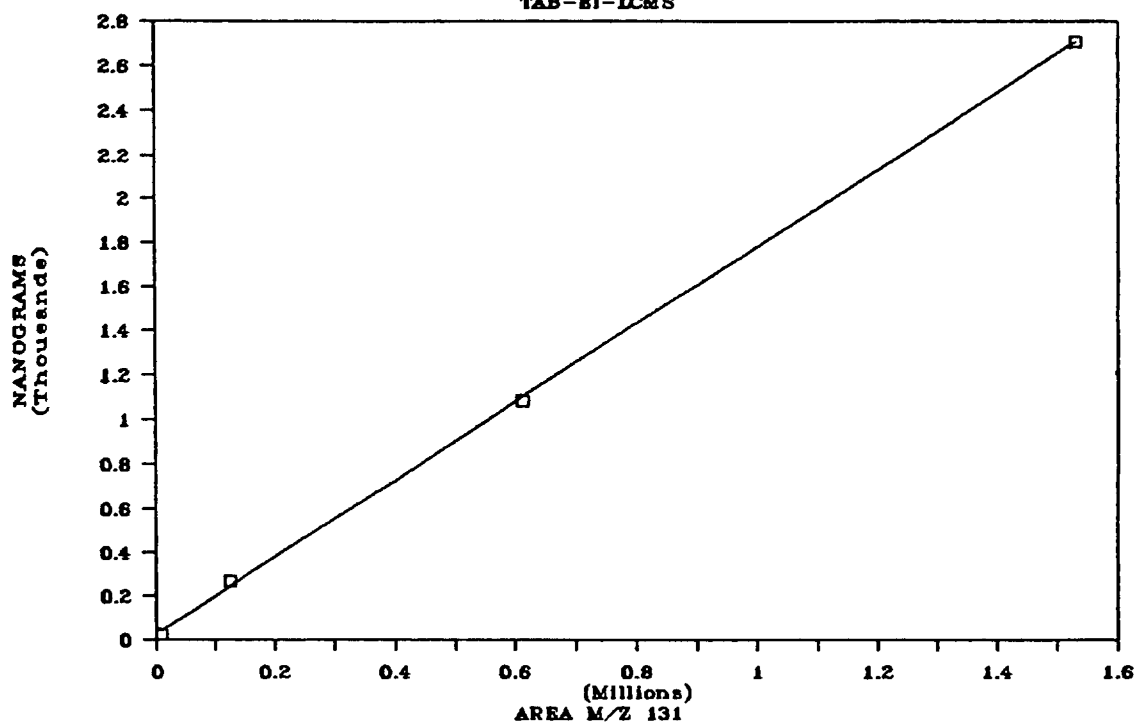


Figure 4.



CARBAMATE AND UREA PESTICIDES BY THERMOSPRAY LC/MS

Bradford A. Anderson, Vice President, Diane W. Anderson, President, Agriculture and Priority Pollutants Laboratories, Inc., 4203 West Swift, Fresno, California 93722

ABSTRACT

A sensitive and specific method for the determination of carbamate and urea pesticides in environmental matrices utilizing thermospray LC/MS is discussed. The method provides a screening procedure for these classes of compounds including but not limited to those listed in EPA methods 531 and 632 with detection limits in the part per billion range. Sample preparation, instrument parameters, analytes, detection levels and recovery information are provided. The positive and negative aspects of thermospray as an analytical tool are reviewed.

INTRODUCTION

Carbamate and urea pesticides have historically been analyzed using liquid chromatography with UV/variable detection and post column derivatization with fluorescence detection. Detection levels in the low nanogram range are achievable using these methods. Thermospray LC/MS can be used to measure carbamate and urea pesticides in the low nanogram range comparable to historic detection levels and simultaneously provide spectral information for confirmation.

Ammonium acetate ionization reagent is used to adjust mobile phase solvents to 0.1M. The thermospray interface introduces the eluent through a capillary tube where it is rapidly heated and vaporized into the source of the mass spectrometer.(Figure 1) The resultant chemical ionization (CI) spectra are reproducible and consists of a quasi-molecular ion and fragmentation ions. The retention times and fragmentation patterns of peaks present in environmental matrices can be compared to those of known standards for both identification and quantitation.

EXPERIMENTAL

Apparatus and Materials

(a) Liquid Chromatograph (Hewlett-Packard 1090L) equipped with a 250 μl injection loop, a 7mm guard column packed with 37-53 230 μm Pellicular ODS Whatman, and a 250 x 4.6 mm Zorbax ODS 10 μ column.

(b) Mass Spectrometer (Hewlett-Packard 5988A) factory equipped for thermospray.

(c) Data system (Hewlett-Packard RTE-A)

(d) Rotary evaporator (Büchi RE111)

(e) Glassware as specified in EPA Methods 632 and 3540.

Reagents

(a) LC solvents: Methylene Chloride, HPLC Grade (Burdick & Jackson); Water, HPLC Grade (Burdick & Jackson); Methanol, HPLC Grade (Burdick & Jackson); Ammonium Acetate, Reagent Grade (Mallincrodt)

(b) High purity Carbaryl, Carbofuran, Methomyl, Oxamyl, Azodrin Aminocarb, Barban, Chloropropham, Diuron, Fenuron, Linuron Fluorometuron, Methiocarb, Monuron, Neburon, Propham, Siduron and Propoxur were obtained from the U.S. EPA Pesticides and Industrial Chemical Repository. Alidicarb, Aldicarb Sulfone, Mexacarbate and Metalaxyl were obtained from Nanogens. Thiobencarb was obtained from IHARA Chemical Company.

Samples

Samples used for recovery data were collected by outside sources and represent true unknown environmental matrices.

HPLC Conditions

The mobile phase, consisting of Methanol and Water containing 0.1 molar Ammonium Acetate, was solvent programmed with linear gradients as follows: initial mixture 5 percent Methanol/ 95 percent Water to 90 percent Methanol/ 10 percent Water with a 10 minute ramp; held for 5 minutes; to 100 percent Methanol/ 0 percent Water with a 1 minute ramp; held for 4 minutes; to a final mixture of 5 percent Methanol/ 95 percent Water with a 5 minute ramp; held for 5 minutes. The flow rate was 1 ml/ minute. The run was isothermal at ambient temperature with a total run time of 30 minutes.

Interface Conditions

The thermospray probe gradient used was survey dependant.

MS Conditions

A 50 ppm solution of polypropylene glycol was used to tune the system. The source temperature was 276°C and the stem temperature was 114°C. The electron energy was 1000 volts. The mass range was 100-1000 amu.

Sample Preparation

Samples were fortified at the levels listed in tables 1 and 2. One liter aliquots of aqueous samples were extracted in accordance with EPA Method 3510 and concentrated to a final volume of 1 ml. Twenty gram aliquots of soil were extracted using methylene chloride for 16 hours and the extracts were taken to dryness. The samples were reconstituted to a final volume of 1 ml. Internal standards were incorporated into the Methanol diluent at a concentration of 1μg/ml. Injection size per sample was 100 μL.

Discussion

A series of controls and variables were used to evaluate the stability and reproducibility of the thermospray method over time. The recovery data was obtained using real world samples over an eight month period of time. The extractions were performed under routine laboratory conditions. The results are are presented in Tables 1 and 2.

A statistical evaluation of area responses was used to monitor the stability of the thermospray mass spectrometer. Internal standards were selected that would encompass the widest range of retention times possible and not interfere with the compounds of interest. The compounds used were Azodrin, Thiobencarb, and Metalaxyl. The results are presented in Tables 5,6 and 7.

The chromatography described does not produce baseline separation of the parameters of interest. Extracted ion profiles were used to qualify and quantify recovery data.

SUMMARY

Thermospray as a routine analytical tool has positive and negative aspects. Instrument maintenance is more involved than GC/MS and as a result is more time consuming. The training necessary to successfully operate a thermospray LC/MS is also more involved. The spectra generated using thermospray is not as defined as electron impact, however, in situations where standards are available the methods works extremely well.

Upon statistical review of the area counts of the internal standards, the system remained stable over a 19 day period under normal operating conditions. The recovery data over a period of time demonstrates the system to be reproducible.

TABLE 1

Compound	Spike Level (µg/L)	Number of Spikes	Average % Recovery	Relative Standard Deviation
Carbaryl	5.0	3	115.0	7.0
Carbofuran	5.0	3	66.1	12.1
Methomyl	5.0	4	92.3	8.8
Oxamyl	5.0	6	86.2	15.8
Diuron	0.3	10	84.8	24.5
Diuron	1.0	10	69.8	17.3
Diuron	2.5	10	88.1	12.6
Diuron	5.0	3	102.0	8.4
Fenuron	0.3	10	88.1	12.6
Fenuron	1.0	10	54.5	16.8
Fenuron	2.5	10	63.6	5.4
Linuron	2.0	10	61.4	13.4
Linuron	5.0	10	95.5	21.0
Methiocarb	5.0	3	99.5	3.4
Monuron	0.9	10	134.3	71.5
Monuron	3.0	10	104.9	45.6
Monuron	7.5	10	84.0	28.8
Neburon	2.5	10	83.1	12.2
Neburon	5.0	3	101.0	6.1
Tebuthiuron	0.15	7	93.3	13.5
Tebuthiuron	0.5	7	141.5	35.9
Tebuthiuron	1.25	10	80.5	24.5
Fluormeturon	0.3	10	116.6	53.9
Fluormeturon	1.0	10	139.9	46.6
Fluormeturon	2.5	10	85.3	24.0
Siduron	0.3	10	79.3	21.7
Siduron	1.0	10	76.1	29.7
Siduron	2.5	10	77.7	10.1
Chloroxuron	9.0	10	76.8	13.9
Chloroxuron	30.0	10	75.2	18.2
Norea	0.3	10	66.9	20.2
Norea	1.0	10	61.8	12.2
Norea	2.5	10	76.7	20.0

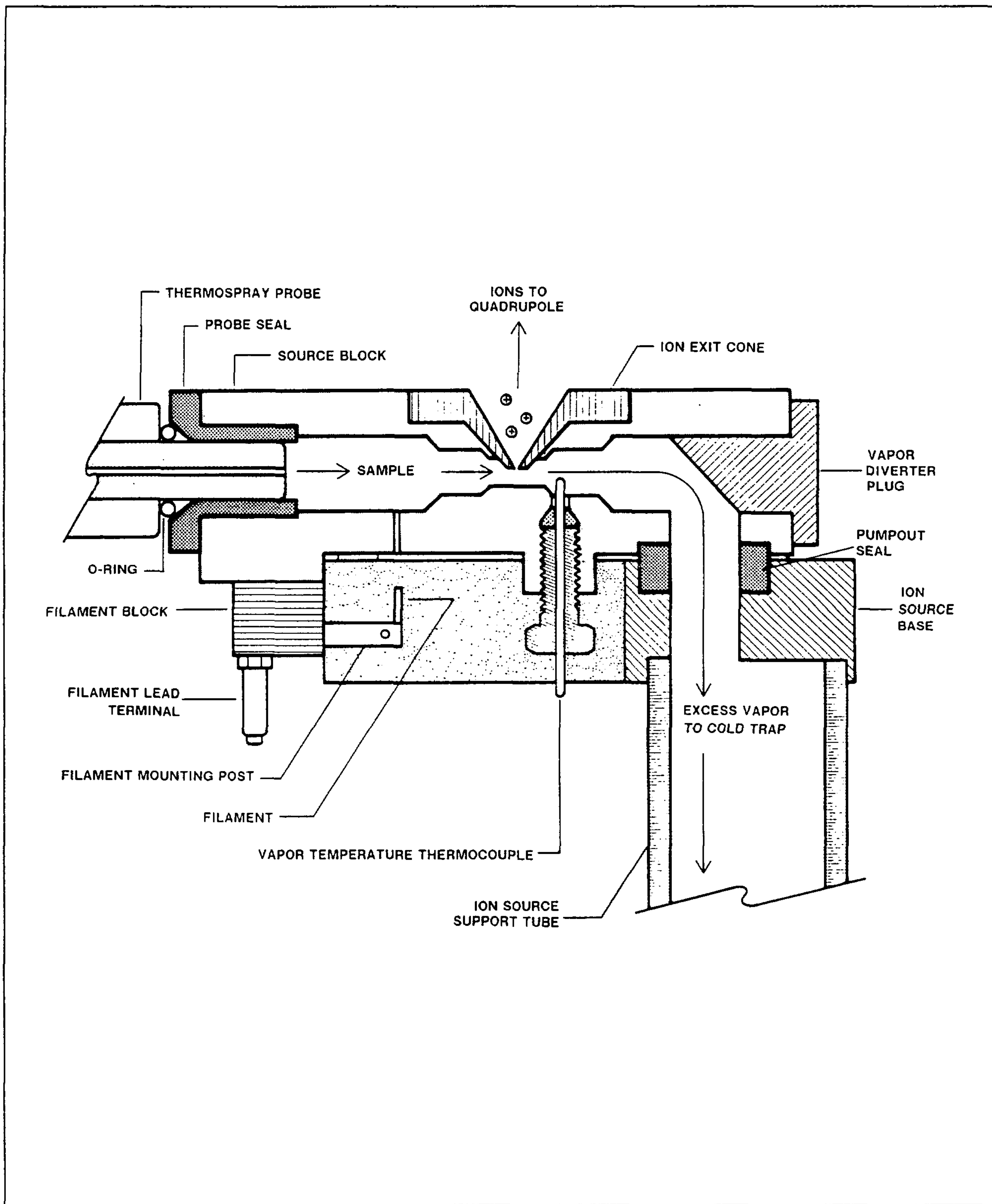
Table 2

Compound	Spike Level (µg/g)	Number of Spikes	Average % Recovery	Relative Standard Deviation
Carbaryl	0.25	6	100.2	15.1
Carbofuran	0.125	12	85.6	16.6
Methomyl	0.125	15	80.6	15.2
Oxamyl	0.25	4	87.5	18.9
Chloropropham	0.25	11	83.9	19.2
Diuron	0.125	10	74.9	18.1
Fenuron	0.125	15	77.9	14.8
Linuron	0.25	11	72.3	18.6
Methiocarb	0.125	9	84.3	10.2
Monuron	0.25	10	94.9	13.2
Neburon	0.125	10	82.7	14.6
Propham	0.25	7	100.0	17.3

Table 3

Compound	Detection Limit µg/L
Aldicarb	0.5
Aldicarb sulfone	1.0
Aldicarb sulfoxide	5.0
Carbaryl	0.5
Carbofuran	0.5
Methomyl	0.5
Oxamyl	0.7
Aminocarb	5.0
Barban	5.0
Chloropropham	5.0
Diuron	0.1
Fenuron	0.1
Linuron	0.2
Methiocarb	0.5
Mexacarbate	5.0
Monuron	0.3
Neburon	0.1
Propham	1.0
Propoxur	1.0
Siduron	0.1
Tebuthiuron	0.05
Fluormeturon	0.1
Siduron	0.1
Chloroxuron	3.0
Norea	0.1

FIGURE 1



Ion Source Sample Path

Table 4

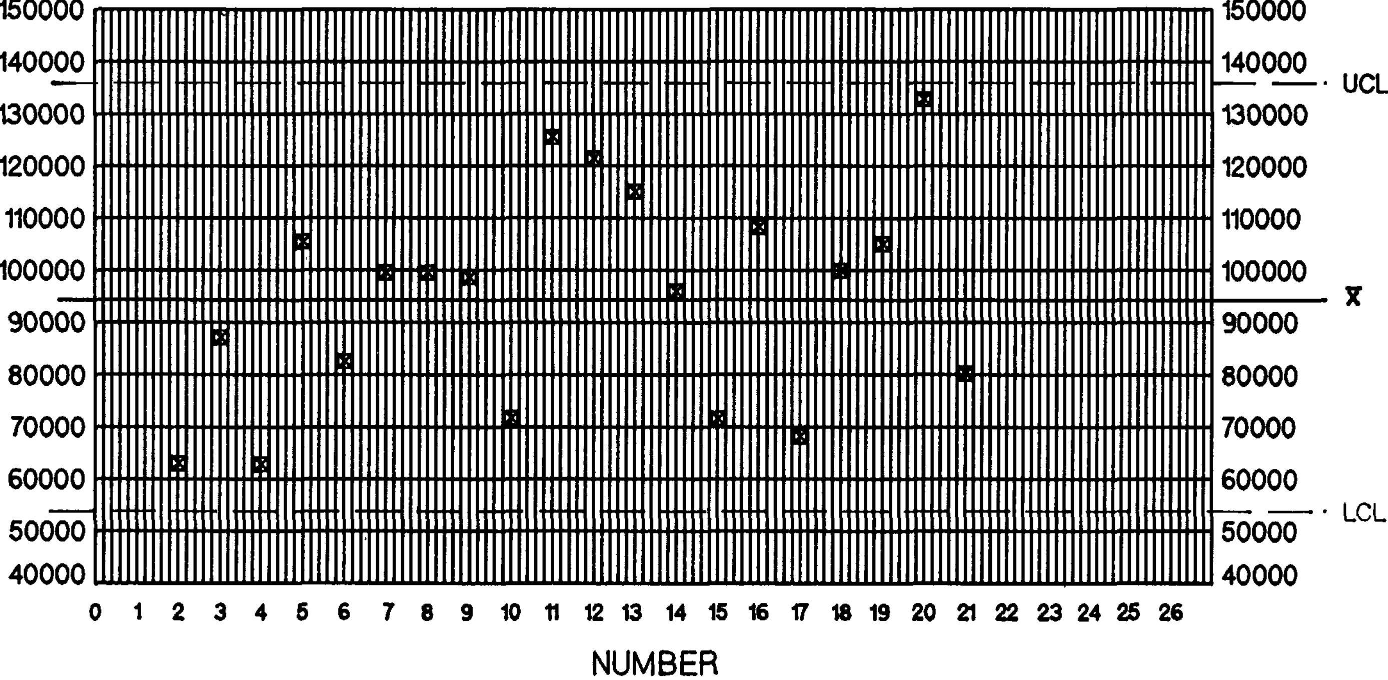
INTERNAL STANDARD

QUALITY CONTROL CHART

METALAXYL

Chemist: Brad Anderson Level: 1.0 ppm Period Covered: 1-8-89 --> 1-27-89

	n	$\bar{X}$	s	CL	UCL	LCL	%R.S.D.
Current	20	94,762	20,753	41,506	136,268	53,256	21.90%



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3	87150	1-8
4	62837	1-8
5	105452	1-8
6	82522	1-11
7	99505	1-13
8	99480	1-13
9	98616	1-15
10	72712	1-15
11	125560	1-15
12	121380	1-15
13	115007	1-15
14	95970	1-20
15	71590	1-20
16	108274	1-20
17	68192	1-20
18	99914	1-20
19	105055	1-20
20	132822	1-27
21	80219	1-27
22		
23		
24		
25		

Table 5

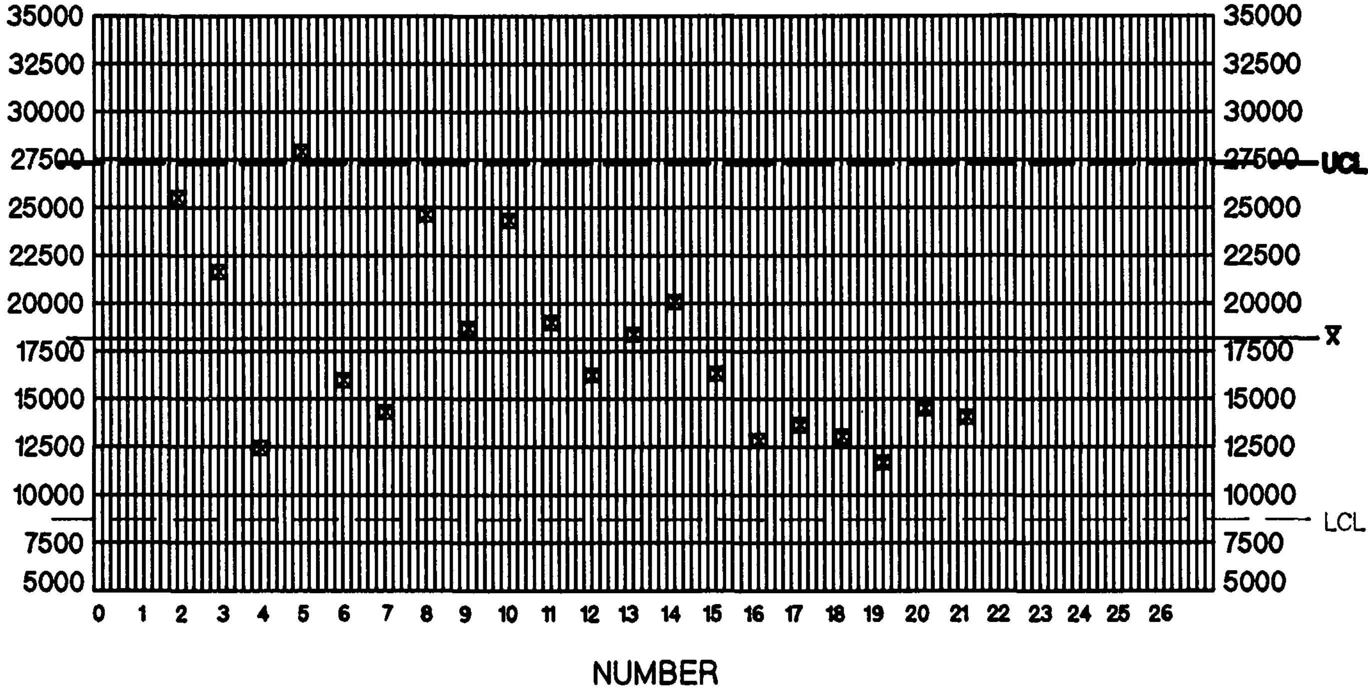
INTERNAL STANDARD

QUALITY CONTROL CHART

THIOBENCARB

Chemist: Brad Anderson Level: 1.0 ppm Period Covered: 1-8-89 --> 1-27-89

	n	x	s	CL	UCL	LCL	%R.S.D.
Current	20	17,733	4,860	9,720	27,453	8,013	27.40%



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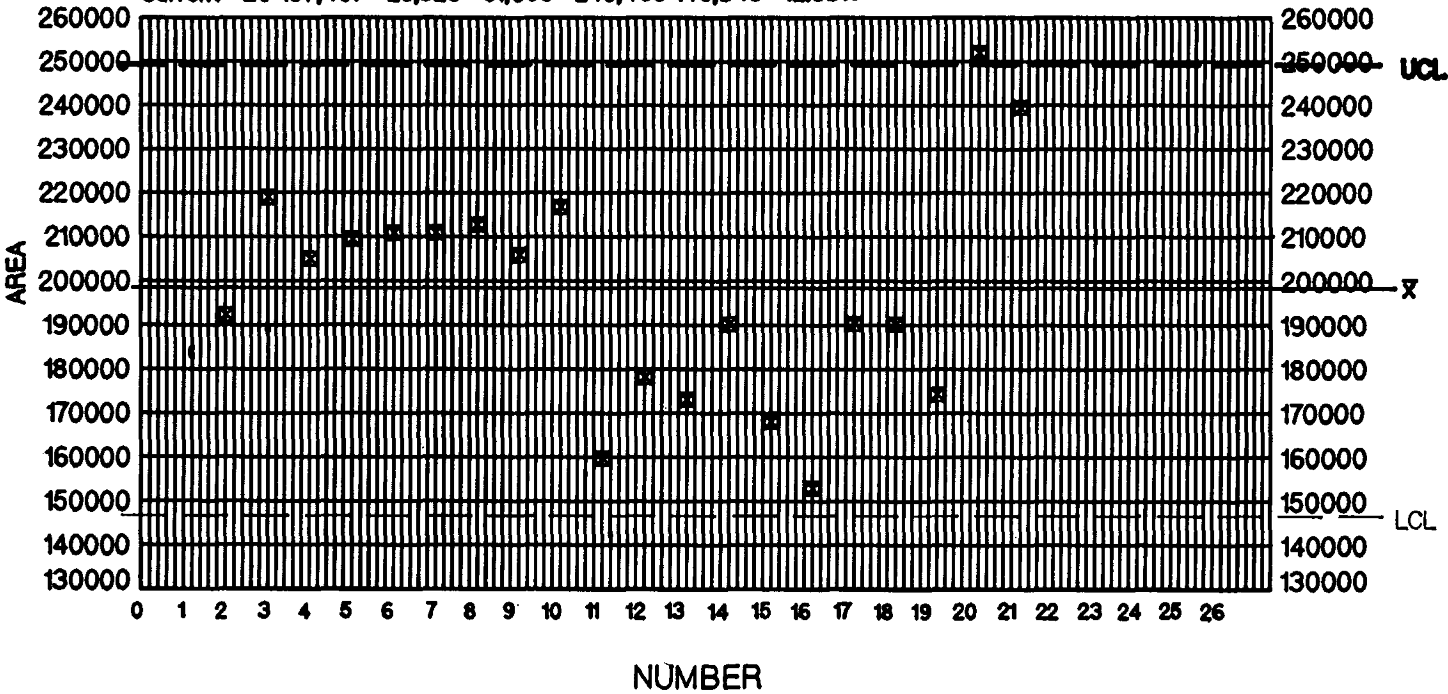
4	12405	1-13
5	27871	1-13
6	15956	1-13
7	14294	1-13
8	24597	1-15
9	18666	1-15
10	24303	1-15
11	18974	1-15
12	16217	1-15
13	18350	1-20
14	20060	1-20
15	16298	1-20
16	12786	1-20
17	13616	1-20
18	13022	1-20
19	11659	1-27
20	14482	1-27
21	14026	1-27
22		
23		
24		
25		

Table 6



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5	209290	1-8
6	210730	1-11
7	210763	1-13
8	212587	1-13
9	205729	1-13
10	216620	1-15
11	159559	1-15
12	178024	1-15
13	172969	1-15
14	190022	1-20
15	167897	1-20
16	152800	1-20
17	190187	1-20
18	190002	1-20
19	174122	1-20
20	251707	1-27
21	239320	1-27
22		
23		
24		
25		

DEVELOPMENT OF SOLID SORBENT COLLECTION TECHNIQUES IN EXPLOSIVES ANALYSES

LANG, KENNETH T. AND RYAN, MARY ANN E., U. S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY, ABERDEEN PROVING GROUND, MARYLAND 21010-5401; BICKING, M.K.L. AND SUMMER S.J., BATTELLE, COLUMBUS DIVISION, 505 KING AVENUE, COLUMBUS, OHIO 43201-2693

ABSTRACT. An analytical method was developed for the determination of eight explosives in ground water. The method employed a Porapak R solid sorbent extraction technique as the sampling method. A reverse phase liquid chromatographic method was developed to provide baseline resolution of all eight explosives in a single injection. Quantification was achieved using a dual detector system consisting of an absorbance detector set at 254nm in series with a photoconductivity detector using a zinc photoionization source. Six of the explosives were quantified using the absorbance detector: HMX, RDX, Tetryl, TNT, 2,6-DNT, and 2,4-DNT. Nitroglycerine and PETN were quantified with the photoconductivity detector. Method detection limits range from 0.50 to 10 ug/L.

ANALYSIS FOR N-METHYLCARBAMATE PESTICIDES BY HPLC IN ENVIRONMENTAL SAMPLES

Howard S. Okamoto, Donald Wijekoon Ph.D., Crisenciana Esperanza, James Cheng, Shinae Park, Jarnail Garcha, Sardara Gill and Kusum Perera Ph.D., Hazardous Materials Laboratory, California Department of Health Services, 2151 Berkeley Way, Berkeley, California 94704

ABSTRACT

This method was developed for the routine analysis of ten N-methylcarbamate pesticides in environmental aqueous and soil samples. Aqueous samples are extracted with dichloromethane, while soils are extracted with acetonitrile. The extracts are solvent exchanged to methanol prior to analysis. Analysis entails an HPLC separation on a C18 reverse phase column, post column derivatization and monitoring the resulting fluorophore by fluorescence detection. The standard derivatization procedure is based on alkaline hydrolysis of the N-methylcarbamate to yield methylamine, which in turn is reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol to form 1-(2-hydroxyethylthio)-2-N-methylisoindole. For routine quantitation the product is excited at 340 nm and the fluorescence emission detected through a 418 nm cut-off filter. Initial laboratory data indicate that method detection limits, precision and accuracy should be reasonable for routine environmental samples. The detection limits for clean water samples are estimated to be in the 1 to 10 ug/L range, while soil samples are estimated to be in the 10 to 50 ug/Kg range.

INTRODUCTION

The use of N-methylcarbamates as effective pesticides by the agricultural community has been increasing mainly due to their lower mammalian toxicity (aldicarb is a notable exception) when compared to organophosphorus pesticides. It is known that this class of compounds, in addition to having a broad spectrum of insecticidal activity, also undergoes fairly rapid biodegradation. The wide use of this class of pesticides has caused concern in the environmental community because of subsequent contamination of soils, surface waters and ground waters.

Several methods have been reported for the analysis of N-methylcarbamate pesticide residues in fruit and vegetable crops. In spite of the thermal lability of these compounds, gas chromatographic analysis has been attempted [1,2,3]. In some cases the gas chromatographic analysis has been carried out following derivatization [4]. Another less sensitive method is hydrolysis of the parent carbamate followed by derivatization and detection by colorimetry [5,6].

However, the most feasible and widely used methods for the separation and detection of these pesticides involve the use of reverse phase high performance liquid chromatography employing suitable detection techniques. UV detection has resulted in the successful monitoring of N-methylcarbamates with detector sensitivities in the low mg/L range [7]

and with wastewater sample detection limits in the ng/L range, after solvent extraction and concentration of the extract prior to analysis [8]. A technique used for the trace level detection of methomyl, (S-methyl-N-[(methylcarbamoyl)oxy]-thioacetimidate), one of the most widely used N-methylcarbamates, and its hydrolytic product, methomyl-oxime, in water is the use of a UV detector in series with an electrochemical detector [9]. An important limitation of UV detection is its non-specificity. Most environmental samples contain significant quantities of UV absorbing components. Even carefully planned sample cleanup procedures sometime do not exclude interferences arising from non-carbamate pesticide residues.

A detection method specific for N-methylcarbamate is the post-column fluorometric labelling technique [10, 11, 12]. In this technique, the resolved individual N-methylcarbamate is passed through a heated base hydrolysis zone (allowing it react with aq. NaOH at an elevated tempeture) to yield methylamine, which in turn is allowed to react with a mixture of o-phthalaldehyde and 2-mercaptoethanol to form 1-(2-hydroxyethylthio)-2-N-methylisoindole (Figure 1).

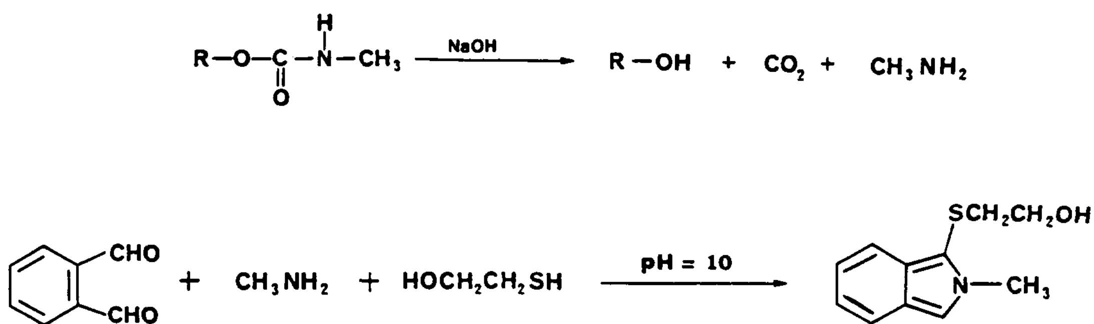


Figure 1

Because of the fluorescent nature of this chromophore, it is easily detected at trace levels. This fluorometric procedure is currently employed in the USEPA Method 531 [13] for measuring carbamates at the low ug/L range in drinking water. In an attempt to reduce band broadening effects, a novel approach was developed, whereby the resolved components were hydrolysed as they passed through a post-column reactor packed with a tetraalkylammonium anion exchanger (Aminex A-28), thus avoiding the need to introduce aq. NaOH solution into the post-column effluent stream before derivatization with OPA [14].

A selective method recently developed involves a coulometric procedure for detection of some N-methylcarbamates which produce phenolic moeties on hydrolysis [15]. Finally, a method applied to the analysis of 19 different carbamates involves HPLC/MS [16]. This method could be valuable (but expensive) in resolving ambiguities arising from coelution of mixtures, and in confirming suspected N-methylcarbamates.

The purpose of this current work was to develop sample extraction and preparation procedures for N-methylcarbamate pesticides in environmental aqueous and soil samples and to utilize HPLC post-column fluorometric detection for the analysis of the prepared extracts. We needed a routine method that would provide high sensitivity and perform with acceptable accuracy and precision. In this study, ten N-methylcarbamate pesticides were spiked into both deionized water and soil samples (field soil samples previously analyzed to be free of N-methylcarbamates) at low levels to determine the method detection limits and at medium levels to determine the accuracy and precision of analyses. The applicable compounds and their structures are illustrated in Figure 2.

MATERIALS and METHODS

Chemicals and Reagents

a) Water, deionized, obtained from a Barnstead Nanopure II Cartridge Water Purification System consisting of prefilter, ion exchange and organic removal cartridges followed by an in-line 0.2 um membrane filter, Barnstead, Newton, MA

b) Dichloromethane, OmniSolv^{R}, EM Science, Cherry Hill, NJ.

c) Methanol, OmniSolv^{R}, EM Science.

d) Acetonitrile, OmniSolv^{R}, UV grade, EM Science.

e) Ethylene glycol, reagent grade, EM Science.

f) o-Phthalaldehyde, reagent grade, Fisher Scientific, Fairlawn, NJ.

g) 2-Mercaptoethanol, reagent grade, Fisher Scientific.

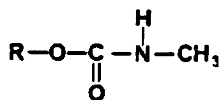
h) pH 10 borate buffer solution, J.T. Baker, Phillipsburg, NJ.

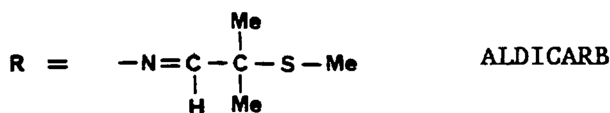
i) Phosphoric acid, reagent grade.

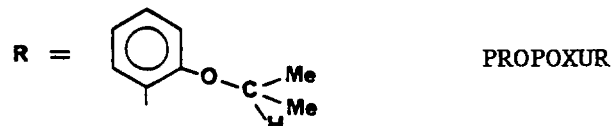
j) NaOH, reagent grade, prepare to yield an aq. 0.05N solution.

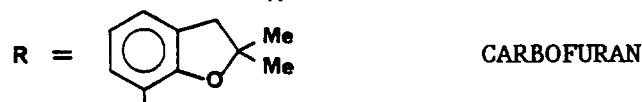
k) Aldicarb, aldicarb sulfone, carbaryl, carbofuran, dioxacarb, 3-hydroxycarbofuran, methiocarb, methomyl, promecarb and propoxur were obtained as reference standards from the U.S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository, Research Triangle Park , NC. The purities were at least 99%, or better.

Individual carbamate stock solutions were prepared in methanol at concentrations of 1000 ug/mL. These stock solutions were further diluted to the mixed working standard concentrations of 0.100, 0.200, 0.500, 1.00, 2.00, 3.00 and 5.00 ug/mL each.









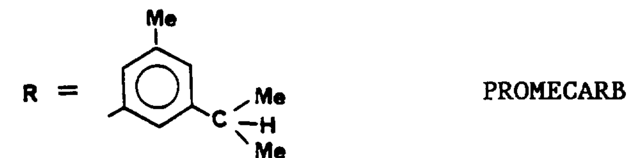


FIGURE 2. CHEMICAL STRUCTURES

The OPA reagent was prepared as follows. O-phthalaldehyde (500 mg) was dissolved in methanol (10 mL) in a 1000 mL volumetric flask. To this solution was added deionized water (900 mL), a borate buffer solution (pH 10, 50 mL), followed by 2-mercaptoethanol (2 mL). After thorough mixing, the solution was made up to 1 liter with deionized water. OPA solutions were prepared fresh on a weekly basis and stored at 4°C when not in use.

Chromatographic System

A pair of Beckman 112 high-pressure pumps provided solvent delivery for the mobile phase while a Beckman 421 Controller module controlled the flow rate and gradient. Sample injection was performed by a Spectraphysics SP8780 autosampler. Chromatographic separation was achieved through a Beckman 4.6 mm I.D. x 25 cm ODS Ultrasphere[R] reverse phase column. The post column system consisted of a pair of ABI Analytical Spectroflow[R] 400 pumps delivering the hydrolysis and OPA reagents, respectively, and an ABI Analytical PCRS 520 temperature controlled post column reaction system consisting of the independently heated hydrolysis and reaction coils (0.5 mm I.D. x 4.9 m, 1 mL vol. each). An ABI Analytical Spectroflow[R] 980 fluorescence detector (Schoeffel design) was used to monitor the resulting fluorophore. Table I provides a summary of the chromatographic system parameters used in this study. Figure 3 illustrates the chromatographic system.

Data System

Fluorometric detector signals were collected through a Perkin-Elmer DCI 2000 A/D converter and processed by a Perkin-Elmer 3210 computer using the 1.7.1 version of LIMS/CLAS software.

Sample Preparation and Extraction

Aqueous samples: A 100 mL aliquot of deionized water in a 250 mL separatory funnel was spiked with the appropriate amounts of carbamate pesticides and extracted three times (2 min each) with 30 mL portions of dichloromethane. The extracts were combined in a 100 mL volumetric flask and made up to volume with dichloromethane. A 10.0 mL portion of the dichloromethane extract was then pipetted into a 10 mL graduated glass vial containing 100 uL of ethylene glycol. The extract was gently evaporated under a stream of dry nitrogen until only the ethylene glycol keeper remained. Methanol was added to the ethylene glycol residue until the total volume was 1.0 mL. After filtering through a disposable 0.45 um filter, the extract was transferred into an autosampler vial in preparation for analysis.

Soil samples: A 20 g portion of soil was weighed into a 250 mL teflon-lined screw-cap Erlenmeyer flask, 50 mL of acetonitrile was added, the flask capped and the sample shaken on a platform shaker for 2 hrs. After allowing the mixture to settle, the extract was decanted into a 250 mL centrifuge tube. The soil residue was extracted two more times with 20 mL aliquots of acetonitrile for 1 hr each on the platform shaker. The

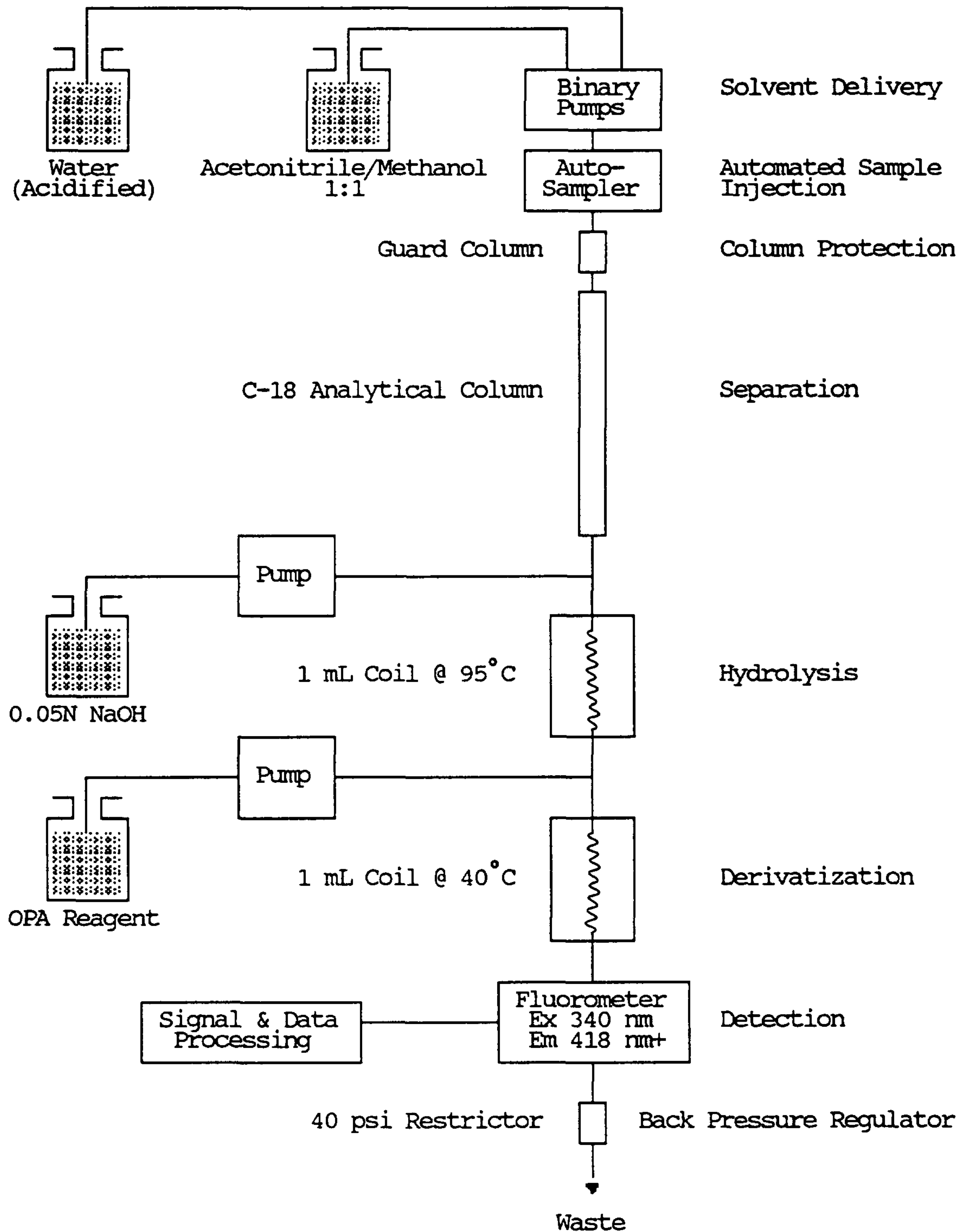


FIGURE 3. HPLC SYSTEM

extracts were decanted as before and combined with the first extract in the centrifuge tube. Clarification of the extract was achieved by centrifuging at 200 rpm for 10 minutes. The supernatant was carefully decanted into a 100 mL volumetric flask and made up to volume with acetonitrile. Approximately 15 mL of this extract was passed through a C18 Sep-Pak^{R} for cleanup. A 10.0 mL aliquot of this extract was then pipetted into a 10 mL graduated glass vial containing 100 uL of ethylene glycol. The extract was gently evaporated under a stream of dry nitrogen until only the ethylene glycol keeper remained. Methanol was added to the ethylene glycol residue until the total volume was 1.0 mL. After filtering through a disposable 0.45 um filter, the extract was transferred into an autosampler vial in preparation for analysis.

RESULTS AND DISCUSSION

Sample Extraction

Aqueous samples: Early trials of direct injection of aqueous waste samples resulted in numerous episodes of blockages in the detector flow cell, which resulted in lengthy down times. Precipitation of dissolved solids from the sample was suspected to be the cause of the blockages. We had also attempted solid phase extraction using disposable C18 reverse phase cartridges, but found poor or no retention of aldicarb sulfone, methomyl, 3-hydroxycarbofuran and dioxacarb on this substrate. In order to circumvent these problems, liquid/liquid extraction was selected. Dichloromethane was chosen as the extraction solvent of choice because N-methylcarbamates are highly soluble in this solvent, its low boiling point makes solvent exchange rapid at ambient temperature and it allows for lower sample detection limits through volume reduction of the extract.

Soils: Acetonitrile was chosen as the solvent of choice for soil extraction due to the high solubility of carbamates in this solvent while maintaining low solubility of potentially interfering nonpolar organic constituents. The acetonitrile extract had to be solvent exchanged to methanol prior to analysis because we found it to be too strong a solvent for the initial mobile phase composition used in the HPLC analysis. Injection of acetonitrile extracts caused peak splitting with aldicarb sulfone, methomyl, 3-hydroxycarbofuran and dioxacarb. The splitting phenomenon disappeared when methanol was used.

Chromatography

Figure 4 illustrates the excellent chromatographic separation obtained using the parameters described in Table I. Retention time and detector response repeatabilities of 0.2% (Table II) and 5% (Table III), respectively, were routinely achievable during continuous automated analysis of the 1.00 ug/mL mixed standard. The linear calibration range extended from 0.100 ug/mL to 5.00 ug/mL for each compound and demonstrated excellent response correlation (Table IV). Relative standard deviations of less than 10% for these average response factors were routinely achieved. Linearity beyond the upper and lower

concentration limits described were not investigated in this study. However, our past experience has shown that by increasing the PMT gain, the Spectroflow^{R} 980 detector is capable of operating within a linear range of 10 ng/mL to 500 ng/mL.

Method Detection Limits

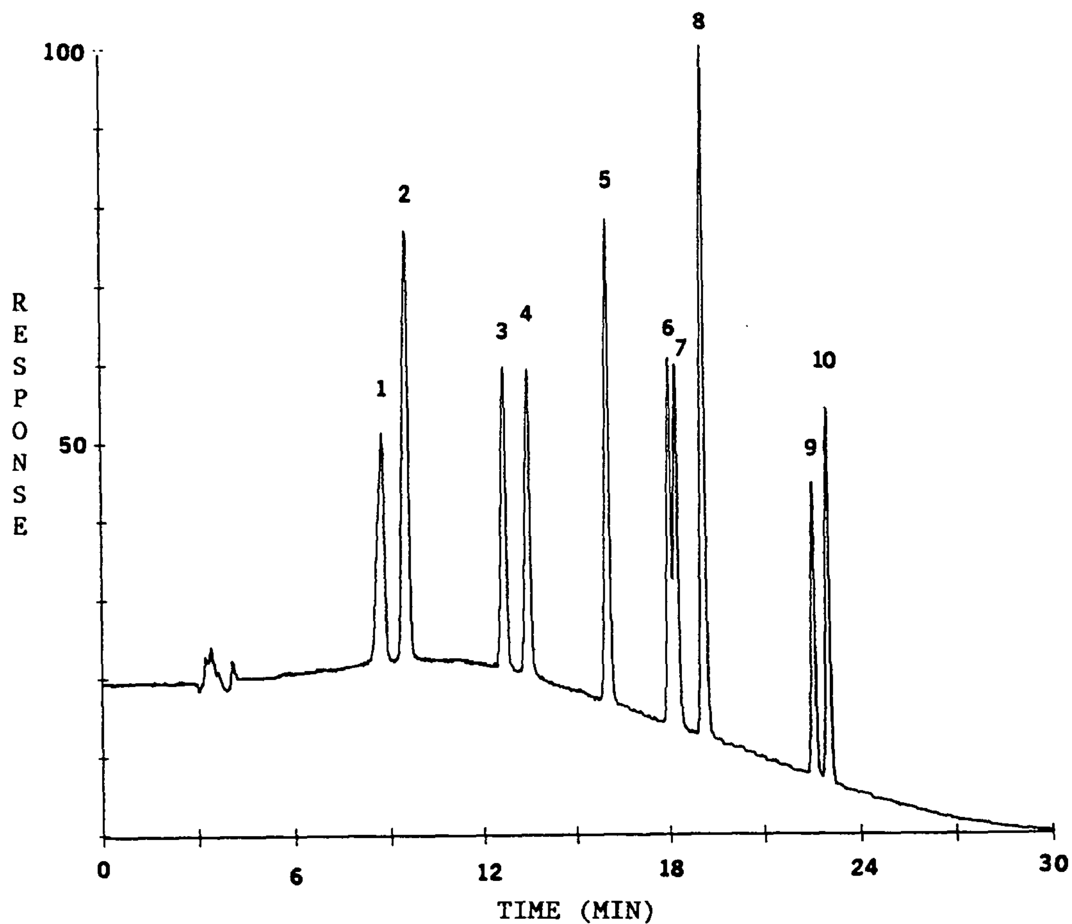
Method detection limits of N-methylcarbamates were determined by low level spikes (10 ug/L aldicarb sulfone, methomyl, 3-hydroxycarbofuran, dioxacarb, propoxur, carbofuran, carbaryl, methiocarb and promecarb and 20 ug/L aldicarb) into deionized water and (50 ug/kg aldicarb sulfone, methomyl, 3-hydroxycarbofuran, propoxur, carbofuran, carbaryl, methiocarb and promecarb and 100 ug/kg aldicarb) into soils. In general, 7 to 10 replicate spike analyses were performed for the two matrices of concern. The recoveries were averaged and the method detection limits were calculated from the respective standard deviations using the student t-test at the 99% confidence level that the analyte concentrations in question are greater than zero [17]. The detection limits for water ranged between 1 to 10 ug/L and 10 to 44 ug/kg for soils (Table V). However, dioxacarb in soil presented a dilemma in that spike levels at 50 ug/kg (n=3) resulted in no recovery, whereas, spike levels at 500 ug/kg (n=7) suggested a contradictory method detection limit of 20 ug/kg. At the present time we feel that the MDL for dioxacarb probably lies between 50 and 100 ug/kg.

Recoveries

Recovery studies of the N-methylcarbamate pesticides were performed by spiking into deionized water and soils at levels approximately 100 times higher than the respective method detection limits determined for each of the two matrices. Recoveries for the ten carbamates ranged from 70 to 81% in water and 64 to 80% in soils (Table VII) with associated precision of analyses ranging from 3 to 6% and 4 to 11%, respectively. The generally lower recoveries and precisions obtained from the soil samples probably reflect the increased matrix effects attributable to the soils such as adsorption, in situ hydrolysis or degradation of the analytes of interest.

CONCLUSION

The analytical performances achieved on spiked deionized water and soils for the ten N-methylcarbamate pesticides in our study indicate that the extraction, sample preparation and chromatography procedures employed should adequately apply to the analysis of routine environmental samples. Analytical performance achieved in other matrix types, such as sludges, will certainly be influenced by sample composition and the performance may deteriorate as the matrix becomes more complex. In waste analysis the potential for matrix interference is especially high. Samples having a content of extractable organics will certainly require some type of cleanup procedure to remove these potential interferences. Work is in progress in our laboratory on examining cleanup procedures utilizing



1.00 ug/mL EACH OF:

1. ALDICARB SULFONE
2. METHOMYL
3. 3-HYDROXYCARBOFURAN
4. DIOXACARB
5. ALDICARB
6. PROPOXUR
7. CARBOFURAN
8. CARBARYL
9. METHIOCARB
10. PROMECARB

FIGURE 4. CHROMATOGRAM

solid phase disposable cartridge technology and polar/nonpolar solvent partitioning effects.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Jerry Muth (USEPA, Region X, Seattle, WA) for the work he performed on carbamate analysis in this laboratory through an inter-agency personnel agreement with the USEPA.

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Table I. Summary of Selected HPLC-Post Column-Fluorometric Parameters

HPLC parameters:

Column	C18 Ultrasphere[R]
Solvent A	water acidified with 0.4 mL H_3PO_4/L water
Solvent B	1:1 (v/v) acetonitrile/methanol
Flow rate	1.0 mL/min
Injection vol	20 uL

Gradient:

Time(min)	%B
0.00	10
20.00	80
25.00	100
30.00	100
33.00	10
40.00	10

Post column reaction parameters:

Hydrolysis:

Solution	0.05N NaOH
Flow rate	0.7 mL/min
Temperature	95°C
Residence time	35 sec (1 mL coil)

Derivatization:

Solution	Buffered OPA/2-mercaptoethanol
Flow rate	0.7 mL/min
Temperature	40°C
Residence time	25 sec (1 mL coil)

Fluorometer parameters:

Cell	10 uL
Excitation wavelength	340 nm
Emission wavelength	418 nm cutoff filter
Sensitivity range	0.05 uA
PMT Voltage	-800 V
Time constant	2 sec

Table II. Typical Retention Time Repeatability (n = 5) for a 1.00 ug/mL (Each Component) Mixed Standard

Compound	Average[a] RT (min)	SD	%RSD
Aldicarb Sulfone	8.83	0.019	0.22
Methomyl	9.59	0.012	0.12
3-Hydroxycarbofuran	12.70	0.022	0.17
Dioxacarb	13.50	0.021	0.16
Aldicarb	16.05	0.017	0.11
Propoxur	18.06	0.032	0.18
Carbofuran	18.28	0.032	0.18
Carbaryl	19.13	0.031	0.16
Methiocarb	22.56	0.036	0.16
Promecarb	23.02	0.039	0.17

[a]Data was taken from a 30 hr analytical run of 44 samples. The 1.00 ug/mL mixed standard was analyzed approximately once every 6 hr for a total of five analyses.

Table III. Typical Detector Response Repeatability (n = 5) for a 1.00 ug/mL (Each Component) Mixed Standard

Compound	Average[a] Area Response	SD	%RSD
Aldicarb Sulfone	113572	5612	4.94
Methomyl	189660	8073	4.26
3-Hydoxycarbofuran	110335	6010	5.45
Dioxacarb	110955	7389	6.66
Aldicarb	153700	6389	4.16
Propoxur	108072	4504	4.17
Carbofuran	106741	4350	4.08
Carbaryl	198472	8983	4.52
Methiocarb	80682	4597	5.70
Promecarb	101715	5566	5.47

[a]Data was taken from the same analytical run as in Table II.

Table IV. Typical Calibration Response Factors

Compound	Ave. RF[a,b]	SD	%RSD
Aldicarb Sulfone	8.38×10^{-6}	0.59×10^{-6}	7.04
Methomyl	5.14×10^{-6}	0.26×10^{-6}	5.06
3-Hydroxycarbofuran	8.80×10^{-6}	0.53×10^{-6}	6.02
Dioxacarb	8.60×10^{-6}	0.72×10^{-6}	8.37
Aldicarb	6.24×10^{-6}	0.42×10^{-6}	6.73
Propoxur	8.76×10^{-6}	0.69×10^{-6}	7.88
Carbofuran	8.90×10^{-6}	0.48×10^{-6}	5.39
Carbaryl	4.82×10^{-6}	0.29×10^{-6}	6.02
Methiocarb	1.15×10^{-5}	1.01×10^{-6}	8.78
Promecarb	9.21×10^{-6}	0.74×10^{-6}	8.03

[a]Response factor = concentration (ug/mL) area response.

[b]Average of response factors from standard concentrations 0.100, 0.200, 0.500, 1.00, 2.00, 3.00 and 5.00 ug/mL.

Table V. Method Detection Limits for Reagent Water and Soil

	Reagent Water		Soil	
Compound	n[a]	MDL (ug/L)	n[a]	MDL (ug/kg)
Aldicarb Sulfone	7	1.9	7	44
Methomyl	10	1.7	10	12
3-Hydroxycarbofuran	10	2.6	7	10
Dioxacarb	10	2.2	7	> 50[b]
Aldicarb	7	9.4	7	12
Propoxur	10	2.4	10	17
Carbofuran	10	2.0	10	22
Carbaryl	10	1.7	10	31
Methiocarb	10	3.1	10	32
Promecarb	10	2.5	10	17

[a]Number of replicate spikes.

[b]See text for explanation.

Table VI. Recovery and Precision for Reagent Water at the Spike Level of 300 ug/L Each Compound, n = 10

Compound	Recovered	%Recovery	SD	%RSD
Aldicarb Sulfone	225	75.0	7.28	3.24
Methomyl	244	81.3	8.34	3.42
3-Hydoxycarbofuran	210	70.0	7.85	3.74
Dioxacarb	241	80.3	8.53	3.54
Aldicarb	224	74.7	13.5	6.03
Propoxur	232	77.3	10.6	4.57
Carbofuran	239	79.6	9.23	3.86
Carbaryl	242	80.7	8.56	3.54
Methiocarb	231	77.0	8.09	3.50
Promecarb	227	75.7	9.43	4.15

Table VII. Recovery and Precision for Soil at the Spike level of 2.00 mg/kg Each Compound, n = 10

Compound	Recovered	%Recovery	SD	%RSD
Aldicarb Sulfone	1.57	78.5	0.069	4.39
Methomyl	1.48	74.0	0.086	5.81
3-Hydoxycarbofuran	1.60	80.0	0.071	4.44
Dioxacarb	1.51	75.5	0.073	4.83
Aldicarb	1.29	64.5	0.142	11.0
Propoxur	1.33	66.5	0.126	9.47
Carbofuran	1.46	73.0	0.092	6.30
Carbaryl	1.53	76.5	0.076	4.90
Methiocarb	1.45	72.5	0.071	4.90
Promecarb	1.29	64.7	0.124	9.61

AZEOTROPIC DISTILLATION METHOD FOR THE DETERMINATION OF POLAR, WATER-SOLUBLE, NONPURGEABLE VOLATILE ORGANICS

Robert Graves, USEPA, Environmental Monitoring Systems Laboratory - Cincinnati
P. Cramer and J. Stanley, Midwest Research Institute

ABSTRACT. The determination of volatile organic compounds (VOCs) is an important step in the assessment of water quality. Although analytical methods have been developed that provide accurate determination of volatile, nonpolar, water-insoluble organics in aqueous samples, analytical methods for the determination of volatile, polar, water-soluble compounds, such as nitriles, aldehydes, alcohols, etc., have not been developed for general, routine applications. Such methods have been lacking because of the difficulties involved in removing (via purge and trap or solvent extraction) and concentrating these compounds from the aqueous matrix.

Azeotropy is a condition that occurs for some chemicals when a boiling mixture of two chemicals produces a vapor with the same composition as the liquid. Azeotropic distillation uses the property exhibited by selected organic compounds to form binary azeotropes with water. Since most azeotropes boil at a lower temperature than either the water or the organic compound, they can be removed from the aqueous sample by careful distillation.

The distillation of binary aqueous azeotropes of selected chemicals from the RCRA Appendix VIII, Michigan, and BDAT lists, including nitriles, ketones, aldehydes, amines, and alcohols have been investigated. The objectives of the program were to: (1) determine the maximum number of target compounds that could be chromatographed simultaneously by direct aqueous injection HRGC, (2) determine the azeotropic properties of those compounds which could be successfully chromatographed , and (3) determine the overall method performance for each compound. Data from the evaluation of azeotropic distillation as a method of concentrating and separating water soluble, polar, nonpurgeable VOCs from water will be presented.

The analytes were tested individually for chromatographic performance on a selection of wide-bore fused silica columns. Direct aqueous injection was performed since the sample would be in aqueous solution after distillation. Gas chromatographic conditions were optimized to resolve the greatest number of analytes simultaneously. The analytes that could be successfully chromatographed were tested for their ability to azeotropically distill. Recoveries were determined versus standard at the same level as if 100% of the analyte had been distilled over in the distillate. Investigations into suitable surrogates and internal standards were made. Precision and accuracy data for those compounds that were amenable to azeotropic distillation were collected at three concentration levels. Method performance and method detection limits were determined using "real-world" samples. Stability of the analytes in chlorinated and dechlorinated waters was also determined over a 14-day holding time.

THE WHY AND HOW OF SUPERCRITICAL FLUID EXTRACTION AND ITS APPLICATION TO ENVIRONMENTAL ANALYSIS

Viorica Lopez-Avila, Acurex Corporation, Mountain View, California 94039-7044; and W.F. Beckert and S. Billets, Environmental Monitoring Systems Laboratory, U.S. EPA, Las Vegas, Nevada 89139-3478

ABSTRACT

The increased interest in the use of supercritical fluids (SFs) is based on a combination of the properties of the supercritical fluids and the increased availability of both off-line and on-line equipment for supercritical fluid extraction (SFE). SFs have low viscosities, and thus the solute diffusivities are much higher for SFs than for solvents currently used in conventional extraction techniques. Consequently, the extraction efficiencies for SFs are much higher, and the extraction conditions can be adjusted so that compounds can be separated according to their volatility, polarity, etc. Furthermore, there is very little organic solvent needed for the collection of the extracted materials, and the supercritical fluid can be completely separated from the extracted material in the release step by reducing the pressure to ambient. This paper will present the why and how of SFE and its application to environmental analysis. Initial efforts were directed at SFE with carbon dioxide with and without modifiers. The effects of pressure, temperature, sample moisture content, sample size, analyte concentration, and matrix on extraction efficiencies were investigated for various classes of compounds.

INTRODUCTION

Several reviews discuss the supercritical fluid extraction (SFE) technique (1-4). Here we will discuss briefly the most important features of supercritical fluids (SF), the concepts of SFE, and several applications gathered from the open literature. This discussion will then be followed by the objectives of our study, and it will conclude with the results of the experiments performed so far.

The supercritical fluid state of a gas refers to those conditions of temperature and pressure under which the gas can be compressed to a density which approximates that of a liquid. Above the critical temperature, the gas will not become a liquid regardless of pressure. The important properties of SFs are summarized below:

- The compressibility of a SF is high above the critical temperature, and slight changes in pressure result in large changes in its density and thus in its ability to solubilize compounds from solid matrices.

- The densities of SFs are typically 100 to 1000 times greater than those of gases, however, their viscosities and diffusion coefficients are intermediate between those of liquids and gases. This allows rapid transfer of solutes into the SF. Consequently, the extraction efficiencies for SFE are higher than those for liquid solvent extractions.

- Many of the SFs in use have low critical temperatures, thus extractions can be performed at relatively low temperatures (e.g., the critical temperature for supercritical carbon dioxide is 31°C).

Among SFs, supercritical carbon dioxide is widely used since it is nontoxic, unreactive, and inexpensive. Furthermore, because of its low critical temperature, extractions with supercritical carbon dioxide can be performed at relatively low temperatures.

Recognition of these unique properties of SFs has been documented recently in the number of applications reported in the technical literature. However, the operating conditions for SFE are still largely a matter of trial and error, and the applications to compounds currently regulated by the Environmental Protection Agency have been quite limited.

Brady et al. (5) have investigated SFE of PCBs, DDT, and toxaphene from contaminated soils using carbon dioxide at 40°C and 100 atm. They showed that approximately 70 percent of the DDT and 75 percent of the toxaphene can be leached from a topsoil, contaminated with 1,000 ppm DDT and 400 ppm toxaphene, in under 10 min by using supercritical carbon dioxide at a flow rate of 0.7 g/sec. The extraction of PCB-contaminated subsoil gave recoveries higher than 90 percent in less than 1 min at the same carbon dioxide flow rate. The organic and the water content of the soil were found to be the two primary factors affecting the extraction efficiency.

Removal of trace organic species from urban particulate matter and sediments was investigated by Schantz and Chesler (6). Samples of 1 to 6 g were extracted with supercritical carbon dioxide at 40°C and 345 atm. The supercritical fluid was depressurized through a combination of capillary and packed-column restrictors. The extracted components were deposited onto a C_{18}-bonded-phase packed column. No breakthrough was found on a second collector column placed in series with the first column. Extraction efficiencies for PCBs from sediments and for PAHs from urban particulate matter were compared to Soxhlet extraction. The data demonstrate that comparable amounts of PCBs and PAHs (except indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene) were extracted by Soxhlet and by SFE. The SFE, however, required less time for completion than did Soxhlet extraction. Furthermore, the values obtained for indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene by SFE were 30 percent and 18 percent respectively, higher than the certified values.

Smith and coworkers (7-10) used SFs for the extraction of high-molecular-weight organics from various adsorbent and particulate matrices. Supercritical carbon dioxide, isobutane, and methanol-modified carbon dioxide were employed for sample extraction. Polar compounds were extracted more efficiently with supercritical carbon dioxide containing methanol as a modifier, whereas isobutane was found to be more efficient for the higher-molecular-weight and the less polar compounds.

Hawthorne and Miller (11-14) used SFs to extract PAHs from urban dust, flyash, and river sediment, and reported that nitrous oxide with 5 percent methanol gave recoveries of 100 percent for fluoranthene and benzo[a]anthracene, of 85 percent for benzo[a]pyrene, and slightly less than 50 percent for indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene from urban dust.

Several researchers reported that a nonpolar fluid, when doped with a small amount of a certain solvent such as acetone or methanol, can become highly selective (15,16). For example, Dobbs et al. (15) reported that the addition of 3.5 mol-percent methanol to carbon dioxide increased the solubility of 2-aminobenzoic acid by 620 percent. In the case of benzoic acid, the solubility enhancement was significantly greater for methanol than for

acetone or n-octane. Dooley et al. (16) studied the use of modifiers such as methanol and toluene and reported that supercritical carbon dioxide with 5 percent methanol is much more effective than supercritical carbon dioxide with 5 percent toluene.

To investigate the practicality of SFE, we conducted a series of experiments designed primarily to evaluate a commercial supercritical fluid extractor, with the focus on classes of compounds of interest to EPA. The goal of our study was to establish conditions (e.g., pressure, temperature, restrictor dimensions, extraction vessel design, collection device) which would give reasonable extraction efficiencies (recovery >60 percent) for 17 organochlorine pesticides, 16 PAHs, 25 organophosphorus pesticides, and 43 neutral/acidic compounds known as the EPA priority pollutants. These compounds were spiked into relatively clean matrices such as sand, NIST Standard Reference Materials (urban dust, coal, and coal flyash), and soil samples prepared by the University of Nevada, Las Vegas. The samples were extracted with supercritical carbon dioxide. Modifier was added directly to the sample. Due to budgetary and time constraints, the kinetics of the extraction were evaluated only to a very limited extent. The idea was to establish conditions that will allow efficient extraction of these 101 compounds. Once these conditions are known, then a protocol for the SFE technique can be written and tested for ruggedness. Finally, the feasibility of interfacing the extractor to an ion trap detector via a gas chromatograph will be considered.

EXPERIMENTAL

Apparatus

(a) Supercritical fluid extractor -- Suprex Model SE-50, consisting of a 250-mL syringe pump with the neccesary valves and connecting lines to the extraction vessel, a control module that contains the microprocessor for control of the SFE system and store up to 25 extraction methods; an oven module consisting of the extraction oven, extraction vessel, and a 4-port valve configured with electronic actuators for automatic operation (Figure 1). Several extraction vessels (Figure 2) were evaluated. Supercritical pressures were maintained inside the extraction vessel by using 60-cm uncoated fused-silica tubing (50 μm ID x 375 μm OD) from J&W Scientific. Other restrictors from Suprex (25 μm ID) and Polymicro Technologies have also been evaluated. Collection of material that was extracted with supercritical carbon dioxide was performed by inserting the outlet restrictor into a 15-mm x 60-mm glass vial containing hexane spiked with a known concentration of an internal standard.

(b) Gas chromatograph -- Varian 6000 equipped with two constant current/pulsed frequency electron capture detectors and two megabore open tubular columns (30-m x 0.53-mm ID DB 608 column and 30-m x 0.53-mm ID DB 1701 column), connected to an 8-inch injection tee.

(c) Autosampler -- Varian Model 8000

(d) Gas chromatograph/mass spectrometer -- Finnigan 4510B interfaced to a data system for data acquisition and processing and equipped with a 30-m x 0.32-mm ID DB 5 fused-silica capillary column.

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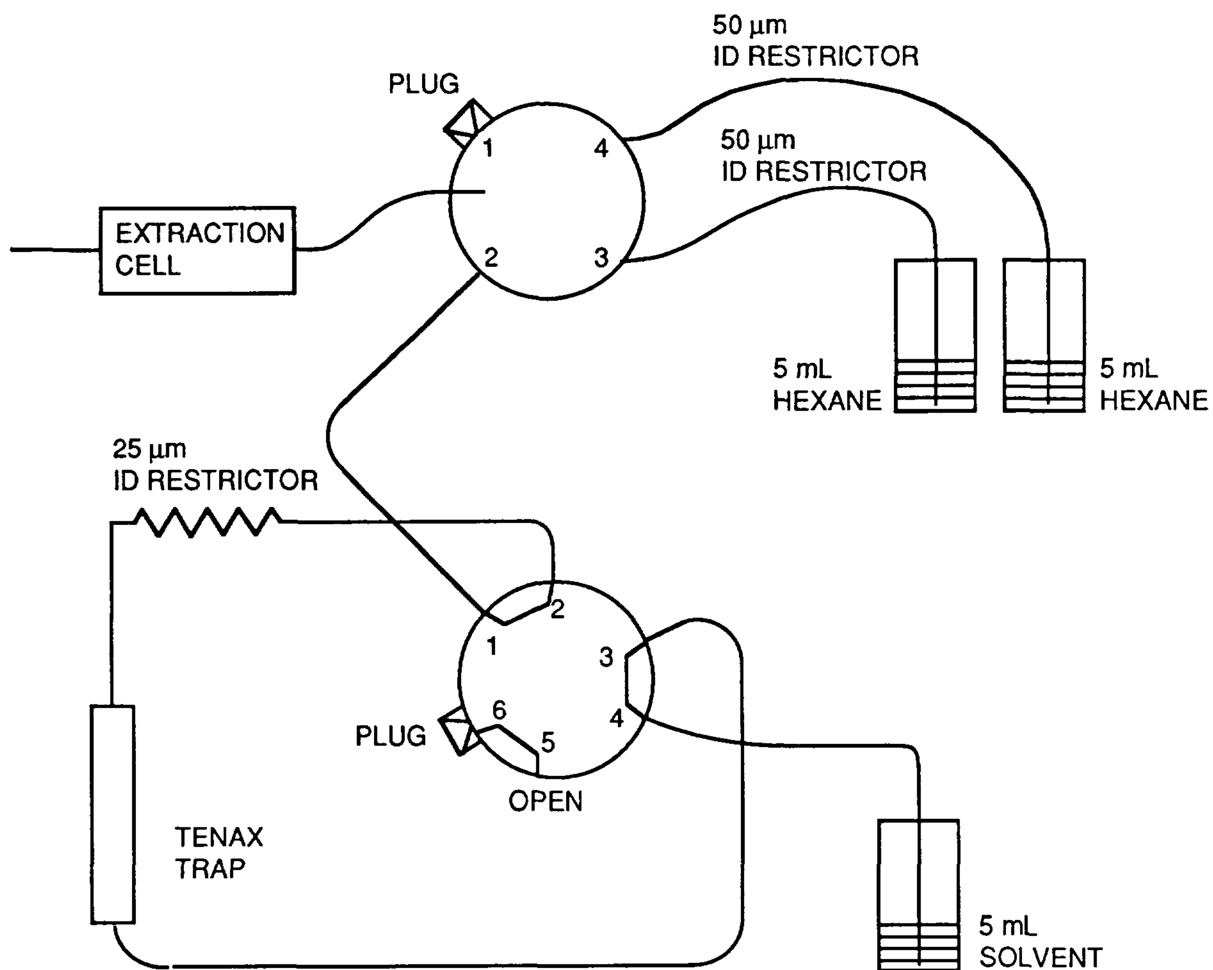

Figure 1. Schematic representation of 4-port and 6-port valve connections

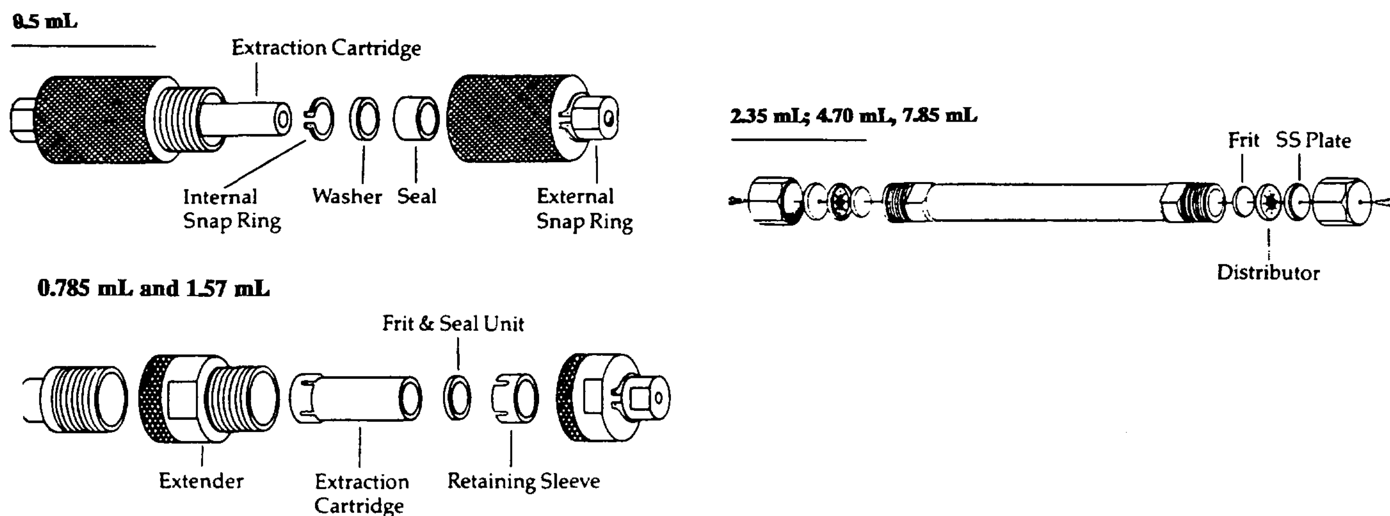

Figure 2. Various types of extraction vessels

Materials

(a) Standards -- Analytical reference standards of the organochlorine pesticides, PCBs, PAHs, phthalate esters, and organophosphorus pesticides were obtained from the U.S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository; Aldrich Chemical; UltraScientific Inc.; Chem Service; and Scientific Polymer Products. Purities were stated to be greater than 98 percent. Stock solutions of each test compound were prepared in pesticide-grade hexane at 1 mg/mL. Working calibration standards were prepared by serial dilution of a composite stock solution prepared from the individual stock solutions.

(b) Carbon dioxide SFC-grade liquid (Scott Specialty Gases)

(c) Sample matrices -- sand; standard reference materials, containing organochlorine pesticides prepared by the University of Nevada, Las Vegas (UNLV), identified as SMY 945, YJU 963, D69 Z3Z, ZVD 497, H59 VW5, and UPV 277; Love Canal soil sample provided by Dr. Larry Butler of the EPA-Las Vegas; and NIST Standard Reference Materials (SRM 1645, SRM 1632a, and SRM 1633a).

RESULTS AND DISCUSSION

The results of our experiments are summarized in Tables 1 through 5. All experiments were performed with the 7.85-mL extraction vessel shown in Figure 2. The amount of sample loaded onto the extraction vessel varied from 4 g for Florisil to 8 to 11.2 g for sand and to 5 to 6 g for the UNLV soil samples. Smaller amounts of sample (e.g., 1 g for urban dust or for coal and 2 g for coal flyash) were also extracted in the 7.85-mL extraction vessel. In this case, the void volume was filled with silanized glass wool or glass beads.

The 7.85-mL extraction vessel has been used continuously for a period of four months without any problems. Other extraction vessels shown in Figure 2, were tested, were found inadequate. The 0.5-mL vessel developed leaks after the fourth extraction, and the 1.57-mL vessel did not pass the leak test. Finally, the 0.785-mL extraction vessel is too difficult to work with because the extraction cartridge is only 1 cm in length and 1 cm in diameter, making the sample loading very difficult.

Since the goal of our experiments was to improve extraction efficiency, the next parameter we tried to optimize was the backpressure device. The instrument was equipped by the manufacturer with a 50-cm x 25-μm ID uncoated fused-silica capillary restrictor. After a series of trial-and-error experiments with the 25-μm ID restrictor, we concluded that in order to achieve reasonable extraction efficiencies in less than 60 min, we needed a larger diameter restrictor. A 50-μm and a 100-μm ID uncoated fused-silica capillary restrictor were then tested. The flow rate through the 100-μm ID restrictor was too high for our collection device to handle; therefore, the 100-μm ID restrictor was no longer evaluated. A thick wall (375-μm OD) 50-μm ID restrictor from J&W Scientific performed adequately. Except for the data shown in Table 1, all the data shown in this paper were obtained with a 50-μm ID uncoated fused-silica capillary restrictor.

Evaluation of the backpressure device is continuing. Currently, our instrument is set up with two 50-μm ID uncoated fused-silica capillary restrictors and a 6-port valve for collection of volatiles and trapping on a Tenax cartridge. One restrictor is used for collecting the

TABLE 1. RESULTS OF THE AROCLOR 1232/1260 EXTRACTIONS USING SUPERCRITICAL CARBON DIOXIDE, A 7.85-mL EXTRACTION VESSEL, AND A 50-CM X 25-μm ID UNCOATED FUSED-SILICA TUBING AS RESTRICTOR (MATRIX: FLORISIL, 4 g)[a]

		Percent Recovery								
		40°C[b]			50°C			60°C		
Pressure (atm)		First Extraction	Second Extraction	Total	First Extraction	Second Extraction	Total	First Extraction	Second Extraction	Total
120	DB-608	15.6	25.8	41.4	11.9	12.0	23.9	8.9	51.4	60.3
	DB-1701	13.6	23.9	37.5	9.6	12.2	21.8	7.7	50.4	58.1
150	DB-608	43.1	34.0	77.1	31.3	36.3	67.6	45.3	63.0	108.3
	DB-1701	41.5	32.3	73.8	29.9	35.5	65.4	44.0	59.8	103.8
200	DB-608	51.5	30.0	81.5	53.3	29.2	82.5	45.4	48.0	93.4
	DB-1701	48.1	27.1	75.2	50.9	27.6	78.5	47.1	50.6	97.7
230	DB-608	70.6	32.5	103.1	74.7	19.1	93.8	48.2	58.2	106.4
	DB-1701	63.5	28.0	91.5	72.7	17.6	90.3	47.5	56.4	103.9

[a]Spiking level of Aroclor 1232/1260 is 5 μg/g Florisil. The first extraction was performed for 20 minutes at the temperature and pressure indicated; the extracted Aroclors were collected in 5 mL hexane at room temperature; the second extraction was also performed for 20 minutes at the temperature and pressure indicated.
[b]The temperature varied slightly from 40°C to 42°C.

TABLE 2. PERCENT RECOVERIES OF THE ORGANOCHLORINE PESTICIDES FROM SAND FORTIFIED WITH THE TARGET COMPOUNDS AND EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE[a]

	Compound	OCP-2[b]	OCP-3[c]	OCP-4[d]	OCP-5[e]
1.	alpha-BHC	102.6	95.9	102.8	101.0
2.	gamma-BHC	97.1	96.8	101.9	98.7
3.	beta-BHC	93.9	92.4	100.5	95.2
4.	Heptachlor	98.4	95.7	101.0	98.7
5.	delta-BHC	92.4	95.3	101.4	97.9
6.	Aldrin	81.6	82.0	90.4	86.4
7.	Heptachlor epoxide	96.9	98.6	103.0	100.8
8.	Endosulfan I	95.4	96.7	102.8	98.7
9.	4,4′-DDE	98.5	97.0	102.3	99.0
10.	Dieldrin	96.3	98.5	103.4	99.1
11.	Endrin	100.2	107.0	114.9	108.8
12.	4,4′-DDD	94.8	95.9	101.9	96.6
13.	Endosulfan II	81.9	97.0	96.2	89.3
14.	4,4′-DDT	89.8	93.2	100.9	95.8
15.	Endrin aldehyde	73.5	76.5	85.8	78.6
16.	Endosulfan sulfate	62.4	72.3	86.9	75.1
17.	Methoxychlor	45.4	58.1	70.7	75.1
	Mean	88.3	91.1	98.1	93.8
	SD	15.3	12.1	9.8	9.6

[a]All experiments were performed with a 7.85-mL extraction vessel. The amount of sand extracted is 8 g. The extraction conditions are specified in footnotes b through e. A 50-μm x 60 cm length ID uncoated fused-silica restrictor (J&W Scientific) was used. Collection was done in 5 mL hexane.

[b]OCP-2: 150 atm/50°C/10 min, static
200 atm/60°C/10 min, dynamic
250 atm/70°C/10 min, dynamic

[c]OCP-3: 200 atm/60°C/30 min, dynamic

[d]OCP-4: 200 atm/60°C/30 min, dynamic with 200 μL acetone modifier

[e]OCP-5: 150 atm/50°C/30 min, dynamic

TABLE 3. PERCENT RECOVERIES OF THE ORGANOPHOSPHORUS PESTICIDES FROM SAND FORTIFIED WITH THE TARGET COMPOUNDS AND EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE[a]

Compound	OPP-A[b]	OPP-F[c]	OPP-G[d]
1. Dichlorvos	54.0	61.3	56.3
2. Mevinphos	66.3	14.7	9.7
3. Ethoprop	66.3	60.0	50.3
4. Naled	28.7	30.7	18.7
5. Sulfotep	60.0	81.3	79.3
6. Phorate	60.7	80.7	78.0
7. Dimethoate	65.0	5.7	--
8. Diazinon	53.7	9.7	--
9. Disulfoton	59.0	81.3	84.3
10. Methylparathion	57.7	74.3	70.7
11. Ronnel	59.3	80.7	85.3
12. Malathion	58.3	70.7	61.0
13. Fenthion	53.7	80.7	84.0
14. Chlorpyrifos	58.7	85.0	87.7
15. Parathion	61.0	79.7	79.7
16. Stirofos	67.3	61.0	47.0
17. Fensulfothion	46.0	--	--
18. Bolstar	66.3	82.0	84.7
19. EPN	66.0	78.3	76.3
20. Azinphos methyl	61.7	13.0	--
21. Coumaphos	65.3	--	--
22. Demeton (I)	55.3	73.0	69.0
23. Demeton (II)	57.6	28.3	21.7
24. Merfos	50.6	65.3	61.3
25. Ethion	58.2	82.7	86.0
Mean	58.1	55.2	51.6
SD	8.0	31.2	33.9

[a] All experiments were performed with a 7.85-mL extraction vessel. The amount of sand extracted is 8 g. The extraction conditions are specified in Footnotes b through i. A 50-μm ID x 60-cm length uncoated fused-silica restrictor (J&W Scientific) was used. Collection was done in 5 mL hexane. When no recovery value is given, the compound was not recovered.

[b]OPP-A 250 atm/70°/5 min static, with 300 μL acetone modifier
250 atm/70°/55 min dynamic

[c]OPP-F 250 atm/70°/5 min static, with 300 μL acetone modifier
250 atm/70°/55 min dynamic

[d]OPP-G 200 atm/60°/45 min dynamic, no modifier

Table 4. PERCENT RECOVERIES OF NEUTRAL/ACIDIC COMPOUNDS FROM SAND WITH SUPERCRITICAL CARBON DIOXIDE[a]

	Compound	Supercritical Carbon Dioxide	Supercritical Carbon Dioxide with 200 µL acetone
1.	Phenol	141	83.5
2.	Bis(2-chloroethyl)ether	37.6	36.3
3.	2-Chlorophenol	73.1	57.9
4.	1,3-Dichlorobenzene	3.9	1.9
5.	1,4-Dichlorobenzene	4.6	2.1
6.	Benzyl alcohol	111	128
7.	1,2-Dichlorobenzene	9.0	5.0
8.	2-Methylphenol	111	129
9.	Bis(2-chloroisopropyl)ether	45.1	42.8
10.	4-Methylphenol	148	96.6
11.	N-nitroso-di-n-propylamine	57.6	67.1
12.	Hexachloroethane	5.7	0
13.	Nitrobenzene	59.4	54.9
14.	Isophorone	59.1	73.6
15.	2-Nitrophenol	67.0	55.3
16.	2,4-Dimethylphenol	93.3	71.7
17.	Benzoic acid	0	0
18.	Bis(2-chloroethoxy)methane	65.7	83.3
19.	2,4-Dichlorophenol	104	75.7
20.	1,2,4-Trichlorobenzene	42.9	36.7
21.	Hexachlorobutadiene	36.9	29.6
22.	4-Chloro-3-methylphenol	176	113
23.	2-Methylnaphthalene	74.2	72.1
24.	Hexachlorocyclopentadiene	67.9	63.3
25.	2,4,6-Trichlorophenol	105	88.5
26.	2,4,5-Trichlorophenol	121	96.1
27.	2-Chloronaphthalene	81.1	82.0
28.	Dimethylphthalate	49.0	71.1
29.	2,4-Dinitrophenol	33.1	26.8
30.	4-Nitrophenol	82.7	111
31.	Dibenzofuran	89.1	92.3
32.	2,4-Dinitrotoluene	71.9	87.5
33.	2,6-Dinitrotoluene	87.8	85.0
34.	Diethyl phthalate	48.5	72.5
35.	4-Chlorophenyl-phenylether	83.6	90.1
36.	4,6-Dinitro-2-methylphenol	49.6	53.3
37.	4-Bromophenyl-phenylether	102	80.0
38.	Hexachlorobenzene	113	79.9
39.	Pentachlorophenol	66.4	58.2
40.	Di-n-butylphthalate	51.9	77.8
41.	Butylbenzylphthalate	32.1	63.3
42.	Bis(2-ethylhexyl)phthalate	59.6	73.6
43.	Di-n-octylphthalate	35.0	69.7
	Mean	68.8	66.0
	SD	39.7	32.6

[a] All experiments were performed with a 7.85-mL extraction vessel. Extraction was performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and then 250 atm/70°C/10 min dynamic. A 50-µm ID x 60-cm length uncoated fused-silica restrictor was used. Collection was done in 5 mL hexane. Modifier (200 µL) was added to the matrix. 9.3 g sand sandwiched between two plugs of regular glass wool was used in each experiment. Spiking levels of neutral/acidic compounds are 200 µg per compound for the neutrals, and 167 µg per compound for the acidic compounds, except for 4-methylphenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol which were spiked at 33.3 µg per compound.

TABLE 5. PERCENT RECOVERIES OF PAH COMPOUNDS FROM SAND AND NIST STANDARD REFERENCE MATERIALS BY SFE WITH SUPERCRITICAL CARBON DIOXIDE

Compound	Sand[a] (9.3 g)	Sand with 200 μL acetone[b] (9.3 g)	Sand[b] (11.2 g)	Sand with 200 μL acetone[b] (11.2 g)	SRM-1649[c,d] Urban Dust (1 g)	SRM-1632a[c,d] Coal (1 g)	SRM-1633a[c,d] Coal Flyash (1 g)
1. Naphthalene	67.2	80.4	41.0	86.2	100	95.0	88.3
2. Acenaphthylene	81.7	78.4	62.7	92.9	95.3	92.8	88.8
3. Acenaphthene	87.8	81.2	65.9	88.7	104	93.0	89.5
4. Fluorene	86.7	80.2	68.6	89.1	101	94.6	89.2
5. Phenanthrene	85.7	79.0	63.0	91.8	118	95.0	87.5
6. Anthracene	84.6	77.5	64.4	88.1	93.8	91.7	85.7
7. Fluroanthene	85.7	78.4	64.2	87.6	88.8	92.6	90.7
8. Pyrene	89.3	82.7	69.5	89.9	70.0	94.8	87.4
9. Benzo(a)anthracene	85.8	82.1	77.0	88.8	14.5	96.7	88.6
10. Chrysene	76.8	82.6	66.3	89.2	26.7	96.7	88.6
11. Benzo(b)fluroanthene	97.0	83.5	70.2	88.5	20.0	104	88.1
12. Benzo(k)fluoranthene	63.7	84.1	62.9	88.6	30.0	98.9	100
13. Benzo(a)pyrene	70.4	81.7	67.2	92.3	19.2	100	92.7
14. Indeno(,2,3-c,d)pyrene	59.5	85.3	50.7	87.2	16.4	99.0	90.1
15. Dibenzo(a,h)anthracene	31.8	80.8	17.9	84.9	15.0	93.9	88.1
16. Benzo(g,h,i)perylene	24.3	79.9	16.6	87.0	12.8	93.8	85.2
Mean	73.6	81.1	58.0	88.8	57.0	95.8	89.3
SD	20.5	2.2	17.9	2.2	42.2	3.3	3.4

[a]All experiments were performed with a 7.85-mL extraction vessel. Extraction was performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and then 250 atm/70°C/10 min dynamic. A 50-μm ID x 60 cm length uncoated fused-silica restrictor was used. Collection was done in 5 mL hexane. Modifier (200 μL) was added to the matrix. 9.3 g sand sandwiched between two plugs of regular glass wool was used in each experiment. Spiking level of PAHs is 200 μg per compound

[b]All experiments were performed with a 7.85-mL extraction vessel. Extraction was performed at 150 atm/50°C/5 min static followed by 150 atm/50°C/55 min dynamic. A 50-μm ID uncoated fused-silica restrictor (J&W Scientific, 60 cm in length) was used. Collection was done in 5 mL hexane.

[c]Values given represent the amounts recovered in the first extraction. No compounds were detected in the second extraction that was performed at 200 atm/60°C/10 min dynamic followed by 250 atm/70°C/10 min dynamic.

[d]Values given represent the amounts recovered in the first extraction. No compounds were detected in the second extraction that was performed at 200 atm/60°C/10 min dynamic followed by 250 atm/°C/10 min dynamic.

first extract. The other restrictor is used to verify that the first extraction is complete; for this purpose, a second fraction is collected either under the same conditions as the first one or under a different set of conditions. The same results can be obtained with one restrictor by changing the collection vessel; however, our setup allows us unattended operation of the instrument during two extractions. A third and a fourth restrictor could be installed in the 4-port valve.

Collection of the material extracted with supercritical carbon dioxide was done by inserting the outlet restrictor into a 15-mm x 60-mm glass vial containing 5 mL hexane spiked with a known amount of an internal standard. Terphenyl-d_{14} was used for the PAHs, organophosphorus pesticides, and the neutral/acidic compounds. Benzyl benzoate was used for the phthalate esters. Recoveries of the internal standards were better than 95 percent when the volume of the solvent was adjusted to 5 mL. During extraction, approximately 60 percent of the hexane is lost by volatilization. We have determined, by using hexane solutions of the test compounds and the extraction conditions specified in Tables 1 through 5, that losses during the sample collection step are less than 2 percent.

Recovery data shown in Tables 1 through 5 for different classes of compounds show that the SFE technique works well at moderate pressures and relatively low temperatures for sand and the NIST Standard Reference Materials. PCBs can be recovered from spiked Florisil (concentration 5,000 ppb) at 150 atm and temperatures >40°C in a 40-min extraction. Organochlorine pesticides can be recovered from spiked sand (concentration 2,500 ppb) in a 30-min extraction at pressures of 150 atm and temperatures of 50°C. An extraction method in which both the pressure and temperature are changed (150 atm/ 50°C/ 10 min static, followed by 200 atm/ 60°C/ 10 min dynamic and then 250 atm/ 70°C/ 10 min dynamic) was evaluated and found to give almost identical results as the 150 atm/ 50°C/ 60 min program.

Extraction of the organophosphorus pesticides from sand (Table 3) requires additional optimization since the average recoveries are only around 55 percent, and compounds such as mevinphos, dimethoate, diazinon, fensulfothion, azinphos methyl, and coumaphos could not be recovered or had very low recoveries. OPP-A and OPP-F (Table 3) are identical experiments; however, we cannot explain why the six compounds mentioned above could not be recovered in the OPP-F experiment.

Forty-three neutral/acidic compounds were spiked into sand samples at concentrations of 21,500 ppb for the neutrals and 3,600 to 18,000 ppb for the acidic compounds. Twenty-eight of the 43 compounds had recoveries >50 percent (Table 4). From the remaining compounds, 10 had recoveries between 25 and 49 percent, and 5 compounds had recoveries below 9 percent. It is interesting to note that the compounds which were not recovered from sand, except for benzoic acid, were recovered from Florisil. We attribute this to a matrix effect and plan to investigate it further.

Finally, the compounds for which the SFE technique seems to work well are the 16 PAHs listed in Table 5. Despite reports by Smith and coworkers (9) that PAHs could not be recovered from solid matrices with supercritical carbon dioxide alone, we achieved recoveries averaging 57 percent for urban dust, 95.8 percent for coal, and 89.3 percent for coal flyash. The addition of acetone to the matrix was found to improve the mean recovery from 58 percent to 88.8 percent (for the 11.2-g experiment) and from 73.6 percent to 81.1 percent (for the 9.3-g experiment).

NOTICE

Although the research described in this paper has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Footnotes

[1]For all other purge and trap GC/MS method details, please follow the U.S. EPA CLP Statement of Work for Organic Analysis, Revision 2/88, exactly.

[2]Actual concentration ranges could be ten to twenty times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[3]The volume of methanol added to the 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 μL added to the syringe.

[4]Dilute an aliquot of the methanol extract and then take 100 μL for analysis.

[5]Weight of container, soil, methanol - weight of container, methanol = g of sample (wet weight).

[6]Outside CLP acceptance criteria.

EVALUATION OF SAMPLE EXTRACT CLEANUP USING SOLID-PHASE EXTRACTION CARTRIDGES

V. Lopez-Avila, S. Yeager, Acurex Corporation, 485 Clyde Avenue, Mountain View, California 94039; and W. F. Beckert, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, 944 East Harmon Avenue, Las Vegas, Nevada 89109.

INTRODUCTION

Fractionation or cleanup of sample extracts prior to instrumental analysis is used to remove coextracted materials that often interfere with the determination of target analytes. Such fractionations are usually accomplished by column chromatography, gel permeation chromatography, or acid/base partitioning. Standardized cleanup procedures such as Method 3610 and 3620 published in EPA SW-846 specify amounts of alumina and Florisil in excess of 10 g and large volumes of eluting solvents (e.g., a 10-g Florisil column and 100 mL of 20-percent diethyl ether in hexane are recommended for cleanup of sample extracts containing phthalate esters). Such large volumes of solvents increase the likelihood of sample contamination by impurities in the solvents. Furthermore, the adsorbent materials and the solvents are not recycled, and although such materials are not overly expensive, the time required for the preparation of the adsorbent, for the packing of the chromatographic columns, for the elution of the target analytes, and for the evaporation of solvents contributes to the overall cost of analysis. The solution to all these problems would be to use disposable cartridges known as solid-phase extraction (SPE) cartridges.

Solid-phase extraction is one of the fastest-growing sample preparation methods (1). The technique has been used primarily for preconcentrating organics from aqueous samples (2,3,4,5,6,7,8). Recent applications of the solid-phase extraction technique include cleanup of sediment and fish extracts known to contain organochlorine and organophosphorus pesticides (9), cleanup of plant material in residual pesticide analysis (10), fractionation of petroleum hydrocarbons from crude oil and product oil (11), separation of additives from various matrices (e.g., 1-methyl-imidazole from epoxy resin, fractionation of petrolatum, isopropyl myristate, and cetyl alcohol from commercial hand cleaners, separation of mineral oil from impact polystyrene, etc.) (12), cleanup of human and bovine adipose tissues (13, 14), extraction of polychlorinated biphenyls (PCBs) from transformer oil (15), and cleanup of environmental sample extracts (16).

Silica-based bonded-phase cartridges seem to have won the environmental market; however, alumina, Florisil, and silica gel are also getting popular, especially for extract cleanup. Polymer-based cartridges are available from several suppliers (Interaction Chemicals, EM Science, Bio-Rad Laboratories) and have several advantages over the bonded-phase silicas which make them quite attractive. These include: higher capacity, ability to withstand a wider range of solvents and pH conditions, and the capacity for reuse, if needed. The typical amounts of adsorbent material are 100 to 500 mg for the bonded-phase silicas,; larger amounts (1 g) are typically used for Florisil, alumina, and silica gel.

The purpose of our study is to evaluate the Florisil, alumina, silica gel, and bonded-phase silica SPE cartridges for cleanup of extracts of environmental samples that contain organochlorine pesticides, phthalate esters, chlorinated hydrocarbons, organophosphorus pesticides, etc. Cartridge loading and the effect of matrix interferents (e.g., lipids, diesel-type hydrocarbons, elemental sulfur) are being addressed. Finally, the feasibility of

automated solid-phase extraction is being evaluated with robotic devices for sample preparation. This paper focuses on two groups of environmental pollutants: organochlorine pesticides/PCBs and phthalate esters. The former group of compounds is dealt with in EPA Method 8080/8081, the latter in EPA Method 8060.

EPA Method 8080/8081 recommends Florisil cleanup (Method 3620) for extracts that are analyzed for organochlorine pesticides and PCBs. The target compounds are eluted from the Florisil column with 6, 15, and 50 percent diethyl ether in hexane. The PCBs are not separated from the organochlorine pesticides under these conditions. Nonetheless, we found that the Florisil procedure gave quantitative recoveries (>75 percent) for 17 organochlorine pesticides, toxaphene, technical chlordane, and 7 Aroclors.

Work done previously in our laboratory with a 3-g silica gel column (the silica gel was deactivated with water at 3.3 percent by weight) allowed the separation of PCBs from most of the organochlorine pesticides (16). However, the column had to be eluted with large volumes of hexane (130 mL) and methylene chloride (15 mL) in order to allow quantitative recovery of PCBs and organochlorine pesticides. Such large volumes of solvents increase the cost of analysis and may also increase the likelihood of sample contamination by impurities in the eluting solvents.

EPA Method 8060 recommends either alumina cleanup (Method 3610) or Florisil cleanup (Method 3620) for extracts to be analyzed for phthalate esters; however, neither method presents recovery data for the target compounds. We have tested both procedures and found that the Florisil cleanup was less desirable because three phthalate esters were not recovered at all.

EXPERIMENTAL

Apparatus

(a) Vacuum manifold -- VacElute Manifold SPS-24 (Analytichem International) or Visiprep (Supelco Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel sample delivery tips, built-in vacuum bleed valve and gauge; the system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing.

(b) Gas chromatographs -- Varian 6000 with constant current/pulsed frequency ECD, interfaced with a Varian Vista 402 data system; Varian 6500 with FID, also interfaced with a Varian Vista 402 data system. For simultaneous analysis, the megabore open tubular columns were connected to a Supelco 6-inch injection tee and to identical ECDs.

(c) Autosampler -- Varian Model 8000

(d) GC columns: DB-608, 30-m x 0.53-mm ID open tubular fused-silica column and DB-1701, 30-m x 0.53-mm ID open tubular fused-silica column for phthalate ester analysis, and DB-5, 30-m x 0.25-mm ID fused-silica capillary column for organochlorine pesticides and PCB analysis.

Materials

(a) Cartridges -- Florisil, alumina, silica gel, or diol (40-μm particles, 60-Å pores) of different sizes (0.5 g, 1.0 g, 2.0 g). The cartridges consist of serological-grade polypropylene tubes, 3 mL or 6 mL in volume; the adsorbent material is held between two polyethylene frits (20-μm pores).

(b) Standards -- Analytical reference standards of the organochlorine pesticides and the phthalate esters were obtained from the U.S. Environmental Protection Agency--Pesticides and Industrial Chemicals Repository; Aldrich Chemical; Ultra Scientific Inc.; Chem Service; and Scientific Polymer Products. Purities were stated to be greater than 98 percent. Stock solutions of each test compound were prepared in pesticide-grade hexane at 1 mg/mL. Working calibration standards were prepared by serial dilutions of a composite stock solution prepared from the individual stock solutions.

(c) Corn oil -- Stock solution was prepared in hexane at 1.1 mg/mL.

(d) Elemental sulfur -- Stock solution was prepared in hexane at 0.28 mg/mL.

Cartridge Cleanup Procedure

Each Florisil cartridge was conditioned prior to use by washing with 4 mL hexane. Diol cartridges were conditioned with 10 percent acetone in hexane (4 mL). Two-mL aliquots of hexane solutions containing the test compounds and the interferents were loaded onto cartridges using a micropipette. To ensure that the packing did not get dry in between cartridge conditioning and sample addition or in between collection of fractions, we always let 1 mm of the last solvent remain on top of the frit. A Supelclean vacuum manifold (Supelco, Inc.) was used to simultaneously prepare as many as 12 samples, and an Analytichem International vacuum manifold (SPS-24) was used to prepare 24 samples simultaneously. When using the Visiprep Supelco vacuum manifold, the vacuum for each cartridge was adjusted manually using chemically inert screw-type valves.

Compounds were eluted with the various solvents identified in the tables that summarize the results. The volume of each fraction was adjusted to 5 mL prior to gas chromatographic analysis.

Gas chromatography operating conditions: 150°C (0.5-min hold) to 220°C at 3°C/min then to 275°C (hold 15 min) at 5°C/min; injector temperature 250°C; detector temperature 320°C.

RESULTS AND DISCUSSION

Organochlorine Pesticides

Two elution schemes were attempted initially. In Scheme A, the charged cartridges were eluted with 3 mL hexane (Fraction 1), followed by 5 mL 26-percent methylene chloride in hexane (Fraction 2) and 5 mL of 10-percent acetone in hexane (Fraction 3); in Scheme B, the charged cartridges were eluted with 3 mL hexane (Fraction 1), 5 mL 4-percent diethyl ether in hexane (Fraction 2), and 5 mL of 56-percent diethyl ether in hexane. The 26-percent methylene chloride in hexane has approximately the same solvent strength as the

4 percent diethyl ether in hexane, and the 10 percent acetone in hexane has approximately the same solvent strength as the 56 percent diethyl ether in hexane. Under the Scheme A conditions, silica gel proved to be superior to Florisil because it allowed complete separation of the PCBs from all but four organochlorine pesticides, quantitative recovery of all compounds, and almost complete separation of the Method 8080/8081 organochlorine pesticides from 16 phthalate esters. The four organochlorine pesticides that eluted with the 16 phthalate esters could be identified and quantified without any difficulty because they were resolved from the phthalate esters on a 30-m x 0.25-mm ID DB-5 fused-silica capillary column.

The solvents used in Scheme B gave almost identical elution patterns for the Florisil and silica gel cartridge procedure with quite a few organochlorine pesticides spread among the three fractions. Because of this, no further work was undertaken using Scheme B.

The procedure given in Scheme A was tested at 2 organochlorine pesticide concentrations in quadruplicate. The results presented in Tables 1 and 2 show elution patterns, compound recoveries, and method precision for 18 organochlorine pesticides. The silica gel SPE cartridges seem to perform better than the Florisil cartridges in separating PCBs from the organochlorine pesticides (Table 1). Four organochlorine pesticides (heptachlor, aldrin, 4,4'-DDE, and 4,4'-DDT) elute in Fraction 1. The remaining organochlorine pesticides, with the exception of endosulfan II and endosulfan sulfate, elute in Fraction 2. Endrin aldehyde and 4,4'-methoxychlor elute in both Fractions 2 and 3. Compound recoveries were quantitative and method precision (%RSD) was better than 10 percent for 14 of the 18 target compounds.

Table 2 presents the results for the Florisil SPE cartridge procedure. Eight pesticides (alpha-BHC, gamma-BHC, heptachlor, aldrin, gamma-chlordane, 4,4'-DDE, 4,4'-DDD, and 4,4'-DDT) elute in Fraction 1. The remaining organochlorine pesticides, with the exception of endosulfan sulfate, elute in Fraction 2. Alpha-BHC, gamma-BHC, gamma-chlordane, endosulfan II, 4,4'-DDD, endrin aldehyde, and 4,4'-methoxychlor elute in both fractions.

Seven Aroclor mixtures were tested individually on the silica and the Florisil SPE cartridges. In each case the cartridge was loaded with 10 μg of the corresponding Aroclor and eluted with 3 mL hexane. The recovery data given in Table 3 indicate that Aroclors are recovered quantitatively from either cartridge with 3 mL hexane. An additional fraction was collected by eluting the cartridge with an additional 3 mL hexane to verify that indeed the PCBs are removed completely from the cartridge with 3 mL hexane. Larger cartridges may require additional solvent to ensure complete removal of the PCBs.

Experiments are in progress to determine if diol cartridges can be used in place of silica gel cartridges. Preliminary experiments conducted with the diol cartridges indicate that they do not separate PCBs from the organochlorine pesticides. Although recoveries of the organochlorine pesticides from a 1-g diol cartridge by elution with 10 percent acetone in hexane are quantitative, except for endrin aldehyde (0 percent recovery), the fact that they cannot separate PCBs from most of the organochlorine pesticides is a disadvantage. In those samples where PCBs are not present and the matrix has high concentrations of lipid material, the diol cartridge may be quite useful because it is polar and would retain preferentially the organochlorine pesticides,while the lipids can be easily washed off.

Table 1. Elution Patterns and Percent Recoveries of the Organochlorine Pesticides Using Silica Gel Solid-Phase Extraction Cartridges[a]

	Amount of 0.5 μg/compound						Amount of 5 μg/compound					
	Fraction 1 (3 mL hexane)		Fraction 2 (5 mL 26-percent methylene chloride in hexane)		Fraction 3 (5 mL 10-percent acetone in hexane)		Fraction 1 (3 mL hexane)		Fraction 2 (5 mL 26-percent methylene chloride in hexane)		Fraction 3 (5 mL 10-percent acetone in hexane)	
Compound	**Avg.**	**%RSD**	**Avg.**	**%RSD**	**Avg.**	**%RSD**	**Avg.**	**%RSD**	**Avg.**	**%RSD**	**Avg.**	**%RSD**
alpha-BHC			111	8.3					111	2.4		
beta-BHC			109	7.8					111	2.7		
gamma-BHC			110	8.5					111	2.3		
delta-BHC			106	9.3					110	3.5		
Heptachlor	98.4	10.8					105	1.0				
Aldrin	96.6	9.9					108	0.9				
Heptachlor epoxide			109	7.9					112	2.8		
gamma-Chlordane			105	3.5					108	6.5		
Endosulfan I			111	6.2					114	2.6		
4,4'-DDE	104	5.7					109	1.1				
Dieldrin			110	7.8					114	2.4		
Endrin[b]												
Endosulfan II					111	2.3					110	3.0
4,4'-DDD			111	6.2					114	3.3		
Endrin aldehyde			48.9	14.0	47.7	12.4			52.4	3.1	41.9	9.9
4,4'-DDT[c]	40.1	25.5	16.7	24.3	63.4	3.2	44.6	10.3	19.4	25.9	63.3	4.1
Endosulfan sulfate[c]												
4,4'-Methoxychlor			84.5	22.2	33.6	29.0			94.3	10.4	26.1	10.2

[a]1-g LC-Silica gel solid-phase extraction cartridges (Supelco Inc.) were used. The amount of pesticides loaded onto the cartridges is 0.5 or 5.0 μg per compound (or 2 mL of a 0.25-μg/mL or 2.5-μg/mL solution in hexane). Fraction 1 was eluted with 3 mL hexane, Fraction 2 with 5 mL 26-percent methylene chloride in hexane, and Fraction 3 with 5 mL 10-percent acetone in hexane. The number of replicates is 4.
[b]Data not available.
[c]These compounds coelute on the 30-m x 0.25-mm ID DB-5 fused-silica capillary column.

Table 2. Elution Patterns and Percent Recoveries of the Organochlorine Pesticides Using Florisil Solid-Phase Extraction Cartridges[a]

	Amount of 0.5 μg/compound						Amount of 5 μg/compound					
	Fraction 1 (3 mL hexane)		Fraction 2 (5 mL 26-percent methylene chloride in hexane)		Fraction 3 (5 mL 10-percent acetone in hexane)		Fraction 1 (3 mL hexane)		Fraction 2 (5 mL 26-percent methylene chloride in hexane)		Fraction 3 (5 mL 10-percent acetone in hexane)	
Compound	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD
alpha-BHC	82.6	3.4	26.3	10.7			79.0	13.7	34.1	5.6		
beta-BHC			102	2.3					104	3.6		
gamma-BHC	35.8	13.3	77.5	3.1			32.0	20.9	82.8	3.8		
delta-BHC			99.6	1.4					103	2.3		
Heptachlor	94.4	2.3					94.8	14.8				
Aldrin	93.1	2.0					94.6	14.2				
Heptachlor epoxide			102	2.4					104	3.9		
gamma-Chlordane	47.6	9.8	65.6	3.5			44.2	18.0	73.2	5.4		
Endosulfan I			101	2.7					104	4.3		
4,4′-DDE	94.5	1.7					96.8	14.9				
Dieldrin			101	2.9					105[b]	4.4		
Endrin			57.2	7.5								
Endosulfan II			58.2	13.3	61.1	9.9			60.3	5.2	58.3	10.8
4,4′-DDD	38.5	12.3	68.8	2.9			37.7	19.9	77.3	4.9		
Endrin aldehyde			36.3	7.2	78.7	2.6			47.5	2.7	72.7	6.7
4,4′-DDT[c]	49.6	1.9	11.2	16.4	59.4	3.1	51.6	15.0	12.2	13.7	56.8	9.8
Endosulfan sulfate[c]												
4,4′-Methoxychlor			96.0	3.4	11.7	3.0			105	5.5	11.2	15.0

[a]1-g LC-Florisil solid-phase extraction cartridges (Supelco Inc.) were used. The amount of pesticides loaded onto the cartridges is 0.5 μg or 5.0 μg per compound (or 2 mL of a 0.25-μg/mL or 2.5-μg/mL solution in hexane). Fraction 1 was eluted with 3 mL hexane, Fraction 2 with 5 mL 26-percent methylene chloride in hexane, and Fraction 3 with 5 mL 10-percent acetone in hexane. The number of replicates is 4.

[b]Data not available

[c]These compounds coelute on the 30-m x 0.25-mm ID DB-5 fused-silica capillary column.

Table 3. Percent Recoveries of the Aroclors Using Florisil and Silica Gel Solid-Phase Extraction Cartridges

	Percent Recovery[a]	
Compound	LC-Florisil (1g)	LC-Silica Gel (1g)
Aroclor 1016	105	124
Aroclor 1221	76.5	93.5
Aroclor 1232	90.1	118
Aroclor 1242	93.6	116
Aroclor 1248	97.2	114
Aroclor 1254	95.4	108
Aroclor 1260	89.7	112

[a] 1-g LC-Florisil or LC-silica gel solid-phase extraction cartridges (Supelco Inc.) were used. The amount of Aroclor loaded onto each cartride is 10 μg (or 2 mL of a 5-μg/mL solution in hexane). Hexane (3 mL) was used as eluent.

Phthalate Esters

Florisil and alumina SPE cartridges were evaluated for their use in phthalate ester analysis. These cartridges were chosen because the current SW-846 Method 8060 recommends use of either Florisil (Method 3620) or alumina (Method 3610) for cleanup of sample extracts containing phthalate esters. In Method 3620, Florisil (60/80 mesh) is activated for 16 hours at 140°C and then deactivated with water (3 percent by weight). The charged Florisil column is eluted with hexane (40 mL) to remove interfering compounds; phthalate esters are then recovered with 100 mL of 20-percent diethyl ether in hexane. In Method 3610, neutral alumina, activity Super I, W206 series, is activated for 16 hours at 400°C and then deactivated with water (3 percent by weight). The charged alumina column is eluted with 35 mL hexane to remove interfering compounds; phthalate esters are then recovered with 140 mL of 20-percent diethyl ether in hexane.

The Florisil procedure with 10-g glass columns was applied for the determination of 16 phthalate esters; bis(2-methoxyethyl), bis(2-ethoxyethyl), and bis(2-n-butoxyethyl) phthalates were not recovered at all, whereas dimethyl and diethyl phthalates gave recoveries of only 40 and 57 percent, respectively.

To improve the recoveries of the five phthalate esters mentioned above, we have taken Florisil and alumina SPE cartridges of 0.5-g, 1.0-g, and 2-g size, charged them with our target compounds and interferents, and eluted them with 10 percent acetone in hexane (for Florisil) and 20 percent acetone in hexane (for alumina). We first attempted the elution of the phthalate esters from the alumina column with 20 percent diethyl ether in hexane. Since none of the phthalate esters was recovered after 10 mL solvent passed through the cartridge, we changed the eluting solvents to 10 percent acetone in hexane and later to 20 percent acetone in hexane to improve the recovery of bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate and bis(2-n-butoxyethyl) phthalate. The results of these experiments are summarized in Tables 4, 5, and 6.

The data shown in Table 4 indicate that all but two phthalate esters can be recovered from a 0.5-g or a 1.0-g Florisil SPE cartridge with 5 mL 10-percent acetone in hexane (Fraction 1) and from a 2.0-g cartridge with 10 mL 10-percent acetone in hexane (no phthalate esters were recovered in Fraction 1, therefore an additional fraction had to be collected). The two phthalate esters that could not be recovered are bis(2-methoxyethyl) phthalate and bis(2-ethoxyethyl) phthalate. When working with the 0.5-g Florisil cartridge, these two phthalate esters were recovered almost quantitatively by eluting the cartridge with an additional 5 mL 10-percent acetone in hexane; however, they could not be recovered from either the 1.0-g or the 2.0-g Florisil cartridge under similar conditions. The alumina cartridge procedure (Table 5) allowed recovery of all 16 phthalate esters except for one compound, bis(2-methoxyethyl) phthalate, from the 2.0-g cartridge.

Matrix interferents such as corn oil, diesel hydrocarbons, elemental sulfur, and organochlorine pesticides (in the case of phthalate esters only) were added to hexane solutions containing the target analytes at known concentrations, and were then subjected to the Florisil or alumina SPE cartridge procedure to establish if there are any changes in the compound elution pattern and in their recovery when matrix interferents are present (Table 6). Such interferents were selected because they mimic typical background contamination in certain environmental sample matrices that could also be contaminated with the target compounds. For example, corn oil would be representative of fatty acid triglycerides, diesel hydrocarbons of petroleum hydrocarbons, and organochlorine pesticides (in the case of phthalate esters only) of compounds of environmental significance that would be expected to behave in the same way as the target analytes chosen for investigation in this study. The data presented in Table 6 indicate that neither corn oil nor diesel hydrocarbons affect the elution patterns of the 16 phthalate esters. Corn oil is also removed from the Florisil cartridge with 10 percent acetone in hexane. Fortunately, its presence does not seem to affect the determination of the 16 phthalate esters. This statement is true only for corn oil concentrations below 0.2 mg/mL of solvent (or 1 mg per cartridge) because this is the maximum concentration we used. Diesel hydrocarbons do not seem to cause problems with the quantification of the phthalate esters because the detector is transparent to aliphatic hydrocarbons. Nonetheless, we are in the process of establishing how much corn oil and diesel hydrocarbons are eluted in Fraction 1.

Use of SPE cartridges reduces solvent and adsorbent requirements and labor cost in sample preparation. Because such cartridges are prepackaged and ready for use, there is no need for adsorbent calibration, activation, or deactivation. Sets of up to 24 sample extracts, depending on the capacity of the vacuum manifold, can be cleaned up simultaneously with no danger of sample contamination. Thus, sample throughput is increased significantly.

Table 4. Elution Patterns and Percent Recoveries of the Target Phthalate Esters from the Florisil SPE Cartridges Using 10 Percent Acetone in Hexane[a]

	0.5-g cartridge						1.0-g cartridge						2.0-g cartridge					
Compound	40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 2		80-µg spike Fraction 2		120-µg spike Fraction 2	
Dimethyl phthalate	98.9	101	81.2	80.8	73.9	76.4	91.1	87.6	42.1	57.7	28.5	35.7	70.9	95.3	37.1	39.5	63.6	72.9
Diethyl phthalate	108	113	91.3	93.1	83.7	85.3	99.5	95.1	81.2	87.3	78.6	76.5	111	94.0	100	101	107	107
Diisobutyl phthalate	109	106	92.8	91.7	87.8	91.8	94.9	88.6	88.7	92.1	90.6	88.1	114	103	92.2	92.8	86.9	86.0
Di-n-butyl phthalate	104	107	87.4	88.5	80.1	83.1	100	105	89.1	87.4	87.9	85.8	108	108	91.4	92.4	82.5	80.9
Bis(4-methyl-2-pentyl) phthalate	106	114	98.2	95.9	86.4	90.2	112	99.1	95.4	94.1	92.5	89.2	115	116	94.8	95.8	105	98.5
Bis(2-methoxyethyl) phthalate[b]	16.0	15.6	11.9	14.8	10.7	15.9	c	c	c	c	c	c	c	c	c	c	c	c
Diamyl phthalate	107	111	94.8	91.5	82.7	87.9	96.8	92.1	89.4	92.5	88.1	85.6	113	106	91.8	92.3	83.4	82.6
Bis(2-ethoxyethyl) phthalate[d]	96.6	97.6	74.7	69.3	65.8	71.6	96.0	91.1	d	d	d	d	d	d	d	d	d	d
Hexyl 2-ethylhexyl phthalate	99.6	98.4	75.6	75.9	65.3	68.9	101	90.8	70.6	70.2	66.1	63.9	83.9	93.8	68.9	84.3	77.8	77.5
Dihexyl phthalate	105	109	91.0	87.6	78.6	86.0	99.4	94.1	88.6	87.9	85.1	82.5	106	103	86.4	90.9	80.6	78.3
Butyl benzyl phthalate	108	109	84.1	82.3	67.5	71.3	99.8	97.3	80.4	82.8	70.1	69.5	109	104	83.2	93.9	101	97.2
Bis(2-ethylhexyl) phthalate	113	117	98.5	94.3	83.2	91.4	105	89.9	95.3	102	97.4	93.5	118	112	98.3	95.9	94.1	87.0
Bis(2-n-butoxyethyl) phthalate	111	111	92.1	87.6	76.5	84.5	95.6	87.4	68.0	74.7	47.1	50.2	111	65.8	82.9	84.4	81.5	77.6
Dicyclohexyl phthalate	91.4	81.6	62.9	61.7	53.5	57.0	97.0	84.1	62.0	53.7	59.0	48.0	69.6	72.0	59.9	57.3	72.2	59.9
Di-n-octyl phthalate	120	114	102	93.2	83.3	95.4	99.9	94.3	98.1	97.9	98.5	93.0	114	115	103	99.4	97.3	86.9
Dinonyl phthalate	118	118	103	92.2	83.1	95.9	111	98.8	98.1	100	98.3	94.8	118	115	101	99.3	92.8	88.5

[a] Each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Fraction 1 was eluted with 5 mL 10-percent acetone in hexane; Fraction 2 with 5 mL 10-percent acetone in hexane. A third fraction was collected from the 2-g cartridge by elution with 5 mL 10-percent acetone in hexane.

[b] Additional bis(2-methoxyethyl) phthalate was recovered from the 0.5-g Florisil cartridge by eluting the cartridge with an additional 5 mL 10-percent acetone in hexane. The recoveries in Fraction 2 were 70.3 and 71.3 percent for the 40-µg spike, 55.4 and 54.3 percent for the 80-µg spike, 53.4 and 54.1 percent for the 120-µg spike.

[c] Compound not recovered even when the cartridge was eluted with an additional 5 mL 10-percent acetone in hexane.

[d] Bis(2-ethoxyethyl) phthalate was recovered by eluting the cartridge with an additional 5 mL 10-percent acetone in hexane. Total recoveries were 75.1 and 79.3 percent for the 80-µg spike (1.0-g cartridge), 57.3 and 56.5 percent for the 120-µg spike (1.0-g cartridge), 94.6 percent for the 40-µg spike (2-g cartridge), 55.4 and 62.0 percent for the 80-µg spike (2.0-g cartridge), 70.2 and 79.0 percent for the 120-µg spike (2.0-g cartridge).

Table 5. Elution Patterns and Percent Recoveries of the Target Phthalate Esters from the Alumina SPE Cartridges of Various Sizes by Elution with 20 Percent Acetone in Hexane[a]

Compound	0.5-g cartridge						1.0-g cartridge						2.0-g cartridge					
	40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1	
Dimethyl phthalate	106	108	67.8	72.6	69.5	71.3	108	117	100	92.1	115	113	98.6	93.8	92.3	73.2	84.1	93.0
Diethyl phthalate	111	112	76.2	78.9	73.1	75.3	139	148	106	125	126	127	106	108	105	102	112	104
Diisobutyl phthalate	92.5	94.3	79.8	80.6	116	115	77.5	85.4	93.8	108	96.9	94.0	84.6	86.5	119	110	99.8	100
Di-n-butyl phthalate	101	103	83.8	86.7	913	89.6	101	109	109	121	103	101	95.4	94.6	108	103	98.2	92.8
Bis(4-methyl-2-pentyl) phthalate	98.8	96.4	81.4	82.6	100	109	75.1	90.4	92.3	107	83.3	81.5	81.8	80.3	101	98.1	81.5	78.8
Bis(2-methoxyethyl) phthalate	98.8	104	76.0	79.4	87.7	88.8	87.1	93.8	92.2	101	90.3	88.5	b	b	b	b	b	b
Diamyl phthalate	103	104	83.6	83.2	99.3	98.7	92.4	101	103	116	95.0	93.0	82.4	84.4	98.6	94.9	87.7	83.3
Bis(2-ethoxyethyl) phthalate[c]	107	110	80.9	84.6	95.2	94.5	96.5	105	97.7	109	103	96.6	81.6[c]	67.9[c]	76.9[c]	55.8[c]	45.6[c]	70.3[c]
Hexyl-2-ethylhexyl phthalate	102	104	68.3	72.0	78.1	69.8	81.1	104	90.3	110	87.4	86.2	74.9	78.8	94.1	87.9	78.5	74.2
Dihexyl phthalate	101	100	81.5	87.4	101	85.4	116	126	94.9	106	118	116	95.5	97.8	87.8	81.6	101	93.7
Butyl benzyl phthalate	113	116	59.2	61.9	62.0	60.5	103	110	99.1	106	104	103	89.3	91.0	96.8	92.8	94.5	88.4
Bis(2-n-butoxyethyl) phthalate	86.4	78.5	83.0	91.1	117	113	88.1	92.5	99.4	110	104	103	73.3	73.9	101	96.5	87.3	79.5
Bis(2-ethylhexyl) phthalate	112	112	77.3	87.8	96.6	913	99.4	107	100	113	93.5	92.0	85.6	87.0	99.1	93.1	90.2	85.6
Dicyclohexyl phthalate	100	102	63.9	62.3	73.5	72.6	99.3	105	92.4	106	90.5	89.9	57.4	59.1	82.1	71.1	60.7	57.5
Di-n-octyl phthalate	84.3	74.3	79.6	90.5	103	101	93.3	108	101	113	103	102	85.6	86.5	101	97.1	93.1	85.9
Dinonyl phthalate	77.1	66.2	80.7	89.5	96.4	94.7	106	114	103	114	113	110	88.9	91.5	100	96.1	102	92.9

[a]Each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Fraction 1 was eluted with 5 mL 20-percent acetone in hexane; Fraction 2 with 5 mL 20-percent acetone in hexane. A third fraction was collected from the 2-g cartridge by elution with 5 mL 20-percent acetone in hexane.

[b]Bis(2-methoxyethyl) phthalate was recovered from the 2.0-g alumina cartridge by eluting the cartridge with two additional 5 mL 20-percent acetone in hexane (Fractions 2 and 3). The recoveries in Fraction 2 are 77.6 and 50.9 percent (40-µg spike), 57.8 and 46.2 percent (80-µg spike), 26.3 and 61.5 percent (120-µg spike). The recoveries in Fraction 3 are 38.1 percent (40-µg spike), 37.9 and 48.1 percent (80-µg spike), 38.1 and 31.9 percent (120-µg spike).

[c]Additional bis(2-ethoxyethyl) phthalate was recovered from the 2.0-g alumina cartridge by eluting the cartridge with an additional 5 mL 20-percent acetone in hexane. The recoveries in Fraction 2 are 13.3 and 30.9 percent (40-µg spike), 28.6 and 55.9 percent (80-µg spike), 62.7 and 28.9 percent (120-µg spike).

Table 6. Percent Recoveries of the Phthalate Esters from Florisil and Alumina SPE Cartridges When Interferents are Present[a]

Compound	Florisil Cartridge: Corn Oil (1000 μg per Cartridge)		Florisil Cartridge: Diesel Hydrocarbons (2000 μg per Cartridge)		Alumina Cartridge: Corn Oil (1000 μg per Cartridge)		Alumina Cartridge: Diesel Hydrocarbons (2000 μg per Cartridge)	
Dimethyl phthalate	119	123	106	111	105	104	92.5	94.4
Diethyl phthalate	133	133	123	129	120	119	92.5	94.4
Diisobutyl phthalate	101	104	111	107	88.8	87.7	82.8	85.8
Di-n-butyl phthalate	111	111	110	114	92.4	91.1	88.7	90.4
Bis(4-methyl-2-pentyl) phthalate	104	104	93.2	95.7	61.2	63.1	69.8	71.0
Bis(2-methoxyethyl) phthalate[b]	[b]	[b]	[b]	[b]	81.4	81.8	74.1	75.8
Diamyl phthalate	96.6	96.8	98.8	98.8	82.7	83.1	74.9	76.9
Bis(2-ethoxyethyl) phthalate[c]	53.3	64.6	43.7	32.3	70.9	71.8	66.0	67.9
Hexyl 2-ethylhexyl phthalate	89.8	91.2	87.1	86.6	74.3	82.9	71.1	73.1
Dihexyl phthalate	108	106	103	104	99.8	98.9	90.3	91.5
Butyl benzyl phthalate	106	107	102	104	93.8	92.6	84.6	87.3
Bis(2-ethylhexyl) phthalate	99.9	99.4	92.1	94.6	83.3	83.1	72.6	74.6
Bis(2-n-butoxyethyl) phthalate	104	104	98.8	100	87.8	87.9	88.3	81.6
Dicyclohexyl phthalate	81.4	81.2	68.2	68.2	81.8	81.3	72.0	73.8
Di-n-octyl phthalate	109	108	102	103	93.1	92.7	80.9	82.7
Dinonyl phthalate	114	114	107	111	98.5	99.2	86.4	88.3

[a] 1-g cartridges were used for this experiment. Each cartridge was preconditioned with 4 mL hexane. Each experiment was performed in duplicate. The Florisil cartridge was eluted with 5 mL 10-percent acetone in hexane. The alumina cartridge was eluted with 5 mL 20-percent acetone in hexane.

[b] Bis(2-methoxyethyl) phthalate was recovered from the Florisil cartridge by eluting the cartridge with an additional 5 mL 10-percent acetone in hexane. The recoveries are 81.9 and 95.6 percent when corn oil was present as interferent and 71.5 and 62.3 percent when diesel hydrocarbons were the interferents.

[c] Additional bis(2-ethoxyethyl) phthalate was recovered from the Florisil cartridge by eluting the cartridge with an additional 5 mL 10-percent acetone in hexane. The recoveries in Fraction 2 are 41.6 and 31.7 percent when corn oil was present as interferent, and 56.8 and 63.4 percent when diesel hydrocarbons were the interferents.

Work is in progress to evaluate commercially available workstations which employ robotic systems for cartridge conditioning, sample loading, and elution.

NOTICE

Although the research described in this abstract has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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THE APPLICATION OF SUPERCRITICAL FLUID CAPILLARY CHROMATOGRAPHY TO THE ANALYSIS OF APPENDIX-VIII AND IX COMPOUNDS

DR. MARK F. MARCUS Director of Analytical Programs, DR. PETER A. POSPISIL Manager Methods Development, MATT A. KOBUS Chemist, Methods Development Chemical Waste Management, Inc. 150 West 137th Street Riverdale, IL 60627

ABSTRACT

Supercritical fluid chromatographic technology, was used to successfully chromatograph over 270 Appendix VIII and IX compounds on a single column, within one hour. Retention times, response factors and chromatographic conditions for the analysis of a very broad range of compound classes are presented.

The Appendix VIII and IX lists define the compounds of major regulatory importance in a broad range of solid wastes and groundwater. They include upwards of several hundred organic substances, covering a broad compositional, polarity, volatility, thermal and hydrolytic stability ranges. Some of the entries are mixtures such as coal tar, creosote, cresols, PCB'S, aflatoxins, and dioxins, which may contain hundreds of individual components. Significant numbers of these compounds can be difficult to determine by existing analytical techniques because of their lack of volatility and low thermal stability. The application of this technology will cost reduce and streamline existing practices and open new avenues of analytical research in the areas of improved calibration and confirmatory analysis.

INTRODUCTION

In July 1982, the Environmental Protection Agency issued interim RCRA regulations setting permit procedures and operating standards for hazardous waste land disposal facilities. The regulations require disposal facility owners to analyze hazardous wastes and ground water for a broad range of materials of major regulatory importance.

The Appendix VIII and IX lists include upwards of several hundred organic and inorganic substances, excluding organic isomers, which are considered by the EPA to present a potential public health hazard. These compounds cover a broad compositional, polarity, volatility, thermal stability and hydrolytic stability range. Some of the entries are mixtures such as coal tar, creosote, cresols, PCB'S, aflatoxins, and dioxins, which may contain hundreds of individual components. The following presents the predominant organic compound types encountered in the lists.

Major Organic Compound Types on Appendix VIII and IX Lists

Chloro, nitro, methyl, amine and hydroxy substituted single ring aliphatics and aromatics
Low carbon number halogenated and oxygenated aliphatics, olefinics and amines.
Fused aromatic ring hydrocarbon and nitrogen compounds. PNA's, PCB's, acridines, including some having halogen substitution.
Phthalates, ethers, ketones, alcohols
Nitrosoamines, nitriles
Organo - arsenic, mercury and selenium compounds
Carbamates, ureas, thioureas, hydrazides
Biochemicals, and biologically derived materials

SW-846 is the principal document for the analysis of these materials for the numerous matrices in which they occur. The methods are primarily based on compound volatility producing methods for volatiles, semi-volatiles, non-volatiles etc. To analyze these diverse analyte types in their broad matrix ranges requires extensive sample preparation and a variety of analytical procedures. The organic component methods may require Soxhlet extraction, sonication or purge and trap procedures to separate the analytes from their matrices and prepare them for analysis. Packed and capillary column, gas chromatographic and liquid chromatographic procedures are used to obtain a separation and mass spectrometry for confirmation.

The implementation of the 3rd third RCRA reauthorization requires that a large number of the Appendix VIII and IX compounds be analyzed. The purpose of this work is to show the feasibility of using supercritical fluid chromatography as an alternate approach to the analysis of the broad range of Appendix-VIII and IX organic compounds. The broad benefit will be the introduction of new technology to the environmental analytical community. The more direct goal is to reduce the number of protocols to decrease analytical time and cost. Overall, the ultimate effect will be to broaden the environmental analytical applicability and use.

The approach to this work was to use supercritical fluid instrumentation to generate retention time and response factor data for a large number of the Appendix VIII and IX materials.

Three hundred and fourtythree organic compounds, were selected from both lists as potential analytes. Representative components were chosen for entries representing mixtures, isomer groups, or cogeners such as coal tars, creosotes, and dioxins. Fifty two compounds were either not available, excessively volatile, chemically reactive or FID insensitive, leaving 291 remaining for the study. An overall numerical summary is presented below. Listings of the compounds in both categories are presented in Tables 1 and 2.

Compound Numerical Summary

Total Organic Compounds applicable to study	343
Non-obtainable, excessively volatile, reactive or FID unresponsive compounds	52
Materials available for study	291

SCF THEORY

Supercritical fluid chromatography combines the best qualities of gas and liquid chromatography into one technique and is well suited for the separation of complex mixtures, whose components cover an extensive physical, volatility and thermal stability range,

Supercritical mobile phases are comprised of non-associated molecules and have unique physical properties intermediate between those of liquids and gases,. Their lower viscosities and higher diffusion coefficients approximate those of gases, resulting in low column pressure drops and rapid mobile/liquid phase equilibration, an improvement compared to HPLC. Supercritical fluid densities and solvencies approach those of liquids, allowing analyte dissolution, and thus partition, between the mobile and stationary phase.

Chromatographic efficiencies approach those of gas chromatography, but the technique is not thermally driven making the technology ideal for the analysis of higher molecular weight, thermally labile, and polyfunctional compounds, insufficiently volatile or too polar for gas chromatography. Both packed and capillary columns can be used with a variety of detectors.

The solvency of the mobile phase is a function of its density, which has the same effect on an SFC separation as temperature and solvent composition have on gas and liquid chromatography. The relation between fluid pressure and density is usually not linear, and when utilizing density programming, the system controller must vary the pressure to linearize the density.

EXPERIMENTAL

REFERENCE MATERIALS

The reference materials were acquired from the Aldrich Co., Chem Service Inc., Sigma Chem Co. and the Quality Assurance Branch of the EPA located in Cincinnati Ohio.

The reference materials were prepared, at a 5000 mg/liter concentration, using carbon disulfide to minimize solvent peak interference. Methanol, acetone, water, toluene, and acetonitrile were used when required for compounds not soluble in carbon disulfide. Because a carbon disulfide impurity elutes at a retention time of about four minutes, the relatively volatile components of the lists eluting close to this interference were run neat.

INSTRUMENTATION

A Lee Scientific, Model-501 supercritical fluid instrument, consisting of the following components, was used for this work:

System Controller - An IBM PC based unit, with a 4.5x5.5 inch screen, directed the control and timing of all chromatographic pressure, density and temperature operations.

Syringe Pump - A 150 mL cooled unit supplying liquid CO_2 to the chromatograph at a maximum operating pressure of 410 atmospheres, (6150 PSI).

Chromatograph - A modified HP-5890 equipped with a flame ionization detector (FID).

Chromatographic Injector - A timed split injector valve was installed, in place of a capillary injector linked to a sample splitter. The unit consists of a high speed, pneumatically actuated, reversible, rotary valve capable of placing variable, but reproducible, amounts of sample on to the capillary column. A 200 nanoliter injection loop was chosen for this work.

Chromatographic column - Biphenyl, 10 meter, 100 micron, 0.15 micron film thickness, linked to a 100 micron frit.

Autosampler - A Micromeritics 728 autosampler with a total capacity of 64 samples.

Data Processing and Storage - An HP 3396A integrator and 9114B disk drive is used to process and store all data and data processing methods.

Cooling Unit - A Neslab RTE-110 constant temperature bath maintains the syringe pump and injector temperature at a temperature of $0^{o}C$. This facilitates filling the syringe pump and minimizes over heating of the injection valve, located adjacent to the chromatographic oven.

Purified Carbon Dioxide - Supplied by the Scott Specialty Gas Co.

EXPERIMENTATION

Carbon dioxide was selected as the mobile phase because of its low critical temperature, inertness, safety (it's nontoxic, nonflammable, nonexplosive), ease of purification, lack of response in an FID, and column compatibility. Samples were injected using a time split injector. The injection duration time of the injection valve was adjusted to transfer 20 % of the loop contents, 40 nanoliters, of the 5000 PPM reference solutions directly onto the column. This was reduced to 3.4 nanoliters for the materials run neat. The chromatographic conditions, shown below, were selected to produce a separation of all the components, with some focus on semi and non-volatile materials, within a chromatographic run time of about one hour.

Supercritical Fluid Chromatographic Operating Conditions

Injector Temperature 0°C. Detector Temperature 350°C
Time split injection duration - 0.1 seconds
Injection volume - 40 nanoliters
Approximate linear velocity range equals 0.8 to 4.5 cm/sec.

Time (min)	Pump Conditions		Oven
	density g/mL	ramp rate g/mL/min	Temperature °Celsius
0.0	0.2300		100
2.0	0.2300	0.0100	
49.00	0.7000		
59.00	0.7000		

59.00 Density and pressure reset to values at time zero within 3 minutes.

The reference solutions were run sequentially, using the autosampler, with a single rinse between the vials. Simple response factors were calculated by dividing the peak area by the mass of material injected onto the column.

Two compounds, which did not elute during the first program, were run using lower oven temperature of 50°.

RESULTS AND DISCUSSION

APPENDIX VIII AND IX COMPOUNDS

Retention time and response factor data were directly generated for 270 of the 291, or 93%, Appendix VIII and IX compounds selected for this study, within a one hour run time using a single column. It is simultaneously applicable to the broad range of volatile, semi-volatile and non- volatile compound summarized in the introduction. Although the retention times for many compounds are very close, the study shows that these types of compounds can be run, thus eliminating the need to approach hazardous material analysis strictly through a compound's volatility. Retention time and response factor data for the compounds are presented in Table 1 in order of increasing retention time.

The study illustrates that supercritical fluid chromatographic technology is flexible enough to encompass the compound class distribution encountered in the area of environmental analysis. To illustrate an application, a mixture of over 40 frequently encountered materials was run

using a method providing better resolution at the lower retention time portion of the chromatogram, Figure 1. The technology is applicable to broad range mixtures such as coal tars, cresotes, and dioxins based on the data generated using selected class representative compounds and PCB's.

Twenty one materials generally having a very high polarity and large molecular weights could not be eluted with this particular chromatographic procedure, part c, Table 2. Daunomycin and nitrogen mustard were initially on the list, but were successfully rerun using a program with a lower oven temperature of 50°C. This success may be due to using a less thermally rigorous environment, or the higher CO_2 density, and thus solvencies, achievable at lower temperatures. This further increases the flexibility of this technology.

Of the 52 compounds presented in parts a and b of Table 2, many have structures very similar to compounds where retention time and response factor data has been generated. Based on these structural similarities, the authors feel that up to 317 of the 343 compounds selected for the study, about 92%, of Appendix VIII and IX organic materials can be analyzed using supercritical fluid technology.

The bulk of the response factors presented on Table 1, cover a range of 0.1 to 6. area units/microgram*10^{+7}. All of the compounds injected neat have significantly lower response factors and the reasons for this difference is under review.

POLY CHLORINATED BIPHENYLS

PCB's are of particular interest because of their occurrence in a broad range of matrices. All eight Arochlor reference materials were analyzed and a chromatogram of a mixture of Arochlors 1221, 1242 and 1260 is presented in Figure 2. The chromatogram is divided into three portions, which clearly compare with the individual, visually unique, Arochlor chromatograms. As with gas chromatography the retention time range corresponds to the molecular weight distribution of the material. The quality of the chromatography is comparable to that of gas chromatography, allowing flexibility to shorten or modify the procedure for specific purposes.

The authors feel that the demonstrated separatory power of supercritical fluid chromatography will cause it to have a very large impact in the area of environmental pollution analysis. It is a technology where the phrase "one method fits all", may have real meaning and application.

Table 1

Fifth Annual Waste Testing And Quality Assurance Symposium, Washington D.C, July 24-28 1989

RETENTION TIME AND RESPONSE FACTORS OF APPENDIX VIII AND IX COMPOUNDS

COMPOUND NAME	RETENTION TIME	RES. FACTOR (area/ug)*(E+7)	COMMENTS
Isobutanol	3.862	0.00280	i
Dichlorodifluoromethane	3.910	0.0965	i
Allyl chloride	4.095	0.000815	i
Acetone	4.149	4.149	i
Chloromethyl methyl ether	4.167	0.000994	i
Allyl alcohol	4.175	0.00283	i
Acetonitrile	4.200	0.00245	i
Acrolein	4.200	0.00350	i
1,1-Dichloroethylene	4.220	0.00117	i
Acrylonitrile	4.224	0.000784	a,i
Ethyl cyanide	4.234		
Methyl chlorocarbonate	4.246	0.00203	i
Bis(2-Chloroethoxy)methane	4.250		
Methacrylonitrile	4.260	0.00196	i
Bromodichloromethane	4.300	0.0000976	i
Dibromochloromethane	4.300	7.92	
1,1,1-Trichloroethane	4.311	0.253	
Acrylamide	4.315	0.0213	
Methyl ethyl ketone	4.335	0.000566	i
1,1-Dichloroethane	4.345	0.000297	i
1,2-Dimethylhydrazine	4.350	0.0136	i
N-Nitroso diethanolamine	4.360	0.0000645	i
Carbon tetrachloride	4.367	0.00147	i
Methy isobutyl ketone	4.373	0.00462	i
2-Nitropropane	4.380	0.00203	i
Ethyl carbamate	4.386	1.01	j
Crotonaldehyde	4.396	0.00433	i
Dimethyl sulfate	4.399	0.540	
Ethyl methacrylate	4.418	0.00278	i
Tetranitromethane	4.460		
Toluene	4.479	0.000917	i
Methyl methacrylate	4.480	0.000570	i
Methylene chloride	4.507	0.000199	i
Benzene	4.550	0.00185	i
Acetyl chloride	4.560	0.00264	i
Bis(chloromethyl)ether	4.563	1.71	i
1,2-Dichloropropane	4.567		j
Paraldehyde	4.567	0.00307	i
1,2-Dichloroethane	4.568		
cis-1,3-Dichloropropene	4.584		
trans-1,3-Dichloropropene	4.584		
Trichloroethene	4.589		
Chloroacetaldehyde	4.594		j
Chloroform	4.600	0.00175	i
Tetrachloroethylene	4.600	0.00163	i
Dibromomethane	4.623	0.238	
N-Nitroso-dimethylamine	4.634	0.00207	i
1,4-Dioxane	4.660	0.640	i
2,4-D	4.680		j
Bromoacetone	4.703	0.000829	i
1,1,2-Trichloroethane	4.711	0.0465	i
2-Picoline	4.724	5.037	i
p-Xylene	4.749	0.00276	i
m-Xylene	4.792	0.000781	i
1,1,1,2-Tetrachloroethane	4.826	0.529	a
o-Xylene	4.922	1.55	
N-Nitroso-methylethylamine	4.925	2.74	
Ethoxyethoxyethanol	5.037	2.45	
1,2,3,4-Diepoxpbutane	5.059	2.41	a
1,2-Dibromoethane	5.068	0.981	
3-Chloropropionitrile	5.079	2.16	
2-Chloro-1,3-Butadiene	5.090	0.488	a
Chlorobenzene	5.099	5.93	
N-Nitroso-diethlyamine	5.104	3.04	a
Dimethyl carbamyl chloride	5.120	1.84	
Ethyl methanesulfonate	5.122	1.79	
N-Propylamine	5.225		
trans-1,4-Dichloro-2-butene	5.282	4.24	a
Styrene	5.418		
1,2,3-Trichloropropane	5.472	2.14	a
1,1,2,2-Tetrachloroethane	5.476	0.561	a
Bis(2-chloroisopropyl)ether	5.530	1.53	
Maleic anhydride	5.547		j
N-Nitroso-N-ethylurea	5.582		j
Phenol	5.599	3.87	
2-Propyn-1-ol	5.700	0.00136	a,i
O,O,O-$(Et)_3$-phosphorothioate	5.750	2.41	
Thioacetamide	5.800	0.676	
Bis(2-chloroethyl)ether	5.875	1.10	
2-Chloroethyl vinyl ether	5.875		
m-Dichlorobenzene	5.900	5.44	
1,1-Dimethylhydrazine	6.005		
Pentachloroethane	6.021	0.388	a
2-Chlorophenol	6.085	2.18	
Hexachloroethane	6.112	0.667	
2,4-Dinitrophenol	6.126		j
Benzene, monochloromethyl	6.147	4.23	
Aniline	6.266	4.46	
p-Dichlorobenzene	6.292	2.27	
Bromoform	6.253	0.144	
p-Benzoquinone	6.305		j
Benzenethiol	6.320	2.66	
o-Cresol	6.345	4.20	
N-Nitroso-dipropylamine	6.392	4.42	
N-Nitroso-N-methyl urethane	6.414	0.330	
Acetophenone	6.542	4.38	
o-Dichlorobenzene	6.639	31.6	
p-Cresol	6.685	7.58	
m-Cresol	6.725	6.82	
N-Nitroso di-N-butylamine	6.889	4.32	
2,4-Dimethylphenol	6.920	4.37	
Benzyl alcohol	6.947	7.12	

Table 1

RETENTION TIME AND RESPONSE FACTORS OF APPENDIX VIII AND IX COMPOUNDS

COMPOUND NAME	RETENTION TIME	RES. FACTOR (area/ug)*(E+7)	COMMENTS
1,2-Dibromo-3-chloropropene	6.955	1.43	
Isophorone	7.032	2.13	d
p-Toluidine	7.075		a,j
N-Nitrosomorpholine	7.121	2.06	
Benzene, dichloromethyl	7.129	0.497	
O-Toluidine	7.305		j
1,3-Hexachlorobutadiene	7.388	1.32	
2,4-Dichlorophenol	7.426	2.81	
Hexachloropropane	7.459	0.847	
1-Nitrosopiperidine	7.660	3.50	
Safrole	7.675	4.52	
2-Chloronaphthalene	7.800	5.59	d
Nitrobenzene	7.926		j
1-Chloro-2,3-epoxypropane	7.945		j
Benzene, trichloromethyl	8.074	4.24	
Naphthalene	8.099	7.26	
o-Toluidine hydrochloride	8.255	0.720	
Hexachloropropene	8.282	2.71	
Nitroso-piperidine	8.459	11.2	
o-Nitrophenol	8.468	3.52	
1,2,4-Trichlorobenzene	8.488	2.61	
N-Nitrosopyrollidine	8.507	3.35	
2,6-Dichlorophenol	8.833	2.69	
Hexachlorocyclopentadiene	9.165	1.19	
Isosafrole	9.432	4.18	a
Nicotine	9.695	3.40	
Dimethyl phthalate	9.761	1.34	d
p-Chloroaniline	9.971	3.37	
p-Chloro-m-cresol	10.404	0.340	
N-Nitrososarcosine	10.522	0.174	
1,3-Propane sulfone	10.653	1.12	
Tolylene diisocyanate	10.742	1.59	
3,4-Toluenediamine	10.865		j
1,2,4,t5-Tetrachlorobenzene	10.958	2.24	
2-Methylnaphthalene	10.994	5.32	
Diethyl phthalate	11.046	3.51	
2,4,6-Trichlorophenol	11.307	2.26	
2,4,5-Trichlorophenol	11.490	2.16	
2-Butanone peroxide	11.817	1.54	
Phthalic anhydride	11.869	1.12	
m-Phenylenediamine	12.013		j
Diallate	12.170	1.29	a
Octamethyl pyrophosormide	12.322	2.40	a
Sulfotepp	12.998	9.17	
1-Acetyl-2-thiourea	13.006		j
1,4-Naphthoquinone	13.023	3.79	
Resorcinol	13.130	4.75	
2,6-Toluenediamine	13.154		j
Hydroxydimethylarsine oxide	13.247		j
2,4-Toluenediamine	13.265	0.387	
2,6-Dinitrotoluene	13.290	0.0167	d
Acenaphthene	13.341	5.48	
3,4-Dichlorophenol	13.652	2.43	
Parathion	13.808	1.87	
Streptozotocin	14.728	1.62	
Methyl isocyanate	14.870	0.0701	
Di-n-butyl phthalate	14.874	1.72	d
Acenaphthylene	15.001	5.45	
2,3,4,6-Tetrachlorophenol	15.290	1.57	
Disolfoton	15.324	2.63	
p-Phenylenediamine	15.356		a,j
4-Chlorophenyl phenyl ether	15.534	5.13	
Pentachlorobenzene	15.600	2.11	
m-Nitroaniline	15.684		j
4-Bromophenyl phenyl ether	15.840	1.01	d
Methomyl	16.037		j
Dibenzofuran	16.080	3.61	
Pronamide	16.163	2.27	d
4-Nitrophenol	16.870		j
2,4-Dinitrotoluene	17.078	3.10	
Phenacetin	17.103		j
1,3-Dinitrobenzene	17.345	3.80	
Tetraethylpyrophosphate	17.409	1.25	
Diphenylamine	17.410	5.87	
a-Naphthylamine	17.565	5.26	
Dimethoate	17.607		j
o-Phenylenediamine	17.758		
Endothal	17.836		j
4,6-Dinitro-o-cresol	18.004	1.73	
N-Nitroso-diphenylamine	18.055		j
1-Naphthyl-2-thiourea	18.280		a
b-Naphthylamine	18.280	5.29	
Fluorene	18.301	5.18	
5-Nitro-o-toluidine	18.429		j
1,3-Nitroaniline	18.554	1.08	
Heptachlor	19.260	0.763	d
Phorate	19.542	2.41	
a-BHC	19.645	1.75	a
DNBP	20.165	11.9	
Methyl methanesulfonate	20.441	0.000374	i
Bis(2-Ethylhexyl)phthalate	20.442	1.42	d
Phenanthrene	20.478	5.33	
Aldrin	20.790	0.952	d
Anthracene	20.800	4.59	
Hexachlorobenzene	21.064	2.02	
4-Aminobiphenyl	21.084		j
p-Nitroaniline	21.145		j
1,2-Diphenylhydrazine	21.208	2.12	a
Methyl parathion	21.225	0.666	g
2-Fluoroacetamide	21.441		j
Octachlorodibenzo-p-dioxin	21.555	1.18	
Gamma-BHC	21.765	1.88	

Table 1

RETENTION TIME AND RESPONSE FACTORS OF APPENDIX VIII AND IX COMPOUNDS

COMPOUND NAME	RETENTION TIME	RES. FACTOR (area/ug)*(E+7)	COMMENTS
Aramite	21.803	1.79	a
Pentachloronitrobenzene	21.844	18.3	
Pentachlorophenol	21.857	1.88	
Heptachlor epoxide	21.891	9.44	d
Vinyl acetate	21.970	0.154	
Phenylmercuric acid	22.075		a,j
Saccharin	22.145	1.52	d
Cyclophosphamide monohydrate	22.925		j
Butyl benzyl phthalate	23.030	2.01	d
Isodrin	23.168	2.94	a
Phenylmercuric acetate	23.332	0.284	a
Di-N-octyl phthalate	23.559	0.876	d
Ethylenethiourea	24.620	1.01	
Silvex	23.780	0.461	d
4,4'-DDE	24.780	1.48	d
2,5,5-T	24.862		
1,3,5-Trinitrobenzene	24.905		j
Dieldrin	25.000	0.0111	d
Chlorobenzilate	25.032	1.78	
Pyridine	25.075	0.0104	
Famphur	26.018	2.38	
b-BHC	26.251	0.0496	
Chlordane	26.351	1.12	a
d-BHC	26.657	1.01	a
Fluoranthene	27.017	3.51	
4-Nitroquinoline-N-oxide	27.277	2.82	
Diethyl stilbesterol	27.354		j
4,4'-DDD	27.759	1.48	d
4,4'-DDT	28.137	1.04	d
Kepone	28.524		j
1-Phenyl-2-thiourea	28.792	1.05	d
Pyrene	28.951	4.82	
p-Dimethylaminoazobenzene	29.140	3.93	a
Endrin	29.376	0.995	d
6-N-Propyl-2-thiouracil	29.515	2.26	h

COMPOUND NAME	RETENTION TIME	RES. FACTOR (area/ug)*(E+7)	COMMENTS
Methoxychlor	29.936	3.90	
Chlorambucil	30.839	3.58	
Endosulfan sulfate	31.242	0.662	
2-Acetylaminofluorene	32.713		j
Warfarin	33.528		j
Benzidine	34.565		j
1,2-Benzanthracene	34.956	1.75	e
4,4'-Methylene bis-(o-chloro-aniline)	35.738	3.82	
Chrysene	35.740	5.55	f
Cycasin	35.740		
Tris(2,3-Dibromopropyl) phosphate	36.755	1.32	
Nitrogen mustard	37.258		k
N-Methyl-N-Nitroso-N'-Nitro guanidine	37.258	0.0532	d
3,3'-Dichlorobenzidine	37.803	0.336	
Hexachlorophene	40.275	2.75	
7,12-Dimethylbenz[a] anthracene	41.464	5.52	
Benzo[b]fuuoranthene	43.100	2.42	e
3,3'-Dimethoxybenzidine	42.381	3.10	d
Benzo[k]fluoranthene	43.510	6.88	
Benzo[a]pyrene	43.804	1.78	f
3-Methylcholanthrene	45.055	5.67	
Strychnine	46.162	2.58	
Benzo[a,j]acridine	46.547	12.5	
Benzo[g,h,i]perylene	47.655	2.89	d
1,2,5,6-Dibenzanthracene	47.820		j
Selenourea	48.170		j
Brucine	48.712	3.00	
Indeno[1,2,3-C,D]pyrene	54.000	7.05	h
Resperine	61.499	0.668	g
1,2,4,5-Dibenzpyrene	62.095		k,l
Daunomycin Hydrochloride	67.698		k

NOTES

- a - This compound contains components,which produce peaks having an area greater than 5% of the major peak.
- b - This material was not soluble in CS_2 and was prepared in an aqueous medium.
- c - The peak for CS_2 may result from impurity.
- d - The solution was 100 ppm in methanol.
- e - The solution was 100 ppm in toluene.
- f - The solution was 100 ppm in methylene chloride.
- g - The solution was 1000 ppm in acetonitrile.
- h - The solution was 5000 ppm in acetone.
- i - This material was analyzed neat because of CS_2 impurity interference.
- j - This material was only partially soluble in CS_2 therefore the response factor is not calculable.
- k - This material was run with a column temperature of 50^oC.
- l - This compound was run as a surrogate for material of suspect composition.

Table 2

APPENDIX VIII AND IX COMPOUNDS

A. Materials not Available to be Analyzed

Azaserine
Benz[c]acridine
Benzo[j]fluoranthene
Chlornaphazine
Citrus Red No. 2
Dibenz[a,h]acridine
2-Cyclohexyl-4,6-dinitrophenol
7H-Dibenzo[c,g]carbazole
Dibenzo[a,h]pyrene
Dibenzo[a,i]pyrene
Dichlorophenylarsine
Diethylarsine
N,N-Diethylhydrazine
Dihydrosafrole
Diisopropyl fluorophosphate
a,a,Dimethylphenylethylamine
Di-N-propylnitrosoamine
Ethylenebisdithiocarbamic acid
Glycidylaldehyde (1-propanol-2,3-epoxy)
Hexaethyl tetraphosphate
Iron Dextran
Lasiocarpine
2-Methyllactonitrile
2-Methyl-2-(methylthio)propioaldehyde-o-(methlycarbonyl) oxime
Nitrogen Mustard N-oxide
Nitroglycerine
Nitrosomethyl vinyl amine
N-Nitrosonornicotine
Phosphorodithioic acid, O,O-Diethyl-S-methyl ester
Phosphoric acid, diethyl p-nitrophenyl ester
Thiofanox
Thionazen
Thiuram
Trichloromethanethiol
Uracil Mustard

B. Excessively Volatile, Reactive or FID Insensitive Compounds

Carbon Disulfide
Chloroethane
Chloromethane
Epinephrine
Ethylene Oxide
Ethlyenimine
Formaldehyde
Formic acid
Methanethiol
2-Methylazridine
Methyl bromide
Methyl iodide
Methyl hydrazine
Mustard gas (Sulfide, bis(2-chloroethyl)-)
Tetraethyl lead
Trichlorofluoromethane
Vinyl chloride

C. Non-Responsive Compounds

Aflatoxin-B_1
Amitrole
Auramine Hydrochloride
Benzoarsonic acid
Chloral Hydrate
1-(o-chlorophenol) thiourea
2,4-Dithiobiuret
Endosulfan
Endrin aldehyde
Fluoroacetic acid sodium salt
Maleic Hydrazide
Melphalan
Methyl pyrilene
6-Methyl-2-Thiouracil
Mitomycin-C
Muscimol
Phthalic acid
Thiourea
Thiosemicarbazide
Toxaphene
Trypan Blue

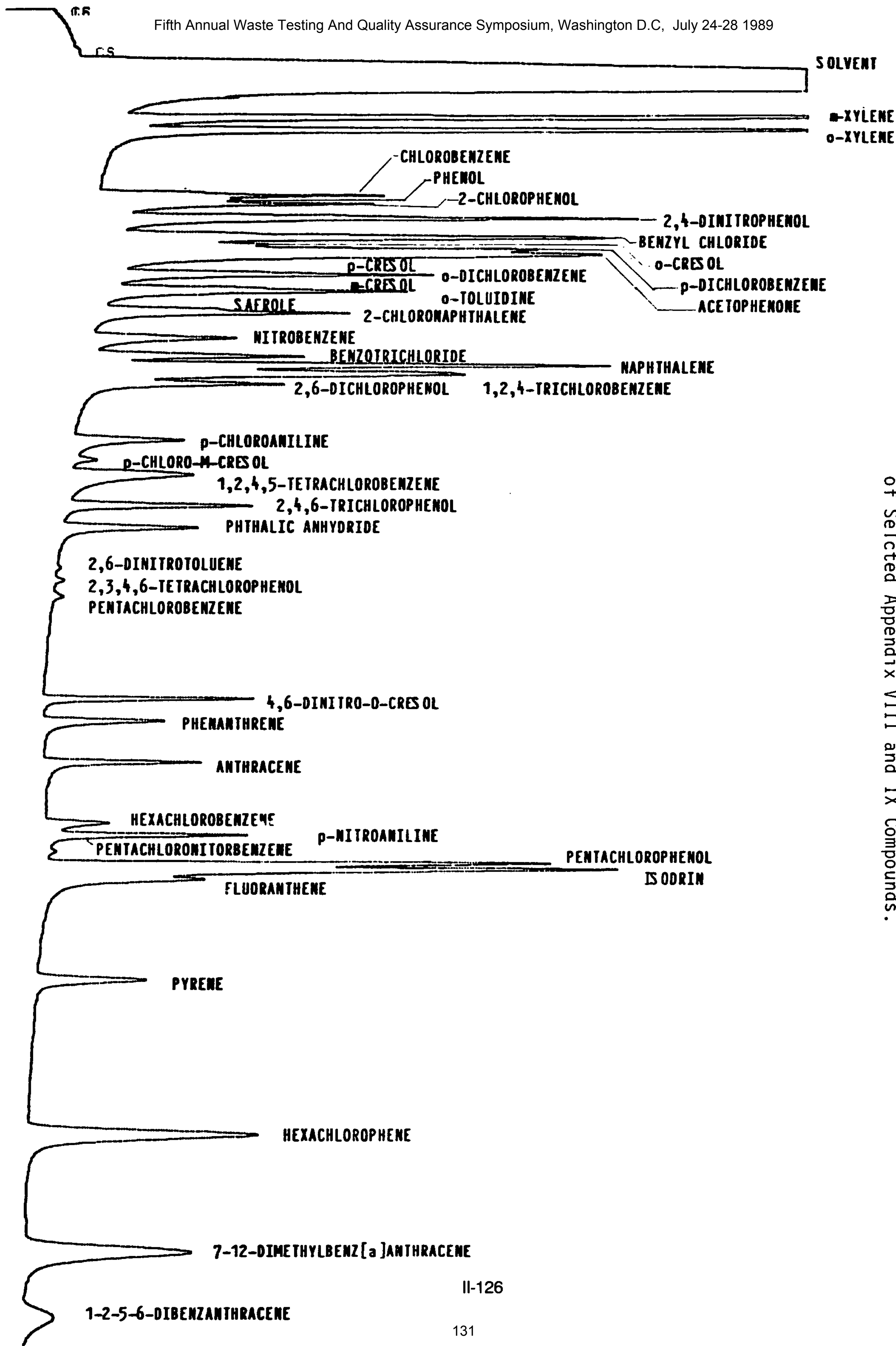

FIGURE 1
Supercritical Fluid Chromatogram of Selcted Appendix VIII and IX Compounds.

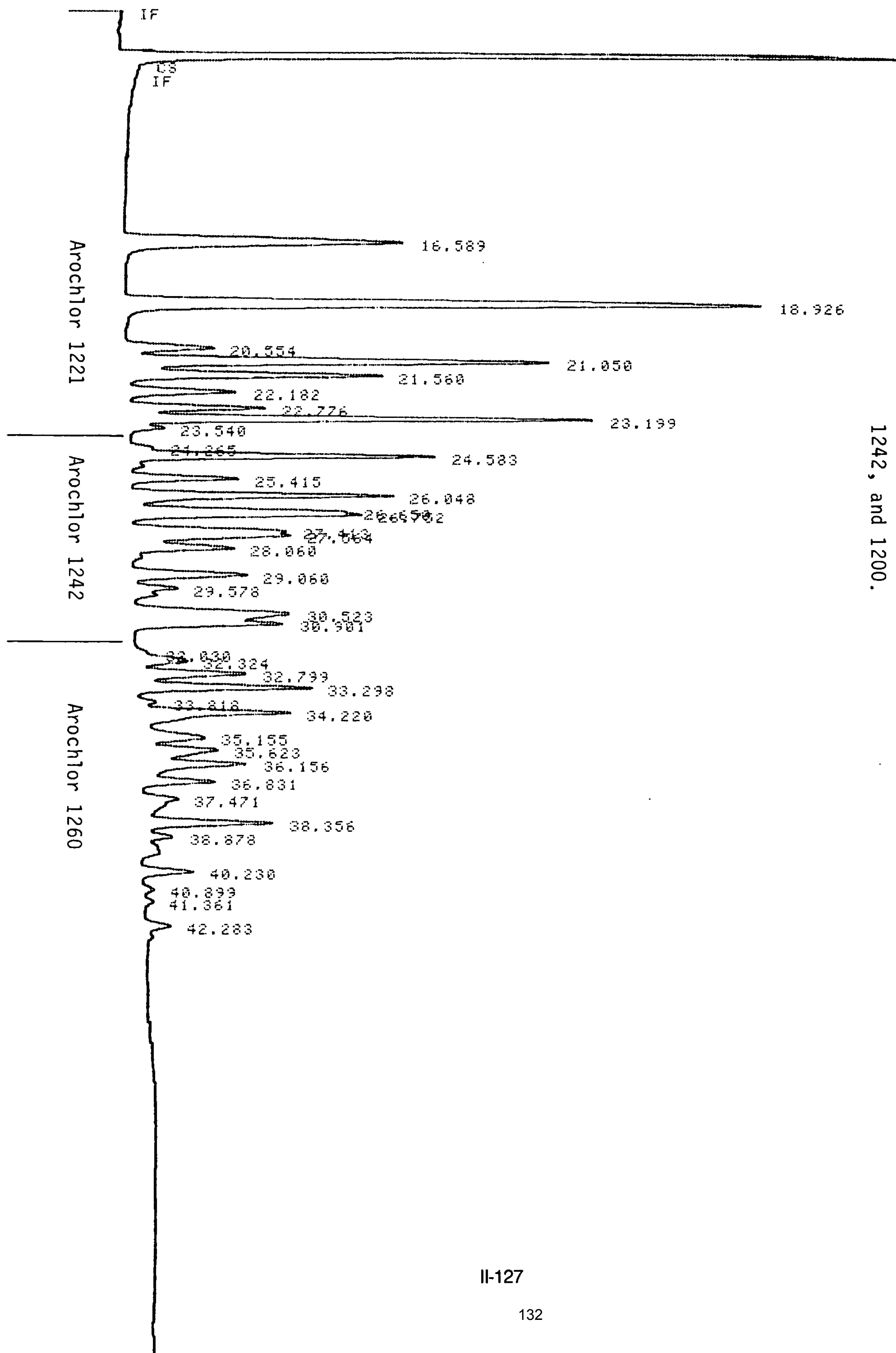

FIGURE 2

Supercritical Fluid Chromatogram of a Mixture of Arochlors 1221, 1242, and 1200.

HEADSPACE SCREENING/CAPILLARY COLUMN GC/MS ANALYSIS FOR VOLATILE ORGANICS: VALIDATION STUDIES AND APPLICATIONS

L. Richard Flynn Development Chemist, Susan W. Bass Manager GC/MS Laboratory, Robert E. Meierer Vice President Quality Assurance, CompuChem Laboratories 3308 Chapel Hill/Nelson Highway, Research Triangle Park, North Carolina 27709

Abstract

A major problem encountered in the analysis of volatile organic compounds is the wide range in concentrations of analytes found in environmental samples. High concentrations of target compounds can contaminate the liquid sampling device and the gas chromatograph/mass spectrometer system requiring cleanup. Compounds generally regarded as being semivolatile (such as naphthalene and the trichlorobenzene isomers) are also purgeable and may appear in subsequent analyses if final column temperatures are not maintained for sufficient times.

The use of megabore capillary columns facilitates the analysis of samples that contain purgeable compounds generally regarded as semivolatile. Higher maximum column temperatures and lower retention indices mean column residence times can be cut by more than half for some compounds.

The use of a headspace sampling device coupled with a gas chromatograph/mass spectrometer (GC/MS) allows the rapid characterization of sample constituents. The MS detector operated in the full scan mode provides adequate sensitivity as well as excellent specificity. Most of the compounds on the volatile target compound list are amenable to analysis using the headspace technique and information on sample constituents not in the analytical standard is available through library searches. The use of the MS as a detector reduces the requirement for chromatographic separation.

Introduction

Megabore capillary columns offer significant advantages to laboratories performing purge and trap analyses. Decreased analysis times as well as improved separations are obtained from their use.

A typical environmental analytical laboratory receives samples from a wide variety of sources and with a wide variety and concentration of purgeable compounds. The EPA Contract Laboratory Program [1] as well as the "Test Methods for Evaluating Solid Waste" (SW-846) define an analytical working range for volatile organic analyses. For most target compounds the maximum sample concentration for both water and soil samples is 200 parts per billion (ppb). Samples containing an excess of 200 ppb of a target analyte must be prepared as a dilution. Additionally, samples often contain high concentrations of non-target volatile compounds. High levels of both target and non-target compounds can contaminate the liquid sampling device and GC/MS system causing loss of analysis time while the sampling device is being cleaned. Late eluting non-target compounds may be retained on the GC column past the end of the analysis and subsequent cooling of the GC only to appear in subsequent analyses. This problem can be especially severe with the SP-1000

packed column. Depending on sample constituents and concentration level, clean-up time can be as long as twenty-four hours.

The laboratory has historically used two methods of identifying samples that might contain unacceptably high levels of either target or non-target compounds. These methods include physical inspection of the sample, noting both the odor and condition (i.e. multiple phases in a liquid sample, oily or tarlike substances in solid samples) of the sample during sample preparation, and determining the concentration of analytes in other samples from the same client. Both methods are somewhat dependent on analyst experience and all allow a significant percentage of high concentration samples to go undetected prior to analysis.

An effective screening method will allow rapid, reproducible sample analysis with a minimum of sample preparation and expense. The screening method recommended in the CLP contract [(2)] requires 40 mL of sample to be extracted with hexadecane and the extract analyzed by GC/FID. Laboratory experience shows this method suffers from poor sensitivity for certain classes of volatile compounds. Also since hexadecane freezes at 19 degrees centigrade, sample storage and handling is difficult.

Recently [(3)] a method was proposed for rapid screening of volatile samples. The method involves sampling and analyzing the headspace above a sample using a gas chromatograph equipped with a megabore capillary column and using a Hall electrolytic conductivity detector and a photoionization detector in tandem. A significant drawback to this method is the lack of information available for unidentified peaks as well as its inability to distinguish coeluting interferences from analytes of interest. In order to address the limitations of the method,it was modified by substituting a mass spectrometer for the PID/Hall detector combination.

Experimental Section

A Hewlett Packard model 19395A headspace analyzer was used as a headspace sampling device. Analytical standards containing the analytes of interest (Table I) were prepared in 15 ml of distilled/deionized, prepurged laboratory reagent water in a 20 mL Hewlett Packard headspace vial. Primary standards containing the analytes of interest were added to the vial to achieve a concentration of 60 parts per billion (ppb) for the target compounds and 10 ppb for the internal standards and surrogate. The standard was immediately sealed with a teflon lined septum, held in place with a crimp sealed cap. Prior to analysis the standard was allowed to equilibrate for a minimum of thirty minutes at 85 degrees centigrade.

Liquid samples were prepared by transferring 15 mL of sample into a 20 mL headspace vial and adding internal standards and surrogate to achieve a concentration of 10 ppb for each. The sample was immediately sealed and allowed to equilibrate for a minimum of thirty minutes prior to analysis.

Soil samples were prepared by transferring 5 grams of soil (+/- 0.5 grams) into a headspace vial and adding enough laboratory water to provide a headspace of approximately 5 mL. Primary standards containing internal standards and surrogate were added to the water to achieve an effective

concentration of 30 ppb in the soil. The samples were immediately sealed and allowed to equilibrate for a minimum of thirty minutes at 85 degrees centigrade and then were mixed at high speed for 15 seconds using a Vortex Genie(TM).

The headspace analyzer was operated with a bath temperature of 85 degrees centigrade and a valve/loop temperature of 90 degrees centigrade. Each sample was pressurized for ten (10) seconds with the vent time set to five (5) seconds. The sample was swept onto the head of the GC column for twenty (20) seconds.

The GC was operated, using liquid nitrogen cryofocusing, at an initial temperature of 0 degrees centigrade with no initial hold, ramped at 15 degrees centigrade per minute to 200 degrees centigrade and held at 200 degrees centigrade for 1 minute. Under these operating conditions the final compound in the evaluation standard (1,3,5-Trichlorobenzene) eluted at approximately twelve minutes. The GC cycle time was approximately 20 minutes. The GC column was a J&W DB-624, 0.53 mm id, megabore capillary column operated with a column flow of 25 mL per minute. A glass jet separator was used to enrich the carrier flow so that approximately 1.5 ml/minute of gas was directed into the mass spectrometer.

The mass spectrometer was operated in full scan electron impact mode scanning from m/z 48 to m/z 250 at 0.70 seconds per scan.

All calculations were made using the internal standard calculation method. Two internal standards, fluorobenzene and D4-1,2-dichlorobenzene were used for quantitations. A surrogate, bromofluorobenzene was added to each sample to measure the effectiveness of the method on a per sample basis.

Results and Discussion

A significant concern using the headspace sampling device is sample integrity. Figure 1 shows the results of the analysis of a series of eight samples analysed over an eight hour period. These samples contained only internal standards and surrogate. The integrated area for both internal standards and surrogate does not show a consistent decrease with increasing time in the headspace sampler thereby indicating that any analyte losses are due to degradation and not the result of leakage around the crimp sealed septum or diffusion across the septum.

The headspace/GC/MS combination exhibited good precision and recovery for most compounds. Table I contains selected analytes with their detection limits and average recovery. Method Detection Limits were determined using the method presented in the October 26, 1984 Federal Register [4] and reflect values at or below the contract required quantitation limit (CRQL) utilized in the CLP. There were, however, several target analytes that did not perform well with this method. Bromodichloromethane, Dibromochloromethane and Iodomethane showed either consistently decreasing recoveries or variable recoveries over time. The headspace sampler used in this study maintains the samples at an elevated temperature from the begining of an analysis sequence to the time the sample is analyzed, therefore a sample may be held at an elevated temperature for a minimum of approximately one hour to a maximum of approximately 8 hours. Table II showes the results of a series of eight sample spikes analyzed for

these compounds. Figure 2 shows a typical standard chromatogram acquired under the conditions described above. Each component in this analysis is at an effective concentration of 60 ppb.

The purge and trap chromatogram in Figure 3 shows a standard analysis acquired according to CLP methods using a DB-624 column. The last three peaks in Figure 3 are 1,2,3-trichlorobenzene, naphthalene coeluting with hexachlorobutadiene and 1,2,4-trichlorobenzene. The chromatogram in Figure 4 shows the same standard using an SP-1000 packed column. Naphthalene and the two trichlorobenzene isomers do not elute in the fifty-five minute analysis time. The last analyte to elute on the SP-1000 column is 1,2-Dichlorobenzene at 49 minutes. 1,2-Dichlorobenzene elutes at 18 minutes on the DB-624 column. Figure 5a shows an extracted ion current profile of mass 146, the key ion for the dichlorobenzene isomers. In an analysis using CLP conditions, near baseline separation is achieved between the 1,3 and 1,4-dichlorobenzene isomers with the DB-624 column. Figure 5b shows the same extracted ion current profile using an SP-1000 column operated under CLP conditions.

Figures 6a shows a chromatogram from a soil sample acquired using the headspace analyzer. Figure 6b shows the same sample acquired using SW-846/CLP analysis conditions. Although the absolute retention times are quiet different, the pattern of chromatographic peaks are very similar. The only target compound found in this analysis is chlorobenzene at scan 466 (Figure 6a) with an estimated concentration of 180 ppb. This level is near the upper limit of the analytical range of the method. The relatively high levels of a target compound as well as the extremely high levels of extraneous compounds eluting between scans 200 and 400 indicates that this sample probably should be diluted prior to analysis and be scheduled during the analytical sequence to minimize instrument down time during cleanup.

Figure 7 shows a headspace screening analysis of a sample containing high concentrations of aromatic volatile compounds. Accurate assessments of the concentrations of ethyl benzene, xylene isomers, styrene and naphthalene were not possible due to significant detector saturation but were above 500 ppb in this sample. Compounds eluting in the last 150 scans of this analysis were identified as methyl naphthalene and substituted indene isomers based on NBS library searches. The information from this screen indicated a dilution was required and that the analyst would have to take particular care in the scheduling of this sample. The late eluting methyl naphthalene and indene isomers could potentially contaminate subsequent samples either from column carryover or sampling device contamination.

Conclusion

The DB-624 column provides the GC/MS analyst a method to improve chromatographic analysis of target analytes while, at the same time reducing, analysis time significantly. The DB-624 column can be used to effectively analyze purgeable compounds that are classically characterized as semivolatile with very little sample preparation.

The headspace analyzer coupled with a GC/MS can provide a rapid, accurate screening analysis for volatile samples. The use of the mass spectrometer as a detector allows for the characterization of unknown components of a sample. Newer designs of headspace analyzer promise to minimize the problems

associated with maintaining high sample temperature for the entire analytical sequence by heating each sample for a predetermined amount of time prior to analysis.

Because of the limited sample preparation required, rapid sample analysis and good overall detection limits this method may be used to identify "hot spots" at sampling sights. Lower sample costs as well as more timely corrective action may result since a large number of field samples can be screened and only those that screen positive will require full CLP analysis.

Acknowledgements

The authors would like to thank Dr. Leroy M. Sutton and Mr. Stephen G. Walburn for their assistance in the preparation of this manuscript.

REFERENCES

1. USEPA, Statement of Work for Organic Analysis, Multi-Media Multi-Concentration, 2/88 p.D-25/VOA.

2. Ibid, p D-10/VOA.

3. USEPA Region IV, Screening Method for Volatile Organic Compounds, Revision 2, January 1987.

4. Federal Register, Vol.49 No. 209, p43430, Friday, October 26, 1984.

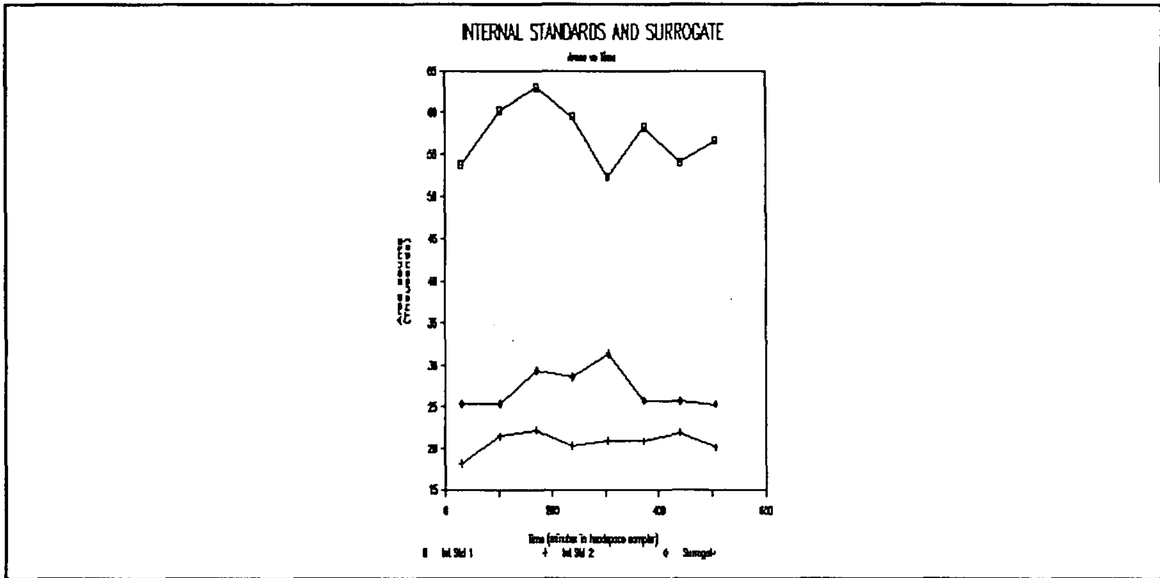

Figure 1 Graph of areas of internal standards and surrogates vs time.
IS 1 = Fluorobenzene IS 2 = D4-1,2-Dichlorobenzene
Surrogarte = Bromofluorobenzene

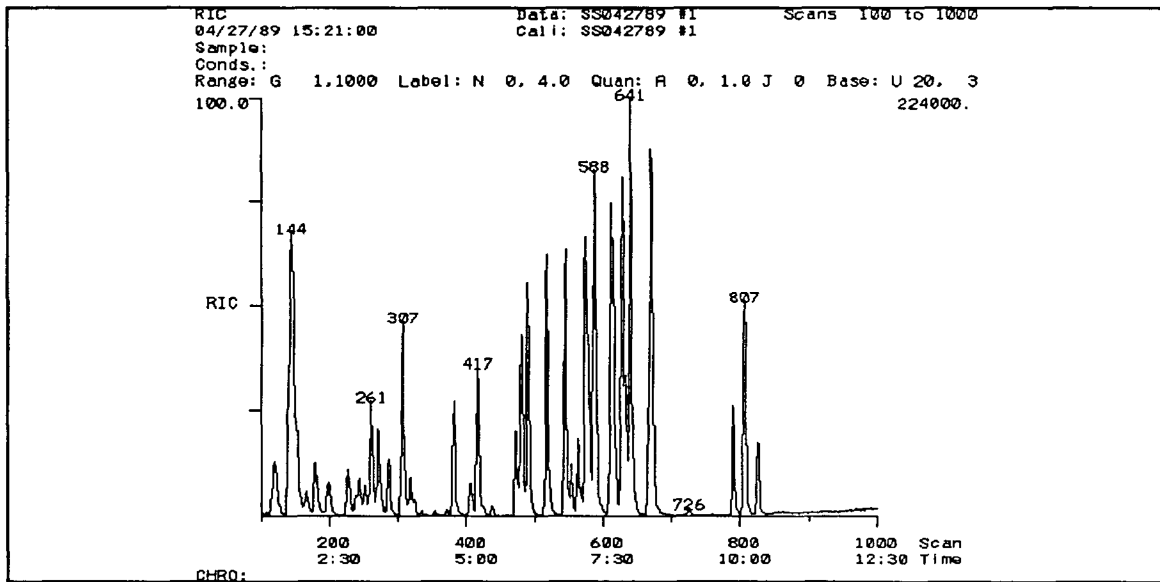

Figure 2 Chromatogram acquired using GC/MS/headspace analyzer. Standard level is 60 ppb.

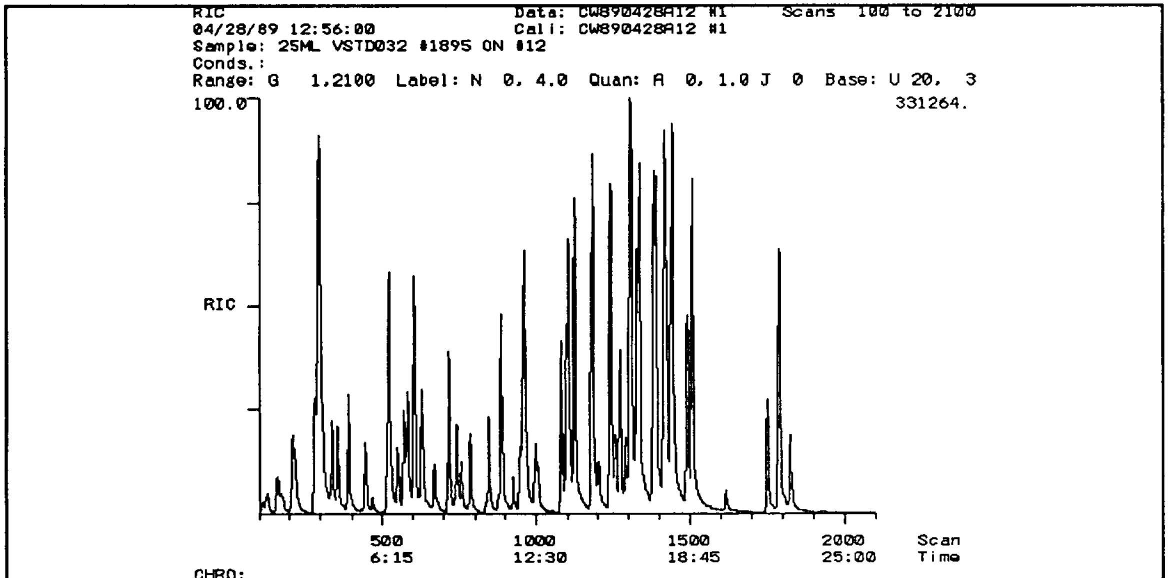

Figure 3 Chromatogram from 524.2 standard analysis. The last three peaks are 1,2,3 Trichlorobenzene, Naphthalene, and 1,2,4 Trichlorobenzene.

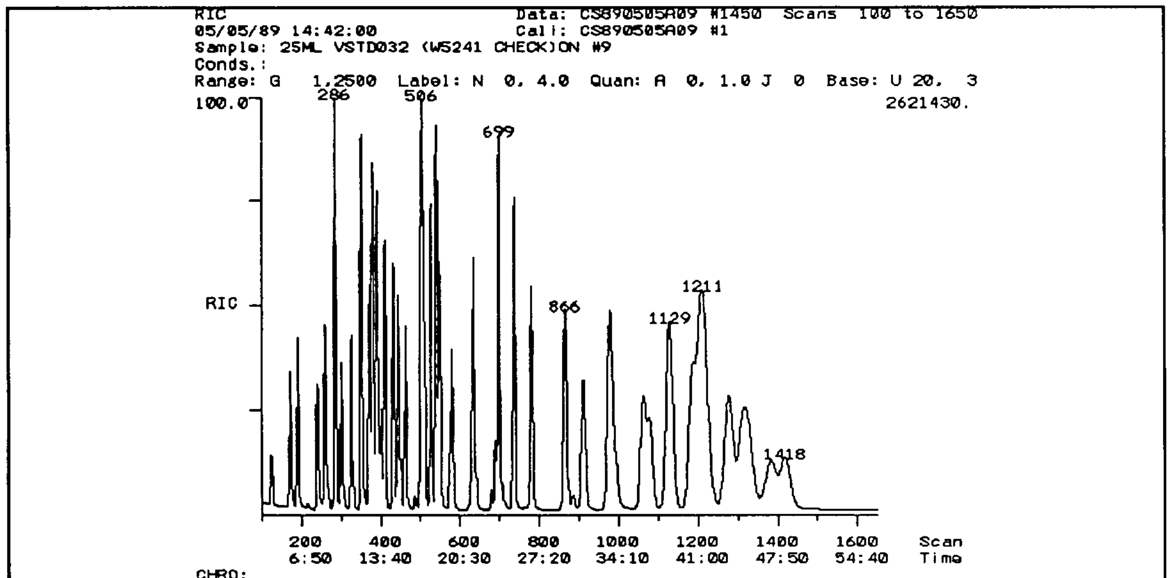

Figure 4 Standard 524.1 Chromatogram using an SP-1000 column. The last eluting peaks are the three dichlorobenzne isomers and the D4-1,2-Dichlorobenzne.

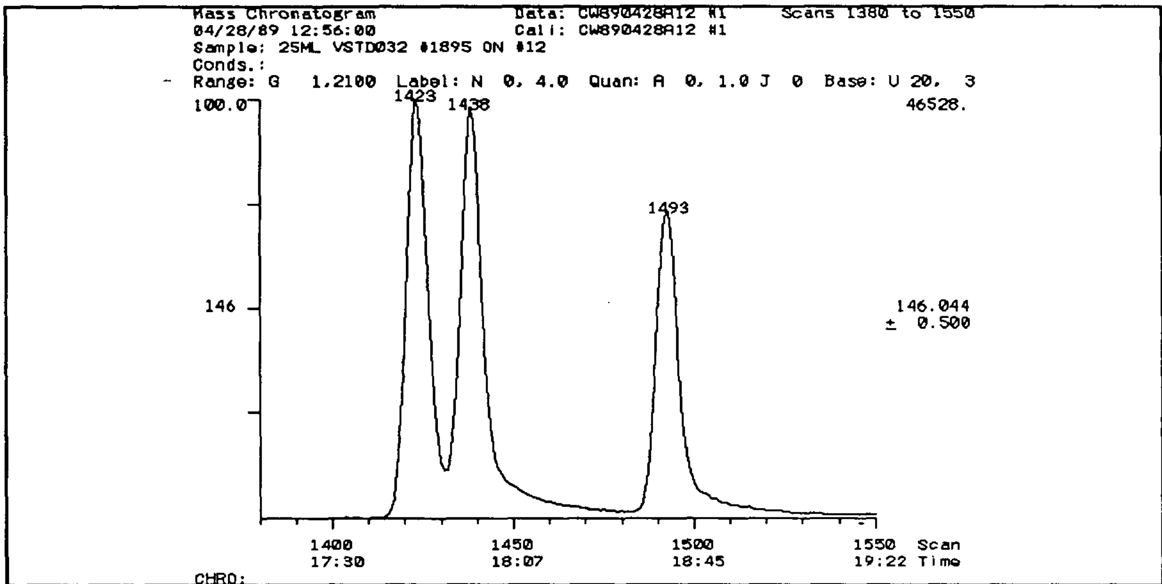

Figure 5a 1,3, 1,4, and 1,2 Dichlorobenzene isomers using a DB-624 megabore column. (Note near baseline resolution between the 1,3 and the 1,4 Dichlorobenzene isomers.)

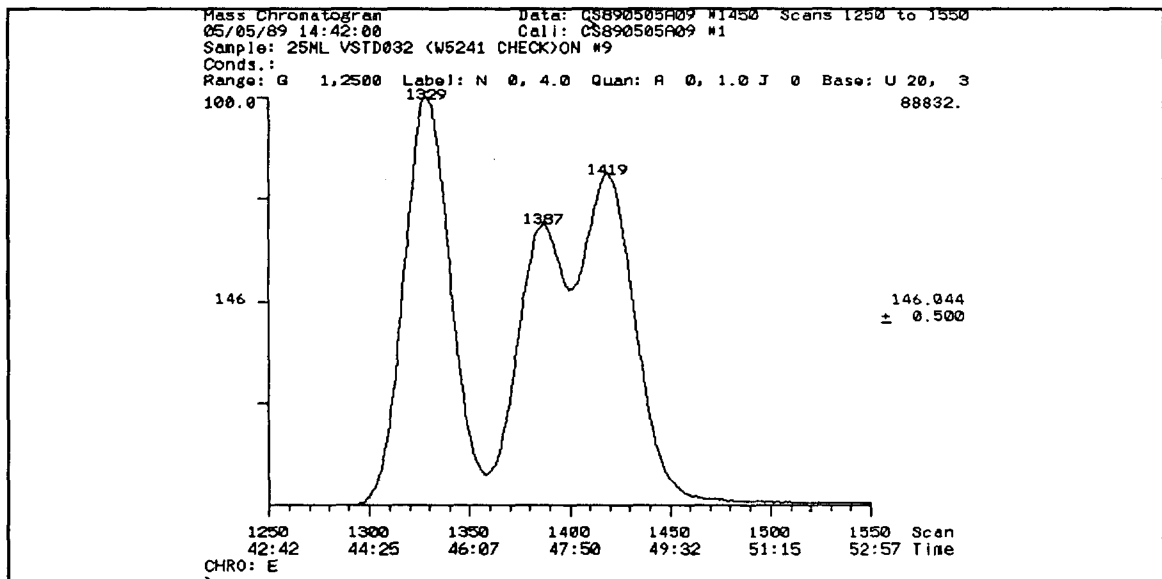

Figure 5b Extracted ion current profile of 1,3, 1,2, and 1,4-Dichlorobenzene using an 6 foot SP-1000 packed column. (Note poor separation between the 1,2 and 1,4-Dichlorobenzene isomers.)

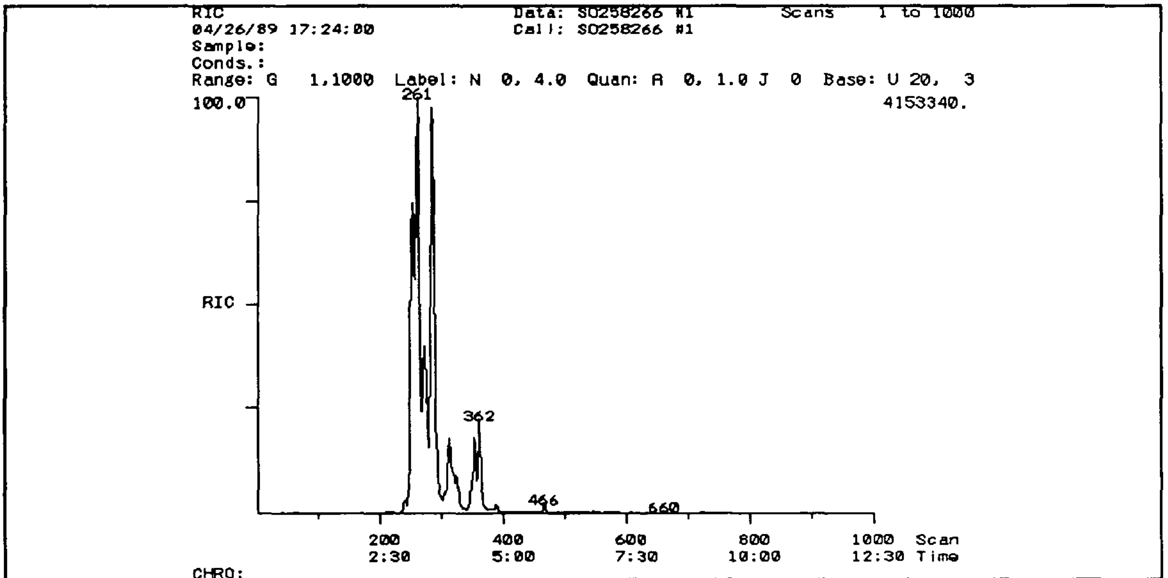

Figure 6a. Headspace sample with high concentrations of early eluting unknown compounds.

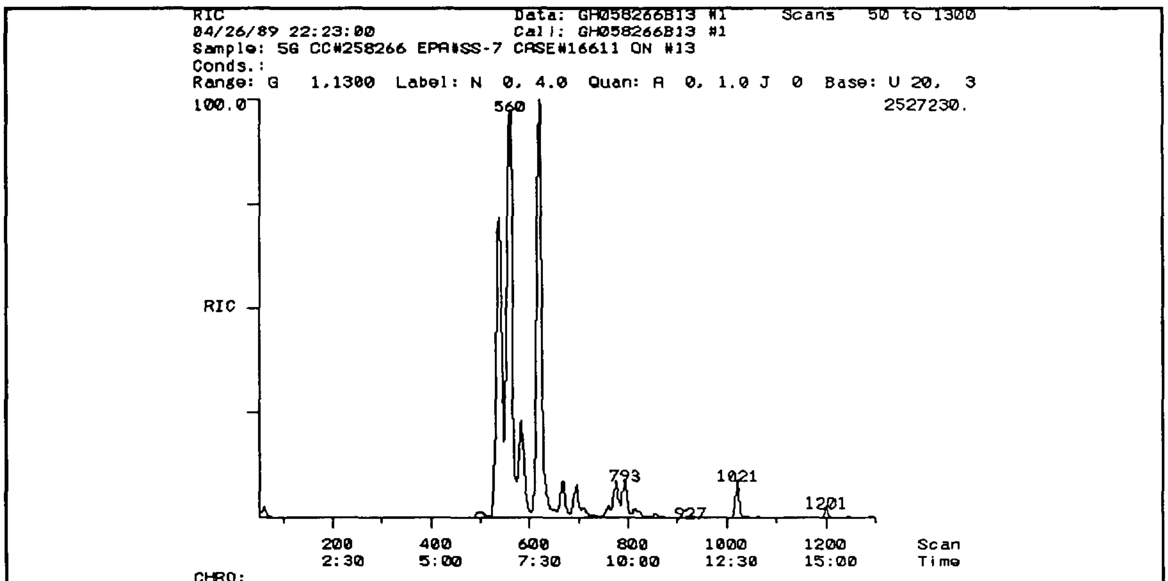

Figure 6b. Normal purge and trap analysis of sample in Figure 6a. (Note the similarities in the chromatograms.)

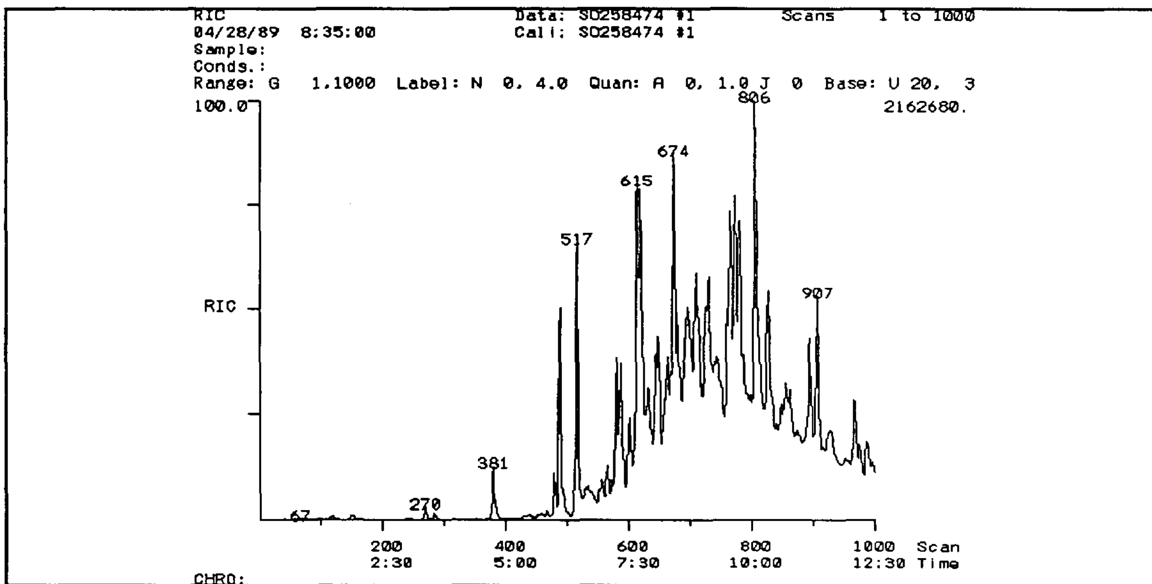

Figure 7 Headspace screen sample containing large quantities of late eluting compounds. Mass spectra from the late eluting peaks indicate methyl naphthalene and indene isomers.

Table I
Recoveries and Method Detection Limits Headspace Analyzer

Compound Name	Average Recovery	Method Det. Limit
TRICHLOROFLUOROMETHANE	115.05	11.51
1,1-DICHLOROETHENE	157.92	22.17
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	124.03	8.95
1,1,1-TRICHLORO-2,2,2-TRIFLUOROETHANE	128.04	7.35
IODOMETHANE	26.15	5.73
3-CHLOROPROPENE	88.14	5.62
METHYLENE CHLORIDE	89.70	3.39
TRANS-1,2-DICHLOROETHENE	105.70	9.55
1,1-DICHLOROETHANE	86.36	8.17
CIS-1,2-DICHLOROETHENE	69.39	6.88
CHLOROFORM	87.30	8.00
1,1,1-TRICHLOROETHANE	65.32	6.68
CARBON TETRACHLORIDE	111.72	12.42
BENZENE	83.40	6.30
1,2-DICHLOROETHANE	83.14	8.08
TRICHLOROETHENE	136.58	12.61
1,2-DICHLOROPROPANE	75.31	6.92
DIBROMOMETHANE	77.48	4.12
BROMODICHLOROMETHANE	43.54	7.84
TOLUENE	94.57	7.09
1,1,2-TRICHLOROETHANE	40.56	7.90
TETRACHLOROETHENE	114.63	11.58
DIBROMOCHLOROMETHANE	43.89	7.68
1,2-DIBROMOETHANE	67.94	3.56
CHLOROBENZENE	86.52	6.74
D4-1,2-DICHLOROBENZENE	50.00	0.00
1,1,1,2-TETRACHLOROETHANE	88.41	6.07
ETHYLBENZENE	121.61	11.77
M,P-XYLENE	191.18	39.17
O-XYLENE	122.50	5.16
STYRENE	109.73	9.52
BROMOFORM	71.51	3.27
BROMOBENZENE	73.39	6.29
1,2,3-TRICHLOROPROPANE	77.61	6.18
2-CHLOROTOLUENE	88.36	8.39
4-CHLOROTOLUENE	80.02	3.50
1,3-DICHLOROBENZENE	84.73	5.26
1,4-DICHLOROBENZENE	74.34	4.02
1,2-DICHLOROBENZENE	76.56	7.61
1,2-DIBROMO-3-CHLOROPROPANE	52.12	9.32
1,2,4-TRICHLOROBENZENE	85.72	2.14
HEXACHLOROBUTADIENE	116.76	11.68
NAPHTHALENE	61.86	7.92
1,2,3-TRICHLOROBENZENE	75.43	2.22

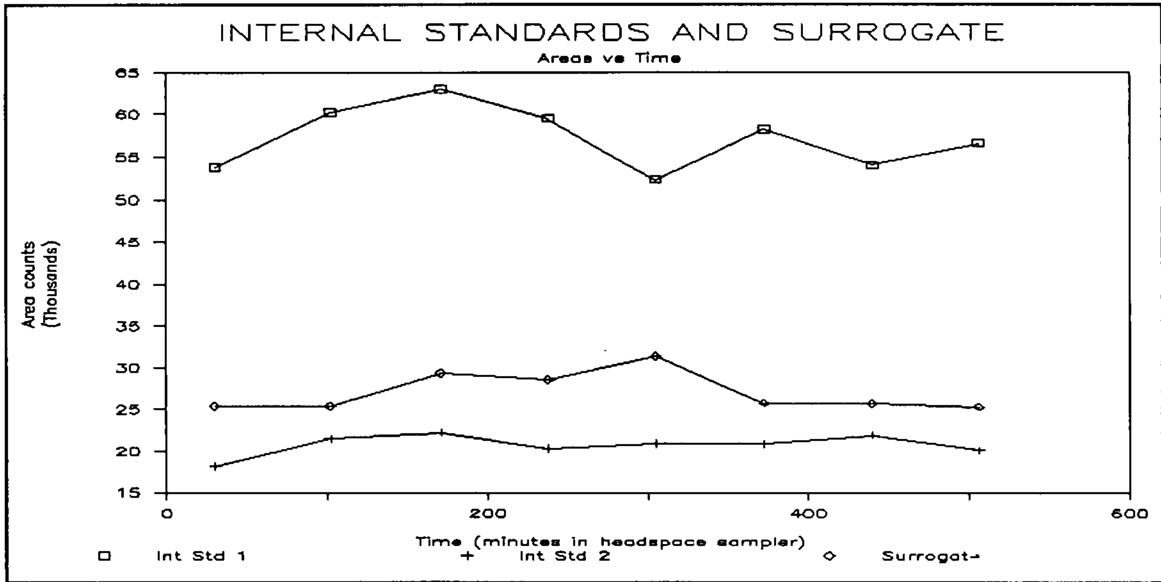

Figure 1 Graph of areas of internal standards and surrogates vs time. IS 1 = Fluorobenzene IS 2 = D4-1,2-Dichlorobenzene

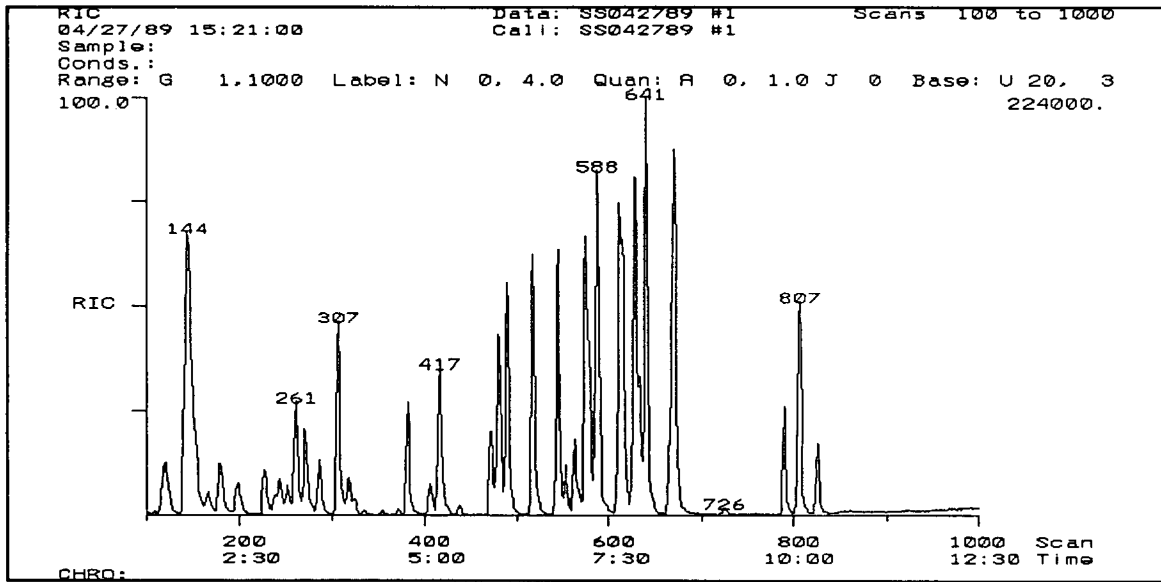

Figure 2 Chromatogram acquired using GC/MS/headspace analyzer. Standard level is 60 ppb.

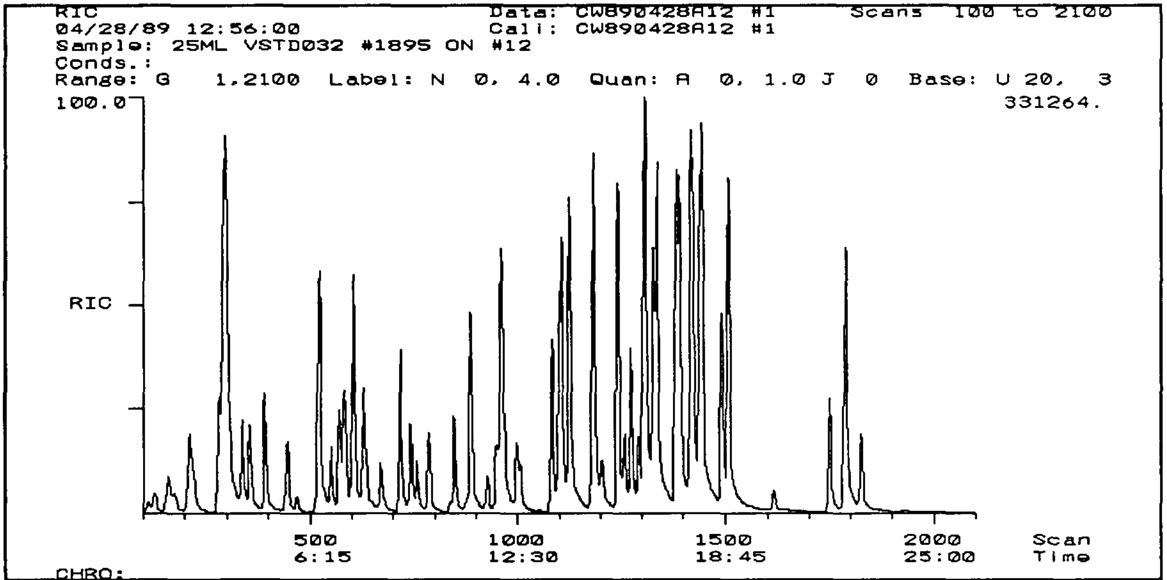

Figure 3 Chromatogram from 524.2 standard analysis. The last three peaks are 1,2,3 Trichlorobenzene, Naphthalene, and 1,2,4 Trichlorobenzene.

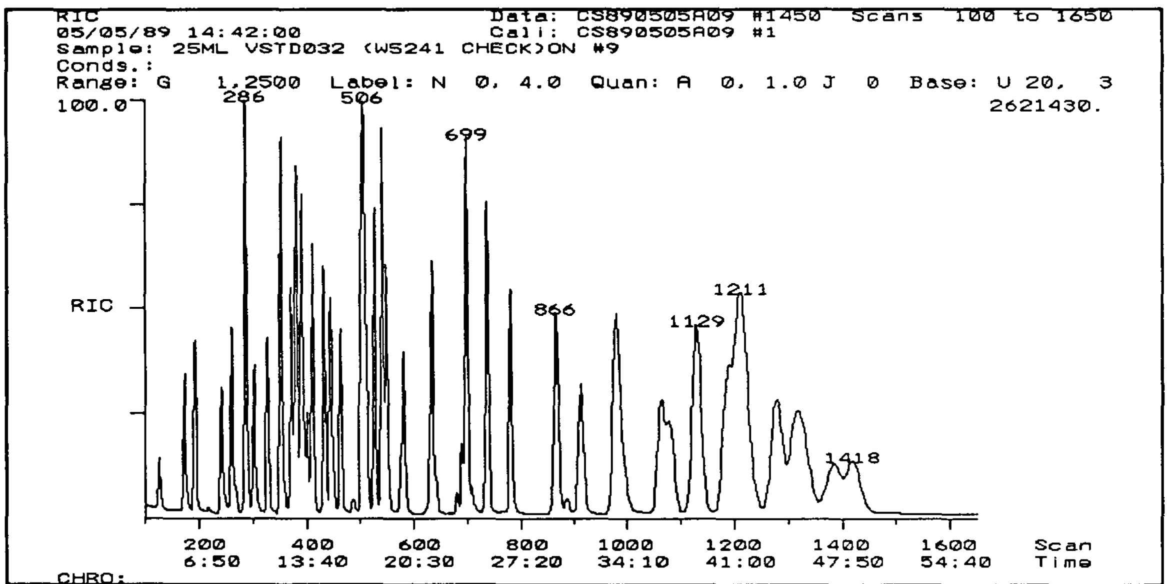

Figure 4 Standard 524.1 Chromatogram using an SP-1000 column. The last eluting peaks are the three dichlorobenzne isomers and the D4-1,2-Dichloro^@^O^C^@^@^@^P

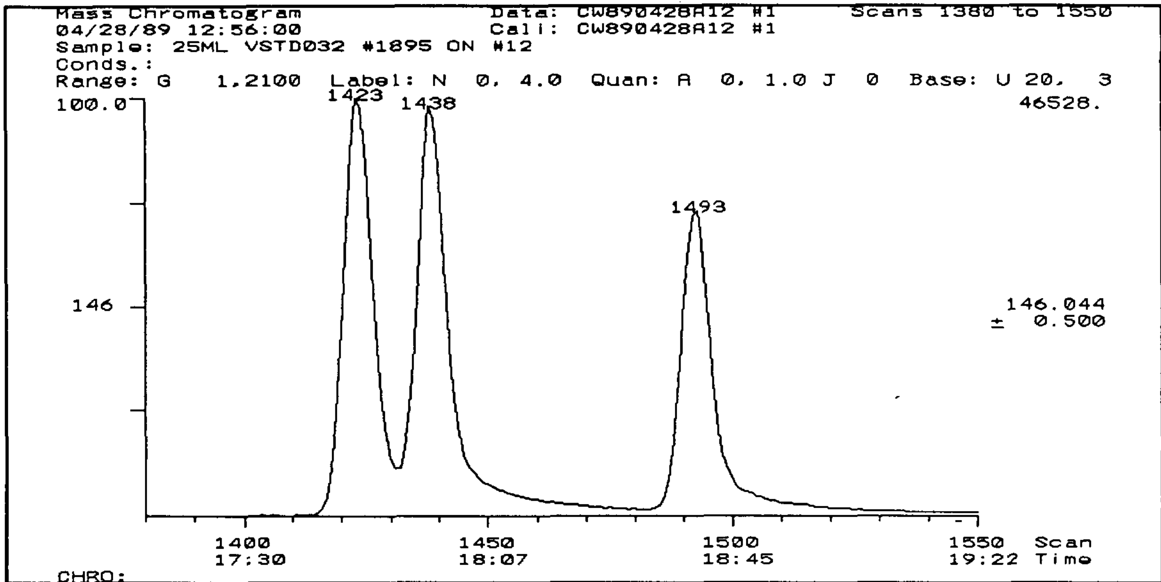

Figure 5a 1,3, 1,4, and 1,2 Dichlorobenzene isomers using a DB-624 megabore column. (Note near baseline resolution between the 1,3 and the 1,4 Di^@^O^C^@^@^@^P^@^A3

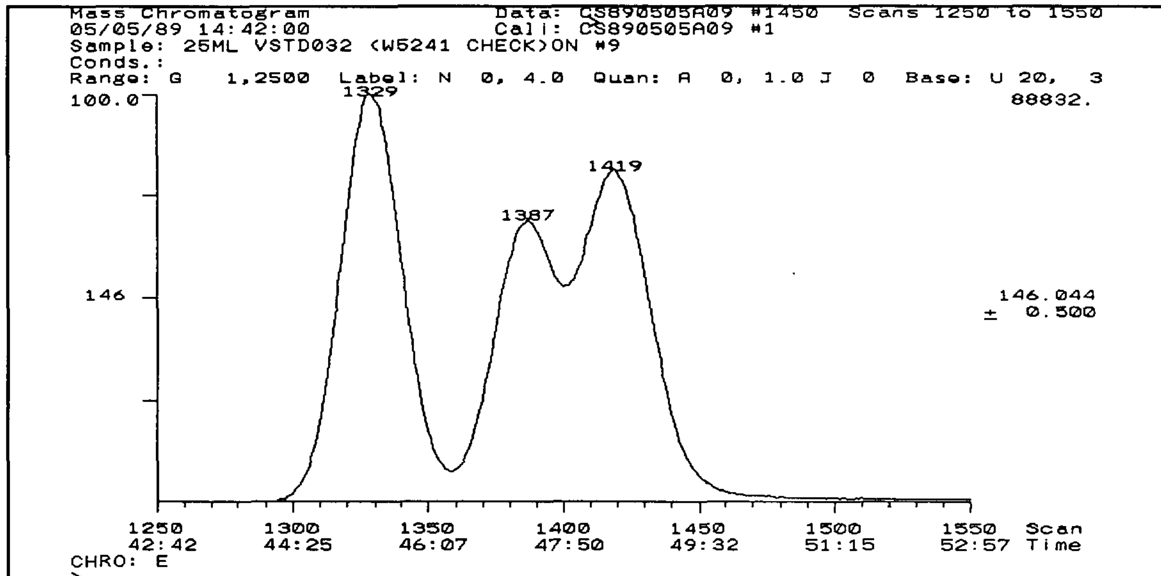

Figure 5b Extracted ion current profile of 1,3, 1,2, and 1,4-Dichlorobenzene using an 6 foot SP-1000 packed column. (Note poor separation b^@^O^C^@^@^@^P^@3K^A3^P^@^@^@^P^@^N^O^@^@ne isome<^A.

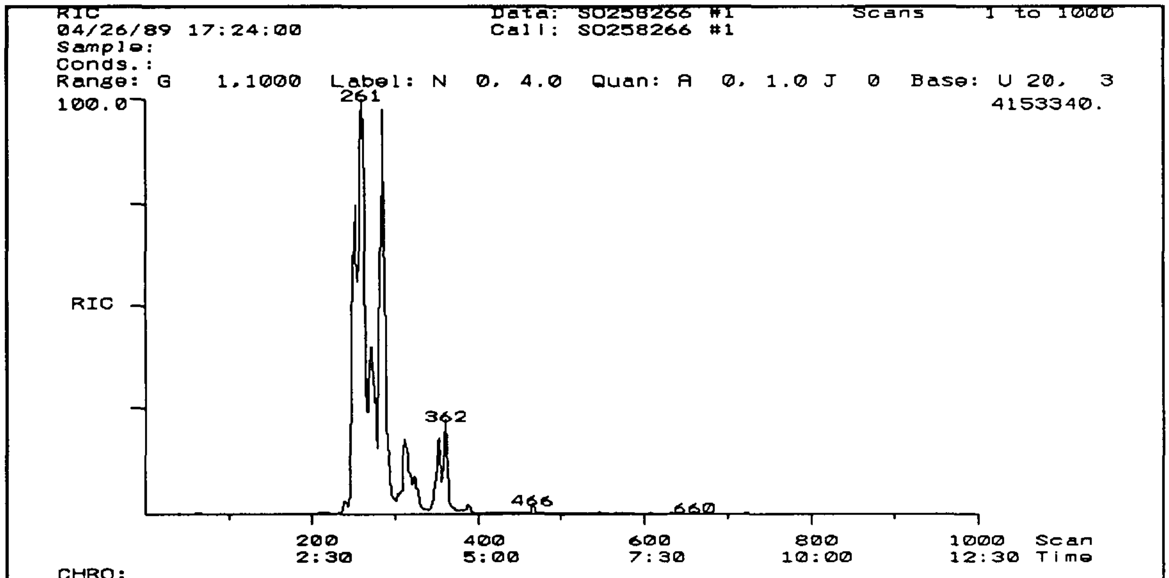

Figure 6a. Headspace sample with high concentrations of early eluting unknown compounds.

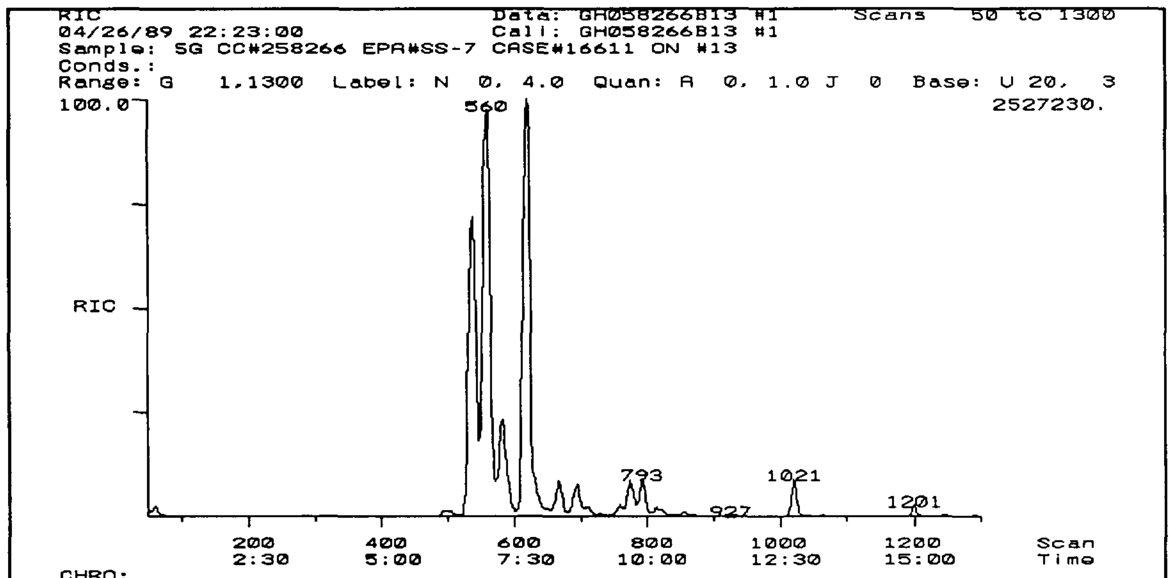

Figure 6b. Normal purge and trap analysis of sample in Figure 6a. (Note the similarities in the chromatograms.)

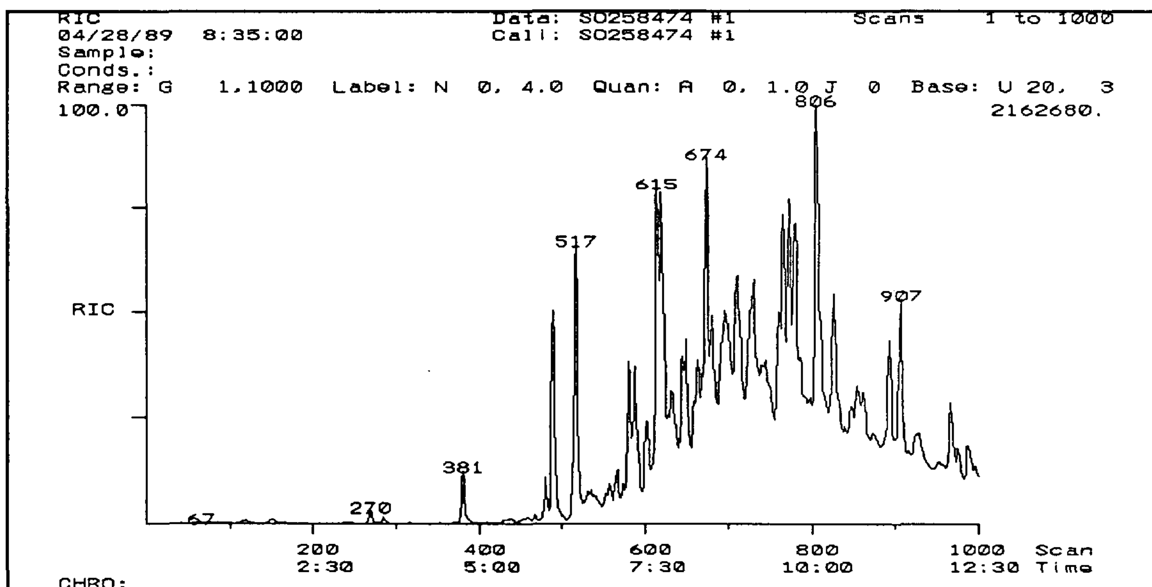

Figure 7 Headspace screen sample containing large quantities of late eluting compounds. Mass spectra from the late eluting peaks indicate ^@^O^C^@^@^@^P^@5K^A5^P^@^@^@^P^@^N^O<^As

EVALUATION OF SW-846 METHOD 8060 FOR PHTHALATE ESTERS

Werner F. Beckert, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nevada 89193-3478; Viorica Lopez-Avila, Acurex Corporation, Environmental Systems Division, 485 Clyde Avenue, P.O. Box 7044, Mountain View, California 94039-7044.

ABSTRACT

SW-846 Method 8060 for the determination of phthalate esters in aqueous and solid matrices was modified and evaluated in a single laboratory. The range of the compounds of interest was expanded to 16 phthalates. A study to determine the sources of phthalate ester contamination in the laboratory, its extent, and ways to minimize background contamination was conducted as part of the evaluation. The packed gas chromatography columns were replaced by two capillary columns (DB-5 and Supelcowax-10, or, optionally, DB-608 and DB-1701) and the isothermal gas chromatography analysis was replaced by a temperature-programmed analysis. Extract cleanup can be performed on alumina or on Florisil, however, three of the target compounds were not recovered from the 10-g Florisil column cleanup step (Method 3620). The use of commercially available disposable Florisil cartridges for the cleanup step was evaluated in order to simplify and standardize the Florisil cleanup procedure; our results indicate that this approach is feasible for all 16 compounds. The interferences represented by organochlorine pesticides were evaluated. Possible internal standards and surrogates were identified. The modified method was tested on a variety of sample matrices. The results obtained indicate acceptable accuracy and precision for most of the target compounds.

INTRODUCTION

Regulations for hazardous waste activities under the Resource Conservation and Recovery Act (RCRA) of 1976 and its elements require analytical methodologies that provide reliable data. The document "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Office of Solid Waste Manual SW-846 (1), provides a compilation of methods for evaluating RCRA solid wastes for environmental and human health hazards. One of the methods in this document, Method 8060, addresses the determination of phthalate esters. This method provides conditions for sample extraction (Methods 3510, 3520, 3540, 3550), sample extract sample extract cleanup (Methods 3610, 3620, 3640) and gas chromatographic (GC) determination of six phthalates in environmental matrices

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NOTICE: Although the research described in this paper has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

including groundwater, liquids, and solids. Analyses are performed by GC using two packed columns at various temperatures, and the compounds are determined with a flame-ionization (FID) or an electron-capture detector (ECD).

Problems with the current Method 8060 include:

- The primary column specified, a 1.8-m x 4-mm ID glass column packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh), needs to be operated at two temperatures (180°C and 220°C) in order to chromatograph the six compounds.

- The confirmatory column specified, a 1.8-m x 4-mm ID glass column packed with 3% OV-1 on Supelcoport (100/120 mesh), also needs to be operated at two temperatures (200°C and 220°C) in order to chromatograph the six compounds.

- Only six phthalate esters are currently listed but other phthalates are also found in environmental samples.

- Surrogate compounds are required to be spiked in the sample matrix prior to extraction, yet no compounds are specified or recommended for this purpose. Likewise, internal standards are required whenever internal standard calibration is used for quantification purposes, yet no internal standards are specified or recommended.

- Extract cleanup is performed according to Method 3610 or 3620, yet no data are included on the recovery of the six compounds from the extract cleanup step.

- Many phthalate esters are present as contaminants in or on laboratory equipment and in solvents and reagents (2). Procedures on how to clean glassware and how to remove phthalate esters from solvents and materials should be tested and incorporated in the protocol. Also, examples of typical background contamination of some common laboratory items should be given to make the analyst aware of such problems.

APPROACH

Because phthalate ester background levels in laboratories are known to be high (2), laboratory solvents (acetone, hexane, diethyl ether, isooctane, methylene chloride, reagent water) and materials (Florisil, alumina, silica gel, anhydrous sodium sulfate, filter paper, paper thimbles, glass wool, and aluminum foil) from a variety of suppliers were analyzed for the most common phthalate esters.

The range of compounds to be determined was extended to the 16 phthalate esters listed in Table 1.

Since GC analysis on packed columns did not give satisfactory results, five fused-silica capillary/megabore columns were evaluated for their

Table 1. Phthalate Esters Included in the Evaluation

Compound	CAS No.
Dimethyl phthalate (DMP)	131-11-3
Diethyl phthalate (DEP)	84-66-2
Di-isobutyl phthalate (DIBP)	84-69-5
Di-n-butyl phthalate (DBP)	84-74-2
Bis(2-methoxyethyl) phthalate (BMEP)	117-82-8
Bis(4-methyl-2-pentyl) phthalate (BMPP)	146-50-9
Bis(2-ethoxyethyl) phthalate (BEEP)	605-54-9
Diamyl phthalate (DAP)	131-18-0
Hexyl 2-ethylhexyl phthalate (HEHP)	75673-16-4
Dihexyl phthalate (DHP)	84-75-3
Benzyl butyl phthalate (BBP)	85-68-7
Bis(2-n-butoxyethyl) phthalate (BBEP)	117-83-9
Dicyclohexyl phthalate (DCP)	84-61-7
Bis(2-ethylhexyl) phthalate (DEHP)	117-81-7
Di-n-octyl phthalate (DOP)	117-84-0
Dinonyl phthalate (DNP)	84-76-4

suitability for this type of compounds. In addition to the sample extract cleanup methods specified (Methods 3610 and 3620), the use of commercially available disposable Florisil cartridges for sample extract cleanup was evaluated in order to simplify and standardize the Florisil cleanup procedure. A suitable surrogate compound and an internal standard were selected and tested.

Because the phthalate esters cannot be separated from the organochlorine pesticides listed in Method 8080/8081 by GC on a DB-5 column, separation of these two groups of compounds was investigated using the Florisil cartridge cleanup procedure.

The revised Method 8060 protocol was evaluated with five environmental materials.

EXPERIMENTAL

Apparatus

(a) Glassware - Essentially as specified in Methods 3510, 3520, 3540, 3550, 3610 and 3620.

(b) Mixxor - Lidex Technologies, Inc.

(c) Sonicator - Heat Systems Ultrasonics, Inc., Model W-375.

(d) Gas Chromatographs - Varian 6000 with constant-current/pulsed-frequency ECD, interfaced with a Varian Vista 402 data system; Varian 6500 with FID, interfaced with either a Spectra Physics 4290

integrator or a Varian Vista 402 data system. For the simultaneous injection on the DB-608 and DB-1701 columns, the Varian 6000 was equipped with a Supelco 6-in injector tee and with dual ECDs.

(e) Autosampler - Varian Model 8000.

(f) GC Columns - (1) DB-5, (2) Supelcowax-10, (3) DB-210, (4) DB-608, (5) DB-1701.

Materials

(a) Solvents and other reagents - As specified in Methods 3510, 3520, 3540, 3550, 3610 and 3620.

(b) Florisil - J. T. Baker, Lot No. 442707, 60/80 mesh, activated at 400°C for 16 hours, then deactivated with water (3% by weight).

(c) Alumina - Alumina Woelm N Super I, activated/deactivated as described for Florisil.

(d) Florisil disposable cartridges - Supelclean SPE tubes consisting of serological-grade 6-mL polypropylene tubes, packed each with 1 g LC-Florisil (40-µm particles, 60-Å pores) held between polyethylene frits.

(e) Standards - DEP was obtained from Scientific Polymer Products, all other phthalates, as well as benzyl benzoate and diphenyl terephthalate, were obtained from Chem Service (distributed by Bryant Laboratories, Inc.). Purities were stated to be greater than 98%. Stock solutions of each compound at 1 mg/mL were prepared in isooctane (Baker Resi-Analyzed, J. T. Baker); working calibration standards were prepared initially in isooctane and later in hexane by serial dilutions of a composite stock solution prepared from the individual stock solutions.

(f) Materials used in contamination evaluation (solvents and other materials used in sample preparation) - Various grades purchased from a variety of suppliers.

(g) Environmental materials -

- Sandy loam soil, obtained from Soils Incorporated, Puyallup, Washington, with the following characteristics: pH 5.9 to 6.0; 89 percent sand, 7 percent silt, 4 percent clay; cation exchange capacity 7 meq/100 g; total organic carbon content 1,290 ± 185 mg/kg.
- A sediment sample of unknown origin. Analysis of the extract by GC/MS indicated the presence of petroleum hydrocarbons.
- NBS SRM-1572, Citrus leaves.

- NBS SRM-1632a, Coal.

- NBS SRM-1633a, Coal flyash.

Contamination Study

Solvent samples (acetone 150 mL, hexane 150 mL, diethyl ether 30 mL, methylene chloride 180 mL) were individually concentrated by K-D evaporation to 10 mL and further reduced to 1 mL with high-purity nitrogen; only isooctane was not concentrated. Two replicate samples of each solvent were prepared and analyzed.

Samples of Florisil (20 g), silica gel (20 g), anhydrous sodium sulfate (50 g) and glass wool (5 g) were immersed overnight in solvent which was then separated and concentrated to 1 mL for GC analysis. Two washings were performed in each case and the concentrates analyzed separately. The effect of baking at 400°C for 4 hours was evaluated for anhydrous sodium sulfate and glass wool.

Samples of filter paper (10 g), paper thimbles (10 g) and aluminum foil (5 g) were cut into 0.5-in x 0.5-in pieces and immersed overnight in solvent which was then separated and concentrated to 1 mL for GC analysis. Two washings were performed in each case and the concentrates analyzed separately.

Gas Chromatography

Operating conditions: DB-5 - 120°C to 260°C (hold 16 min) at 15°C/min, injector temp. 275°C, detector temp. 320°C; Supelcowax-10 - 150°C (hold 2 min) to 220°C at 15°C/min, then to 260°C (hold 16 min) at 4°C/min, injector temp. 270°C, detector temp. 270°C; DB-210 - 125°C (hold 1 min) to 240°C (hold 16 min) at 5°C/min, injector temp. 250°C, detector temp. 250°C; DB-608 and DB-1701 - 150°C (hold 0.5 min) to 220°C at 3°C/min, then to 275°C (hold 15 min) at 5°C/min, injector temp. 250°C, detector temp. 320°C.

Sample Extraction

The extraction efficiencies of Methods 3510 (separatory funnel) and 3520 (continuous liquid-liquid extraction) for the target compounds were determined with reagent water. Microextraction of 50-mL samples using a Mixxor device and hexane (10 mL) was also tested.

Solid samples were extracted either in a Soxhlet extractor with hexane/acetone (1:1) (Method 3540) or by sonication with methylene chloride/acetone (1:1) (Method 3550).

Extract Cleanup

Florisil and alumina chromatography: Glass columns were packed each with 10 g deactivated Florisil or alumina and topped with 1 cm of precleaned anhydrous sodium sulfate. The charged columns were first eluted with 40 mL hexane which was discarded; the phthalate esters were

eluted with 4:1 hexane/diethyl ether (100 mL for the Florisil column, 140 mL for the alumina column).

Florisil disposable cartridges: The cartridges were washed with 4 mL pesticide-grade hexane prior to use. The eluting solvents used were hexane, mixtures of hexane and diethylether, and mixtures of hexane and acetone. Removal of organochlorine pesticides in the presence of phthalates was attempted with mixtures of methylene chloride and hexane.

Surrogate Compound and Internal Standard Evaluation

Ten compounds were evaluated as possible internal standards and surrogates for Method 8060.

RESULTS AND DISCUSSION

A. Phthalate Ester Contamination Study

Only a brief summary of the results is presented here. Detailed results of the study will be published elsewhere (3).

Solvents

Five organic solvents from up to six different commercial suppliers were analyzed for 11 phthalate esters. As can be seen from the summary results listed in Table 2, six phthalate esters were detected in some or all of these solvents. The only phthalate ester detected in any of the methylene chloride samples above 6 ng/mL was DOP at 8.8 ng/mL in one sample.

Since typical volumes of hexane and acetone used in sample preparation are 200 to 300 mL, the amounts of phthalate esters that can be introduced as contaminants with solvents could be considerable.

Materials

The phthalate contamination summary values (averaged across brands) for the materials listed in Table 3 represent averages of second washings. Florisil, alumina and silica gel showed significant levels of phthalates even in the second washing. Florisil disposable cartridges (not listed in Table 3) showed in the first washing levels from 10 to 460 ug per cartridge for 8 of the 11 phthalate esters listed in Table 3. However, washing of the cartridges just prior to use with 4 mL hexane resulted in acceptable method blanks. Washing alone is not sufficient for sodium sulfate and glass wool, but baking these materials at 400°C for 4 hours followed by solvent washing gave acceptable blanks. High levels were found in filter paper and paper thimbles.

Precleaning of these materials is a must when phthalate esters at low nanogram levels are to be quantified.

Table 2. Phthalate Ester Contamination in Common Solvents[a] (ng/mL)

Phthalate	Acetone	Hexane	Diethyl ether	Isooctane	Methylene[b] chloride
Dimethyl	<0.10	<0.10	<0.20 - 3.45	<10	<6
Diethyl	<0.10 - 0.40	<0.10	<0.20	<10	<6
Diisobutyl	<0.10 - 0.35	<0.10 - 0.35	<0.20	<10	<6
Di-n-butyl	<0.10 - 0.50	<0.10	<0.20 - 2.9	<10 - 103	<6
Diamyl	<0.10	<0.10	<0.20	<10	<6
Dihexyl	<0.10 - 0.45	<0.10 - 0.87	<0.20 - 0.75	<10 - 42	<6
Benzyl butyl	<0.10 - 0.46	<0.10	<0.20	<10	<6
Dicyclohexyl	<0.10	<0.10	<0.20	<10	<6
Bis(2-ethylhexyl)	<0.10 - 0.45	<0.10 - 0.40	<0.20 - 2.2	<10 - 69	<6
Di-n-octyl	<0.10	<0.10	<0.20	<10	8.8
Dinonyl	<0.10	<0.10	<0.20	<10	<6
# of diff. brands	8	8	8	8	8
Below det. limit	1	2	0	0	7
Concentr. factor	150	150	30	1	180

[a]Averages of two to four determinations.
[b]Analyzed by GC/FID which resulted in high detection limits.

Table 3. Phthalate Ester Contamination of Laboratory Materials (ng/g)

Phthalate	Florisil[a]	Alumina[b]	Silica gel[c]	Sodium sulfate[d]	Glass wool[e]	Filter paper[f]	Paper thimbles[g]	Aluminum foil[h]
Dimethyl	6.2	129	i	0.7	27.4	67.5	35	24
Diethyl	5.3	28	15	1.8	2.2	<1.0	2.3	0.6
Diisobutyl	0.9	29	0.6	0.8	3	11.5	2.3	0.7
Di-n-butyl	<0.5	14	0.8	3.5	<2.0	6.5	<2.0	0.5
Diamyl	<0.5	5.8	<0.5	0.5	<2.0	<1.0	<2.0	<0.5
Dihexyl	0.8	1.2	3.8	3.3	13	15.5	17.0	3.0
Benzyl butyl	<0.5	0.6	18	4.7	4	3.3	3.0	2.5
Dicyclohexyl	<0.5	<0.5	<0.5	<0.5	<2.0	<1.0	<2.0	<0.5
Bis(2-ethylhexyl)	2.3	4.8	1.3	1.0	4.4	11	2.8	2.5
Di-n-octyl	1.5	<0.5	0.7	<0.5	5	<1.0	<2.0	1.1
Dinonyl	2.3	<0.5	<0.5	<0.5	<2.0	<1.0	<2.0	1.0
# of different brands	2	2	2	2	2	1	1	2

[a] 20 g Florisil, second immersion with 200 mL hexane/diethyl ether (4:1).
[b] 20 g alumina, second immersion with 300 mL hexane/diethyl ether (4:1).
[c] 20 g silica gel, second immersion with 300 mL acetone.
[d] 50 g anhydrous sodium sulfate, second immersion with 300 mL hexane/acetone (1:1).
[e] 5 g glass wool, second immersion with 300 mL hexane/acetone (1:1).
[f] 10 g filter paper, second immersion with 100 mL hexane/acetone (1:1).
[g] 10 g paper thimbles, second immersion with 100 mL hexane/acetone.
[h] 5 g aluminum foil, second immersion with 200 mL hexane/acetone (1:1).
[i] not able to quantify because of interference.

B. Method 8060 Evaluation

GC Column Evaluation

Of the fused-silica capillary columns evaluated, the DB-210 column was found to be the least desirable because of a significant baseline drift during column programming and was therefore eliminated from further consideration.

The retention times of the 16 phthalates of interest on the DB-5 and the Supelcowax-10 column are presented in Table 4. The GC conditions were chosen such that all compounds are resolved and the total analysis time is approximately 20 min. All phthalate esters were resolved on the DB-608 and DB-1701 columns; the retention times are included in Table 4.

Table 4. GC Retention Times for the Phthalates[a]

	Retention time (min)			
Phthalate	DB-5	Supelco-wax-10	DB-608	DB-1701
Dimethyl	3.42	5.62	6.72	6.73
Diethyl	3.45	6.11	8.69	8.85
Diisobutyl	6.48	7.26	12.74	13.36
Di-n-butyl	7.14	8.43	14.68	15.13
Bis(2-methoxyethyl)	7.40	12.05	17.24	16.96
Bis(4-methyl-2-pentyl)	7.96	8.14	15.76	16.73
Bis(2-ethoxyethyl)	8.17	12.41	18.93	18.80
Diamyl	8.41	10.15	17.94	18.64
Hexyl 2-ethylhexyl	8.63	11.13	19.70	19.56
Dihexyl	9.62	12.21	21.50	22.48
Benzyl butyl	9.69	16.36	24.64	23.76
Bis(2-n-butoxyethyl)	10.53	16.94	25.71	25.96
Dicyclohexyl	10.98	16.66	28.33	27.06
Bis(2-ethylhexyl)	11.13	13.31	24.94	26.35
Di-n-octyl	13.03	17.25	29.14	30.57
Dinonyl	16.00	20.73	32.97	34.71
Benzyl benzoate	5.77	7.87	12.13	11.50
Diphenyl terephthalate	12.76	[b]	[c]	[c]

[a]The GC conditions have been specified under "Gas Chromatography."
[b]No response during 60-min analysis.
[c]Values not available.

Sample Extraction

The extraction of reagent water spiked with each of the 16 phthalates (50 µg/L each for separatory funnel and continuous liquid-liquid

extraction, and 1 mg/L for the Mixxor extraction) gave the following results:

- The continuous liquid-liquid extraction technique had unacceptable reproducibilities for all compounds; for five of the phthalate esters the average recoveries were only 20 to 45 percent.

- Extraction with hexane in the Mixxor device gave unacceptable recoveries and reproducibilities.

- The separatory funnel extraction produced recoveries >70 percent for most compounds, and reproducibilities were better than 10 percent for two-thirds of the compounds.

Further evaluation of the separatory funnel extraction technique at lower spiking levels (25, 10, and 1 μg/L) confirmed its usefulness. At 25 μg/L, the recoveries ranged from 90 to 130 percent, with 11 recoveries between 90 and 110 percent, and at 10 μg/L, the range was 73 to 117 percent, with 10 recoveries between 90 and 110 percent. At 1 μg/L, the recoveries ranged from 53 to 152 percent; only four values were between 90 and 110 percent.

Phthalate recoveries from soil samples, spiked at 1 ppm with the 16 phthalates, using Method 3540 (Soxhlet extraction), ranged from 54 percent for BEEP to 135 percent for DHP with 11 recoveries >70 percent. When sonication was used, the recoveries ranged from 32 percent for BMPP to 112 percent for DMP, with 13 recoveries >70 percent.

Extract Cleanup

Alumina and Florisil chromatography were performed with standards in hexane according to Methods 3610 and 3620, respectively (Table 5). For the Florisil cartridge cleanup, various solvents and solvent combinations were tried on standards in hexane and on standards in the presence of organochlorine pesticides. It was found that the organochlorine pesticides can be removed efficiently from the cartridges with hexane/methylene chloride (4:1); under these conditions, the phthalate esters are retained on the Florisil cartridge and can be recovered with hexane/acetone (9:1). The recoveries are presented in Table 5. Additional details on the Florisil cartridge cleanup method can be found in Reference 4.

Surrogate Compound and Internal Standard

Of ten compounds evaluated, benzyl benzoate was selected as internal standard and diphenyl terephthalate was considered as surrogate compound. The selection was based primarily on the observation that both compounds are resolved from the other phthalate esters under the conditions of the GC analysis.

Table 5. Extract Cleanup Recoveries (in Percent)

			Florisil Cartridges[b]	
Phthalate	Florisil[a]	Alumina[a]	Fraction 1	Fraction 2
Dimethyl	43	65	0	130 (52)
Diethyl	57	62	0	88 (2.8)
Diisobutyl	80	77	0	118 (16)
Di-n-butyl	85	77	12	121 (13)
Bis(2-methoxyethyl)	0	70	0	32 (31)
Bis(4-methyl-2-pentyl)	85	89	0	123 (5.7)
Bis(2-ethoxyethyl)	0	67	0	82 (19)
Diamyl	82	75	3.3	94 (8.3)
Hexyl 2-ethylhexyl	105	91	0	126 (6.4)
Dihexyl	74	73	0	62 (15)
Benzyl butyl	90	87	0	98 (6.5)
Bis(2-n-butoxyethyl)	0	63	0	135 (34)
Dicyclohexyl	84	84	0	106 (3.3)
Bis(2-ethylhexyl)	82	91	0	110 (2.7)
Di-n-octyl	115	108	0	123 (7.0)
Dinonyl	73	71	0	102 (8.7)

[a]Average of two determinations.
[b]Averages of three determinations; RSDs given in parentheses. Fraction 1 was eluted with 5 mL hexane/methylene chloride (4:1) and Fraction 2 with 5 mL hexane/acetone (4:1).

Draft Protocol Evaluations with Environmental Materials

The revised draft protocol (cleanup on Florisil cartridges, analyses on DB-5) was tested for the 16 phthalate esters with five environmental materials. The recoveries (Table 6) were >74 percent for all phthalate esters but BEEP.

Parameters Being Further Evaluated

The following parameters are still being investigated. Depending on the results, the draft protocol may be further modified.

- Water sample extraction: Analytichem International has made available the "3M-Empore™ Extraction Disks" that adsorb organic constituents from water samples. The method is fast, and only small amounts of solvents are required. Preliminary results for phthalate esters in water are encouraging.

- Internal standards and surrogate compounds: A number of additional compounds are under consideration to allow better coverage of the total range of phthalate esters.

Table 6. Percent Recoveries of Phthalate Esters from Various Matrices by Florisil Cartridge Cleanup with Hexane/Methylene Chloride (4:1) and Hexane/Acetone (9:1) as Eluants[a]

Phthalate	Sandy Loam Soil	Sediment	NBS SRM-1572	NBS SRM-1632a	NBS SRM-1633a
Dimethyl	78	75	80	76	82
Diethyl	79	79	89	79	84
Diisobutyl	79	82	90	108	86
Dibutyl	74	78	84	83	83
Bis(4-methyl-2-pentyl)	77	84	102	91	86
Bis(2-ethoxyethyl)	37	24	62	32	33
Diamyl	82	86	100	76	89
Hexyl 2-ethylhexyl	80	88	95	93	81
Dihexyl	78	88	86	92	80
Benzyl butyl	82	99	114	102	98
Bis(butoxyethyl)	86	94	98	106	98
Dicyclohexyl	91	96	106	98	95
Bis(2-ethylhexyl)	74	85	108	88	112
Dioctyl	80	92	104	95	88
Dinonyl	84	96	106	111	92

[a]Spiking level is 50 ng/mL for each compound. Data shown are for Fraction 2 which was eluted with 5 mL hexane/acetone (9:1).

- GC analysis: Additional GC columns are being evaluated, and attempts are made to use the split injection technique with identical GC conditions for the DB-5/Supelcowax-10 column pair (as has already been done for the DB-608/DB-1701 pair). This will further simplify the GC analysis step. A preliminary evaluation of the column pairs PTE-5/SP-2380 and Rt_x-5/Rt_x-2330 indicated that, under dual-column analysis conditions, basically complete separation of the phthalate esters can be achieved on both column pairs.

- Detection limits: It seems impractical to determine method detection limits for the phthalate esters because some of the phthalates are ubiquitous contaminants. More useful would be practical quantification limits (or levels of quantification, LOQs). Efforts are under way to define satisfactory LOQs for the phthalate esters.

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DETERMINATION OF OCTACHLORODIBENZODIOXIN AND OCTACHLORODIBENZOFURAN IN SOILS AND BIOLOGICAL SAMPLES BY ELECTRON CAPTURE/GAS CHROMATOGRAPHY

William M. Draper, Ruth R. Chang and Robert D. Stephens,
State of California Department of Health Services,
Hazardous Materials Laboratory, 2151 Berkeley Way, Berkeley, CA 94704

ABSTRACT

We previously reported the development of a gas chromatography-electron capture detector (GC/ECD) method for determination of octachlorodibenzodioxin (OCDD) in soil (see Proceedings of the Fourth Annual WTAQAS). OCDD was used as a marker for the toxic polychlorinated dibenzodioxins and furans (PCDD/PCDF) produced in an industrial pentachlorophenol fire.

This paper describes advancements in the use of OCDD and a second compound, octachlorodibenzofuran (OCDF), as markers and surrogates for highly toxic PCDD/F in both environmental and biological samples. The current procedure allows baseline separation of OCDD and OCDF on DB-17 capillary narrow bore or megabore columns. OCDD and OCDF are relatively involatile, but can be successfully injected using capillary on-column or packed column inlets (for megabore columns), and the latter can be automated. Soil method detection limits (MDL) have been reduced by a factor of ten to 0.4 to 0.8 ng/g for OCDD and OCDF, respectively, sensitivity comparable to GC/MS procedures. An optional Florisil cartridge cleanup isolates OCDD and OCDF from chlorinated pesticides, polychlorinated biphenyls and other coextracted environmental chemicals.

Use of the GC/ECD screening procedure on biological samples was evaluated. A supplemental defatting procedure was required for trace level determination of OCDD and OCDF in egg yolks which contain 25 - 30% lipid by weight. A Biobeads S-X3 gel permeation chromatography (GPC) column in a commercial, automated GPC system was used to separate the octa compounds from lipids. Estimated instrument detection limits for OCDD and OCDF in eggs are in the 0.5 - 1.0 ng/g lipid range after defatting.

INTRODUCTION

Over the past four years ultratrace analytic procedures for PCDD/PCDF have been implemented in the State of California Department of Health Services laboratory. This capability has been critical in dealing with complex human health issues involving dioxins in a variety of exposure scenarios and from a variety of sources. Irregardless of the laboratory's resources, however, the demand for PCDD/F analyses has always outstripped capacity. Because of this dilemma and the need to decrease turnaround time and control costs, our laboratory has placed a high priority on the development of screening procedures for PCDD/F.

Screening procedures are used to extend laboratory resources in two ways. Markers distinguish highly contaminated samples from those with

low-level contamination allowing prioritization of analyses. If the correlation between the test compound and the chemicals of concern is sufficiently strong, they may be used as a surrogate. A dioxin surrogate must be able to predict concentrations of the lesser chlorinated PCDD/PCDF or TCDD toxic equivalents.

Korfmacher and coworkers first reported a GC/ECD method for determination of OCDD in surface wipe samples and building dust (1). In Korfmacher's procedure hexane extracts are subjected to cleanup by acid/base extraction and chromatography on active carbon, prior to the GC/ECD determination. These investigators also proposed a strategy for characterization of dioxin-contaminated sites (1,2). Gas chromatgraphy/mass spectrometry (GC/MS) analysis of a limited number of samples define the PCDD/PCDF congener patterns and establish OCDD:PCDD/PCDF or OCDD:TCDD toxic equivalent ratios. The extent of PCDD/PCDF contamination at the site is then established solely by OCDD screening.

Our laboratory extended this approach in investigating environmental PCDD/PCDF contamination resulting from an industrial pentachlorophenol fire that potentially affected a 2,000 km^2 area (3). Screening OCDD in soil by GC/ECD without any supplemental cleanup proved sufficiently sensitive (MDL = 6 ng/g) for detection of OCDD above expected background levels (3).

The objective of the current work is to improve laboratory screening for chlorinated dioxins and furans by: 1) including a second marker, octachlorodibenzofuran; 2) developing alternatives to on-column sample injection that allow automated GC analysis; 3) lowering method detection limits in soil; and 4) adaptation of the procedure to biological samples. Such improvements in laboratory determination of OCDD and OCDF will further their use as both markers and surrogates for their lower chlorinated, more toxic analogues.

EXPERIMENTAL SECTION

Chemicals. Reference standards of OCDD and OCDF were obtained from Cambridge Isotope Laboratories (Woburn, MA) and The Foxboro Co. (North Haven, CT), respectively. Primary standards were prepared at 1. mg/mL in toluene and secondary and working standards were made by serial dilution in isooctane. Extraction and chromatography solvents were pesticide residue grade.

Gas Chromatography. A Hewlett Packard Model 5890 gas chromatograph (Avondale, PA) fitted with a ^{63}Ni electron capture detector, a packed column inlet and a 7673A autosampler/injector was used routinely. A Spectra Physics 4290 chromatography digitizer (San Jose, CA) and Spectra Physics Winner computerized data system were used for acquisition and processing of chromatography data.

For manual injections a J & W Scientific capillary on-column injector (Folsom, CA) and narrow bore capillary column were used to obtain optimum chromatographic efficiency and lowest instrument detection limits. Two narrow bore capillary columns were evaluated: 30 m X 0.3 mm ID fused silica columns with 0.25 um DB-17 (J & W Scientific

Folsom, CA) and 0.25 um SPB-5 (Supelco, Bellefonte, PA) bonded phases. The DB-17 capillary was operated with an isothermal oven temperature of 290°C giving OCDD and OCDF retention times of 12.6 and 13.8 min, respectively.

For automated GC operation a 15 m X 0.53 mm ID fused silica column with a chemically-bonded, one um methylphenyl silicone stationary phase (DB-17, J & W Scientific, Folsom, CA) was used. The column was installed in a packed column port and operated under the following conditions: inlet temp., 280°C; detector temp., 325°C; detector gas, 60 ml argon-methane/min; and column head pressure, ~6 psi helium. Isothermal operation with a 240°C column and 6 mL/min carrier gas flow rate gave retention times (t_R) of 35 and 38 min for OCDD and OCDF, respectively. At 255°C t_R were 22 and 24 min. A column temperature program was most effective at eluting high-boiling, electron-capturing compounds occasionally detected in highly contaminated environmental and biological samples: initial column temp., 240°C for 2 min; temp. ramp, +3°C/min to 290°C and hold for 15 min; return to initial conditions at -25°C/min. With a helium carrier gas flow rate of 3.2 mL/min t_R were typically 21 and 22 min for OCDD and OCDF, respectively.

Quantitation of OCDD and OCDF. For quantitative analysis, external calibration by peak height relative to a 24 pg/ul mixed standard in isooctane was used. The autosampler injection volume was 2.0 uL and the instrument was recalibrated every seventh run to bracket retention times and detector responses. Baselines were inspected and adjusted manually due to the complexity of some of the chromatograms.

Soil Extraction. We previously reported on the analysis of OCDD in soil (3), but in the present work modifications were made in sample handling to improve sensitivity. As before soil was passed through a #18 sieve (1.0 mm openings) to give fine and coarse fractions. A slow step in processing has been cleaning and drying sieves which requires a detergent wash, rinsing with demineralized water, and a final rinse with acetone. The fine fraction is agitated and 20.0 +/- 0.1 g is extracted in a Soxhlet device with 200 mL of hexane. The soil is contained in paper thimbles with a glass wool plug and extraction proceeds for 4 hr after the first cycle. Extracts are cooled, reduced to about 5 mL on a rotary flash evaporator and dried by passage through a mini anhydrous sodium sulfate column prepared in a Pasteur pipet. Two mL of isooctane are added and the samples are concentrated to ~1.5 mL under a stream of dry nitrogen and adjusted to give a final sample volume of 2.00 mL of isooctane (1.00 mL for manual on-column injection). Extracts were not allowed to go to dryness to avoid adsorption losses (4). Extracts were stored at room temperature in amber vials with Teflon liners prior to analysis.

An alternate extraction procedure described by Albro et al. (5) was compared for measurement of OCDD and OCDF in two soils from industrial sites. Ten g of anhydrous sodium sulfate, 20 g of soil and 10 g of anhydrous sodium sulfate were layered in a 125 mL separatory funnel with a Teflon stopcock and a glass wool plug. The contents of the funnel were eluted with 14 mL of acetone followed by 50 mL of ethyl acetate and then 100 mL of methylene chloride. Solvents percolated

slowly and were collected in a single 250 mL round bottom. The extract was combined with 3 mL of isooctane, concentrated to about 3 mL on a rotary evaporator, and further concentrated to one mL under a stream of nitrogen. An equal volume of toluene was added to dissolve precipitates formed.

Method Detection Limit in Soil. A soil sample from the Rosamond/Mojave area of Kern County, CA was used to estimate the MDL (U. S. EPA, Test Methods for Evaluating Solid Waste, 1982). In this area sandy soils are typical and a fine textured, high surface area sample was selected for study. Soil samples (20 g) were spiked by adding 20 uL of a hexane solution containing 1.0 ng/uL each of OCDD and OCDF. Samples sat at room temperature for about an hour after evaporation of the solvent before extraction. Five replicates were analyzed in order to obtain precision data needed to estimate the MDL.

Soil Extraction Efficiency. The adequacy of Soxhlet extraction with hexane and the comparability of the screening method were examined by analysis of soils from an industrial incinerator/metal recovery plant in Kern County. PCDD/PCDF determinations used the standard EPA method 8280 as modified by Professor C. Rappe and coworkers. In this procedure a more vigorous 8 hr, Soxhlet extraction with toluene is used.

Optional Florisil Cartridge Cleanup. Florisil cartridge cleanup separates polychlorinated biphenyl (PCB) and chlorinated pesticides from OCDD and OCDF and may be useful for some types of combustion samples including those from PCB fires. A Florisil Sep Pak cartridge (Waters Associates, Milford, MA) is attached to a 50 mL Leur-lock syringe and washed with 10 mL of hexane. The soil extract in 5.0 mL of hexane is added to the syringe and the solvent allowed to percolate to the surface of the adsorbent bed. The adsorbent is washed with 20 mL of hexane to elute PCB and chlorinated pesticides (6) and then 40 mL of diethyl ether to recover OCDD/OCDF. The ether eluate is combined with 1.5 mL of isooctane, concentrated to about 1.0 mL and adjusted to 2.0 mL with isooctane for GC analysis.

Extraction of OCDD and OCDF from Biological Samples. Previous studies of foraging livestock and poultry (7) have demonstrated the importance of food chain contamination in areas of dioxin releases. In particular, laying hens take up and excrete chlorinated dibenzodioxins and furans in eggs. The yolk, with up to 30% lipid by weight, contains the bulk of these lipophilic pollutants. The coextracted lipids must first be removed for analysis of trace constituents.

A 15 - 20 g egg yolk sample is added to a tarred Teflon centrifuge bottle to obtain the sample weight. The sample is homogenized with 100 mL of acetone-hexane (2:1, v/v) using a Polytron homogenizer and agitated vigorously for 15 min on a wrist-action shaker. The bottle contents are then rolled gently with 30 mL added water and centrifuged for 5 min at 3,000 rpm. The hexane layer is drawn off by pipet and filtered through anhydrous sodium sulfate into a 100 mL round bottom. The egg yolk is reextracted with 50 mL of hexane in the same manner and the volatile solvent removed from the combined extract on a rotary flash evaporator.

A less elaborate extraction procedure involving grinding a 15 - 20 g egg yolk sample with granular sodium sulfate and 4 X 50 mL hexane in a mortar and pestle was investigated, but could not be used because it extracted only about 25% of the egg yolk lipid.

Fat Determination and Defatting Biological Samples. The egg yolk extract was dissolved in 25 mL of methylene chloride-cyclohexane (1:1, v/v) and 5.0 mL were transferred to a tarred Griffin beaker. Overnight evaporation at room temperature gave lipids for weight determination.

Extracts were defatted using gel permeation chromatography (GPC) with an Analytical Bio-chemistry Laboratories Autoprep Model 1002 chromatograph (Columbia, MO) using a modified version of a published procedure (4). The Biobeads SX-3 resin was swelled in methylene chloride-cyclohexane (1:1, v/v) and the flow rate was 5.0 mL/min of this mobile phase. The GPC retention volume of OCDD and OCDF was stable over a 4 month period with a typical dump time of 33 min followed by a 10 min collection time.

The GPC column was periodically calibrated with a mixture of 20 g corn oil, 5 ug OCDD and 5 ug OCDF in 100 mL methylene chloride-cyclohexane mobile phase. Twenty three 10 mL fractions were collected and the first 15 allowed to evaporate giving the lipid elution profile. The remaining fractions were combined with 2.0 mL toluene, reduced to 1.5 mL in a nitrogen evaporator, and adjusted to 2.0 mL for determination of OCDD and OCDF elution by GC/ECD.

With the egg yolk extracts in 25 mL of mobile phase, the instrument's 5.0 mL sample loops contain the maximum GPC column capacity of approximately 1.0 g of lipid, but for this study a single loop was used. Larger samples require multiple sample loops and chromatographic cycles. The OCDD/OCDF column eluate was reduced to about 5 mL on a rotary flash evaporator and the remaining volatile solvent removed under a stream of dry nitrogen after addition of 20 uL of tetradecane keeper. The residue was taken up in 180 uL of isooctane for GC analysis.

RESULTS AND DISCUSSION

Gas Chromatography of OCDD and OCDF. In our previous work we analyzed OCDD using a fused silica capillary column with a 5% diphenyl:94% dimethyl:1% vinyl polysiloxane (SPB-5) bonded stationary phase. This column provides inadequate selectivity for resolution of OCDD and OCDF (Fig. 1). At 280°C the two compounds are separated by only 0.16 min and at 260°C the resolution is not improved. OCDD and OCDF are resolved to baseline on a more polar 50% phenyl silicone DB-17 column (Fig. 1). The chromatogram shown for the narrow bore DB-17 column used an isothermal oven temperature of 300°C where the compounds are separated by over 0.9 min. This temperature is above the recommended DB-17 operating range by 20°C, the SPB-5 column has an operating limit of 320°C.

OCDD cannot be satisfactorily chromatographed using purged splitless capillary injection, even at inlet temperatures as high as 250°C (3).

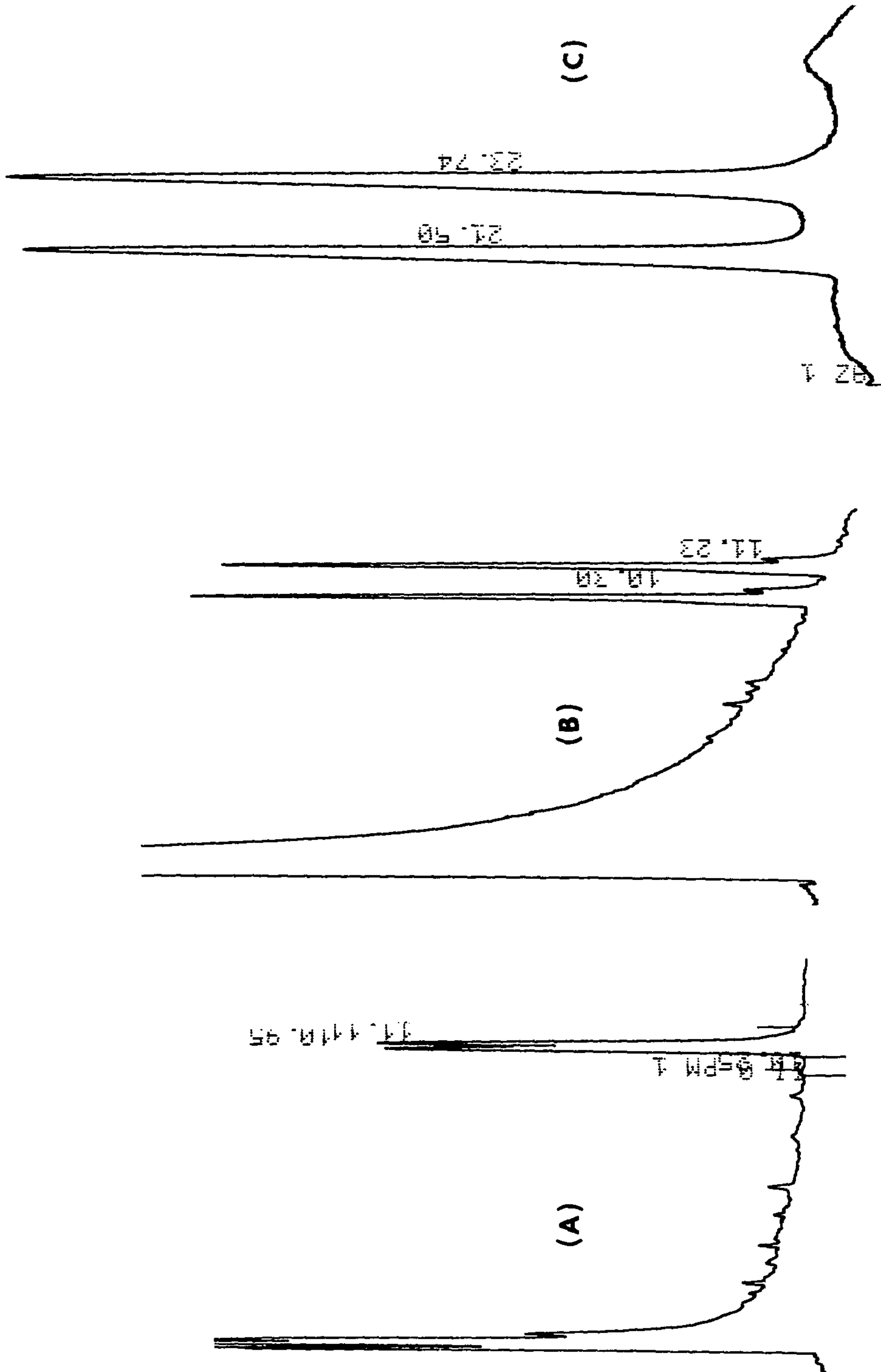

Figure 1. (A) GC/ECD chromatogram of 24 pg each of OCDD and OCDF on a 30 m SPB-5 capillary at 280°C using on-column injection; (B) GC/ECD chromatogram of 24 pg each of OCDD (10.30 min) and OCDF (11.23 min) on a 30 m DB-17 capillary at 300°C; (C) 75 pg each of OCDD and OCDF using a packed column inlet, a 15 m DB-17 megabore and a 255°C column temperature.

On-column injection affords good peak shape (Fig. 1) and reproducibility, but is not automated. OCDD and OCDF can be analyzed using a conventional packed column GC port operated at a high temperature (Fig. 1). The chromatogram depicted represents 75 pg each of OCDD and OCDF using the packed column inlet, a 15 m DB-17 megabore column, and a 255°C column oven. For routine automated GC analysis a 35 min oven temperature program was used. Automated GC operation is particularly desirable in screening where large numbers of samples are encountered.

Infrequently, the peak shapes and sensitivity degraded, particularly after analysis of high concentration sample extracts. The chromatographic performance was restored by replacing the glass inlet liner and removal of the front 5 - 10 cm of the column. Soil was a clean matrix in general, although in screening 150 soil composites for PCDD/PCDF, about 5% of sample extracts had to be rechromatographed due to ghost peaks from the previous chromatographic run. In every case the preceding sample had large amounts of electron-capturing coextractive interferences. A longer plateau in the oven temperature program may minimize this problem.

Soil Extraction Efficiency and Method Detection Limit. The initial selection of Soxhlet extraction with hexane for analysis of OCDD in soils (3) was based on its previous use in the extraction of OCDD from building dust (1). However, more information is needed regarding the efficiency of this procedure for extracting OCDD and OCDF from soil. Matrix extraction efficiency is difficult to determine absolutely because "true" concentrations are not known in real samples. Matrix fortification in the laboratory does not adequately incorporate chemical residues, or fully expose them to binding sites where chemisorption or nonspecific binding may occur. Therefore, most laboratory recovery data can only reveal gross deficiencies in extraction efficiency or other large systematic errors.

Organic carbon is the principal soil determinant of binding for most organic pollutants (8). OCDD is soluble in water at only 400 parts-per-quadrillion (9) and has an octanol-water partition coefficient of 10^{12} to 10^{13} (10) indicating the extreme lipophilicity of highly chlorinated dibenzodioxins and furans, as well as their affinity for soil organic matter. The soil binding constant, K_{OC}, for OCDD is estimated from the relationship to K_{OW} (8) to be about $2 X 10^{8}$. Thus, OCDD and OCDF are bound more strongly to soil surfaces than the less chlorinated PCDD/PCDF.

Equation 1.

$$K_{OC} = \frac{\text{ug adsorbed/g organic carbon}}{\text{ug/mL solution}}$$

$$\log K_{OC} = 0.544 \log (5 X 10^{12}) + 1.377 = 8.3$$

$$K_{OC} = 1.9 X 10^{8}$$

The efficiency of hexane Soxhlet extraction for OCDD and OCDF in soil was evaluated in various ways. The conventional approach of laboratory spiking to determine recovery was conducted with soils from Kern County. Extraction efficiency was also evaluated empirically by comparison of other extraction techniques including Soxhlet extraction with toluene and a single contact soil extraction using consecutive elution with acetone, ethyl acetate and dichloromethane (5).

A fine grained soil from Kern County when spiked at 1.0 ug/kg gave average recoveries of 108 and 101% for OCDD and OCDF, respectively (n = 5). The method detection limits calculated using the appropriate Student's t-value for four degrees of freedom were 0.75 and 0.41 ng/g for OCDD and OCDF, respectively. These MDLs are comparable to instrument detection limits achievable by EPA method 8280. In a recent batch of soil samples analyzed by a commercial laboratory, average OCDD and OCDF detection limits were 0.42 (n = 20) and 0.56 ng/g (n = 19), respectively.

Soxhlet extraction with toluene, a more polar solvent than hexane, did not appreciably affect recovery of OCDD from Kern County soils (Fig. 2). The soils studied were collected from sites where industrial and manufacturing wastes were incinerated for metals recovery, resulting in a range of soil OCDD concentrations. Aside from polarity, toluene has a much higher boiling point than hexane (BP = 111°C vs 69°C) meaning that the soil in the Soxhlet thimble is contacted by a much hotter extractant. Lastly, the duration of extraction for toluene was 8 hr vs 4 hr for hexane. In spite of the major differences in polarity, extraction temperature, and duration, hexane extraction gives comparable measurements in the Kern County soil.

The data depicted in Fig. 2 also demonstrate the comparability of the screening technique for OCDD determination with the more elaborate GC/MS procedure, EPA method 8280. These particular samples had average OCDF concentrations less than 10% of the OCDD levels, and this combined with the lack of ^{13}C-OCDF internal standard recoveries precluded similar comparisons for OCDF. The ^{13}C-OCDD internal standard recoveries averaged 64%.

The Albro <u>et</u> <u>al.</u> extraction procedure is rapid when compared to Soxhlet extraction. Industrial site soil extracts, however, were highly colored, possibly due in part to extraction of endogenous humic materials. On concentration in isooctane the extracts became cloudy with a precipitate that was soluble in isooctane-toluene (1:1, v/v). The GC/ECD chromatogram for the Albro method soil extract was extremely complex with major interferences that necessitated dilution of the extract. Hexane Soxhlet extracts were clean in comparison and did not require dilution. A second sample from a carbon black plant that looked like powdered asphalt yielded a tarry extract by either extraction procedure. Chromatograms of this sample using either extraction technique showed indistinguishable patterns of interfering coextractives. Little could be concluded from this experiment regarding extraction efficiencies.

The data available demonstrate that hexane is an effective and relatively selective extractant for OCDD and OCDF in soil. Some

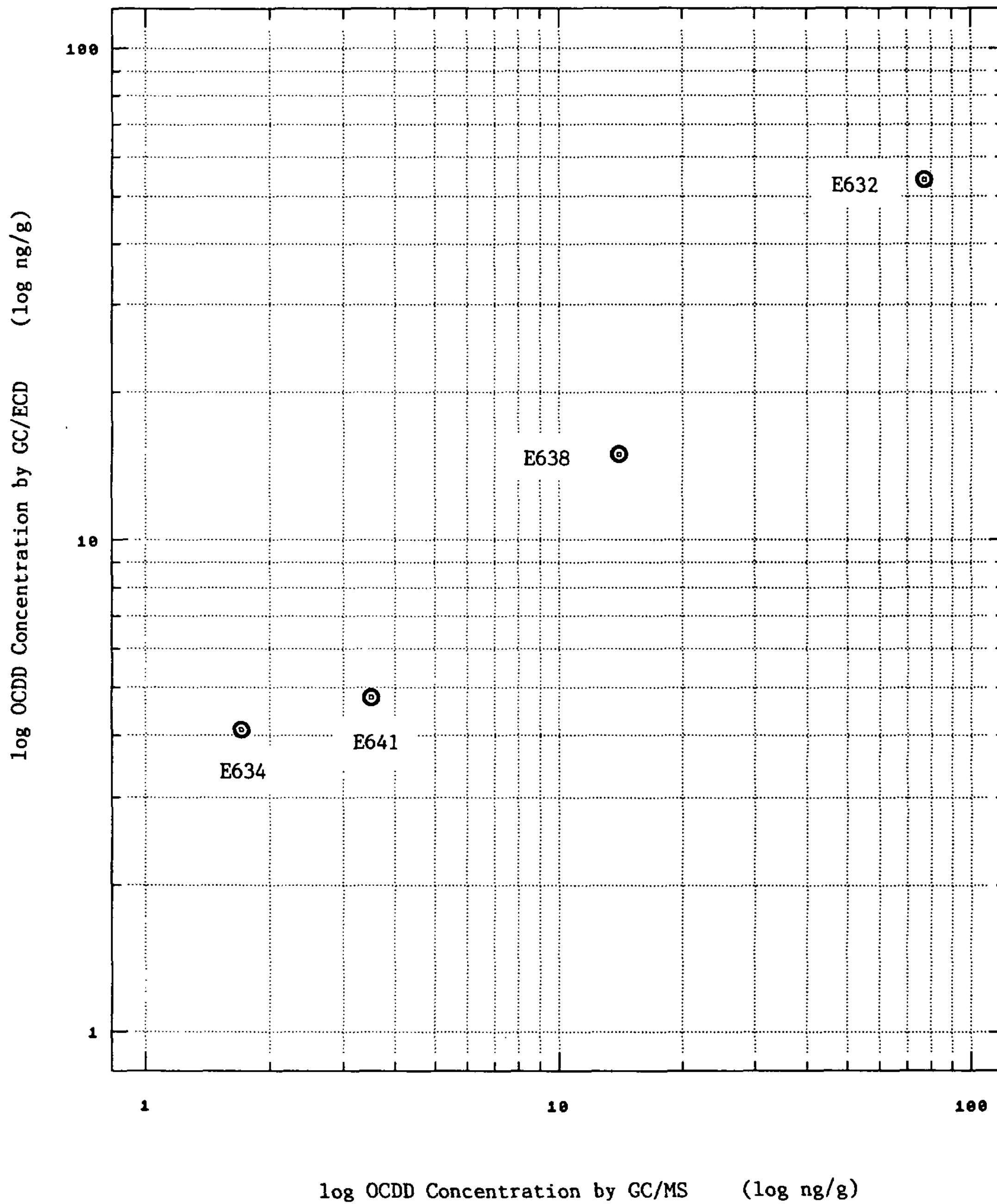

Figure 2. Comparability of OCDD determinations in Kern County industrial site soils by U. S. EPA method 8280 ("GC/MS") and using the OCDD/OCDF screening procedure.

samples, very few in our experience, are too complex for determination of trace levels of OCDD and OCDF by GC/ECD and become candidates for EPA method 8280.

Typical Chromatograms for Soil Samples and Quality Control. Examples of the application of the screening procedure are shown in Fig. 3. The soil samples were part of a community-wide study in Kern County in which a total of over 150 soil samples were tested. The laboratory data were obtained by one technician who completed the project in five weeks. In the chromatograms depicted, and all others from the study which included residential and nonindustrial sites, no supplemental sample cleanup was required.

A colocated sample at site E1095 submitted as a blind duplicate contained 5.7 ng OCDD/g and 0.59 ng OCDF/g. The analysis of E1162 was replicated with each sample batch as a positive control and indicated a high degree of reproducilibity as follows: 1.9 +/- 0.46 ng OCDD/g and 2.1 +/- 0.45 ng OCDF/g (n = 9). Analyses of a second soil sample from the study area and spiked with 1.0 ng/g of each octa compound also showed acceptable accuracy and precision as follows: 0.96 +/- 0.19 ng OCDD/g and 0.96 +/- 0.31 ng OCDF/g (n = 4). Method blanks in which an empty thimble was extracted contained no detectable residues (n = 4). Thus, the method appears to be rugged and reproducible.

Optional Florisil Cartridge Cleanup. Elaborate sample cleanup is not suitable for screening, but a simple cleanup may extend the applicability of the method to a broader range of samples or lower detection limits. The Florisil cartridge is useful for removing nonpolar interferences from OCDD and OCDF. OCDD is not eluted from the cartridge with hexane or 6% diethyl ether in hexane (Fig. 4.). OCDD begins to elute with 15% diethyl ether, although in the elution profile plotted, over 60% of the OCDD was still sorbed on the column. Elution with 40 mL of diethyl ether recovers 70 - 100% of OCDD and OCDF.

The Florisil cartridge separation has been used to remove lipids from biological samples (6). The 20 mL hexane eluate contains chlorinated pesticides and PCBs while up to 100 mg of coextracted lipids are retained. The data presented here in combination with reference 6 demonstrate that the Florisil cartridge separation is effective for isolating both OCDD and OCDF from PCB. This cleanup may be useful in screening PCDD/PCDF contamination produced in transformer fires and or PCB spills.

When testing the Florisil cartridge cleanup on an Oroville soil sample spiked with 1.2 ng/g each of OCDD and OCDF, recoveries were only 34 - 40% and 37 - 41%, respectively. These low recoveries were confusing initially, and led to questions about the soil extraction efficiency. In fact, OCDD/OCDF recoveries from the Florisil cartridge are strongly influenced by the absolute quantity of analyte adsorbed (**Table I.**). Recoveries are excellent above 200 ng, but drop to only about 35% in the low ng range. Recoveries from the soil matrix were in the same range expected where 24 ng of OCDD and OCDF are added directly to the Florisil bed. The chromatographic elution profiles for OCDD and OCDF were also affected by the spike level (**Table II.**). At higher

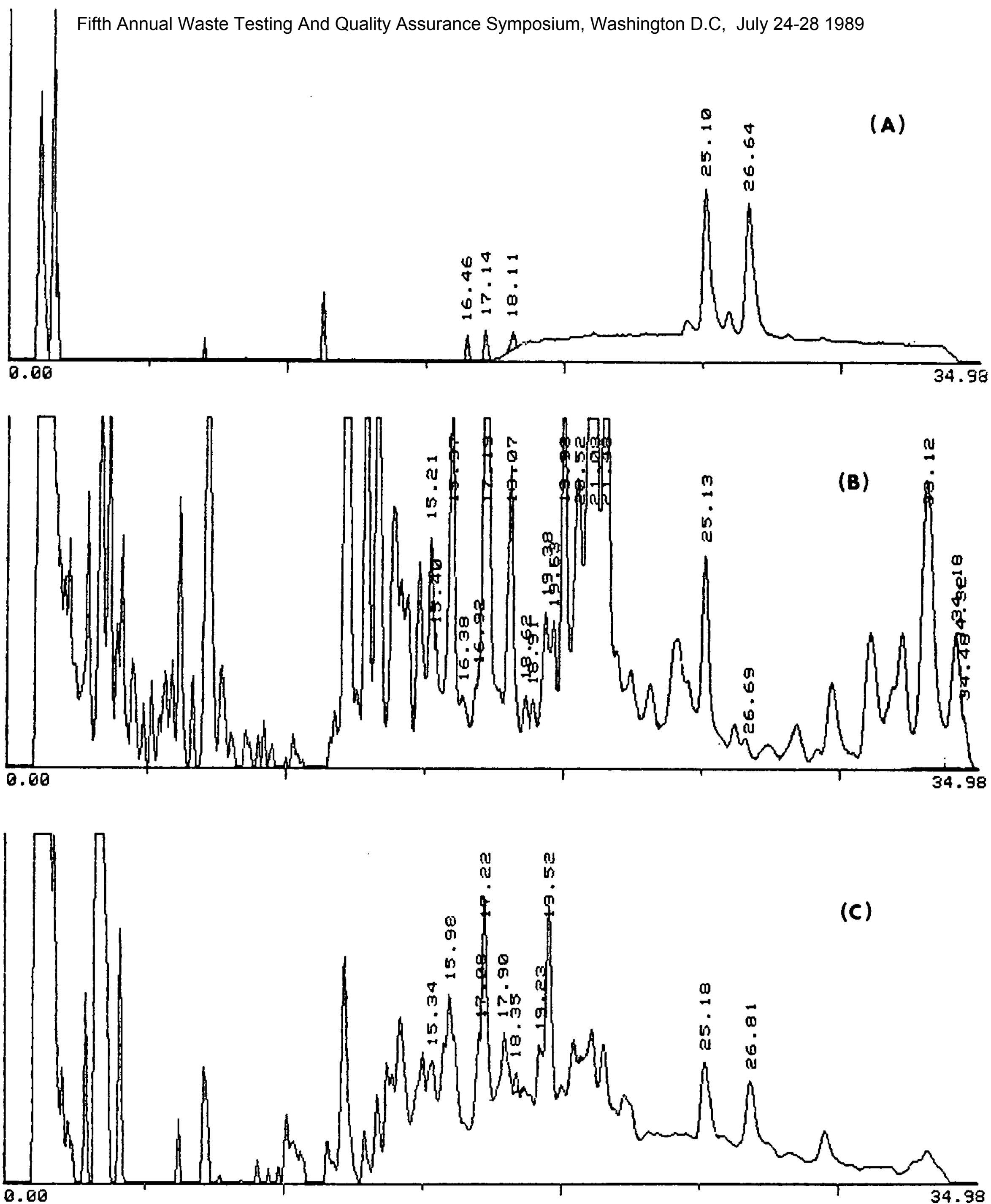

Figure 3. (A) GC/ECD chromatogram of 48 pg each of OCDD and OCDF (attenuation 4); (B) Kern County soil sample E1095 containing 4.3 ng/g OCDD and 0.35 ng/g OCDF (attenuation 6); (C) Kern County soil E1162 containing 1.4 ng/g each of OCDD and OCDF (attenuation 4).

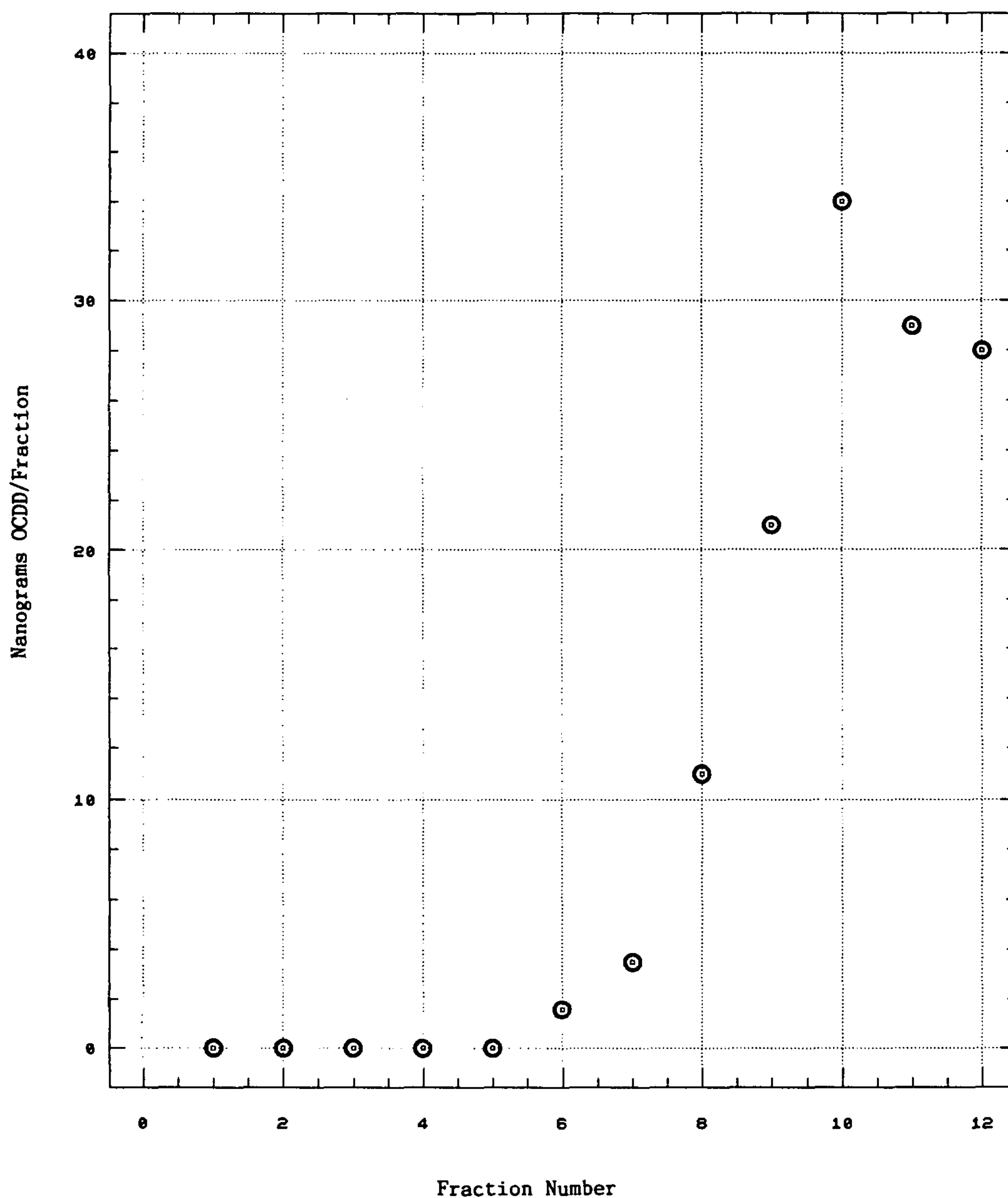

Figure 4. Elution of OCDD from a Florisil SepPak cartridg Fractions 1 - 4 are each 5.0 mL of hexane, 5 - 8 are 5.0 mL 6% dieth ether in hexane, and 9 - 12 are 5.0 mL 15% diethyl ether in hexane.

concentrations most OCDD/F is eluted with the first 20 mL of diethyl ether, but at lower levels the second 20 mL of diethyl ether is most important.

Table I. Effect of Spiking Level on the Recovery of OCDD and OCDF from Florisil Cartridges.

Analyte Added (ng)			Recovery (%)	
OCDD	OCDF	Replicates	OCDD	OCDF
220	-	1	100	-
220	220	1	70	72
24	24	3	50 ± 5.5	54 ± 7.0
3.5	3.5	3	38 ± 4.9	43 ± 5.7
3.5[a]	3.5[a]	3	32 ± 3.1	34 ± 4.6

a Florisil packing removed and transferred to a glass column

Table II. Effect of Spike Level on the Chromatographic Elution of OCDD and OCDF from Florisil Cartridges.[a]

	% OCDD Eluted			% OCDF Eluted		
Spike Level	F1	F2	F3	F1	F2	F3
220 ng	0	58	12	0	58	14
3.5 ng	0	7.3	22	0	6.3	23

a F1 = 20 mL hexane, F2 = first 20 mL of diethyl ether,
F3 = second 20 mL of diethyl ether

Florisil cartridge cleanup of the carbon black plant soil extract produced a clean hexane eluate. Unfortunately, diethyl ether eluted the electron-capturing interferences making trace-level OCDD/OCDF determination impossible. Nevertheless, the Florisil cleanup may be effective with other matrices.

Determination of OCDD and OCDF in Egg Yolk. Because ingestion is a major route of human exposure to environmental dioxins, biological samples including human milk, fish, dairy and poultry products and red meat are frequently encountered in the laboratory. Our preliminary attempts to analyze OCDD and OCDF in biological matrices were promising.

Some form of defatting (e.g., solvent partitioning, oxidation, saponification or chromatography) is critical for analysis of trace constituents. Egg yolks studied here contained between 22 and 27% lipid by weight. GPC provided good separation of corn oil or egg yolk lipids from the octa compounds (Fig. 5). GPC separation with the column used is limited to ~one gram of lipid and therefore ultratrace analysis or analysis of matrices very high in lipid like adipose may require multiple runs. Using one sample loop and chromatographic cycle, instrument detection limits of about 0.5 to 1.0 ng/g lipid were possible.

Egg yolk extracts without further cleanup showed a broad, featureless rise in the baseline (Fig. 6). Distinct chromatogaphic peaks for both OCDD and OCDF are observed at the 1.1 and 3.6 ng/g lipid spike level. The method as described is sufficiently sensitive to detect OCDD in some egg samples, for example, those collected from contaminated areas in the northern California community of Oroville (7). The available recovery data are limited (**Table III.**), but are in the range of 73 - 130% for OCDD and 53 - 110% for OCDF.

Table III. Quantitative Analysis of OCDD and OCDF in Egg Yolk Lipid.[a]

Sample	Egg Yolk Lipid (g)	OCDD/F Fortification (ng each/g fat)	OCDD/F Found (ng/g Lipid) OCDD	OCDF	OCDD/F Recovery (%) OCDD	OCDF
1395.A	4.14	3.6	3.3	2.8	92	76
1395.B	4.14	3.6	2.6	1.9	73	53
0298.A	4.38	1.1	1.3	1.3	120	110
0289.B	4.38	1.1	1.5	1.3	130	110
1365.A	5.15	0	ND	ND	-	-
1365.B	5.15	0	ND	ND	-	-
Method Blank A	0	0	ND	ND	-	-
Method Blank B	0	0	ND	ND	-	-

a Lipid content in the egg yolk samples varied between 22 and 27%.

SUMMARY

1. Improvements in screening methodology allow OCDD and OCDF determination with sensitivities comparable to EPA method 8280.

2. Screening OCDD and OCDF in soil is useful in defining environmental contamination by PCDD/PCDF. The extent to which sources have been characterized by GC/MS determines their applicability as markers or surrogates.

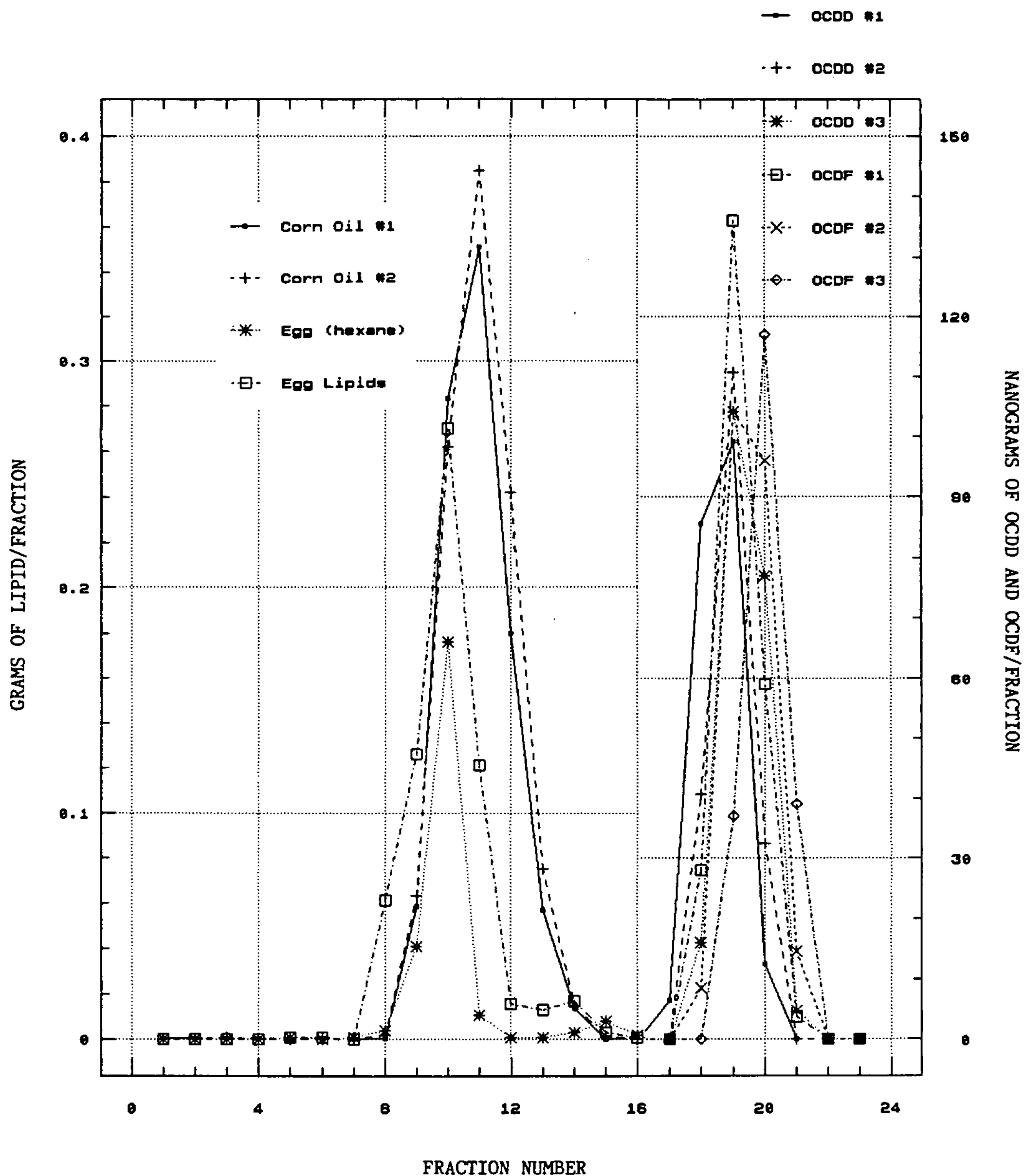

Figure 5. Separation of corn oil or egg yolk lipids from OCDD and OCDF by gel permeation chromatography using Biobeads SX-3 and methylene chloride-cyclohexane (1:1, v/v) mobile phase. Replicates are plotted for corn oil and the octa compounds over a several month period. Total and hexane-extractable egg yolk lipids are plotted and approximately coelute with corn oil.

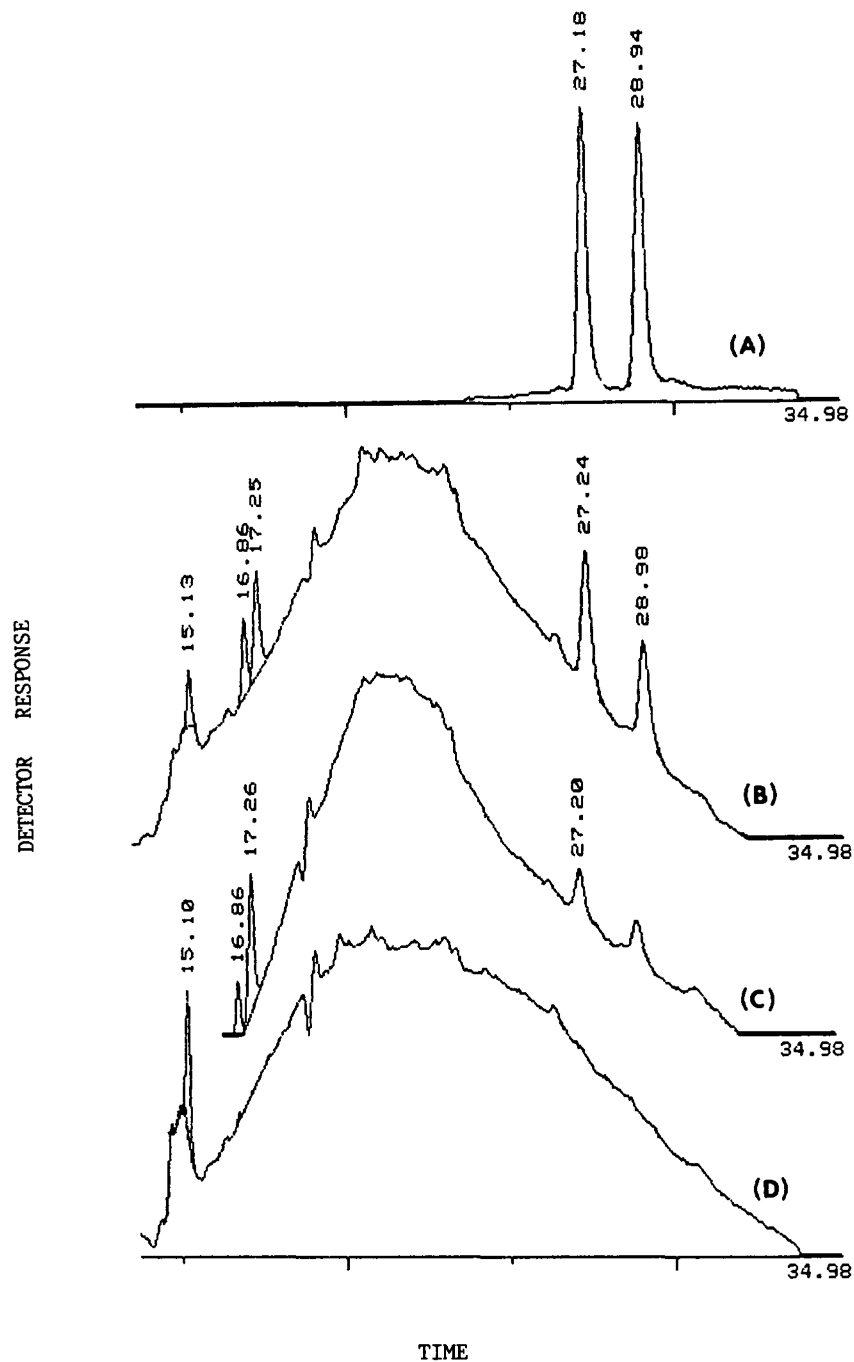

Figure 6. (A) 48 pg each of OCDD and OCDF; (B) egg yolk spiked wi 3.6 ng OCDD and OCDF each/g lipid; (C) egg yolk spiked with OCDD a OCDF at the 1.1 ng/g lipid level; and (D) unspiked egg yolk sample same dilution. Egg yolk extracts were spiked before the GPC clean step and no further cleanup was used.

3. Use of Florisil cartridge separation isolates OCDD and OCDF from nonpolar intereferences like PCB, but recoveries are reduced at low ng levels.

4. Screening techniques are useful for biological samples including egg yolks after sample defatting.

ACKNOWLEDGEMENT

Hyun Park, Gillian Wild and Charles King of the California Public Health Foundation provided technical assistance. Martha Harnly and Myrto Petreas organized the community study in Kern County and provided various samples for study.

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PRESCREENING MARINE SEDIMENT SAMPLES USING CAPILLARY GC/MIP ATOMIC EMISSION DETECTOR TO EFFECT MORE EFFICIENT SAMPLE CHARACTERIZATION BY CAPILLARY GC/MS

Billy Bob Potter. George Michael Brilis, William C. Brumley, Irene M. Meyer-Farnham, U.S. EPA, EMSL-LV, P.O. Box 93478, Las Vegas, NV 89193-3478.

Abstract. The EPA-LV and Hewlett Packard have collaborated to assess the potential of a prototype element specific gas chromatograph detector to analyze target compounds and to provide empirical formula information on non-target compounds in environmental samples. This prototype detector is similar to the recently commercialized HP 5920A atomic emission detector. This detector uses a microwave-induced plasma to produce highly energetic atoms from a GC effluent, and the concentrations of these atoms are then determined with an emission spectrometer. This technology has recently been applied to the analysis of extracts from sediments contaminated with creosote oil. These sediments pose a challenge to the analyst because they contain large amounts of polynuclear aromatic hydrocarbons (PNA's) as well as a complex mixture of naturally occurring organic constituents. The six data channels from the element selective atomic emission detector were found to simplify the analysis of this complex matrix by eliminating hydrocarbon responses and focusing the attention of the analyst on organic compounds that contained specific elements of interest (e.g., chlorine, nitrogen, sulfur and oxygen). This approach was used to direct the interpretation of the gas chromatograph mass spectrometry data, and resulted in the identification of two compounds, quinaldine and naphthalene nitrile, that were not detected initially because their signals were obscured by PNA responses. This approach can be extended to provide data on organometallic species (i.e., tin, mercury, and arsenic) in samples and to provide additional information on compounds that are not positively identified in mass-spectral search routines such as the tentatively identified compounds of the Contract Laboratory Program.

NOTICE: Although the research described in this article has been funded by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

The Environmental Monitoring Systems Laboratory, Las Vegas (EMSL-LV) of the U.S. Environmental Protection Agency (EPA) is assisting the EPA Region 10 Laboratory, Manchester, Washington in developing an efficient method to monitor clean-up efforts of the Eagle Harbor Superfund site in Puget Sound. Sediment samples collected from this Superfund site contain creosote oil which is used by the wood treatment industry. The EPA Regional Laboratory staff requested assistance in improving the current screening method, which is based on the technique used in a study by Krone et al.(1). Krone, using a combination of gas chromatograph/nitrogen-phosphorus detector (GC/NPD) and gas chromatograph/mass spectrometer (GC/MS) to analyze Eagle Harbor sediment samples, was able to identify over 200 distinct nitrogen-containing aromatic compounds (NCAC). This technique is laborious and time consuming. The GC/NPD is used to screen for samples that should receive confirmatory analysis by GC/MS. The GC/NPD often produces false positive identification of target compounds. These trigger unnecessary GC/MS confirmation analyses, thus increasing the cost for monitoring clean-up efforts.

Region 10 Laboratory supplied sample extracts, NCAC standards and the results of their GC/NPD analysis of samples NCAC #519, NCAC #535 and NCAC #545. These samples were reanalyzed at EMSL-LV using two different instrument systems. The first instrument used to characterize these samples was an HP 5890A gas chromatograph/full scan electron impact mass spectrometry using a VG 7070EQ magnetic sector instrument, and will be referred to as simply GC/MS. The second instrument system was used to analyze the Eagle Harbor sediment samples. This instrument system was provided by Hewlett Packard (HP) and consists of an HP 5890A gas chromatograph and the HP prototype (commercial model HP 5920A) atomic emission detector and it is referred to as GC/AED.

EXPERIMENTAL

The elemental chromatograms produced by the GC/AED of the EMSL-LV, were compared to those produced by GC/NPD at the EPA Region 10 laboratory. This report describes the results of our analyses of the sample extracts for Appendix 9 compounds. These analyses were completed using GC/AED and GC/MS. The GC/AED is capable of monitoring several element-specific signals simultaneously per injection, and during this preliminary characterization of the samples, eight channels were selected. They are carbon (495.7nm), hydrogen (486.1nm), chlorine (479.5nm), bromine (478.6nm), sulfur (181.4nm), nitrogen (174.3nm), and oxygen (777.3nm). An additional channel for carbon (193.03nm) was selected because of its selectivity and sensitivity. The high intensity from carbon emission saturated carbon (193.03nm) channel producing truncated peaks, whenever high concentrations of hydrocarbons were present in a sample. Even so, this channel was monitored in order to provide instrument sensitivity for blanks and samples containing

little or no creosote waste. The gas chromatographic and atomic emission detector conditions may be reviewed in Tables 1 and 2.

Table 1
Gas Chromatographic Parameters

Instrument Configuration (Model Numbers)	
Gas Chromatograph:	HP 5890A
Autosampler:	HP 7673A
AED Detector:	HP prototype
Computer/Workstation:	HP 300/9153C
Gas Chromatograph Parameters	
Injection Port Type:	SPLIT/SPLITLESS
Injection Port Temperature:	200°C
Injection Type / Mode	
Autosampler:	10 μl/3 wash
Splitless Mode	
Purge Flow:	100 ml/min
Purge Time:	0.5 min
Injection Volume:	1 μl
Column:	DB-5, 30 M X .32 mm 0.25 μm film thickness No. BC 8182514 J&W
Column-Detector Coupling:	Direct to Detector
Oven Temperature Program:	intl.50°C/hold 1 min 5°C/min/300°C hold 5 min
Column Flow Rate (ml/min)	1 ml/min
Column Linear Velocity (cm/sec)	34 cm/sec

Table 2
Atomic Emission Detector Parameters

Elements Analyzed:

ELEMENT	SPECTRA LINE	REAGENT GAS	VENT OFF ml/min	VENT ON ml/min	INJECTION NO.
Carbon	495.724	O_2	21.8	21.1	1
Hydrogen	486.133	O_2	"	"	"
Chlorine	479.465	O_2	"	"	"
Bromine	478.553	O_2	"	"	"
Carbon	193.031	O_2/H_2	21.8/27.0	21.1/26.8	2
Sulfur	181.354	O_2/H_2	"	"	"
Nitrogen	174.261	O_2/H_2	"	"	"
Oxygen	777.302	H_2/AUX*	1.05	1.05	3

* AUX=reagent gas mixture

Total number of injections for all elements: 3 @ 40 min. each

Spectrometer purge flow: Nitrogen @ 2 L/min
Window purge: Helium @ 40 ml/min

Solvent back flush used, Yes/No: Yes

Transfer line temperature: 250°C

Cavity temperature: 250°C
pressure: 1.5 psi

Water temperature: 65°C

Reagent Gas pressure:
Aux 60 psi
Hydrogen 70 psi
Oxygen 25 psi

RESULTS AND DISCUSSION

Using the GC/AED and GC/MS instrument systems, it was found that GC/NPD results as provided by Region 10 Laboratory in some instances did not agree with EMSL-LV Laboratory results. There appears to be at least one mis-identification in the sample NCAC #535, the peak identified as benzonitrile in the GC/NPD analysis

appears to be due to 2,4,6-trimethylpyridine (tentative identification). Several compounds were tentatively identified using the GC/MS that had not been observed previously including 2,4-dimethylpyridine, other isomers of dimethylpyridine, methyl- and dimethylnaphthalene, and benzo- and dibenzothiophene and dibenzofuran. Confirmation of many compounds by GC/MS was complicated by chromatographic problems. Poor peak geometry and non-resolved peaks were encountered for quinoline, indole, benzoquinoline and acridine. Attached are the GC/MS results from the first analysis for samples #535 and #545 (Table 3). Sample #519 contained a large amount of elemental sulfur; this increased background noise and precluded reliable analysis by GC/MS.

A comparison of the results between GC/MS and GC/AED indicated that some of the nitrogen and sulfur compounds had not been observed in the first GC/MS analysis. Specifically, the atomic emission detector indicated that two nitrogen compounds and one sulfur compound were located in the same area of the chromatogram where the responses of polynuclear aromatic hydrocarbons (PNA's) were 10 to 20 times greater than peak responses for these nitrogen and sulfur containing compounds. As a result, total ion chromatographic trace from the PNA's overwhelmed the responses of the nitrogen and sulfur compounds.

TABLE 3
GC/MS RESULTS

PNA	Scan Number	Retention Time	Concentration Sample #545 ng/µl	Concentration Sample #535 ng/µl
Naphthalene	167	6:24	0.68	>290
Acenaphthylene	302	9:10	0.05	26
Acenaphthene	397	11:06	0.26	330
Anthracene/Phenanthrene	621/636	15:40/15:46	>13	980
Chrysene/Benzoanthracene	929	21:57	>19	140
Fluorene	485	12:54	1.0	300
Pyrene/Fluoranthene	764/787	18:35/19:03	24	710
Benzofluorene/	1076/1100	24:57/25:26	24	95
d8-Naphthalene	167	6:24	8.0*	8.0*
d10-Phenanthrene Benzopyrene	624	15:44	5.0*	8.0*
NCAC				
Benzonitrile	67	4:22	n.d.	n.d.
Benzothiazole	190	6:53	1.0	n.d
Quinoline	198	7:02	n.d.	n.d.
Isoquinoline	212	7:20	n.d.	n.d.
Indole	234	7:47	n.d.	n.d.
7, 8-Benzoquinoline	623	15:43	n.d.	n.d.
Acridine	630	15:51	0.64	n.d.
9-Methylcarbazole	642	16:06	n.d.	n.d.
Carbazole	650	16:16	2.4	31

* - amount injected

n.d. - not detected (no detection limit has been established at this time)

The nitrogen-containing compounds were subsequently located in the total ion chromatogram of the GC/MS by using the GC/AED traces of the carbon elemental chromatogram and the nitrogen elemental chromatogram. By comparing the patterns of the GC/MS, carbon and nitrogen chromatograms, the peaks of interest were isolated with respect to major PNA peaks. Using this information, the GC/MS analyst confirmed the existence of nitrogen-containing compounds which were obscured by the responses of the PNA's. It was found that the direction for the intensified search of GC/MS analyses of Eagle Harbor samples was best provided by the graphic presentations of the GC/AED elemental chromatograms for carbon, nitrogen, oxygen and sulfur channels. A discussion of attached plots which were produced by the GC/AED's computer follows:

Plot No. 1 is of Eagle Harbor sediment sample NCAC #535. This is a four channel chromatogram (carbon 496nm, sulfur 181nm, oxygen-777nm, and nitrogen 174nm). The sediment sample is a complex matrix containing carbon, sulfur, oxygen and nitrogen-containing compounds. The plot is a combined plot of the four AED channels of interest. It may initially seem confusing to the eye and mind; however, it demonstrates the amount of information which the AED is capable of producing. This plot was normalized in order to place the four channels on one plot thus, the scale does not represent relative channel responses.

Plot No. 2 demonstrates how the selection of only one channel (nitrogen 174nm) can simplify the analysis for NCAC #535 by focusing the analyst's attention on specific target compounds. Note that toward the center of the chromatogram there are two compounds which were not observed on the first scan and library search of the GC/MS. These NCAC's were either co-eluted with, or were small shoulders of, much larger PNA peaks (i.e. methyl naphthalene and acenaphthalene). After these peaks were observed in the AED analysis, the nitrogen-containing compounds were tentatively identified by GC/MS as a quinaldine and an isomer of naphthalene nitrile.

Plot No. 3 is the sulfur 181nm channel, which has a large peak located at 12 minutes on the chromatogram. This peak was also observed on the first analysis by GC/MS as benzo[b]thiophene, even though this sulfur-containing compound was located on the shoulder of the naphthalene peak. Two peaks (A & B) were not identified by GC/MS.

Plot No. 4 is the oxygen 777nm channel which has a major peak located at 19 minutes. This peak was also identified in the first analysis by GC/MS as dibenzofuran.

Plot No. 5 is the carbon channel 496nm. This plot contains the peak clusters which obscured benzo[b]thiophene, quinaldine and naphthalene nitrile thus making it difficult to identify by GC/MS.

These clusters contain naphthalene, isomers of methyl-naphthalene and acenaphthene.

CONCLUSION

The atomic emission detector is an effective tool for prescreening sediment samples and can direct GC/spectral analyses by locating areas within the mass spectral scans where nitrogen-containing compounds may be located. The complexity of these Eagle Harbor samples is evident by the number of peaks detected by the AED carbon channel. Region 10's nitrogen phosphorus detector produced between 100 to 200 peaks which were presumed to be nitrogen-containing compounds. Our results indicate that many of these peaks were actually hydrocarbon which resulted when the NPD selectivity was exceeded by high concentrations of PNA's. Thus, the GC/NPD may not be a suitable screening detector for nitrogen-containing compounds found in creosote contaminated sediment samples. The possibility of false positive peaks as a result of overcoming detector selectivity demonstrates that identifications of target compounds should not be made on the basis of retention time matches in GC/NPD analyses. The GC/AED is much more selective for nitrogen-containing compounds, but it is less sensitive than the GC/NPD and therefore may miss NCAC's at lower concentration levels.

Two compounds were missed by the GC/MS in the initial investigation. The GC/AED had strong responses for both these compounds, and they were later identified by the full scan electron impact mass spectrometer using the atomic emission detector's nitrogen chromatogram to assist in the search. In this way, the GC/AED can be used for the purpose of prescreening complex sample matrices and can supply additional information to GC/MS analysts, who then can make more efficient use of mass spectral search methods to locate hidden peaks. If the GC/AED had received the Eagle Harbor samples before the GC/MS analyses, approximately 2 to 3 hours of data review would have been saved, thus making the mass spectral search more efficient.

ACKNOWLEDGEMENTS

The HP 5921A Atomic Emission Detector, project staff of the Hewlett Packard Company, Avondale Pennsylvania for providing the prototype AED and engineering support for this study.

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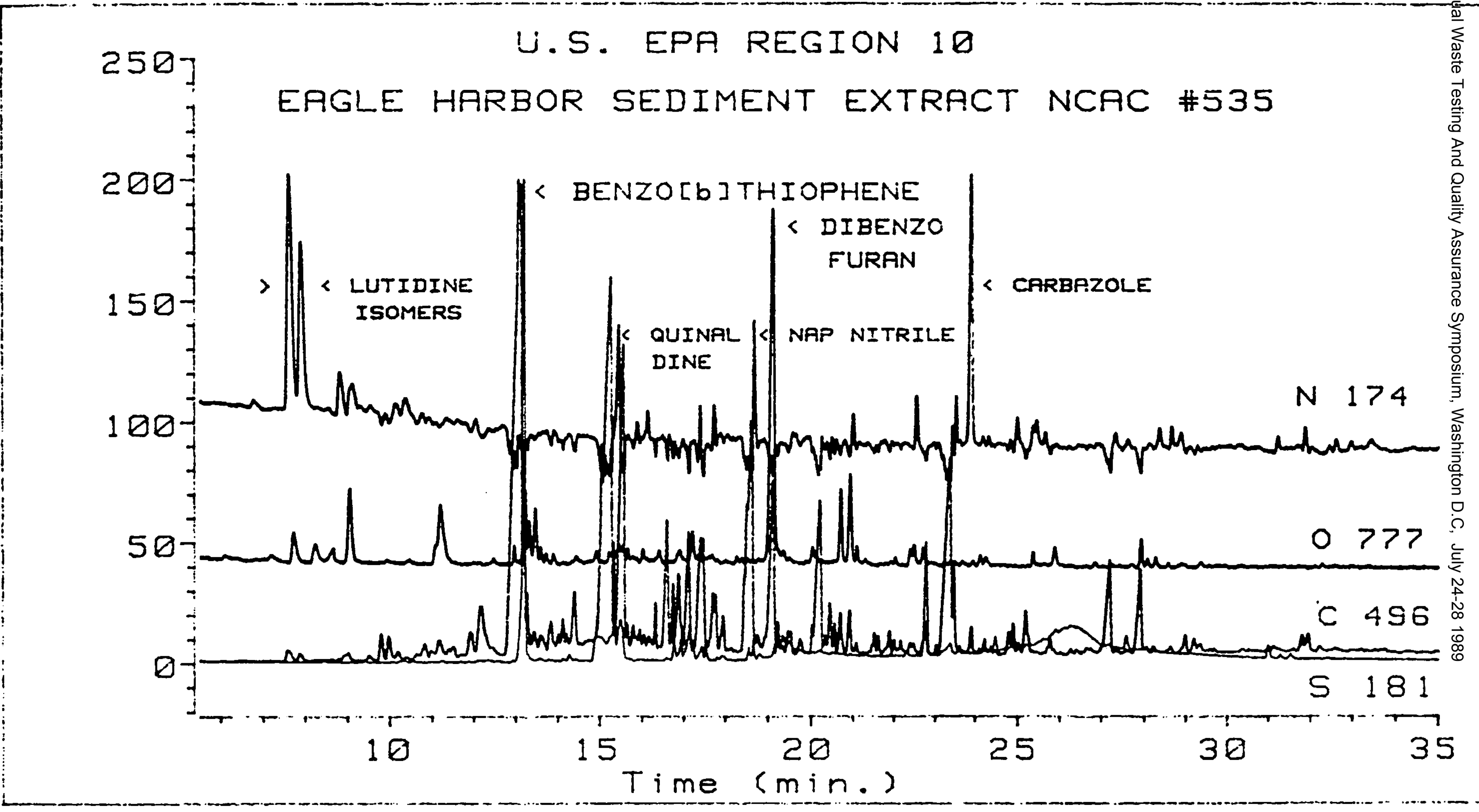
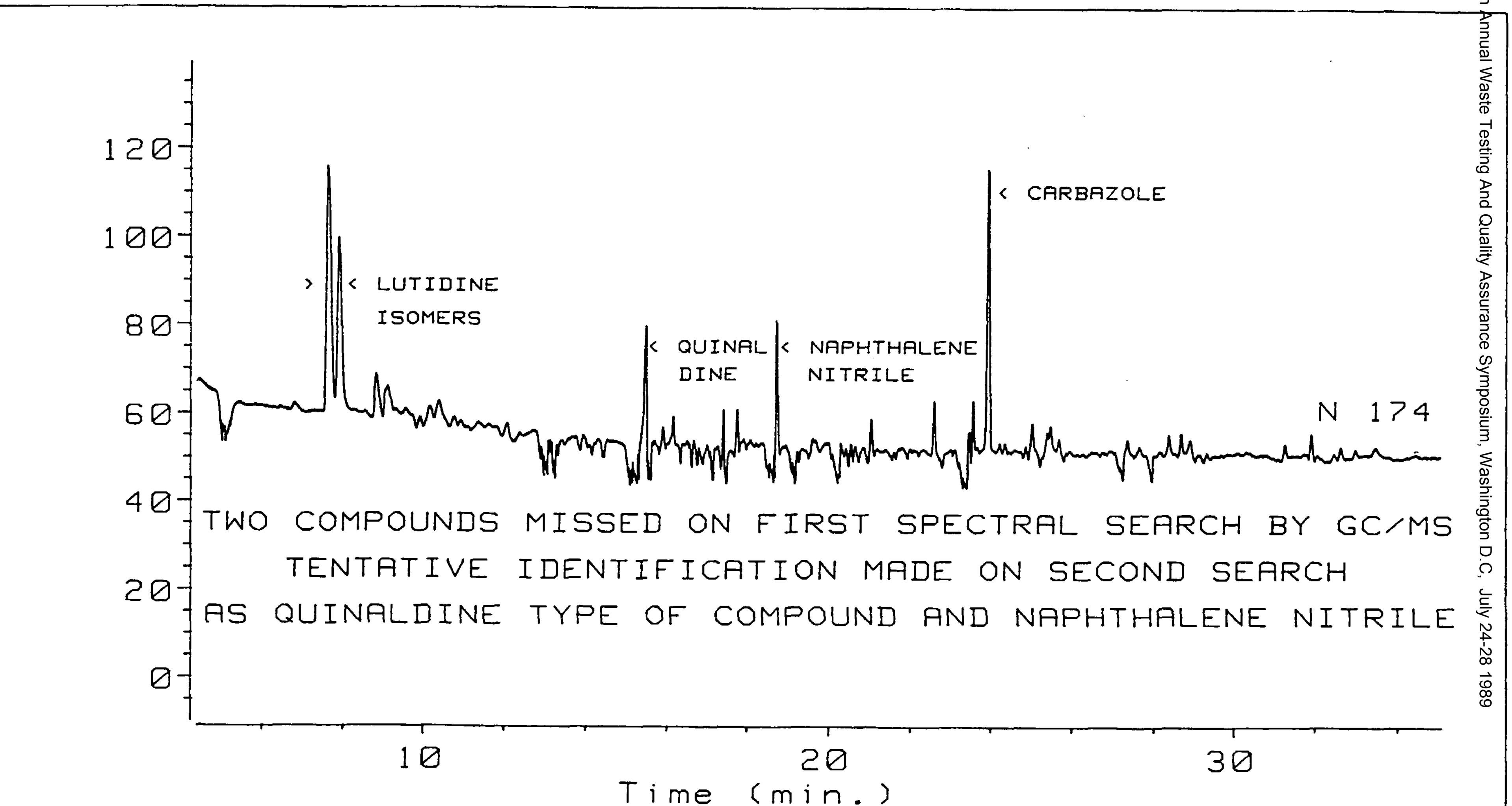


Plot 1



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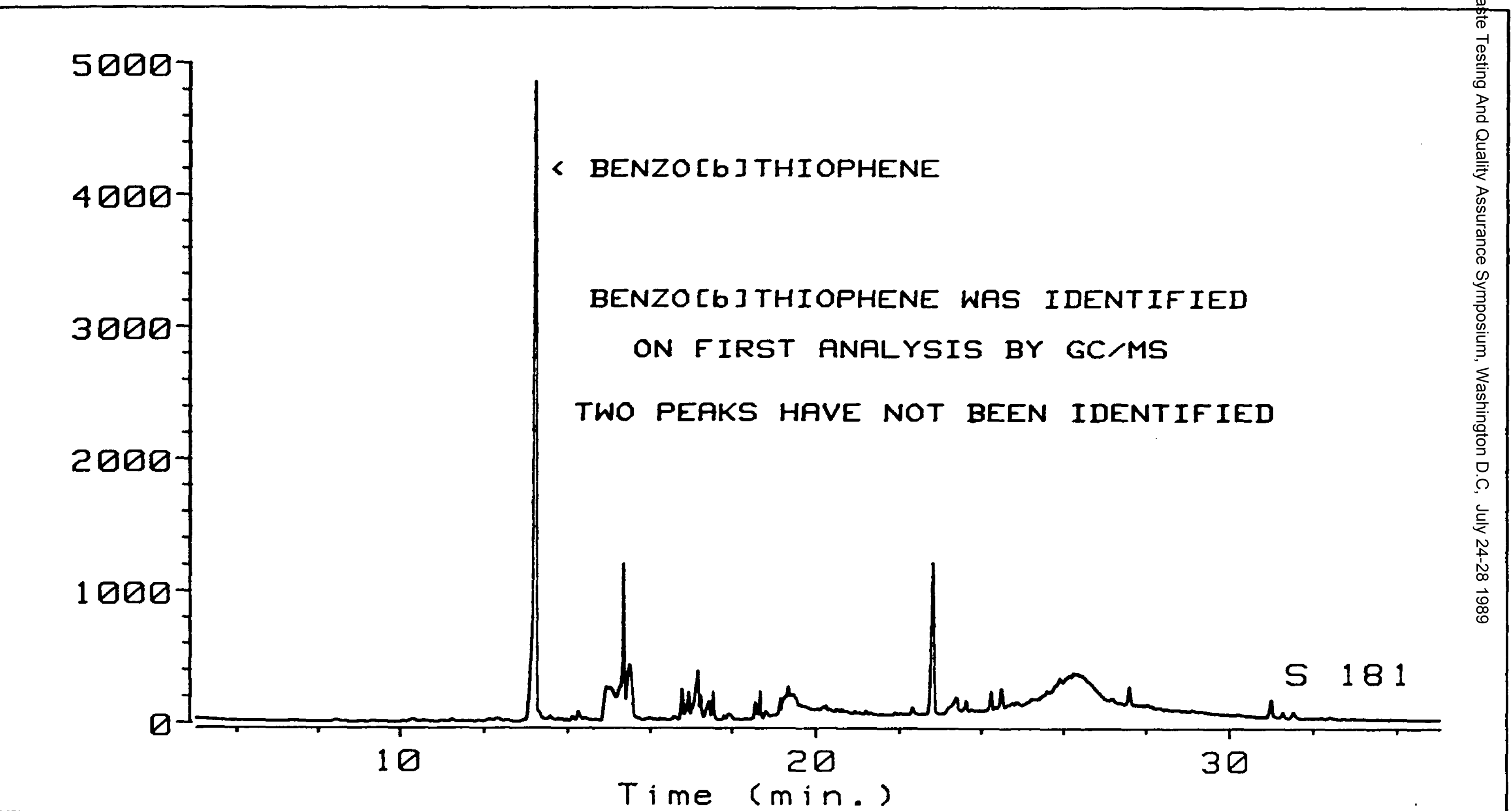
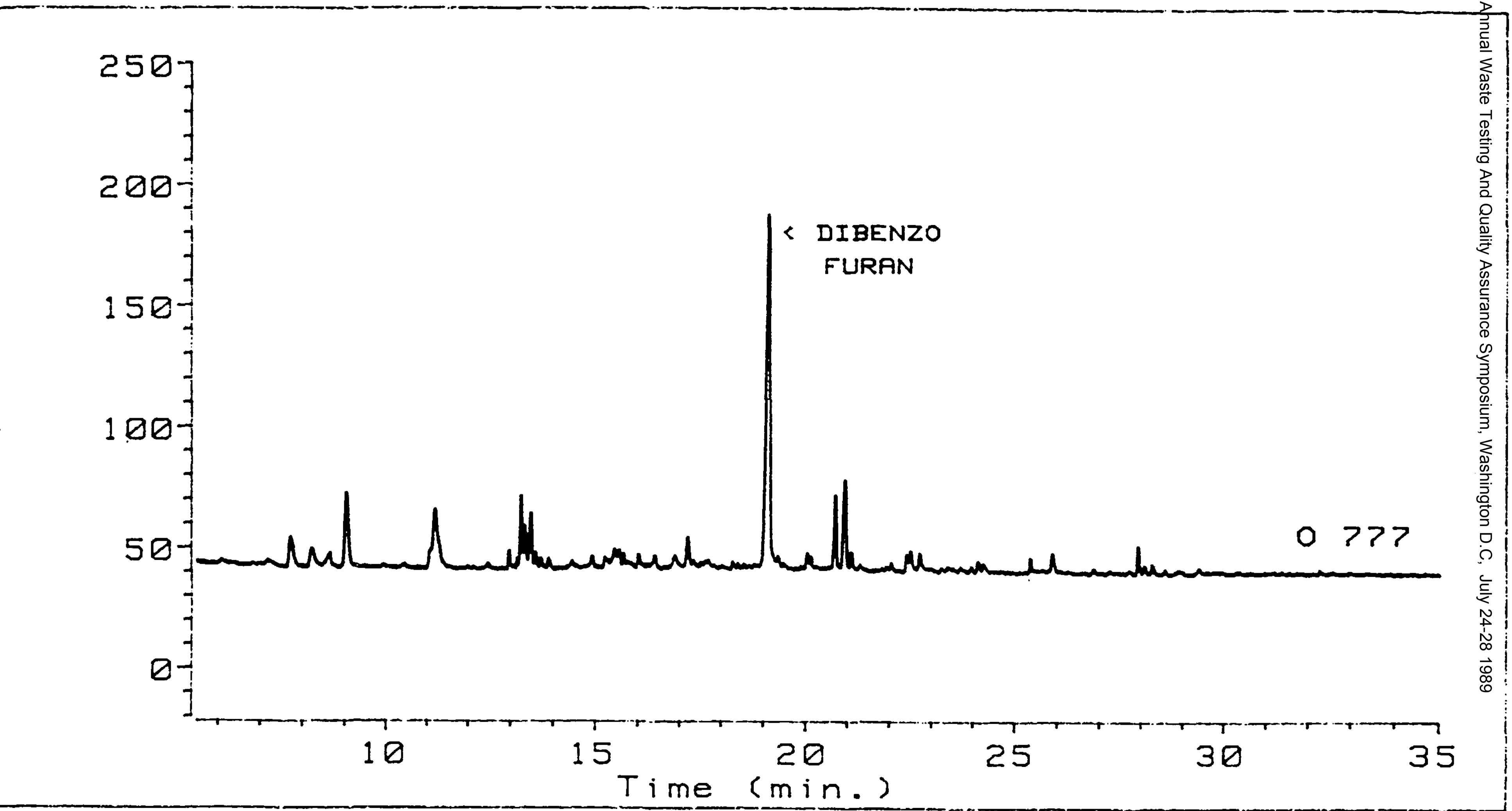
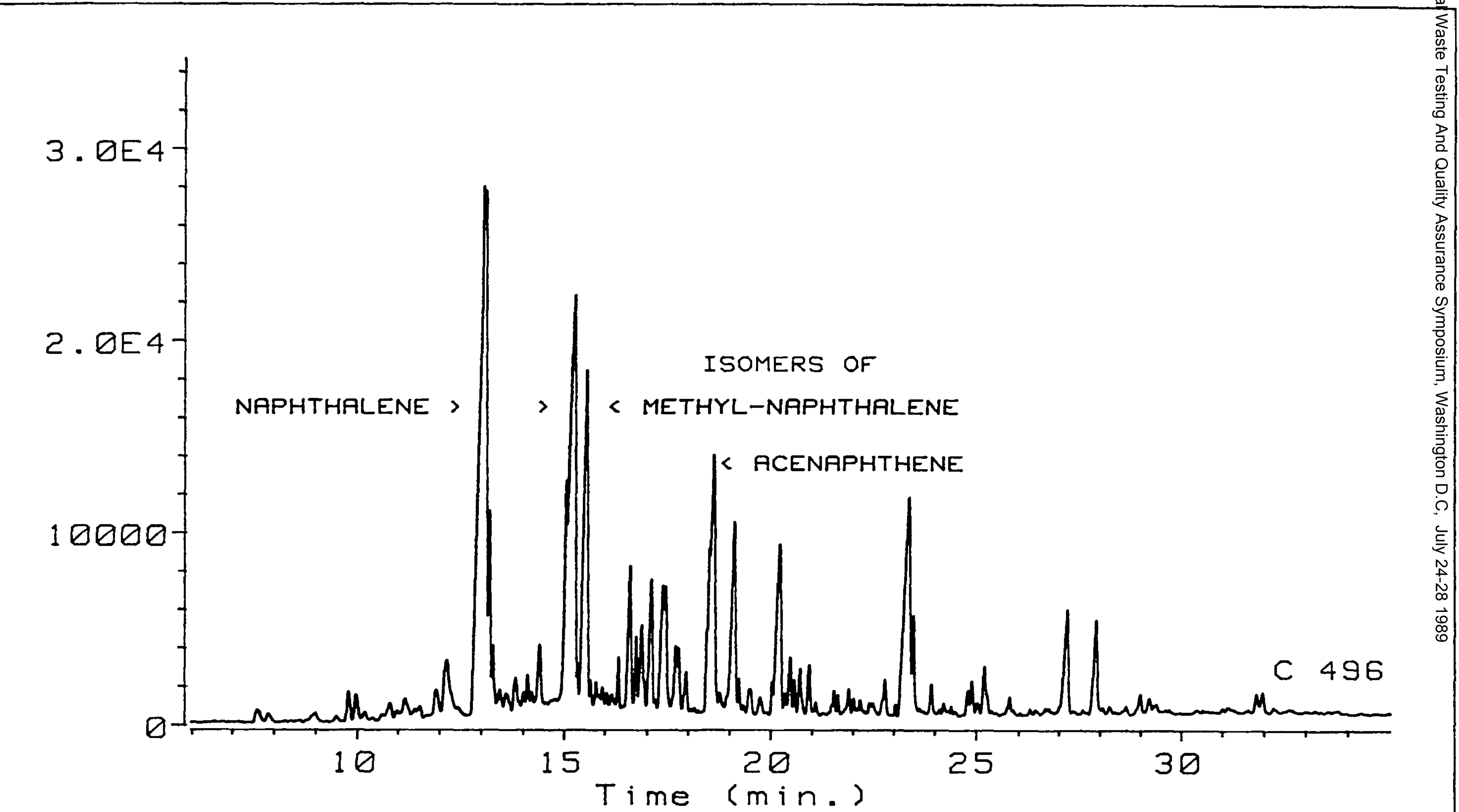


< BENZO[b]THIOPHENE
BENZO[b]THIOPHENE WAS IDENTIFIED
ON FIRST ANALYSIS BY GC/MS
TWO PEAKS HAVE NOT BEEN IDENTIFIED
S 181
5000
4000
3000
2000
1000
0
10
20
30
Time (min.)



Plot 4



Plot 5

Fifth Annual Waste Testing And Quality Assurance Symposium, Washington D.C, July 24-28 1989

QUALITY ASSURANCE CONSIDERATIONS IN THE SOLID PHASE ADSORBENT CLEAN-UP FOR PESTICIDE ANALYSIS

V. A. ECKER, D. A. MILLER, Ph.D., T. C. CHIANG, Ph.D., LOCKHEED ENGINEERING AND SCIENCES COMPANY, 1050 EAST FLAMINGO ROAD, LAS VEGAS, NEVADA 89119; P. J. MARSDEN, Ph.D., G. W. SOVOCOOL, Ph.D., UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, 944 EAST HARMON AVENUE, LAS VEGAS, NEVADA 89120.

ABSTRACT. The packed column gas chromatographic method for organochlorine pesticides/PCBs required as part of the Environmental Protection Agency's Contract Laboratory Program (CLP) has been improved. The new pesticide analytical procedure for the CLP utilizes liquid-liquid (for water) or ultrasonic (for soil) extraction procedures and wide-bore capillary column (0.53 mm id) analysis with electron capture detection (ECD). Extract cleanup procedures include gel permeation chromatography, Diol bonded silica adsorption columns, and optional techniques for sulfur removal. Additional method quality control (QC) criteria are required for these clean-up procedures.

The use of wide-bore capillary columns provides increased resolution for organochlorine pesticides/PCBs. However, due to the decreased sample capacity of these columns versus packed columns and the sensitivity of the ECD to halogenated compounds, the performance of the extract cleanup techniques becomes a critical factor in overall method performance.

Work is now in progress to evaluate various solid phase extraction (SPE) products for pesticide extract cleanup and to develop QC criteria to ensure reliable method performance. The recoveries of the method analytes processed through various SPE materials (Diol, silica and florisil) will be reported, along with the effect of halogenated phenol and phthalate standards as indicators of the potential for interferent break-through. During the course of these evaluations we will investigate optimization of sorbent performance, improved technical procedures, and QA/QC requirements for this method.

A COMPARISON OF THE PERFORMANCE CHARACTERISTICS OF SORBENT COLUMN PACKING MATERIALS USED FOR PURGEABLE ORGANICS ANALYSIS.

CHARLES WESTON - SENIOR CHEMIST
DAVID SPEIS - MANAGER, NEW PRODUCT DEVELOPMENT

ENVIRONMENTAL TESTING AND CERTIFICATION CORPORATION
284 RARITAN CENTER PARKWAY
P.O. BOX 7808
EDISON, NEW JERSEY 08818-7808

RICHARD ALBERT - OPERATIONS MANAGER

ETC TOXICON LABORATORIES
3213 MONTERREY BOULEVARD
BATON ROUGE, LOUISIANA 70814

ABSTRACT. The use of silica gel as a component of the sorbent column trap for the determination of volatile organics by GC/MS (SW-846 Method 8240) has been found to lead to water vapor buildup in the instrument vacuum system which results in loss of sensitivity, inaccuracies in the data and in some cases automatic shutdown of the MS due to excess pressure in the ion source.

Several alternative sorbent trap packings have been investigated as a means of alleviating the detrimental effects resulting from the retention of excess water vapor in the GC/MS system. The most successful combinations have excluded silica gel as a sorbent column component.

Instrument response data was generated for the volatile organic target compounds listed on the USEPA Contract Laboratory Program (CLP) and several gaseous Freons using sorbent traps with and without silica gel. Method detection limits were experimentally determined on each trapping system and evaluated for statistically significant differences. Statistical comparisons of trapping efficiency were also performed for the two systems. The method calibration requirements (SPCC and CCC) were evaluated against the method criteria for the silica gel-free sorbent column.

Statistically significant deviations in silica gel-free trap performance were minor and did not adversely affect the achievement of the method performance criteria for SW-846 Method 8240.

INTRODUCTION. A progressive deterioration of GC/MS performance has been observed during routine, continuous analysis of water samples for volatile organics. Symptoms of the deterioration include an overall loss of sensitivity, inaccuracies in quantitative data and in some extreme cases, automatic shutdown of the MS due to excess pressure in the ion source.

An investigation into the causes of these symptoms has revealed an increasing water vapor background within the ion source during a 12 hour sample acquisition period. The purging step of the analysis volatilizes water in addition to the organic compounds of interest. The purged water is absorbed by the silica gel contained in the sorbent trap used to concentrate the volatilized organics. The water is thermally desorbed into the GC/MS system after the completion of the purging process.

The vacuum pumps used in GC/MS systems do not pump water from the analyzer as efficiently as they can pump solvents. Turbo-molecular pumps are less efficient for pumping water vapor than oil diffusion pumps. As a result of performing continuous purge and trap analysis, water vapor buildup occurs in the vacuum system, leading to the observed symptoms.

A possible remedy to this problem is to employ sorbents for trapping which do not contain silica gel. Several experiments were performed to determine if silica gel could be eliminated from the sorbent trap without adversely affecting the trapping characteristics required to determine the target analytes.

EXPERIMENTAL. Two experiments were designed and performed to determine if silica gel could be eliminated from the sorbent trap without affecting the analytical performance of the method. Each experiment was performed using silica gel-containing traps and silica gel-free traps. The experiments were based on the simple premise that the sorbent characteristics of the trap described in SW-846 Methods 5030 and 8240 were satisfactory for purge and trap analysis and that silica gel neither enhanced nor detracted from the absorption efficiency of the trap.

Experiment one was designed to determine if differences in method detection limit (MDL) and trapping efficiency existed between the two trap configurations. For this determination, seven volatile organic analyses were performed on each trap using 5 ml of reagent water spiked at 25 nanograms (5ug/l). The spiked samples were analyzed using the gas chromatograph and mass spectrometer parameters required for SW-846 Methods 5030 and 8240 with the exception of the trap modifications used for one set of seven spiked replicates.

Experiment two was designed to determine if there were significant differences between the compound/internal standard response factor of the silica gel-containing trap and the non-silica gel-containing trap. For this determination, the GC/MS system was calibrated 28 separate times using each trapping system for each target parameter of SW-846 method 8240. A five-concentration calibration procedure was used to determine the calibration response factor. With the exception of the variations in trap components, the analysis was conducted using the gas chromatograph and mass spectrometer parameters required by the method.

DISCUSSION.

Experiment One. The MDL for each compound was determined using the "Definition and Procedure for the Determination of the Method Detection Limit" 40 CFR Part 136, July 1, 1988, Appendix B. The calculation for MDL is based on the standard deviation s of the replicate data set as described in equations 1,2 and 3.

1) $$S_x^2 = \frac{\sum_{i=1 \text{ to } n} (\overline{C}_x - C_{xi})^2}{n-1}$$

2) $$S_x = [S_x^2]^{.5}$$

3) $$MDL_x = t\,(n-1,\ 1-\alpha = .99)S_x$$

Where:

n = number of replicates

$\overline{C}_x$ = mean concentration of analyte x.

C_{xi} = Concentration of analyte x in replicate.

S_x = Standard deviation of analyte.

t = Student t distribution for 99% single tailed confidence interval.

The calculated MDL data for each compound on each trapping system are tabulated in Table 1 (See Note 1). These MDL's were tested to determine if statistically significant differences existed between the two trapping systems. The procedure used to calculate an MDL is based upon the calculation of the variance (s^2) of replicate measurements for spiked samples. To determine if the variances of the two data sets are equivalent, an F test was performed for the calculated variance pairs of each compound using equation 4 (See Note 2).

Equation 4

$$F = S_1^2/S_2^2$$

The calculated F Test values were compared to the predicted values at the 99% confidence interval. If the calculated F value is below the predicted value, the two MDL's are not significantly different at the 99% confidence interval (Thus, at a probability of 1%, the hypothesis that the MDL's may be the same cannot be rejected). Individual compound variance pairs which are not significantly different form each other are indicated with a minus sign on Table 1.

Table 1: MDL and Trap Efficiency Comparison

	MDL (NG)		Significance of Difference (F)		Efficiency Ratio Trap B/Trap A	
	Trap A	Trap B	95% Conf.	99% Conf.		(Sig. 99% conf.) of difference
Bromochloromethane	-	-	-	-	1.59	+
Methyl chloride	7.04	7.25	-	-	1.41	+
Methyl bromide	20.32	24.81	-	-	.862	-
Dichlorodifluoromethane	15.44	11.72	-	-	1.47	+
Vinyl chloride	13.03	13.09	-	-	1.24	-
Chloroethane	13.73	12.79	-	-	1.15	-
Methylene chloride	29.70	9.68	+	-	1.00	-
Acetone	29.42	11.35	+	-	1.53	+
Carbon disulfide	8.92	6.18	-	-	2.55	+
Trichlorofluoromethane	9.14	6.25	-	-	1.21	+
1-1-Dichloroethylene	11.31	7.49	-	-	.680	+
1-1-Dichloroethane	11.02	5.83	-	-	.662	+
1-2-Trans-dichloroethylene	11.67	7.38	-	-	.667	+
Chloroform	10.60	6.47	-	-	.671	+
1-2-Dichloroethane-d4 (SURR)	-	-	-	-	1.22	+
1-2-Dichloroethane	9.61	5.61	-	-	.633	+
1-4-Difluorobenzene	-	-	-	-	1.28	+
Methyl ethyl ketone	-	-	-	-	-	-
1-1-1-Trichloroethane	11.23	6.34	-	-	.709	+
Carbon tetrachloride	9.53	6.30	-	-	.725	+
Vinyl acetate	17.81	5.42	+	-	1.66	+
Dichlorobromomethane	9.84	6.73	-	-	.671	+
1-2-Dichloropropane	11.25	6.23	-	-	.610	+
cis-1-3-Dichloropropylene	10.02	4.85	-	-	.625	+
Trichloroethylene	8.23	8.38	-	-	.719	+
Chlorodibromomethane	6.22	5.13	-	-	.654	+
Benzene	5.87	4.72	-	-	.581	+
1-1-2-Trichloroethane	5.51	6.64	-	-	.641	+
trans-1-3-Dichloropropylene	5.63	3.68	-	-	.562	+
2-Chloroethylvinyl ether	5.10	6.72	-	-	1.00	-
Bromoform	8.18	3.89	-	-	.676	+
Chlorobenzene-d5	-	-	-	-	1.34	+
Methyl-iso-butyl-ketone	6.78	5.14	-	-	1.66	+
2-Hexanone	8.99	8.09	-	-	1.55	+
1-1-2-2-Tetrachloroethane	9.56	5.93	-	-	.595	+
Tetrachloroethylene	10.21	5.26	-	-	.741	+
Toluene-D8 (SURR)	-	-	-	-	1.29	+
Toluene	9.57	4.78	-	-	.654	+
Chlorobenzene	8.55	5.93	-	-	.662	+
Ethylbenzene	8.75	5.93	-	-	.625	+
p-Bromofluorobenzene (SURR)	-	-	-	-	1.17	+
Styrene	9.48	8.36	-	-	2.00	+
m-Xylene	14.34	6.78	-	-	2.43	+
o+p-Xylenes	19.65	-	-	-	-	-

Trap A - Tekmar 14-0124-003, Tenax, Silica Gel, charcoal
Trap B - Tekmar 14-1457-003, Tenax, charcoal

Calculated F values for a compound variance pairs which are greater than the predicted value at the 99% confidence interval indicate that the MDL values obtained for the two traps are significantly different. Compounds in this category are indicated by a plus sign on Table 1.

The F test for MDL differences at the 99% confidence interval indicated that were no significant differences using the two trapping systems. The F values at the 95% confidence interval indicated that three study compounds; acetone, vinyl acetate and methylene chloride showed significant differences for the silica gel-free trapping system. Although the confidence interval overlap for these compounds is less than 5%, the calculated MDL easily exceeded the practical quantitation limits (PQL) listed in SW-846 Method 8240. Furthermore, response factor and RSD data from experiment two does not indicate significant differences at the 99% confidence interval for these compounds using the silica gel-free system.

The data collected for the MDL determinations of each compound on each trapping system were also used to determine if statistically significant differences in compound trap/desorb efficiency for each trap were being observed. Trapping and desorption efficiency is commonly determined by comparing the area of an individual compounds chromatographic peak obtained through purge and trap analysis to the chromatographic peak area of the same compound obtained by direct injection of a standard solution of the compound.

The comparison of trap/desorb efficiency for two different trapping systems can be performed by direct comparison of the individual compound peak areas in one system versus the other system. Because these experiments were designed to determine equivalency to an existing standard (traps containing silica gel), the differences in purge/trap efficiency are calculated based on the required silica gel-containing trap as described in equation 5.

Equation 5.

$$\text{Efficiency} = B/A$$

Where A = Mean Compound Peak Area with silica gel
Where B = Mean Compound Peak Area without silica gel

The mean area of the chromatographic peak of each compound was calculated from the respective seven-fold replication for each trapping system. The trapping efficiency ratio for the mean areas of each compound were calculated using the above equation and listed in Table 1.

A Student's T test was applied to the mean area pairs for each individual compound to determine if the trap/desorb efficiencies of the two systems were significantly different as described in the following:

1. Calculate the mean, $\overline{X}_1$ and $\overline{X}_2$, of each population.

2. Calculate the variance S_1^2 and S_2^2 of each population

   $$S^2 = \frac{\Sigma(\overline{x} - x_i)^2}{n-1}$$

3. Obtain Se^2, the pooled variance from the variances of each population, S_1^2 and S_2^2.

   $$Se^2 = [\nu_1 (S_1^2) + \nu_2 (S_2^2)] / (\nu_1 + \nu_2)$$

   Where ν_1 and ν_2 are the degrees of freedom of each population mean.

4. Calculate the t-statistic.

   $$t = \Delta X / [Se^2 (1/n_1 + 1/n_2)]^{.5}$$

   Where n_1 and n_2 are the respective sample sizes of each population.

   Δx is the difference between the means.

5. Compare the calculated t-value with the value from a table of percentage points of the t-distribution for a double tailed confidence interval of 99% at $\nu_1 + \nu_2$ degrees of freedom.

The calculated Student's T value was compared to the predicted T value at the 99% confidence level (See note 4). Calculated T values which are below the predicted value indicate that the mean peak areas of the two trapping systems are not significantly different at the 99% confidence interval. Individual compound mean peak area pairs which are not significantly different from each other are indicated with a minus sign on Table 1. Thus in this case, at a probability of 1%, the hypothesis that the trap desorb efficiencies may be the same cannot be rejected.

A calculated T value for a compound mean area pair which is greater than the predicted value at the 99% confidence interval indicates that the trap/desorb efficiency values obtained for the two traps are significantly different. Compounds in this category are indicated by a plus sign on Table 1.

The trap/desorb efficiency ratios (Table 1) indicated that 18 compounds exhibited an increase in efficiency while 22 exhibited decreases in efficiency using a silica gel-free trap. The reasons for the increase or decreases appeared to be random and could not be attributed to a compound specific or compound class related reason.

The T test values for trap/desorb differences as measured by mean peak area indicated that the mean peak areas of 37 of the 44 compounds tested were statistically different at the 99% confidence level using the silica gel-free trap. Although this data indicates a high frequency of peak area difference, the differences were not always detrimental to the method performance. Forty-three percent of the tested compounds showed increased trap/desorb efficiency using silica gel-free traps while 50% showed efficiency decreases.

Experiment Two. Average response factor data for each test compound was determined from an initial five-point calibration performed on each trapping system. The mean response factor data for each trapping system is listed in Table 2. These data were pooled and statistically evaluated to determine if the mean response factors are equivalent. This determination was performed using the Student's T Test at confidence intervals of 95% and 99%. The equations used to determine the equality of two population means were previously described in experiment one.

Student's T test values were calculated for average response factors of each compound on each trapping system to determine if the individual compound response factors of the two systems were significantly different (See Note 3). The calculated Student's T value was compared to the predicted T value at the 95% and 99% confidence levels.

Calculated T values which are less than the predicted value for the individual compound response factors of the two trapping systems indicate no significant difference at the specified confidence intervals. Compounds in this category are indicated with a minus sign on Table 2.

Calculated T values for individual compound response factors that are greater than the predicted value at the specified confidence intervals indicate that the response factors obtained for the two traps are significantly different. Compounds in this category are indicated by a plus sign on Table 2. For example, if a compound has a minus sign in the 99% confidence interval column, then at a probability of 1% the hypothesis that the respective mean values for that compound may be the same cannot be rejected.

Table 2: Response Factor and RSD Comparison

	Mean Resp. Factor		Sig. of Difference Conf. Interval (%)		Mean RSD		Sig. of Difference Conf. Interval (%)	
	Trap A	Trap B	95	99	Trap A	Trap B	95	99
Methyl chloride	.897	.654	+	-	12.89	22.24	+	-
Methyl bromide	.286	.380	-	-	10.02	20.74	+	-
Dichlorodifluoromethane	.450	.511	-	-	18.57	31.22	+	+
Vinyl chloride	.540	.673	-	-	16.73	27.62	+	-
Chloroethane	.594	.639	-	-	11.26	11.70	-	-
Methylene chloride	1.17	1.40	+	-	13.65	15.15	-	-
Acetone	.566	.548	-	-	19.25	24.82	-	-
Carbon disulfide	3.18	4.01	+	+	10.45	9.38	-	-
Trichlorofluoromethane	2.81	2.28	+	-	10.21	9.09	-	-
1-1-Dichloroethylene	1.08	1.28	+	+	5.45	7.93	+	-
1-1-Dichloroethane	2.88	3.30	-	-	5.28	8.20	+	-
1-2-Trans-dichloroethylene	1.60	1.59	-	-	5.80	9.07	+	-
Chloroform	3.60	3.81	-	-	6.12	7.76	-	-
1-2-Dichloroethane	3.12	3.24	-	-	7.02	7.14	-	-
Methyl ethyl ketone	.0319	.0319	-	-	16.58	16.98	-	-
1-1-1-Trichloroethane	.558	.568	-	-	8.35	6.28	-	-
Carbon tetrachloride	.592	.567	-	-	7.89	7.24	-	-
Vinyl acetate	.505	.441	-	-	46.06	39.15	-	-
Dichlorobromomethane	.672	.651	-	-	6.28	5.58	-	-
1-2-Dichloropropane	.428	.415	-	-	6.30	5.78	-	-
cis-1-3-Dichloropropylene	.625	.573	-	-	6.83	5.89	-	-
Trichloroethylene	.372	.401	+	-	6.20	6.55	-	-
Chlorodibromomethane	.575	.538	-	-	6.74	7.09	-	-
Benzene	1.07	1.04	-	-	5.95	6.07	-	-
1-1-2-Trichloroethane	.330	.312	-	-	6.75	7.16	-	-
trans-1-3-Dichloropropylene	.536	.529	-	-	7.68	6.61	-	-
2-Chloroethylvinyl ether	.255	.237	-	-	9.98	8.10	-	-
Bromoform	.449	.391	+	+	9.22	11.31	-	-
Methyl-iso-butyl-ketone	.651	.512	+	-	10.49	12.52	-	-
2-Hexanone	.496	.380	+	-	13.29	15.84	-	-
1-1-2-2-Tetrachloroethane	.692	.604	+	-	7.70	7.03	-	-
Tetrachloroethylene	.579	.491	+	+	6.92	6.69	-	-
Toluene	.995	.906	+	+	5.28	5.28	-	-
Chlorobenzene	1.29	1.18	+	+	5.38	4.74	-	-
Ethylbenzene	.633	.604	+	-	5.24	5.61	-	-
Styrene	1.29	1.20	+	+	6.08	5.03	-	-
m-Xylene	.767	.765	-	-	6.54	6.62	-	-
o+p-Xylenes	.725	.734	-	-	6.65	5.86	-	-

Trap A - Tekmar 14-0124-003, Tenax, Silica Gel, charcoal
Trap B - Tekmar 14-1457-003, Tenax, charcoal

The mean calibration response factors obtained using the silica gel-free trap exhibited a trend towards lower response factors. Twelve of the thirty-eight test compounds exhibited calibration response increases in comparison with the silica gel-containing trap while 26 exhibited a decreased calibration response.

Although the calibration response trend was downward, the response change was statistically significant for only seven test compounds. Five of these seven had statistically significant decreases, while two had increases.

The trend towards decreased response emerged much more clearly at the 95% confidence level where 13 test compounds exhibited statistically significant calibration response factor differences, nine of them lower using the silica gel-free system. Although the response factor trended towards decreased response, the calibration response factor criteria minimum of 0.3 was achieved for all test compounds with the exception of methyl ethyl ketone and 2-chloroethylvinyl ether. These compounds also did not achieve the calibration response factor criteria using the silica gel-containing trap. Furthermore, some of the observed lower response factors in the silica gel free system can be attributed to significantly higher responses for all internal standards.

The mean relative standard deviation (RSD) of the calibration response factor data were also calculated and listed in Table 2 (See Note 3). This data was also evaluated for statistically significant differences between the two trapping systems. The test for significance employed for the RSD data is identical to the test used for the response factor data and is reported on Table 2 using the identical system that was used for the calibration response factors.

The statistical evaluation of the calibration response factor RSD indicated a slight trend towards increasing RSD. A larger calibration RSD for the calibration factor increases the quantitative measurement error. Twenty-two of the thirty-eight test compounds had increased RSD's while sixteen had decreased RSD's using the silica gel-free trap. Dichlorodifluoromethane was the only compound that showed a statistically significant increase in RSD at the 99% confidence level. The number of test compounds which exhibited statistically significant differences at the 95% confidence level increased to seven. The calibration response factor RSD criteria was achieved for all compounds except dichlorodifluoromethane and vinyl acetate. Vinyl acetate also did not meet the RSD criteria using a silica gel-containing trap.

Although response factor and response factor RSD criteria for SW-846 Method 8240 were achieved in all but a few cases, several compounds may show an increased frequency of failing to meet the method RSD criteria using a silica gel-free trap . The compounds of concern in this category are the gases methyl chloride, methyl bromide and vinyl chloride. However, it should be noted that these compounds all exhibit response factor values that are in general equivalent to the silica gel containing trap.

CONCLUSION. Sorbent traps without silica gel offer a reasonable solution to the symptomatic problems associated with water vapor buildup in GC/MS vacuum systems during continuous purgeable organics analysis. The calibration and response criteria of SW-846, Method 8240 were easily achieved using the silica gel-free trapping system even though trap performance differences were observed. These differences, while being statistically significant did not have an adverse affect on achieving the method performance criteria and in some cases indicated performance improvements .

While the general trend of the silica gel-free trap performance does indicate lower relative response for some compounds, this trend is partially a function of the significantly improved response for internal standards. The calibration precision RSD was generally poorer using the silica gel-free trap. However, the method RSD criteria were easily achieved. The compounds which exhibited the greatest effect were the volatile gases. As a result, the calibration criteria for the volatile gases may be more difficult to achieve in some cases.

Based on this study, the silica gel-free trap can be used as a substitute to avoid water buildup in the GC/MS system during volatile organics analysis by purge and trap without adversely affecting the achievement of method performance criteria for SW-846 Method 8240.

Statistical Data Evaluation Notes

Note 1: **MDL Calculations**

Data Set 1 (3 component trap) - 7 data points per analyte

Data Set 2 (2 component trap) - 7 data points per analyte

t-distribution for 7-fold replication.
(ν = 6 degrees of freedom) at 99% single tailed confidence interval = 3.14.

Note 2: **MDL Comparisons**

Data Set 1 (3 component trap) - 7 data points per analyte

Data Set 2 (2 component trap) - 7 data points per analyte

Compare calculated F vs. a table of percentage of F distribution. The reference value is taken as the 95 and 99% double tailed confidence interval with both S_1 and S_2 having 6 degrees of freedom.

95%, F = 5.82
99%, F = 14.2

Note 3: **Mean Response Factor Comparison and Mean RSD Comparison**

Data Set 1 (3 component trap) - 28 data points

Data Set 2 (2 component trap) - 28 data points

Pooled variance - 56 data points

95% confidence range double tailed t factor ($\nu_1 + \chi_2 = 54$) - 2.18

99% confidence range double tailed t factor ($\nu_1 + \nu_2 = 54$) - 3.06

Note 4: C. Trap Efficiency Comparison

Set 1 (3 component trap) - 7 data points per analyte

Set 2 (2 component trap) - 7 data points per analyte

95% confidence range double tailed t-factor (ν= 12) - 2.18

99% confidence range double tailed t-factor (ν= 12) - 3.06

Acknowledgement: The authors gratefully acknowledge the assistance of Alice Preville, Greg Mazurek and the ETC CLP Work Group for providing us with the resources and time to perform the experiments that were used in this study.

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AN ADVANCED AUTOSAMPLING SYSTEM FOR GAS CHROMATOGRAPHY-MASS SPECTROMETRY

John DeWald, Commercial Analytical Services Manager, S-CUBED, A Division of Maxwell Laboratories, Inc., 3398 Carmel Mountain Road, San Diego, California 92129; Charles A. Koch, Sales Support Engineer, Hewlett Packard, 1421 South Manhattan Avenue, Fullerton, California 92631

ABSTRACT

The authors have developed a software enhancement for the Hewlett-Packard RTE gas chromatograph/mass spectrometer (GC/MS) data system that allows for feedback from quality control (QC) samples to control the autosampler sequencing. In addition, the system automatically produces numerous QC data summary reports for analyst evaluation. The enhancements were developed in an Environmental Protection Agency (EPA) contract laboratory where strict tuning and calibration criteria must be met before any samples can be run and where significant review of the data by the analysts is required. One of the advantages of such a system is the ability to produce successful multiple shift runs. This ability allows for 24-hour and weekend operation of GC/MS systems with limited analyst intervention, thus increasing the utilization of limited resources. A second advantage of the system is its ability to automatically produce summary reports. These aid the analyst in evaluating data quality for such parameters as surrogate recovery and target analyte identifications. In addition, the production of these reports in a format to aid quick review of data quality allows the analysts to perform more complete reviews in much less time. This paper discusses the design of this software (referred to as *SMART*), its application to real-world laboratory situations, and suggestions for future improvements.

INTRODUCTION

There is a continual drive in environmental analytical services for faster, cheaper, and higher quality services. This demand is driven both by the increased competition among laboratories and the increased demands of the data users. In order to meet these demands, laboratories must continually look for ways to automate complex analysis systems to increase sample throughput and decrease analyst time. The software enhancement described here is an attempt to satisfy these needs by increasing sample capacity on GC/MS systems while decreasing analyst time required for data acquisition and data review. This system was designed specifically to meet EPA Contract Laboratory[1] requirements for GC/MS analysis, and is referred to as SMART.

DISCUSSION

The SMART system was developed on the Hewlett Packard RTE 1000 GC/MS Data System and utilizes RPN programming language and the Aquarius Batch Software[2] to control autosampler function. SMART consists of a series of procedure files which is run after each sample to direct autosampler sequence control, quantitation, data evaluation, and report preparation. The SMART system is easily incorporated into the Aquarius software. The name of a particular SMART procedure file is entered into the sample form of BEDIT, the batch editor program used to sequence autosampler runs. These procedure file coordinates report preparation, checks tuning and calibration sample results, and alters the autosampler sequence accordingly.

Figure 1 illustrates SMART's algorithm for semivolatile organics analysis. After an optional wash sample, a decafluorotriphenylphosphine (DFTPP) sample is injected. Following data acquisition, the procedure file TUN010 checks these results using a series of nested procedure files to

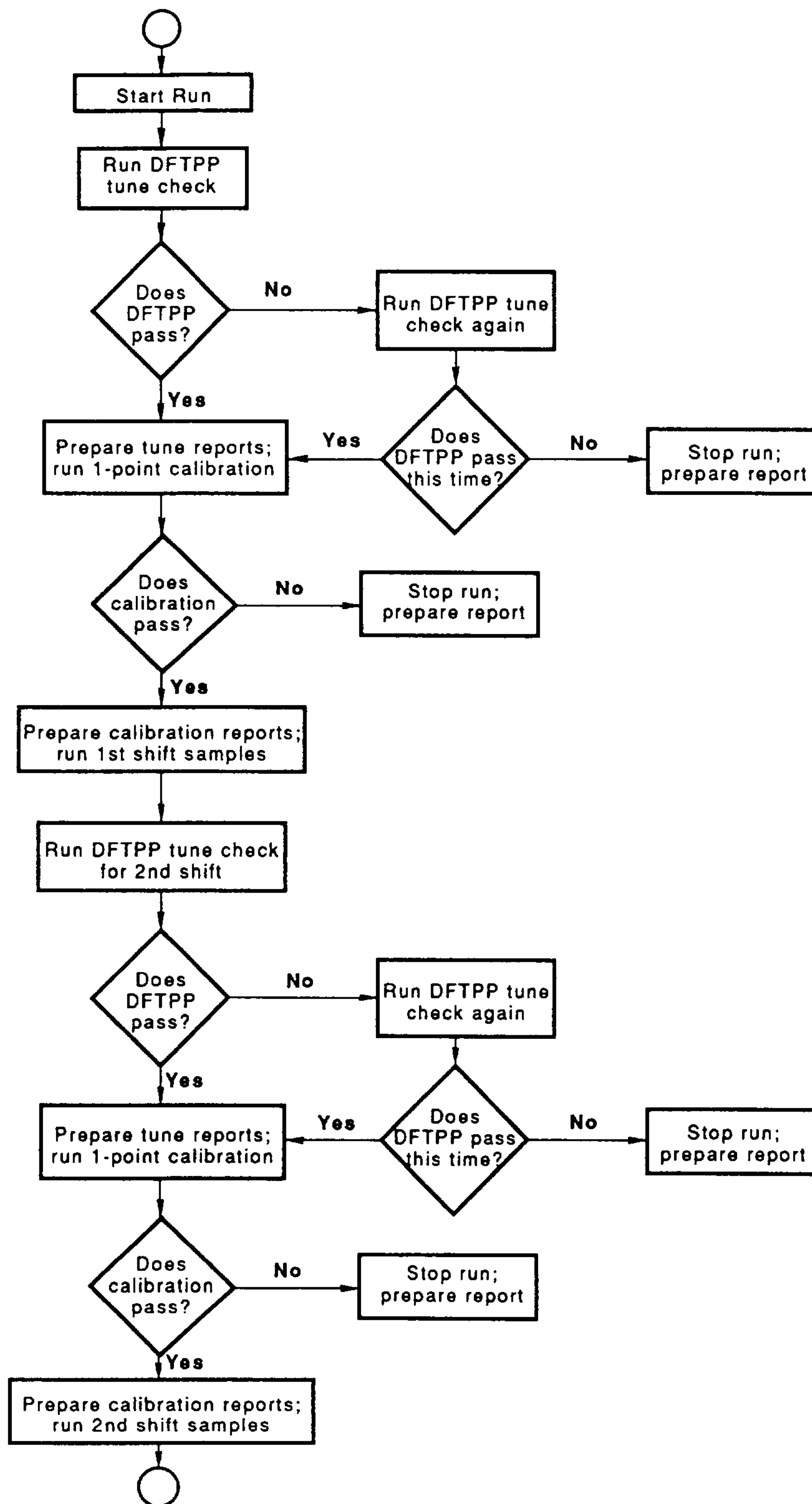


Figure 1. SMART's algorithm for semivolatile organic analysis.

determine whether tuning and mass calibration QC requirements are met. If the tune check fails, the procedure file directs the autosampler to inject a second DFTPP sample. After data acquisition, this second tune check is evaluated. If it fails, the sequence is terminated. If either tune check passes, the autosampler is directed to inject the one-point calibration check sample. The data system begins preparing hardcopy reports of the tuning results and initiates preparation of Form 5, the CLP tune report form. Figure 2 illustrates some of the command language used in the tune check procedures.

After data acquisition of the single-point calibration check sample, a procedure file called CALC50 checks the percent difference of the response factors of the calibration check compounds (CCC) against the average response factors from the current five-point calibration to determine whether QC criteria is met. It then checks the system performance check compounds (SPCC) to see if minimum relative response factor levels are met. If any criteria are not met, the sequence is terminated, or the calibration check is injected once again. If all calibration criteria are met, the calibration reports are prepared, the calibration response factors are updated, and the retention times and areas for the internal standards are stored for comparison to samples. The autosampler is then directed to start the first shift samples.

As each sample is run, a number of reports are prepared. Some of the reports will be used in the hard copy report package, and some will be used by the analyst to quickly evaluate whether sample data meet QC requirements. Figure 3 illustrates some of these reports. While some of these reports must be revised after their review by an analyst, most or all of them will be ready for inclusion in the data package as soon as the run is complete.

When the initial 12-hour sequence is completed, a second shift is started and the tuning and calibration data are checked again following the procedures shown in Figure 1. As long as the system remains in control, additional shifts of samples may be run. S-CUBED has been successful with triple-shifts and routinely runs double-shifts using this software.

There are a number of critical hardware, software, and system requirements that must be met in order for this type of automation to be successful: (1) The autosampler system must be controlled by the data system and must have the ability to skip or return to and repeat any sample. For this system a Hewlett Packard 7673 autosampler was utilized. (2) The data system must be capable of accessing the sequence software and altering its execution during the run. (3) The environment in which the system operates must be well-defined and well-managed. The CLP protocols are well suited for automation as the analytical and QC requirements are strictly defined. However, management practices such as daily instrument maintenance and file management must be strictly defined and adhered to, to fully realize the benefits of this type of automation.

CONCLUSION

This software enhancement has been successful in providing increased sample throughput by substantially increasing the number of successful multiple shift runs achievable and reducing time spent in data review by the analyst. The system is only successful, however, when applied to an analysis with strictly defined QC requirements and when run in a well managed environment.

This system can also be applied to volatile GC/MS analysis. However, the full extent of the automation will not be realized until the interfacing of the data system to more sophisticated purge and trap instruments is complete.

Many other applications of this software are possible, including use with other EPA GC/MS methods such as Method 625[3] and Method 8270.[4] As long as QC requirements are strictly

Autosampler Control After DFTPP Evaluation

```
:**                         $LABEL:BROKEN_NEEDLE
:**
:RU,CRT::RP,1,HC,CA
:DP,
:DP,
:DP,YOU MIGHT HAVE A BROKEN NEEDLE
:DP,THERE WAS NO  M/E  198 {DFTPP} IN THE SAMPLE
:DP,SMART WILL TRY DFTPP AGAIN ANYWAY AUTOMATICALLY
:DP,
:RU,BAMON,ST
:RU,CRT::RP,1,AL,FF
:**
:**
:**                         $LABEL:FAILED_DUCK
:**
:DP,start auto on dftpp again, or, the next sample
:**
:**         FIND OUT WHAT SAMPLE JUST RAN    STORE AS 9G
:TR,LASTRN
:**         NOW, START-UP NEXT SAMPLE, OR, 9G+1
:CA,9,9G,+,1
:**         START UP AUTOSAMPLER AGAIN
:RU,BAMON,PA,1,OF
:RU,BAMON,PA,1
:RU,BAMON,SA,1,9G
:RU,BAMON,GO,1
:RU,BAMON,PA,1
:**          SEND MESSAGE TO USER WHAT'S GOING ON
:RU,CRT::RP,1,HC,CA
:DP,FAILED DFTPP TUNING   TRY AGAIN AUTOMATICALLY
:DP,
:RU,BAMON,ST
:RU,CRT::RP,1,AL,FF
:**
:TR
:**
:**
:**                         $LABEL:PASSED!
:**
:**  it passed, start daily cal run
:**
:**         FIND OUT WHAT SAMPLE NUMBER JUST RAN    STORE AS 9G
:TR,LASTRN
:**         NOW, START-UP DAILY CAL SAMPLE, OR, 9G+2
:CA,9,9G,+,2
:**         START UP AUTOSAMPLER AGAIN
:RU,BAMON,PA,1,OF
:RU,BAMON,PA,1
:RU,BAMON,SA,1,9G
:RU,BAMON,GO,1
:RU,BAMON,PA,1
:**         TELL OPERATOR WHAT'S GOING DOWN, MAN
:RU,CRT::RP,1,HC,CA
:DP,
:DP,
:DP,YOU PASSED DFTPP TUNING  FIRST TRY  START DAILY CAL RUN
:DP,
:RU,BAMON,ST
:RU,CRT::RP,1,AL,HC,CA
:**
:** tunrep will do all the data reporting for us when we pass dftp
```

Figure 2. Command language used in tune check procedures.

Evaluation of DFTPP Data

```
:RU,FI::RP,1G
:RU,NEW::RP
:RU,STW,1
:PU,GOODMS:VI
:RU,RSE::RP
:RU,TIM::RP
:RU,EC::RP,442
:RU,RRH::RP,BA
:**                          minor error checking here - is m/e 198 he

:RU,RIF::RP,0R,GT,27
:IF,1P,EQ,1,4   ,          CONTINUE_GOOSE
:**        SEND BACK BROKEN NEEDLE MESSAGE TO VARFI-   (1P=7)
:CA,1:P,7
:TR
:**
:**                        $LABEL:CONTINUE_GOOSE
:**
:RU,INT::RP,,,1
:RU,PF::RP,1,,-1,,,70
:RU,RTG::RP,70
:CA,3,4P
:CA,3,3G,+,1
:RU,RTG::RP,74
:CA,4,4P
:CA,4,4G,-,1
:RU,SCA::RP
:RU,ES::RP,3G
:**
:**                        $LABEL:TRY_GOOSE_AGAIN
:**
:RU,ES::RP
:RU,TUNER::AQ,=DFTPP::AQ
:IF,1P,EQ,0,6  ,           PASS_GOOSE
:CA,3,3G,+,1
:IF,3G,LE,4G,-7  ,         TRY_GOOSE_AGAIN
:**
:**      it failed -  1p is going back to varfy as 1
:**
:TR
:**                        $LABEL:PASS_GOOSE
:**
:**      it passed - 1p is 0 - let's get back to varfy now
:TR
```

Figure 2. (Continued).

Internal Standard Check Report

Sample File = >MSP54
Cal Check File = >DC511
Date and Time = 5/11/89 20:35
Name = EBP54MS
Miscellaneous = HP3,CASE 11790,EBP54MS,IV 1L,FV 2ml,04/24/89,,$ BTL# 5

I. Areas

Name of the BNA Internal Standard	The Sample ISTD Area	Daily Check ISTD Area	Daily Check ISTD Area / 2	Daily Check ISTD Area x 2	Status of the Sample ISTD Area Precision
1,4-Dichlorobenz-d4	9741	6963	3482	13926	OK
Naphthalene-d8	42714	29593	14797	59186	OK
Acenaphthene-d10	32119	20803	10402	41606	OK
Phenanthrene-d10	65210	45510	22755	91020	OK
Chrysene-d12	74403	37825	18913	75650	OK
Perylene-d12	79984	41903	20951	83806	OK

II. Retention Times

Name of the BNA Internal Standard	The Sample ISTD R.Time	Daily Check ISTD R.Time	Daily Check ISTD RT - 0.5	Daily Check ISTD RT + 0.5	Status of the Sample ISTD R.T. Precision
1,4-Dichlorobenz-d4	10.44	10.43	9.93	10.93	OK
Naphthalene-d8	14.21	14.22	13.72	14.72	OK
Acenaphthene-d10	19.65	19.66	19.16	20.16	OK
Phenanthrene-d10	24.19	24.20	23.70	24.70	OK
Chrysene-d12	32.46	32.49	31.99	32.99	OK
Perylene-d12	36.60	36.61	36.11	37.11	OK

Figure 3. Examples of sample run reports.

Surrogate Recovery Check Report

[OPERATOR REPORT]

[GC/MS LAB SEMIVOLATILES]

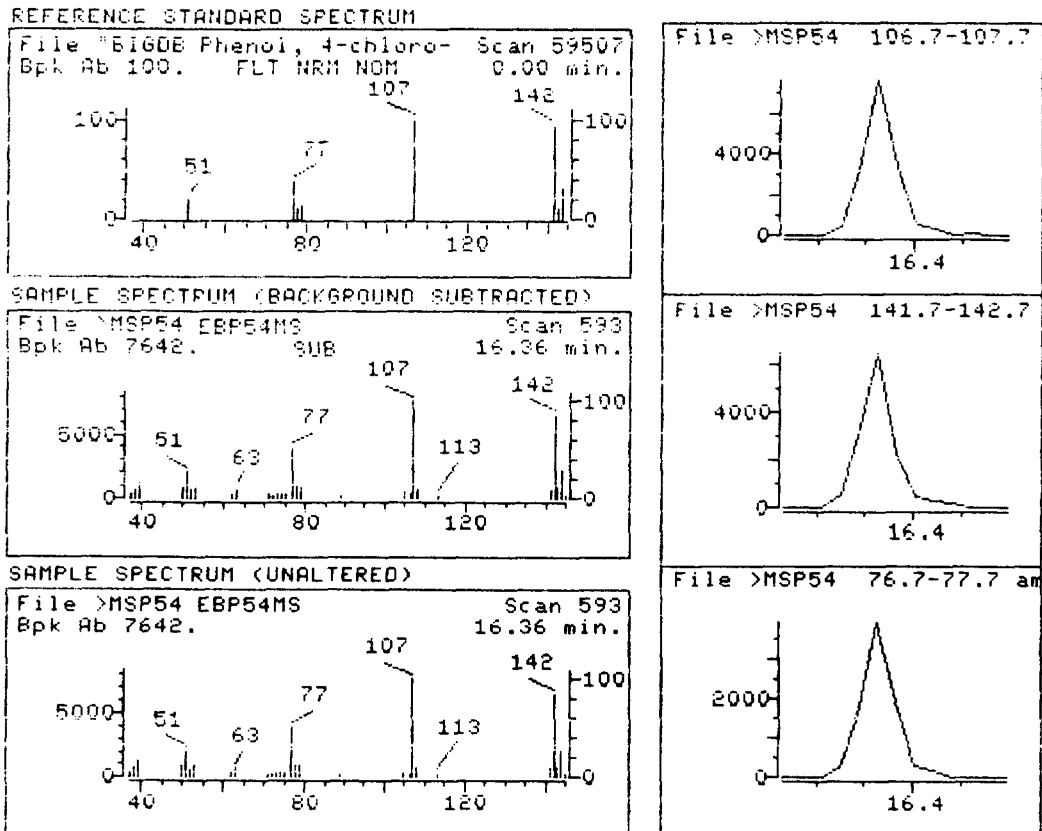
[Preliminary Surrogate Report]

```
DATA FILE    = >MSP54::D4
SAMPLE       = EBP54MS
MISCELLAN    = HP3,CASE 11790,EBP54MS,IV 1L,FV 2ml,04/24/89,,$       BTL# 5
DATE         =  5/11/89 20:35
PROCEDURE    = RBNA
OPERATOR     = DENNIS     SUPER GRP
```

SURROGATE	AS FOUND IN SAMPLE	WAS SPIKED AS	WATER LIMITS	SOIL LIMITS	% RECOVERY
2-Fluorophenol	57.63	100.00	21-100	25-121	57.63
Phenol-d5	58.75	100.00	10-94	24-113	58.75
Nitrobenzene-d5	53.72	50.00	35-114	23-120	107.43
2-Fluorobiphenyl	48.79	50.00	43-116	30-115	97.58
2,4,6-tribromo-phenol	71.80	100.00	10-123	19-122	71.80
p-Terphenyl	45.70	50.00	33-141	18-137	91.39

Figure 3. (continued).

Target Compound Identification Check Report




```
Data File: >MSP54::D4                    Quant Output File: ^MSP54::SC
Name: EBP54MS
Misc: HP3,CASE 11790,EBP54MS,IV 1L,FV 2ml,04/24/89,,$          BTL# 5
Quant Time: 890512 08:51                   Quant ID File: ID_BCA::SC
Injected at: 890511 20:35              Last Calibration: 890512 08:42

Compound No: 29
Compound Name: 4-Chloro-3-methylphenol
Scan Number: 593
Retention Time: 16.36 min.
Quant Ion: 107.0
Area: 18642
Concentration: 42.43 ng/uL
q-value: 93
```

Figure 3. (continued).

defined, the software can be easily altered to meet them. Additional improvements can also be made to the corrective actions that are possible when the QC requirements are not met. These improvements may include predetermined instrument adjustments and the notification of a remote analyst of a failure.

REFERENCES

1. Statement of Work for Organics Analysis, WA-87K236 (EPA Contract Laboratory Program, October, 1986).

2. "Aquarius User's Reference Manual," 4th Edition, Hewlett Packard (Palo Alto, California, 1986) Publication No. 05990-90202.

3. Federal Register 49, 153 (October 26, 1984).

4. Test Methods for Evaluating Solid Wastes. SW-846 (EPA, September 1986).

SIMPLIFIED SAMPLE PREPARATION AND CLEAN-UP FOR PCB/PESTICIDE ANALYSES IN SOILS AND SOLID WASTES

A. L. LATADY, K. M. WALSH, E. W. PICKERING, AND J. D. OKUN, GOLDBERG-ZOINO & ASSOCIATES, INC., 320 NEEDHAM STREET, NEWTON, MASSACHUSETTS 02164

ABSTRACT

The EPA SW 846 Method for the analysis of PCBs and priority pollutant pesticides (Method 8080) requires either extended soxhlet extraction with methylene chloride (a highly toxic solvent) or a cumbersome sonication step to prepare an initial sample extract. An alternative has been developed to this sample preparation regime based on a small scale liquid/liquid extraction using less toxic solvents. The alternative provides comparable extraction efficiencies, a clean extract and a considerable reduction in the volume of solvent and solvent handling needed to perform the analysis. A two stage liquid/liquid extraction from hydrated methanol to hexane is followed by a mini-column liquid chromatographic clean-up step. The cleanup extract is injected directly onto a gas chromatograph equipped with an electron capture detector configured according to EPA Method 8080. The method yields adequate spike recoveries (70-130%) of EPA recommended surrogate standards and detection limits (50 $\mu g/kg$) which are usually well within overall project quality assurance needs. Most interferences are eliminated by the elutriation of the extract through the florisil/sodium sulfate column. When used in conjunction with an autosampler, the precision of this method is optimized. The use of blanks, daily calibration curves, and duplicate sample runs provide the level of quality control backup needed to scientifically defend results. Analyses have been obtained by this procedure at a considerable savings of time and energy without compromising accuracy and precision.

INTRODUCTION

An important goal of an efficient environmental testing procedure is the development of accurate results safely with a minimum of time and resources. The EPA methodology for extracting soils and solid waste samples for subsequent analysis of PCBs and pesticides specified in SW-846 involves a lengthy procedure using relatively large volumes of toxic solvents. This paper presents an alternative which obtains comparable results while reducing analysis time and minimizing toxic solvent handling and waste generation.

Thomas J. Spitler of the U.S. EPA Lexington, Massachusetts Laboratory first proposed a simplified method for sample preparation as a field screening tool to estimate PCB levels in soils. This method involved measuring an aliquot of sample into a capped test tube, the addition of a 4:1 methanol:water solution, followed by agitation, and subsequently

the addition of hexane with further mixing. The hexane extract was injected into a portable gas chromatograph equipped with an electron capture detector. EPA Method 8080 was used to confirm the field screening results.

Refinements to this early method, as presented here, show results comparable to those achieved with EPA Method 8080. Samples are carefully weighed into glass test tubes with Teflon seals. The extraction regime is as used by Spitler. The resulting extract is cleaned up on a florisil/anhydrous sodium sulfate column. The sample is introduced to the GC with an autoinjector for greater precision, and state of the art gas chromatograph equipped with an electron capture detector is used for analysis.

There are a number of advantages to this simple analysis, with most related to reduced solvent use and handling. Extractions involve only 4 milliliters of hexane and 1.5 milliliters of methanol, as opposed to the ± 200 milliliters of methylene chloride required per SW-846. Hexane is a notably less toxic solvent than methylene chloride (a suspect carcinogen). This substitution considerably reduces the potential hazards to laboratory staff and others. In addition, many laboratories have the semi-volatiles and volatiles laboratories are in close proximity to each other; the detection limit for methylene chloride in the purgeables 'analysis is often increased due to cross contamination from the PCB/Pesticide extractions. The use of hexane as the primary solvent significantly reduces this problem.

Method SW-846 proposes the use of complex glassware and apparatus to perform the extraction procedure. Soxhlet apparatus are fragile and expensive; and therefore require deft handling. Because of the many joints and internal bends, there are numerous opportunities for residual contamination, resulting in the need for thorough cleaning. The suggested alternative is sonication. These instruments are also expensive and, due to the piercing noise of the horn, a sound proof box is usually needed. The simplified method presented here requires only test tubes with Teflon caps and pasteur pipets as materials; lessening the costliness and complexity of the analysis.

The presented procedure also permits many samples to be prepared in a short amount of time in our small laboratory. Results for thirty to forty samples can be processed within 48 to 72 hours. This added processing efficiency is passed on to the laboratory's clients which assists them in directing their environmental projects. With an auto injector and tray set-up, we routinely run blanks, calibration standards and duplicates to monitor analytical quality.

METHODOLOGY

A 5 g. air-dried soil or solid waste sample is weighed out into Fisher Scientific Kimax brand 16 by 125 mm borosilicate glass tube with teflon lined caps to +/-0.001 g. for a two phase extraction process. Phase one is the addition of 2 milliliters of a 4:1 solution of Fisher

Scientific Pesticide Grade methanol/ASTM Type III reagent water. After agitating this mixture for 1 minute using a Vortex Genie, the second solvent, 4 milliliters of Fisher Scientific Pesticide grade hexane is added and the sample is reagitated. The phases are allowed to separate for at least 15 minutes and Fisher Scientific purified copper metal powder is added to dissipate emulsions and remove sulfur interferences. The hexane phase extract is cleaned up with a preparative column made from Fisher brand 5-3/4-inch disposable pasteur pipets. The column is constructed by inserting a plug of Pyrex brand 8 micron glass wool in the tip of the pipet and filling the body of the tube with 3" of Fisher PR Grade (60/100 mesh) Florisil (to remove polar constituents) that has been oven dried at 130° overnight followed by the addition of 1/2" of Fisher certified A.C.S. grade anhydrous sodium sulfate (to remove residual water). The column is then tapped to eliminate air pockets and another plug of glass wool placed in the top. The prepared column is pre-wet with pesticide grade hexane; and then a two-stage elutriation is performed. Stage 1 is the addition and collection of 2 milliliters of the extract (hexane layer). Stage 2 is the addition and collection of the final rinse of 2 milliliters of 10 percent Fisher certified spectranalyzed ethyl ether in hexane to remove the PCBs and pesticides. The sample is eight fifths times diluted (volume/ weight) cleaned, and ready for GC analysis.

The prepared extract is analyzed for PCB/pesticide content using a HP-5890A Gas Chromatograph. The GC is equipped with a Nickel 63 Electron Capture Detector and a 3 percent SP-2100 on 100/120 Supelcoport 1/4-inch glass column or alternatively a 1.5 percent SP-2250 plus 1.95 percent SP-2401 on Supelcoport glass column: the column specified in EPA Methods 608 and 8080. The gas chromatographic conditions are set for a 200 degree isothermal run with an argon/methane 95/5 percent carrier gas flow of 40 cc/min. through the column. The half hour automatic analysis is electronically controlled by an HP-7673A Autosampler and data is acquired with a Nelson Analytical Series 2600 Software System. The coherent data yielded by this system is interpreted by the analyst who determines through relative retention times and peak patterns the identity of the PCB/pesticide present and through average areas, the concentration of the unknown.

RESULTS AND DISCUSSION

Based on available results the effectiveness of the presented method for extracting PCBs and pesticides from soils and solid wastes is comparable to the SW-846 Methods. Statistical analysis of spike recoveries for a period of one year demonstrates the reliability and consistency of the results. With three different gas chromatograph operators the average spike recovery was 104 percent with a 10 percent standard deviation. When data developed using this procedure were compared to data from another lab using EPA Method 8080 on similar, but not necessarily duplicate samples, the results were consistent (Table 1). The discrepancies in the data within a single laboratory and between one laboratory and another can primarily be attributed to sample heterogeneity which is a frequent problem with waste and soil

analyses. Although this method has not been used as extensively for extracting pesticides from soils and solid wastes as it has been for PCBs, there is strong supporting evidence that the results would be of comparable quality since at least 10 percent of the samples to be tested for PCBs are spiked with EPA recommended surrogate pesticides, and the recoveries are within 70-130 percent, 99 percent of the time.

Interferences can be a major problem in analytical methods involving complex environmental samples. Petroleum distillates and plasticizers such as phthalates are the primary interferences in analyzing for PCBs and pesticides with an electron capture detector (ECD). The extraction procedure outlined above includes a quick clean-up step with a florisil/anhydrous sodium sulfate column to reduce petroleum distillates, but some of the lighter hydrocarbons elute with the PCBs and pesticides when using a 10 percent ethyl ether in hexane solution as the eluent. Presently, we are experimenting with tandem solid phase extraction columns to optimize the polarity gradients to further reduce contaminating petroleum distillates.

Phthalates are sufficiently similar to PCBs and pesticides in their polarities that relying on polarity gradients in a clean-up scheme is not sufficient to remove them from the extract. Their presence in environmental samples to be tested for PCBs and pesticides presents difficulties in the identification and quantification of the aroclors or pesticides in the chromatogram since the electron capture detector is sensitive to this class of compounds. A possible solution to this problem is the use of an electrolytic conductivity detector (ELCD) instead of an ECD. The ELCD has considerably greater sensitivity to the chloride in the PCBs and pesticides than to the carboxyl functional groups in the plasticizers. Unfortunately, ELCDs require more maintenance and monitoring, thus an optimal arrangement could be to use both the ELCD and the ECD with sample splitting into each. We are currently working on such a set up where a gas chromatograph with two capillary columns fitted to one injection port, each leading to different detectors, an ECD and a ELCD.

Other possible sources of error due to interferences involve sulfur compounds. The addition of copper powder to the sample extract helps to alleviate this problem. The copper combines with sulfur precipitating out of the extract as copper sulfide (CuS). Powdered copper also has the serendipitous side effect of dissipating emulsions.

SUMMARY

A method for the analysis of PCBs and priority pollutant pesticides is presented. The sample preparation involves a small scale two-phase liquid/liquid extraction and permits low detection limits and adequate spike recoveries (104 percent ± 10 percent SD) of EPA recommended surrogates. For most samples the detection limit is 50 ug/kg which usually within project quality assurance objectives.

The method reduces the amount of toxic waste generated compared to the

requirements of EPA Method 8080, and thus lowers the costs and risks of disposing of the waste. The hazardous nature of the extraction itself is reduced since hexane is the primary solvent instead of the suspect carcinogen methylene chloride.

The simplified sample preparation protocol allows a shorter total analysis time permitting results to be used in making environmental clean-up decisions in an expedited manner. Overall the "modified Method 8080" presented here has a number of notable advantages over traditional Method 8080. It plays a significant role in our work in delineating areas of environmental contamination.

Acknowledgements:

The authors would like to express their appreciation for the assistance of Jeff Munic, Goldberg-Zoino & Associates, Inc., 320 Needham Street, Newton Upper Falls, Massachusetts 02164.

References

Spitler, T.M., "Field Measurements/PCBs in Soil and Sediment Using a Portable Gas Chromatograph," paper presented at the 4th National Conference on Management of Hazardous Waste Sites -- Washington, DC, October, 1983.

Boe, B. and Egaas, E., "Qualitative and Quantitative Analyses of Polychlorinated Biphenyls by Gas-Liquid Chromatography," 180 (1979), 127-132.

Method 8080, Federal Register, "Guidelines for Established Test Procedures for the Analysis of Pollutants," July, 1982.

Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019, United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Cincinnati, OH, March, 1979.

TABLE 1

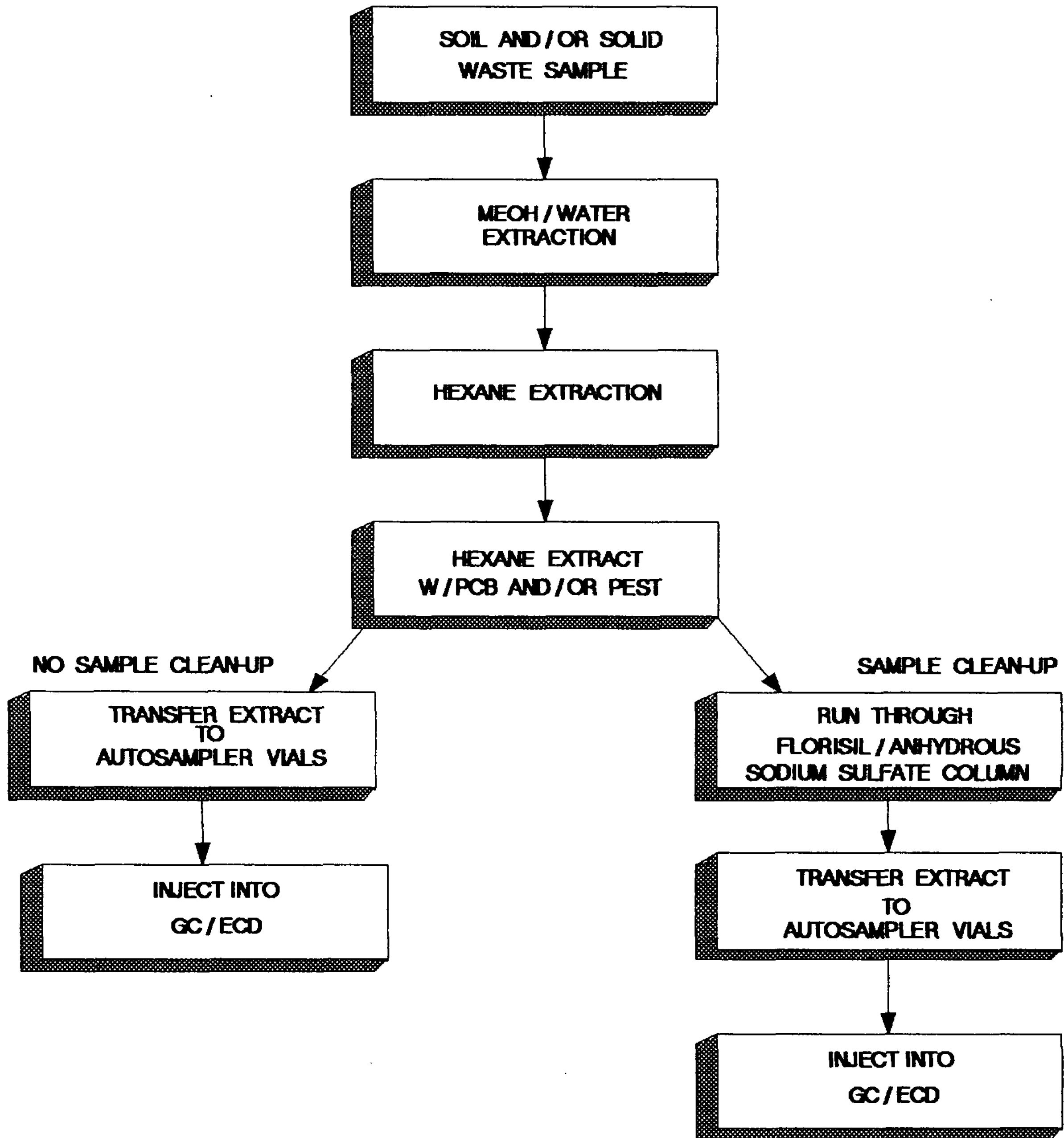
SUMMARY OF INDEPENDENT ANALYTICAL LABORATORY RESULTS AND MODIFIED EPA METHOD 8080 RESULTS

Sample I.D.	GZA Results (ppm)	Independent Laboratories Results (ppm)	Parameters
Composite #1	75.0	57.0	Aroclor 1260
Composite #9	0.58	0.8	Aroclor 1260
Composite #13	110	24.0	Aroclor 1260
Composite #29	1.3	2.2	Aroclor 1260
Composite #37	5.5	13.0	Aroclor 1260
Composite #39	7.6	6.0	Aroclor 1260
T-8	1.4	0.43	Aroclor 1260
T-85.5	0.63	3.7	Aroclor 1242
	ND[1]	0.66	Aroclor 1254
T-107/T-108B	8.5	5.8	Aroclor 1260

Notes:

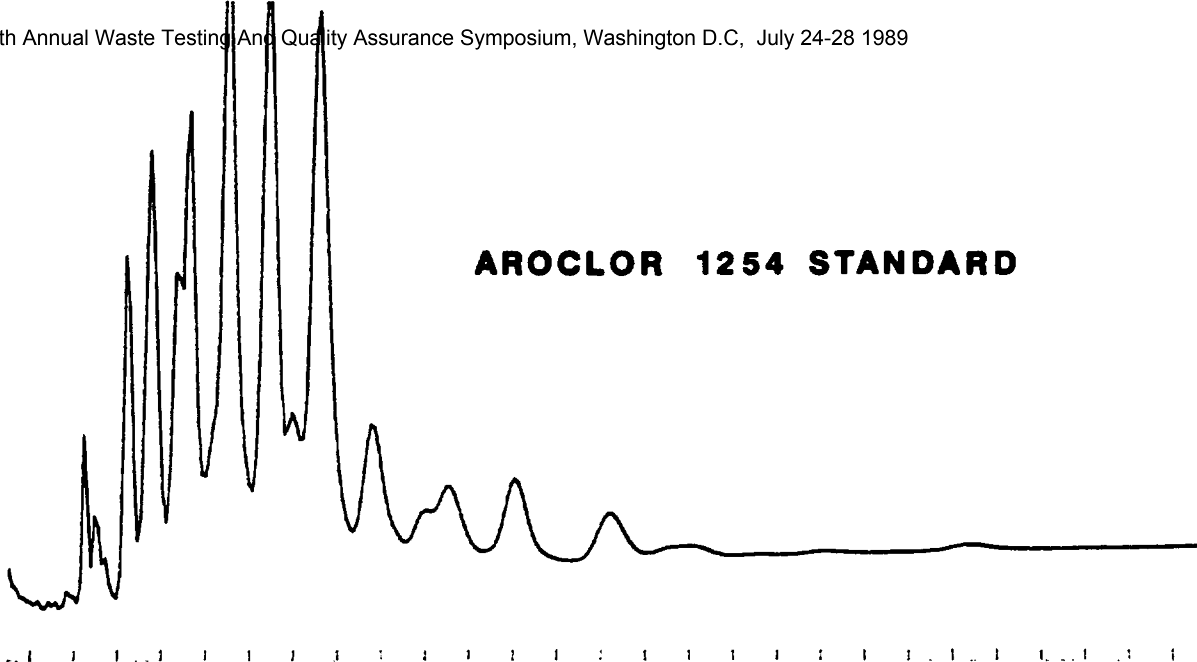
1. Modified EPA Method 8080 detection limit is 0.05 ppm, levels detected below detection limit are reported as ND (not detected).

FLOW CHART - SIMPLIFIED PCB / PESTICIDE EXTRACTION PROCEDURE

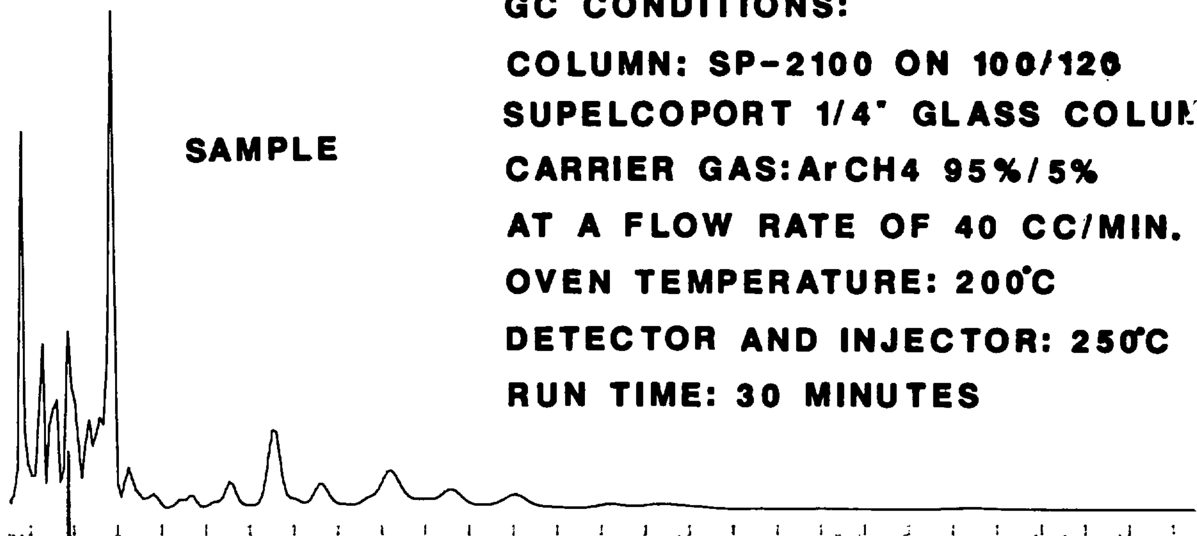


CHROMATOGRAMS OF SAMPLE WITH TWO PCB'S

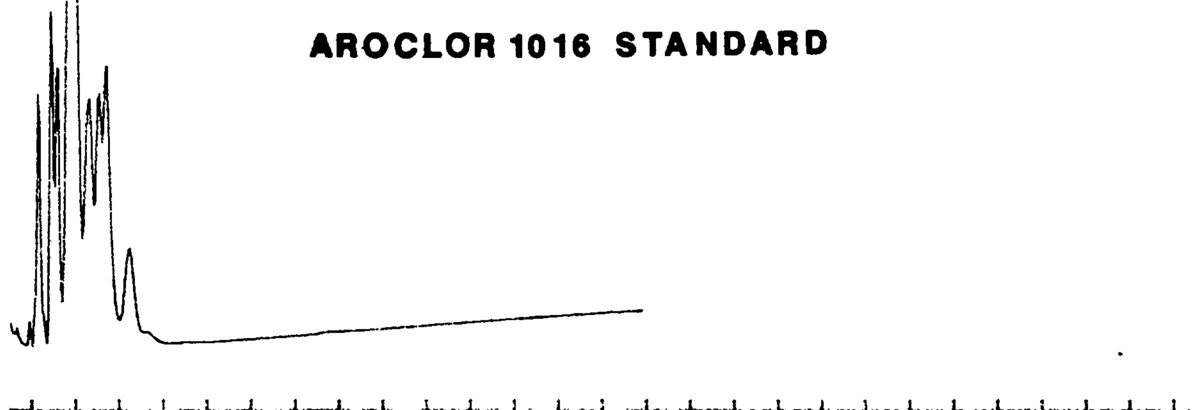
< 215423 >
0.5- 30.0 MIN
40 MV FULL
10 OFFSET



< 020646 >
0.5- 30.0 MIN
140 MV FULL
15 OFFSET



< 1215132 >
0.5- 30.0 MIN
50 MV FULL
10 OFFSET



AUTOMATED EVAPORATION FOR PRIORITY POLLUTANTS

Nancy Schwartz Henegar and W. Frank McCullough, Application Chemists, Analytical BioChemistry Laboratories, Inc., P.O. Box 1097, Columbia, MO 65205.

ABSTRACT

The Autovap® (ABC Laboratories,Inc., Columbia, MO) offers a method for automated concentration of priority pollutant samples. The Autovap® can be used in conjunction with the Autoprep GPC. In this mode, it accepts a continuous flow from the GPC column, concentrating the desired portion as it elutes, under reduced pressure and precisely controlled temperature. A small amount of "keeper" solution may be added to hold the more volatile analytes. Evaporation ceases when the Autovap senses that all solvent has been removed. At this point, the sample is resuspended in a desired solvent and transferred to a sealed vial. The Autovap® can also operate without a GPC, using a Sample Input Module. Samples from 10-250 mLs are pumped into the Autovap®, where they are concentrated, resuspended and transferred as previously described.

Semivolatile priority pollutant spikes were prepared and processed using the GPC-Autovap® system 601, to simulate cleanup of sludge, soil and wastewater samples. After concentration by the Autovap®, the samples were analyzed by GLC/FID as in U.S.E.P.A. Method 8270. Recoveries from these samples, were quantitative and were well within the acceptance criteria established in Method 8270, except for a few compounds which occasionally exceeded their limits of normal range for maximum recovery.

INTRODUCTION

Gel Permeation Chromatography is known to be "the most universal cleanup technique for a broad range of semivolatile organics and pesticides. It has been used successfully for all semivolatile base/neutral and acid" Priority Pollutants(1). The recommended apparatus, the Autoprep automated GPC, allows for up to 23 samples to be sequentially processed unattended.

Unfortunately, steps in sample preparation such as GPC or liquid-liquid extraction result in an excessively large sample volume. The suggested method for subsequent solvent evaporation utilizes Kuderna-Danish concentrators. This procedure is time-consuming because it requires constant supervision. The Autovap® (ABC Laboratories, Inc, Columbia, MO) offers a method for automated concentration of priority pollutant samples. Not only does the Autovap® reduce labor costs, but when used with GPC it merges two steps in sample preparation into one.

AUTOMATED SOLVENT CONCENTRATION

The Autovap® Model 600 sequentially processes up to 23 samples, as in the Autoprep GPC. The actual evaporation takes place in a glass chamber with a temperature sensor built into its ceramic bottom. In the chamber, a partial vacuum is applied and temperature is precisely controlled to

maintain a steady evaporation rate. All parameters are programmed into the microprocessor, which controls all activities of the system. Three pressurized tanks containing the diluent solvent, rinsing solvent, and keeper solution are attached to the instrument's side. These solutions will be transferred to the chamber at appropriate times.

Samples are pumped from a GPC or Input Module into the evaporation module at a rate of 5.0 mL/min. At the designated time, the Autovap begins collecting sample and dumping 2.5 mL portions into the chamber every 30 seconds to be concentrated cumulatively. This is accomplished by the use of two sample input loops, one which fills while the other empties its contents into the chamber. When used with GPC, the input loop system effectively isolates the GPC column from the partial vacuum in the chamber.

At the beginning of the evaporation cycle, a small amount of keeper solution may be added to the chamber. This will prevent excessive loss of the more volatile analytes. The compound used varies, depending on application and method of GLC detection.

The Autovap continues to concentrate the aliquots of sample until all of the sample has been pumped into the chamber, or in the case of GPC, when the desired fraction has completed elution. After the last portion of sample has been dumped into the chamber, the microprocessor begins monitoring the energy input into the chamber. It senses when all solvent has been removed and then resuspends the analytes in a new solvent from the diluent tank. After mixing, the Autovap transfers the sample to a sealed vial. All transfer lines, input loops, and the evaporation chamber are rinsed thoroughly before the next sample is processed.

601 SYSTEM

The Autovap ® Model 600 may be coupled with existing Autoprep GPC Models 1002, 1002A,or 1002B, or both modules may be bought as a system, which includes its own GPC module. All of these combinations are referred to as 601 Systems. The operation of this system is very similar to that of the Autoprep GPC when used alone. Immediately after each sample is automatically measured and loaded onto the GPC column, a rinsing procedure begins. All lines travelled by the sample are rinsed thoroughly with fresh solvent which is dispensed from a rinse solvent reservoir in the GPC module. Concentration of the desired fraction occurs as it elutes from the column, during what is referred to as "Evaporation time". This is directly analogous to the GPC "Collect time". The evaporation rate is about 5 mL/minute, the same as for GPC. Consequently, little or no additional time is required for on-line evaporation. The detection of evaporation endpoint, resuspension, transferring and rinsing processes occur during the GPC "Wash time".

602 SYSTEM

Operating in the 602 mode, the Autovap® can also provide concentration for samples which require no GPC cleanup, by interfacing with a Sample Input Module. Such a module is available with options for convenient conversion between the 601 and 602 Systems. The 602 System allows for samples from 10-250 mL to be pumped into the Autovap® module from pear-shaped flasks. Operation is very similar to 601 System, except that no dump time is necessary and, of course, the GPC column is absent. The sample is pumped into the Autovap® and evaporated at 5 mL/minute. After the sample has been pumped from the flask, 25 mLs of rinse solvent is emptied into the flask. It follows the sample into the evaporation chamber, and is evaporated with it, to assure a quantitative transfer of sample and rinsing the path of flow to the chamber.

The 602 System has the potential for many diverse applications. Among others, the system is very appropriate for groundwater extracts and similar sample types which are routinely tested by contract laboratories.

PROCEDURE

Methylene chloride was spiked with each of the following to reach a final concentration of 20 uG/mL:

> 2-Fluorophenol, p-Dichlorobenzene, Hexachloroethane, Naphthalene, Fluorene, Pyrene and Benzo(a)pyrene

Solutions containing 100 uG of each compound (5.00 mL) were loaded onto the GPC module and automatically injected onto the column of a 601 System. Three sets of at least 20 of these samples underwent cleanup and concentration by this method. Each set was ran unattended and overnight.

Next, spikes containing 0.50 G of corn oil and 100 uG of the same compounds were loaded onto the column to simulate cleanup of wastewater sludge, soil and sediment samples. Corn oil is commonly used for column calibration and represents a typical sample matrix requiring GPC cleanup. Three sets of these samples were also processed unattended and overnight. Samples were analyzed following equipment specifications listed for GC/FID in EPA Method 8270, except for the absence of a mass spectrometer.

Tests were also performed with each of the semivolatile compounds at a lower level. Prepared spikes containing 20 uG of each pollutant and 0.50 G of corn oil were automatically loaded onto the GPC column and processed by the 601 System as previously described. Samples were resuspended to a final volume of 2.50 mL and analyzed by GLC/FID.

EQUIPMENT PARAMETERS

A Model 601 System was used, which consisted of an Autovap® Model 600 and a Model 600-1 Sample Input Module, using Option 600-2, which allows for conversion into a GPC module for 601 System operation.

EQUIPMENT PARAMETERS CONTINUED)

The GPC column was glass, 60 cm x 2.5 cm I.D., packed with 70 G of Bio-Beads® S-X3, 200-400 mesh (Bio-Rad Laboratories, Richmond,CA). The GPC solvent used was 100% Methylene Chloride. The column was calibrated according to EPA Laboratory Manual SW-846, Method 3640(1), using a Shimadzu SPD-6A UV Detector.

Solvent pump flow rate: 5.0 mL/min.
Diluent Addition flow rate: 0.50 mL/second
Keeper Solution: 6 mLs of 0.3% Tricaprin in Methylene Chloride
Diluent Solvent: Methylene Chloride
Vacuum pressure setpoint: 300 Torr

Dump time: 24 minutes
Evaporation (Collect) time: 30 minutes
Evaporation Temperature: 31.8-32.0°
Cool Dry Time: 01 sec
Diluent Addition Time: 10.0 secs. (5.00 mLs), 5.00 secs for low level
Mixing Time: 05 secs, 03 secs. for low level.
Transfer Time: 10.0 secs, 3.0 secs. for low level.
Rinse Time: 20 secs.
Wash Time: 3 min., 26 secs.
Wash Temperature: 30°

GAS-LIQUID CHROMATOGRAPHY EQUIPMENT AND PARAMETERS

Varian Model 3700 with flame ionization detector and split/splitless capillary injector with frit-type splitter insert.

GLC Column: 30 meter x 0.25mm fused silica capillary, DB-5, 1 micron film thickness.

Oven Temperature: 60°C for 2 minutes, then 10°C/minute to 270°C.
Injector Temp.: 290°C, Detector Temp.: 300°C

Split Ratio: 15:1, Carrier Gas: Nitrogen at 1.2 mLs/min, Purge gas: Nitrogen at 28 mLs/min., Air: 300 mLs/min., Hydrogen: 30 mLs/min.

Autosampler: Varian Series 8000, Injection Volume: 1 microliter

Samples were automatically analyzed using the Computer Automated Laboratory System (CALS®) by Beckman, Beckman Digimetry® MK-5 Instrument Coupler, and a Hewlett Packard 1000 Computer Mainframe.

REAGENTS

Methylene Chloride: High purity solvent, Baxter Corp., Burdick & Jackson, Muskegon, MI

Tricaprin: Sigma Grade, Approx. 99%, Sigma Chemical Co., St. Louis, MO
Keeper Solution: 0.33 grams Tricaprin per 100 mLs Methylene Chloride

REAGENTS (CONTINUED)

Priority Pollutant standards: Neat compounds, Supelco, Inc., Bellefont, Pa

2-Fluorophenol:98%, Aldrich Chemical Co, Milwaukee, WI

RESULTS

The three overnight runs of samples containing the semivolatile compounds (no oil) yielded the following results. In the first set of the three, three reagent blanks were interspersed among samples. In this case, as in all previous work done (2), and in work done by Hopper and Griffit (3), no detectable cross-contamination has been found.

TABLE 1

AVERAGE PERCENT RECOVERIES OF SEMIVOLATILES
IN METHYLENE CHLORIDE FROM 601 SYSTEM (GPC-AUTOVAP)
100 micrograms

	n=20		n=23		n=23	
COMPOUND	AVG	STD	AVG	STD	AVG	STD
2-Fluorophenol	76.4	8.4	78.6	8.7	72.4	9.0
p-Dichlorobenzene	85.9	6.4	87.5	6.2	82.7	6.7
Hexachloroethane	89.1	6.1	90.1	5.8	86.4	6.2
Naphthalene	105.6	5.3	107.7	5.6	104.0	6.3
Fluorene	83.6	8.7	88.7	4.8	84.0	5.8
Pyrene	103.4	7.0	108.2	7.3	105.2	7.4
Benzo(a)pyrene	122.5	9.7	128.9	6.8	121.7	8.8

The following results were obtained from the three sets of samples containing the semivolatiles at the same level in a corn oil matrix:

TABLE 2

AVERAGE PERCENT RECOVERIES OF SEMIVOLATILES (100ug)
WITH CORN OIL (0.50 g) FROM 601 SYSTEM (GPC-AUTOVAP)

	n=21		n=23		n=22	
COMPOUND	AVG	STD	AVG	STD	AVG	STD
2-Fluorophenol	80.8	8.0	81.8	9.1	76.8	5.6
p-Dichlorobenzene	90.2	7.2	93.3	8.5	85.2	4.7
Hexachloroethane	92.6	6.4	95.1	8.6	87.6	4.7
Naphthalene	112.4	6.8	110.8	8.8	103.9	4.7
Fluorene	100.8	8.4	97.3	8.4	87.4	3.8
Pyrene	112.8	12.1	118.4	13.9	106.1	7.4
Benzo(a)pyrene	134.0	12.8	135.8	14.9	123.5	9.3

RESULTS (CONTINUED)

The following recoveries were obtained by loading 20 uG of each semivolatile compound in a corn oil matrix onto the GPC column:

TABLE 3

AVERAGE PERCENT RECOVERIES OF SEMIVOLATILES
AT A LOWER LEVEL (20uG) WITH CORN OIL (0.50 G)
601 SYSTEM

COMPOUND	n=20 AVG	STD
2-Fluorophenol	84.6	8.6
p-Dichlorobenzene	91.9	10.9
Hexachloroethane	95.8	9.0
Naphthalene	114.9	10.7
Fluorene	94.0	9.0
Pyrene	120.9	12.4
Benzo(a)pyrene	154.5	14.5

The values given by the U.S.E.P.A. as acceptance criteria for the selected compounds, as they appear in the EPA Laboratory Manual SW-846, Method 8270, Table 6, "QC ACCEPTANCE CRITERIA"(1), are tabulated below. These values are based on data from four determinations.

TABLE 4

QC ACCEPTANCE CRITERIA

COMPOUND	Range for AVG	Limit for SD	Min.-Max.
2-Fluorophenol	NA	NA	21-100%
p-Dichlorobenzene	37.3-105.7	32.1	20-124%
Hexachloroethane	55.2-100.0	24.5	40-113%
Naphthalene	35.6-119.6	30.1	21-133%
Fluorene	71.6-108.4	20.7	59-121%
Pyrene	69.6-100.0	25.2	52-115%
Benzo(a)pyrene	31.7-148.0	39.0	17-163%

SUMMARY

For all compounds tested at a 100 uG quantity, the results were well within the established limits for acceptance, except for pyrene, which occasionally exceeded its upper limit of 100.0. However, none of the compounds were below their lower limit. The more volatile compounds are apparently being sufficiently held and solvent removal is very efficient. All sample sets were ran unattended and overnight, demonstrating the system's abilities of automation. For all compounds tested, at both levels, standard deviations were well within the allowable limits.

The set of samples ran at a lower level of semivolatile compounds also yielded favorable results, although pyrene and benzo(a)pyrene slightly exceeded their upper limits. At this point, testing of samples at this level is still incomplete. Additional data may be available at the time of presentation.

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PREANALYTICAL HOLDING TIME STUDY - VOLATILES IN WATER

Fifth Annual Waste Testing and Quality Assurance and Symposium

D. Bottrell, J. Petty US EPA , Quality Assurance Research Branch, QAD, EMSL-LV
J. Fisk, C. Dempsey, US EPA, Analytical Operations Branch, OERR
G. Robertson, M. Bartling, Lockheed Engineering and Sciences Co.

INTRODUCTION

Pre-analytical holding times are currently a legal and/or contractual consideration. They can be program specific and do not necessarily reflect analyte stability. Published holding times have been based upon minimal analyte- and matrix-specific information (1,2). Current efforts to meet various data needs relate to requirements for analyte- and matrix-specific holding time and method performance evaluations.

Three separate studies were part of this investigation and evaluation. This presentation represents an overview of the information gathered. Results of holding times and the effects of preservation/holding time conditions at a single laboratory have been investigated at Oak Ridge National Laboratory (ORNL) and reported by Dr. M.P. Maskarinec (3,4,5). The ORNL study also generated sufficient sets of preserved (sodium bisulfate) and unpreserved samples for storage and distribution to Contract Laboratory Program (CLP) facilities. These samples were used in an interlaboratory evaluation of analyte-specific stability and an evaluation of the preservation technique recommended by ORNL(3). A third area of activity has been the use of quarterly blind (QB) performance samples to evaluate method performance and preanalytical holding times for volatile target compounds in unpreserved samples on an analyte-specific basis. Descriptions of each study's samples, conditions, and materials are included in Tables 1, 2, and 3.

DISCUSSION

The results of the QB studies demonstrate that nearly all target analytes are stable over a 16 week period. Inter- laboratory performance was determined to be a much greater source of variation than holding times, even for unpreserved samples. Table 4 presents the mean recovery and the acceptance windows as percent recovery from a homogeneous sample set. The samples had an initial concentration of 150 ug/L and were distributed immediately after production and again after three months (maintained at 4 degrees C). Nearly all analytes were stable over the period of study. Table 5 provides a list of the analytes for which significant loss was observed over the 90-100 day duration. From the acceptance windows, it is evident that analytical variation is larger than analyte loss for all but seven of the target compounds included in the study. This was determined by a t-test of reported concentrations over the period

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DEVELOPMENT OF AN INSTRUMENT-INDEPENDENT MS/MS DATABASE BASED ON CHARACTERISTIC BRANCHING RATIOS OF IONIC SUBSTRUCTURES (CBRIS)

Richard I. Martinez and B. Ganguli, Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

ABSTRACT

Dynamically-correct (i.e., instrument independent) branching ratios can be measured in XQQ (QQQ, BEQQ, etc.) tandem mass spectrometers (MS/MS) under single-collision conditions. To do so, the key MS/MS parameters must be properly selected to compensate for (a) the reaction-induced mass discrimination within Q2 (the rf-only quadrupole mass filter which contains the collision region) and for (b) the intrinsic mass discrimination within the Q3 mass analyzer. For the collisionally activated dissociation (CAD) of CH_3CO^+ at a center-of-mass interaction energy $E_{CM} \approx 2.4-38.6$ eV [the range of collision energies used for CAD], the sum of the **absolute** branching ratios equals 1.00±0.05 for all the fragment ions observed. That is, measurements were made with the MS/MS parameters selected so that the rate of reactant ion decay equals the rate of product ion formation (for each product ion, the extent of reaction of the parent ion was measured under the same ion containment conditions that are mandated by the CAD dynamics for each respective product ion). For the source compounds studied [ethanol, oxirane, and CH_3CO-X (where X= H, CH_3, CH_3CH_2, CH_3CO, CH_3COCH_2, and C_6H_5)], the reactant ion entering Q2 appears to be mainly CH_3CO^+. The collisional activation converts a small fraction of the CH_3CO^+ entering Q2 into the other $C_2H_3O^+$ isomers prior to their fragmentation. The product ion distribution for the CAD of $C_2H_3O^+$ at $E_{CM} \approx 2.4-38.6$ eV is quite different from that observed at 4-8 keV. The energy dependence of the branching ratios for $C_2H_3O^+$ from CH_3CO-X source compounds is quite distinct from that observed for $C_2H_3O^+$ from ethanol or ethylene oxide (a carcinogen), or for the isobaric $C_3H_7^+$ from n-pentane. Hence, one can use the CAD of 43^+ to distinguish CH_3CO-X compounds from other source compounds, including sources of the isobaric $C_3H_7^+$. Therefore, the energy dependence of the branching ratios may provide a MS/MS "fingerprint" for ionic substructures. The "CBRIS" database format (Table 1) is proposed for the development of an instrument-independent CAD database of Characteristic Branching Ratios of Ionic Substructures.

INTRODUCTION

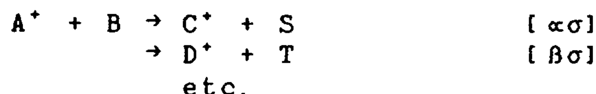
XQQ instruments (QQQ, BEQQ hybrid, etc.) are complex ion-optical devices.[1-8] There are currently more than 400 XQQ MS/MS instruments worldwide, representing a capital investment of more than $170M. To develop an instrument-independent MS/MS database (library) for XQQ instruments one must obtain an undistorted (dynamically-correct) representation of any reaction studied within such instruments [8]. The prerequisites for obtaining dynamically-correct branching ratios within XQQ instruments have been detailed elsewhere [8].

We have proposed a kinetics-based measurement protocol [9] which was incorporated into the protocol used for the NIST-EPA International Round Robin [10]. The round robin data from six participants showed that at least 50% of the QQQ instruments which have been sold and are currently in the field can provide a dynamically-correct (i.e., instrument-independent) representation [10]. Thus, we have successfully developed a kinetics-based measurement protocol which can provide, for the first time, accuracy and precision for measurements within XQQ tandem mass spectrometers. The protocol can be used to develop an instrument independent CAD database for XQQ tandem mass spectrometers. A case study is provided by the energy dependence of the branching ratios (measured with our protocol) for the low energy (2-40 eV) CAD of $C_2H_3O^+$ from several source compounds.

EXPERIMENTAL

All experiments were carried out in the NIST QQQ instrument.[11] Briefly, the instrument consists of (i) a standard electron impact ionizer, (ii) three standard quadrupole rod assemblies (Q1, Q2, Q3) operated in phase at 1.2 MHz and mounted in tandem on a special multipurpose track, and (iii) a continuous-dynode electron multiplier which incorporates a conversion dynode. Q2 is surrounded by a collision chamber enclosure.

With reference to the following general reaction sequence,



$$\mathrm{Ln}\ Y \equiv \mathrm{Ln}\ \{[A^+]_0/[A^+]\} = \sigma[B]L \quad (1)$$

$$\mathrm{Ln}\ W_{\alpha} \equiv \mathrm{Ln}\ \{\alpha[A^+]_o/(\alpha[A^+]_o-[C^+])\} = \sigma[B]L \quad (2)$$
$$\mathrm{Ln}\ W_{\beta} \equiv \mathrm{Ln}\ \{\beta[A^+]_o/(\beta[A^+]_o-[D^+])\} = \sigma[B]L \quad (3)$$

equations (1)-(3), etc. are applicable under pseudo-first order $\{[B]_o>>[A^+]_o\}$, single-collision conditions for a reaction zone of length L wherein the number density of the target gas is [B] and the "target thickness" is [B]L. Here σ $(=\alpha\sigma+\beta\sigma+...)$ is the total cross section for the A^++B interaction, and the sum of the branching ratios $\alpha+\beta+...$ is equal to 1. Reaction cross sections σ were derived by using equation (1).

Note that if there are no scattering losses, no mass discrimination, etc., then Ln Y= $\mathrm{Ln}\ W_{\alpha}$ = $\mathrm{Ln}\ W_{\beta}$, etc., and the branching ratios α, β, ... can be determined experimentally by using equations (4), (5), etc.

$$\alpha=[C^+]/\{[A^+]_o-[A^+]\} \quad (4)$$
$$\beta=[D^+]/\{[A^+]_o-[A^+]\} \quad (5)$$

In this paper, A^+, B, α, β, γ, δ, ϵ, ζ, and η, correspond, respectively, to CH_3CO^+ (m/z 43), Ar, CH^+ (m/z 13), CH_2^+ (m/z 14), CH_3^+ (m/z 15), $C_2H_2^+$ (m/z 26), $C_2H_3^+$ (m/z 27), CO^+ (m/z 28), and HCO^+ (m/z 29). CH_3CO^+ ions were generated by 70 eV electron ionization of each source compound, and the CH_3CO^+ projectiles were selected by Q1.

RESULTS

Table 1 shows typical results for the energy dependence of the branching ratios for all the fragment ions produced by the CAD of $C_2H_3O^+$ from several source compounds for $E_{CM} \simeq$ 2.4-38.6 eV. No other product ions were observed up to m/z 300. For other CH_3CO-X source compounds (X= H, CH_3CH_2, CH_3COCH_2, and C_6H_5), the results were substantially identical to those shown for biacetyl and acetone. Table 2 shows the energy dependence of the branching ratios for all the fragment ions produced by the CAD of $C_3H_7^+$ from n-pentane. No other product ions were observed up to m/z 300.

1. For the CAD of $C_2H_3O^+$:
   (a) For a given E_{CM}, the branching ratio for each fragment ion is substantially the same for all CH_3CO-X source compounds. However, the branching ratios for fragment ions from CH_3CO-X source compounds differ significantly from the branching ratios observed for $C_2H_3O^+$ from other source

compounds.

(b) For every source compound, CH_3^+ is the major fragment (branching ratio $Y > 0.75$) for $E_{CM} \simeq 2.4$-38.6 eV. Near threshold, $Y \simeq 1$.

(c) HCO^+ is the only other (very minor) fragment observed near threshold.

(d) Fragment ions other than CH_3^+ and HCO^+ start to form as E_{CM} is increased above 2.4 eV.

(e) CH^+ and CH_2^+ are significant minor fragments in every case.

(f) The CO^+ fragment is neglible in every case (branching ratio is less than 0.0055).

2. For the CAD of $C_3H_7^+$:

(a) $C_2H_3^+$ is the major fragment for $E_{CM} \simeq 2.4$-38.6 eV.

(b) CH^+ and CH_2^+ are not formed.

3. General observations:

(a) The energy dependence (magnitude and direction) is distinctly different for the isobars $C_2H_3O^+$ and $C_3H_7^+$. Hence, one can readily distinguish $C_2H_3O^+$ from $C_3H_7^+$.

(b) One can readily distinguish ethanol and oxirane from each other, and from CH_3CO-X source compounds.

<u>DISCUSSION</u>:

1. Result 1b indicates that near threshold the reactant ion entering Q2 appears to be mainly CH_3CO^+ in every case, but with different rovibronic distributions, as evidenced by the product distributions (see 3. below).

2. For $E_{CM} > 2.4$ eV, the collisional activation converts a small fraction of the CH_3CO^+ entering Q2 into the other $C_2H_3O^+$ isomers prior to their fragmentation.

3. Table 1 indicates that the CH_3CO-X source compounds (e.g., biacetyl, acetone, etc.) do share a common behavior in the energy dependence of the branching ratios for the CAD of $C_2H_3O^+$. These energy dependences are quite distinct from those observed for $C_2H_3O^+$ from ethanol or ethylene oxide, or for the isobaric $C_3H_7^+$ from pentane. Hence, one can distinguish 43^+ from CH_3CO-X compounds and from other source compounds, including sources of the isobaric $C_3H_7^+$. Therefore, the energy dependence of the branching ratios may provide a MS/MS "fingerprint" for ionic substructures. Hence, the "CBRIS" database format of Table 1 is

proposed for the development of a standardized instrument-independent CAD database of Characteristic Branching Ratios of Ionic Substructures.

SUMMARY

A kinetics-based measurement protocol can provide accuracy and precision for CAD measurements within XQQ tandem mass spectrometers. This protocol can be used to develop a dynamically-correct (i.e., instrument-independent) MS/MS database (library) for XQQ instruments based on Characteristic Branching Ratios of Ionic Substructures (CBRIS). A standardized CAD database is feasible.

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Table 1. Branching Ratios (α-η) vs. Center-of-Mass Collision Energy (E_{CM}) for the CAD of ($C_2H_3O^+$) from Different Source Compounds [1]

Parent Ion: $C_2H_3O^+$ (m/z 43)

Source Compound: 2,3-Butanedione (99.9%) [2]

Ionization Mode: 70 eV electrons

E_{CM} (eV)	σ_{LnY} (Å^2)	α (13^+)	β (14^+)	γ (15^+)	δ (26^+)	ε (27^+)	ζ (28^+)	η (29^+)
2.4	15 [20]	0	0	0.999 [2]	0	0	0	0.0010 [50]
19.3	22 [10]	0.0127 [15]	0.0493 [6]	0.915 [2]	0.0101 [7]	0.0013 [10]	0.0005 [35]	0.0114 [7]
38.6	21 [10]	0.0227 [10]	0.0750 [6]	0.839 [2]	0.0436 [6]	0.0055 [20]	0.0055 [20]	0.0086 [15]

Table 1. (Continued)

Parent Ion: $C_2H_3O^+$ (m/z 43)

Source Compound: 2-Propanone (>99.7%)[2]

Ionization Mode: 70 eV electrons

E_{CM} (eV)	σ_{LnY} ($Å^2$)	α (13^+)	β (14^+)	γ (15^+)	δ (26^+)	ϵ (27^+)	ζ (28^+)	η (29^+)
2.4	15 [25]	0	0	0.999 [6]	0	0	0	0.0008 [65]
19.3	23 [20]	0.0118 [15]	0.0487 [8]	0.911 [3]	0.0119 [6]	0.0018 [40]	0.0018 [40]	0.0130 [6]
38.6	22 [20]	0.0242 [15]	0.0681 [10]	0.846 [3]	0.0409 [7]	0.0069 [30]	0.0050 [20]	0.0089 [20]

Table 1. (Continued)

Parent Ion: $C_2H_3O^+$ (m/z 43)

Source Compound: Oxirane (>99.95%) [2]

Ionization Mode: 70 eV electrons

E_{CM} (eV)	σ_{LnY} ($Å^2$)	α (13^+)	β (14^+)	γ (15^+)	δ (26^+)	ϵ (27^+)	ζ (28^+)	η (29^+)
2.4	20 [15]	0	0	0.990 [2]	0	0	0	0.0096 [15]
19.3	26 [15]	0.0204 [20]	0.0667 [15]	0.872 [3]	0.0111 [10]	0.0041 [25]	0.0020 [50]	0.0234 [10]
38.6	25 [20]	0.0218 [20]	0.1041 [9]	0.796 [3]	0.0337 [10]	0.0071 [35]	0.0024 [100]	0.0352 [15]

Table 1. (Continued)

Parent Ion: $C_2H_3O^+$ (m/z 43)
Source Compound: Ethanol (100%)[2]
Ionization Mode: 70 eV electrons

E_{CM} (eV)	σ_{LnY} ($Å^2$),	α (13^+)	β (14^+)	γ (15^+)	δ (26^+)	ε (27^+)	ζ (28^+)	η (29^+)
2.4	16 [25]	0	0	1.000 [6]	0	0	0	0
19.3	24 [25]	0.0152 [35]	0.1143 [15]	0.795 [4]	0.0361 [15]	0	0	0.0331 [10]
38.6	25 [15]	0.0135 [80]	0.1216 [15]	0.766 [6]	0.0528 [10]	0.0041 [50]	0	0.0419 [30]

Table 1. (Continued)

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1 The numbers in the square brackets represent the maximum uncertainty in σ_{LnY} and in the branching ratios (α-η), expressed as a percentage of each σ_{LnY} and of each branching ratio {e.g., for biacetyl at E_{CM}=2.4 eV, the maximum uncertainty in Y is ±([2%]/100)•Y; i.e., Y= 0.999 ± 0.02}.

2 For the CAD of any given parent ion (e.g., $C_2H_3O^+$), appropriate corrections must be made for contributions from the concurrent CAD of isobaric ions (e.g., $C_3H_7^+$), regardless of their source. The isobaric ions may be co-produced in the ion source (i) from the source compound (e.g., ionization of $CH_3C(O)C_3H_7$ will produce both CH_3CO^+ and $C_3H_7^+$) and/or (ii) from a neutral impurity in a source compound (e.g., for a butanol impurity in a 2-butanone source compound, the butanol generates $C_3H_7^+$, while the 2-butanone generates CH_3CO^+). Fortunately, the CAD spectra of CH_3CO^+ and $C_3H_7^+$ are easily distinguishable. That is, for the CAD of $C_3H_7^+$, $C_2H_3^+$ (m/z 27) is the major CAD fragment for $E_{CM} \approx$ 2-80 eV. By contrast, for the CAD of $C_2H_3O^+$, $C_2H_3^+$ is not produced at E_{CM}= 2.4 eV, and is only a very minor fragment for $E_{CM} >$ 2.4 eV. Unfortunately, even minor impurities can contribute disproportionately to the CAD spectrum of a source compound because of differences in the CAD dynamics of isomeric and/or isobaric ions. Because of this problem, it is advisable that both the source compound and the target gas be of high purity (> 99.95%). Otherwise, the impurities must be characterized so that appropriate corrections can be made for their contribution to the observed CAD spectrum. In this Table, the CAD spectra of $C_2H_3O^+$ have been corrected, where appropriate, for contributions from the isobaric $C_3H_7^+$.

Table 2. Branching Ratios (α-ι) vs. Center-of-Mass Collision Energy (E_{CM}) for the CAD of ($C_3H_7^+$) from n-Pentane [1]

Parent Ion: $C_3H_7^+$ (m/z 43)
Source Compound: n-Pentane (99.3%) [2]
Ionization Mode: 70 eV electrons

E_{CM} (eV)	σ_{LnY} ($Å^2$)	α (13^+)	β (14^+)	γ (15^+)	δ (26^+)	ϵ (27^+)	ζ (28^+)	η (29^+)	θ (39^+)	ι (41^+)
2.4	20 [20]	0	0	0.0457 [10]	0	0.8190 [1]	0	0	0.0031 [8]	0.1322 [7]
9.6	31 [10]	0	0	0.1506 [3]	0.0145 [8]	0.7095 [1]	0.0373 [4]	0.0045 [15]	0.0152 [2]	0.0686 [2]
38.6	28 [15]	0	0	0.3401 [5]	0.1063 [15]	0.4381 [3]	0.0265 [25]	0	0.0164 [4]	0.0725 [4]

1 The numbers in the square brackets represent the maximum uncertainty in σ_{LnY} and in the branching ratios (α-ι), as defined for Table 1.

2 The purity of the source compound.

QUALITY ASSURANCE AND QUALITY CONTROL

THE DEFINITION AND CLASSIFICATION OF HAZARDOUS WASTE MATRICES

DR. PETER A. POSPISIL Manager, Methods Development, DR. MARK F. MARCUS Director of Analytical Programs, Chemical Waste Management, Inc. 150 West 137th Street Riverdale, IL 60627

ABSTRACT

Analytical chemistry plays a major role in the hazardous waste field, but the analyte/matrix relation generates an additional dimension of sample complexity not encountered in other disciplines. Hazardous waste analytes are clearly defined by regulations, but no classification systems exist for hazardous waste matrices.

Twenty four basic hazardous waste classes have been defined based on materials most frequently occurring in waste management operations. The definitions are based on the physio-chemical composition of about 1000 samples received at the CWMI Technical Center. The system can classify 90 to 95 per cent of the samples received in the analytical laboratory. Multiphase mixtures can easily fit into the system by considering each phase as a unique matrix. All of the components defined with D, F and K hazardous waste codes be fit onto the classification. The development of a uniform, systematic waste classification system parallels and facilitates advances in the areas of hazardous materials disposal research, analytical methods development, and QA/QC programs, by providing by providing uniform and realistic reference material classifications.

INTRODUCTION

Waste comprises the vast category of undesirable by-products of our industrialized society: things for which we have little or no value. For decades these materials have simply been dumped and hidden away, but there is now a growing awareness that these materials need to be safely re-assimilated into our environment.

The Chemical Waste Management Company, CWM, effects this task through its 19 disposal sites located throughout the United States. CWM handles a broad range of legally disposable wastes and out of specification materials, excluding hard radioactive materials and explosives. Paint sludge, plating waste and polychlorinated biphenyl disposal comprise a considerable part of our business, but there are thousands of individual substances arising from unique and diverse sources requiring disposal. Both the magnitude of the sources and samples are increasing annually. Many CWM sites annually receive tens of thousands of samples, and this number is increasing as the definition of hazardous waste broadens, the number of regulated components increases, and the detection limits of these components is reduced.

CWM employs modern waste disposal techniques focusing on incineration, chemical treatment, stabilization and landfilling. Its waste disposal technology is also being expanded through the development of new processes for the extraction and degradation of hazardous materials. Paralleling this expansion is a corresponding increase in analytical methods development, quality assurance and quality control implementation and data processing in the areas of sample identification and tracking.

Analytical chemistry plays a major role in the hazardous waste area, through both wet and conventional instrumentation. But there is an complicating factor in this work because of an additional dimension of complexity in the analyte/matrix relation.

Hazardous waste analytes are clearly defined by a broad range of Federal, State and Local regulations. The specific components presented in documents such as: Appendix-3, Appendix-8, Appendix-9, CCWE, List of Lists etc. They can be classified and categorized as required into organic, inorganic, volatile, semi-volatile, non-volatile, water stable etc. groups.

In most industries many analytical problems revolve around the analysis of 1 to 12 parameters in a relatively consistent matrix. In the hazardous waste business there is no single matrix but rather combinations of an extremely broad range of residua having minimum compositional similarities. Unrelated materials such as water, petroleum distillates, paint residues, plating sludges, soils, and numerous mixtures thereof are common occurrences.

Unlike the clearly defined hazardous analytes, the waste matrices in which they occur are not clearly defined at all. Because of the increased analytical requirements arising from expanding technical efforts in the hazardous waste area, there is a need to know more about the fundamental compound classes comprising that broadly defined entity termed "chemical waste."

PURPOSE

The purpose of this work is to define a set of hazardous waste classes, based on materials encountered in waste management operations. The study approaches waste from a broad qualitative compositional overview and does not focus on its minor variations. The measurement of success will be to produce a reasonably sized set of chemically descriptive matrices, which describe 90 to 95 per cent of the single and multiphase samples received in our business. The institution of a uniform, systematic waste matrix classification system will facilitate research in the areas of analytical method development programs, QA/QC development and process engineering operations, by providing a better understanding of basic waste composition.

TECHNICAL APPROACH

There are few waste matrix definitions, but the scope of their range can be extreme. One type of definition views each uniquely composed waste as an individual matrix making their number incalculable. Another reduces all samples to their basic physical state of solid, liquid or gas. Other definitions depend on the use of a physical or chemical test, such as Freon solubility to produce a matrix of Freon solubles. The matrix can be implied by regulation: if the PCB content of a soil is greater than 500 ppm the material is considered to be a pure PCB matrix. Although these definitions may have application in specific situations, this work attempts to approach matrix definition from a balanced standpoint.

This approach to this matrix definition study is through a waste's physio-chemical composition. In this study the term matrix is defined as a micro-homogeneous, physio-chemically unique material describable in chemical terms, which can accommodate the presence of minor amounts of contaminants.

Matrix classification was based on the sample types received in the Analytical Laboratory over a several month period. Approximately 1000 samples were examined, and the waste stream names described in the analytical sample control system were examined. The review showed that distinct sample compositions consistently appeared. These formed the basis of the 24 matrix definitions presented in Table 1. Each matrix is classified under a single heading with a physio-chemical description including examples where possible.

DISCUSSION

There are 24 entries: 11 for solids, 12 for liquids and one for all gases. The solids portion mainly contains variations of inorganic and organic materials and the liquids aqueous and organics. As an example sand, soil, earth, clay, gravel, mud, silt and till all have a common terrestrial origin and are all considered as being an earthen matrix. Any one of the items may be contaminated by oil, arsenic, cyanides, PCB's, resins, solvents, pesticides etc., but the basic earthen matrix remains their common link.

Multiphase samples are considered to be mixtures of matrices. In effect, the defined matrices are building blocks for mixtures. For example, a three phase mixture of soil, fuel oil and water would be considered as a single mixture comprised of three matrices. Replacing the water with an aqueous acid produces a new mixture merely having one matrix different from the first. Small amounts of a stable water-oil emulsion at the interface it can be ignored. But, if the size of the emulsion becomes significant, then it might then be considered as a fourth matrix.

The number and compositional variety of the matrices is sufficient to accommodate samples which may contain a broad variety of chemical classes. For example, components of a sample named "paint solvent" containing chemical types such as hydrocarbons, oxygenates, heteroatom, halogenates and water all fit within the system.

This broader matrix definition rapidly classifies 90 to 95 per cent of the materials received at the Technical Center, along with wastes classified by the D, F and K waste codes. Tests such as Freon solubility can be described as being responsive to most liquid organic matrices and possibly some solid organic matrices.

The authors believe that this classification system of 24 matrices is applicable to 90 to 95 per cent of the wastes received within CWMI. It is applicable to complex samples by considering each phase to be a unique matrix, and flexible enough to be expanded as the need arises. The establishment of a uniform, systematic waste matrix classification system will facilitate research in the areas of analytical method development programs, QA/QC development and process engineering operations, by providing a better understanding of basic waste composition.

Table 1

Classification and Description of Hazardous Waste Matrices

SOLIDS & SLUDGES

Solid or semisolid, nonflowing materials, which may contain some liquids. Including items commonly referred to as bottom sediments, bottom streams, treatment sediments, treatment sludges, muds, residues, filter cakes, and solid slops.

ACID

Reaction products and residues from processes using mineral or organic acids, solidified acids or acid products, such as sulfuric, hydrochloric, phosphoric, acetic and nitric acids. The sludges have a low pH and may contain significant amounts of carbonaceous polymers or insoluble metal salts.

ALKALI

Reaction products and residues from processes using mineral or organic alkalis, solidified alkalies or alkali products, such as sodium and potassium hydroxides, ammonia, quaternary amines and lime residues. The sludges have a high pH and may contain significant amounts of carbonaceous polymers or insoluble metal salts.

EARTHEN

Solid materials of terrestrial origin including sand, soil, earth, clay, gravel, mud, silt, till etc. These are usually silicaceous or alumino-silicaceous but may contain carbonates in the form of limestone. Contaminants are typically organic materials.

COMBUSTION PRODUCTS

Solid products of combustion or production such as incinerator ash, solid ash, fly ash, bottom ash, kiln clinker, synthetic grits and bag dust which are usually composed of metallic oxides, some carbonaceous polymers and trace quantities of organic material.

INORGANIC - PLATING WASTES

A broad range of solid inorganic chemicals whose prime component might be cyanide. The waste might also contain some soluble or insoluble organic material. Nickel and copper waste would be an example.

INORGANIC - RESIDUES

A broad range of inorganic chemicals, metallic or non-metallic elements. Components would range from pure inorganic elements or compounds to a broad range of common and complexed inorganic species, where the central ion is inorganic but the complexing species may vary. The waste might also contain some organic material. Items would include mill scale, plating residue, inorganic pigments, arsenic sulfide.

ORGANIC/INORGANIC

Solids which may contain organic polymers and inorganic materials at roughly equal concentrations, including paints and possibly some inks, dyes, organometal pigments and certain chemical residues.

ORGANIC - HYDROCARBON

Solid organic materials comprised mainly of carbon, hydrogen and some oxygen including still bottoms, carbon, charcoal, many plastics, waxes, tars.

ORGANIC - HETEROATOM

Solid organic materials having a significant sulfur, phosphorus, nitrogen and halogen content such as herbicides, pesticides, cleaning and degreasing residues and bottoms, chemical and grease additives and their respective residues.

BIO-ORGANICS

Biochemicals and materials derived from biological processes and products including sewage sludge, starch, pharmaceuticals and many gelatinous materials having a high water content.

CELLULOSIC

Paper or cloth products including uniforms, clothing, fiberboard, some filters.

LIQUIDS

Liquid or semi-liquid pourable materials, which may also contain suspended solids. Including items commonly referred to as distillation side cuts, stripping still streams, reactor washings, waste treatment streams, scrub waters, pot cleanings, tub washings and leach solutions.

AQUEOUS - ACIDIC

Aqueous solutions of reaction products and residues from processes using mineral or organic acids, liquid acids or acid products. Examples include sulfuric, hydrochloric, phosphoric, acetic and nitric acids. The liquids have a low pH and may also contain some soluble organics and metal salts.

AQUEOUS - ALKALI

Aqueous solutions of reaction products and residues from processes using mineral or organic alkalis, liquid alkalies or alkali products. Examples include sodium and potassium hydroxides or carbonates, quaternary amines and lime residues. The sludges have a high pH and may contain soluble organics and metal salts.

AQUEOUS - CYANIDE, HIGH SOLIDS

Aqueous solutions having a high solids and cyanide ion content. Examples would be copper or nickel plating solutions.

AQUEOUS - NEUTRAL, HIGH SOLIDS

Aqueous solutions having a high solids content and a broad pH range including aluminum, nickel and zinc solutions.

AQUEOUS - NEUTRAL

Aqueous solutions having a low solids content and possibly containing some organics, including groundwater, well water, rain water, runoff, and leachates.

ORGANIC/AQUEOUS SOLUTIONS/SUSPENSIONS

Mixtures of water and significant amounts of water miscible organic materials, which produce a stable single phase, or emulsion, including water containing miscible solvents, surfactants, emulsifiers.

ORGANIC - HYDROCARBON

Liquid petroleum based organic materials and related products comprised mainly of carbon, hydrogen, including liquid still bottoms, naphtha, Stoddard solvent, fuel oil, gasoline, aromatic solvents, quench oil, soaps, surfactants.

ORGANIC - HETEROATOM

Liquid organic materials having a significant sulfur, phosphorus, nitrogen, oxygen and halogen content such as herbicides, pesticides, chemical additives and their respective residues, chlorinated or nitrated phenols, cresols, cresylic acids.

ORGANIC - HALOGENATED

Liquid aliphatic or aromatic hydrocarbons containing one or more halogens, but no other heteroatoms. Including carbon tetrachloride, chloroform, trichloroethylene, bromoform, chlorinated benzenes, degreasing and cleaning solvents, but excluding PCB's.

ORGANIC - HALOGENATED BIPHENYLS

All halogenated biphenyl isomers.

ORGANIC - OXYGENATED

Liquid oxygenated organics generally comprising products such as alcohols, ketones, aldehydes, cellosolves, glycols, ethers, furans, varnishes, shellacs.

ORGANIC/INORGANIC

Liquids which may contain organics and inorganics at roughly equal concentrations, including paints and possibly some inks, dyes, pigments and certain chemical residues.

GASES

The complete range of organic and inorganic, flammable, toxic or corrosive materials requiring containment in any size of gas cylinder or pressurized vessel.

QA/QC Data Management System

Peter Chong - Programmer, Joan Slabaugh - QA/QC Technician, David Rosenbacher - Programmer/Analyst, John Hicks - Manager, Analytical Systems, Chemical Waste Management, Inc., 150 W. 137th St., Riverdale, IL 60627

ABSTRACT

The Quality Assurance department for Chemical Waste Management, Inc. monitors the quality of data generated by CWM laboratories and contract laboratories. As more stringent regulatory measures are proposed from federal agencies, the need to maintain an efficient and accurate QA/QC data collection system has become a formidable task. At Chemical Waste Management, Inc., the Analytical Systems section has developed a computerized QA/QC Data Management System (QA/QC DMS) to improve processing of the QA/QC data.

Monthly and quarterly QA/QC data from all sites are reported and reviewed at CWM's Technical Center in Riverdale, Illinois. The QA/QC data received are evaluated from a defensibility standpoint. This system is also capable of performing tracking and reporting analysis of data trends, various statistical analyses, and providing pre and post audit documentation. This paper describes how the QA/QC Data Management System (QA/QC DMS) is organized and structured in both hardware and customized software. Both hardware and software architectures are in the PC environment because of its data portability and connectivity to other systems. A relational database and integrated spreadsheet are used to process and prepare data for further statistical analysis and graphical presentation. Access to this system provides management with the assurance that corporate QA/QC policies and procedures are adhered to by all sites.

INTRODUCTION

A tremendous amount of data is associated with the evaluation of the quality of work performed by an analytical laboratory. Quantitative data (e.g., qc check samples, fortified sample analyses, parallel analyses), coupled with qualitative data (e.g., record keeping, training, method maintenance) must be evaluated to determine the defensibility of the results generated by a lab. The timely reporting, analysis and collation of the data are critical to the success of an

analytical program.

Chemical Waste Management's Quality Assurance Program has grown from monitoring the performance of 8 laboratories to its current task of 26 CWM laboratories and over 70 contract labs throughout the U.S. and Mexico. During this time, the QA/QC program has not only grown in size, but also in complexity. QA/QC Auditors travel 30 weeks per year, performing laboratory audits and generating data from each audit that needs to be evaluated with proper action taken. Inefficient information management created bottlenecks in preparing for future site audits and reporting the results of audits to the participating labs and management.

The Analytical Systems section of Chemical Waste Management has developed a Data Management System to expedite the collection, collation and evaluation of the QA/QC data. The system is a combination of integrated spreadsheet applications for data collection, a relational database management system to manage and report data, and statistical packages to analyze and graphically represent the compliance and overall performance of a lab when compared to other facilities.

DATA DESCRIPTION

Briefly stated, the QA/QC data generating procedures consist of site audits to determine conformance with corporate policy and procedures, and the collection and analysis of a variety of quality control data. Examples of the data managed are described below:

QC Check Samples: QC check samples are analyzed at least once daily. These samples demonstrate that the calibration and standardization of the measurement process are within acceptable limits.

Duplicate Analyses: Within an analytical method, every tenth sample must be analyzed in duplicate to determine the reproducibility of the result.

Fortification Analyses: Every tenth sample in a procedure is fortified to measure the accuracy of the analytical method as well as, to assist in the identification of matrix interferences.

Round Robin Analyses: Proficiency samples are submitted to all CWM facilities and Contract labs participating in the laboratory approval program by the Director of Quality Assurance. This allows the QA department to compare laboratory performance across the company and evaluate the proficiency of all laboratories used by CWM.

Parallel Analyses: One sample, representative of all parameters analyzed by a lab, is submitted to the Technical Center Laboratory for the identical analysis. The results are compared to the submitting Lab's results for accuracy of analysis.

Laboratory Performance Data: Results from Laboratory audits. The data contains qualitative descriptions of audit results and the corrective actions recommended.

QA/QC Base Software

LOTUS Symphony[R]: The applications used to collect the Quality Control data from participating labs were written in LOTUS Symphony[R]. Symphony[R] was selected as the base software because it is a multi-functional integrated software package which includes; spreadsheet, graphing, database and data communication capabilities that does not require extensive programming. In addition, it is relatively inexpensive, works on the variety of PC's we have in the field, and provides a tool for site laboratories to develop their own applications.

R:base for DOS[R]: The QA/QC database system has been implemented by using R:Base[R]. This system is used to manage collected laboratory audit data and to act as a general information database. R:base[R] was chosen because its flexibility in data handling, data portability and querying characteristics. It has also proven to be cost effective for implementation on our Local Area Network.

RBBS: RBBS (Remote Bulletin Board System) is an inexpensive way to achieve data communications with the Technical Center and our site laboratories. This public domain bulletin board software allows a PC with a modem and a dedicated phone line to act as a host computer. Remote computers can then access the host system and upload or download computer files. This method is used to electronically transfer our quality control files from CWM labs to the Technical Center. In addition, the bulletin board acts as an electronic mailbox where messages between the sites can be exchanged. The remote bulletin board system has enabled us to solve the connectivity problem between our remotely located sites and the staff of the Corporate Technical Center.

Statistical & Graphics Software: A variety of statistical and graphics software packages (e.g., Energraphics[R], StatGraphics[R], Harvard Graphics[R]) are used to analyze the data and graphically present trends in the Quality Assurance programs.

QA/QC Hardware Configuration

The QA/QC Data Management System is a customized integrated system that runs on a PC hardware/software environment(Figure 1). The QA/QC Data Management System and data reside on a HP StarLan^R local area network file server (HP RS/20, 20Mhz-80386 microcomputer with 103 megabytes hard disk storage). The HP StarLan^R network is a 10 megabits/sec network which runs over regular telephone twisted pair wiring. The PC workstations (HP ES/12, 12Mhz-80286 microcomputer with 40 megabytes of hard disk storage) are configured with network interface cards and reside on mobile carts. This configuration allows a single workstation to be shared by several auditors. This arrangement also allows the workstations to be used as standalone PCs. Network implementation has also proven to be a cost effective way to share workstations and printers for the QA/QC unit.

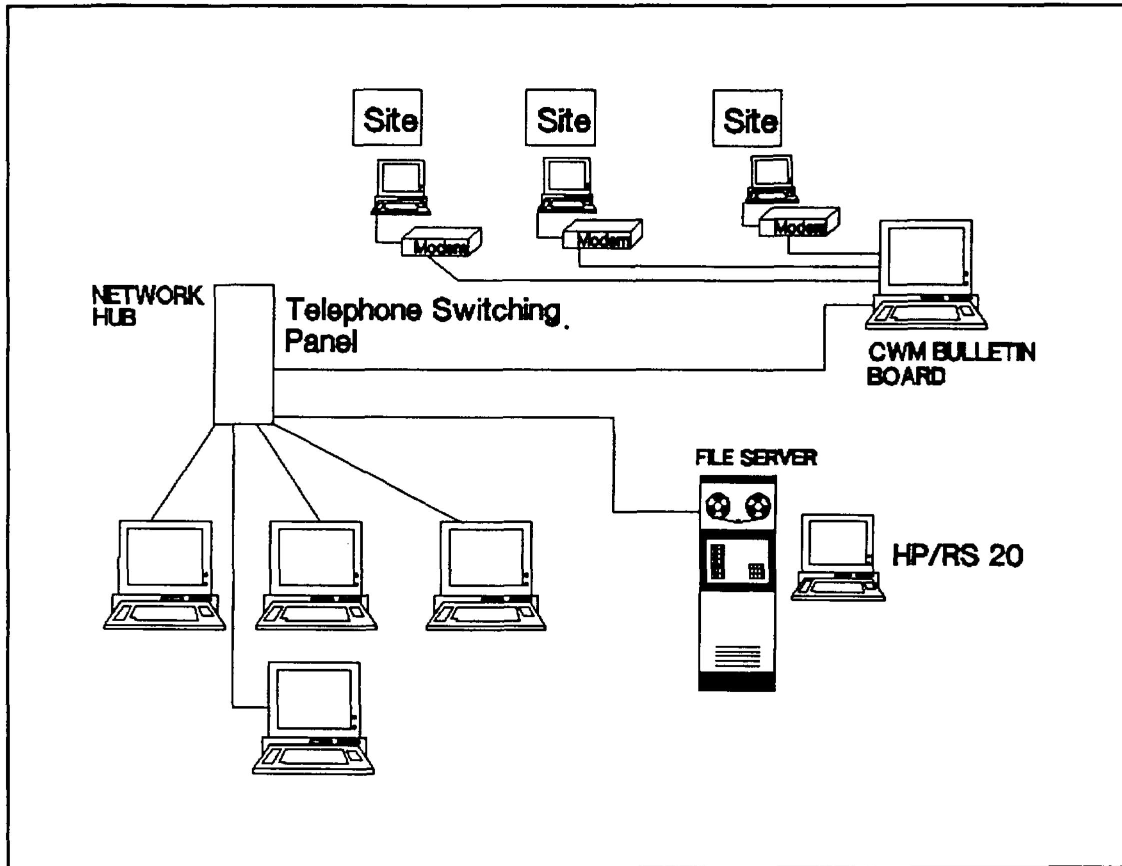


Figure 1: The QA/QC Local Area Network Configuration.

DATA COLLECTION SOFTWARE

QC Program: The QC program is a user configurable application which manages all the QC data for one analytical method. Daily QC samples are entered into a database in which simple statistical methods are employed to determine if the calibration and standardization of the method are within acceptable limits. Duplicate and fortified sample analyses are maintained in a separate database. The mean of the duplicate analyses, % error, and % recovery of the method are calculated during processing. The most current data population is used for statistical analysis by maintaining a moving data population (eg., at least 15 datapoints per month, or the last 15 datapoints). Cumulative statistics from the prior month are maintained to compare with the current month. The QC program has a built in graphical interface which allows the analyst/lab manager to view the results of the assays. These graphs include; a plot of the daily QC sample results, frequency distribution of the QC results, and percent error and percent recovery of the method(Figure 2). A report which summarizes the QC statistics for the method is also available.

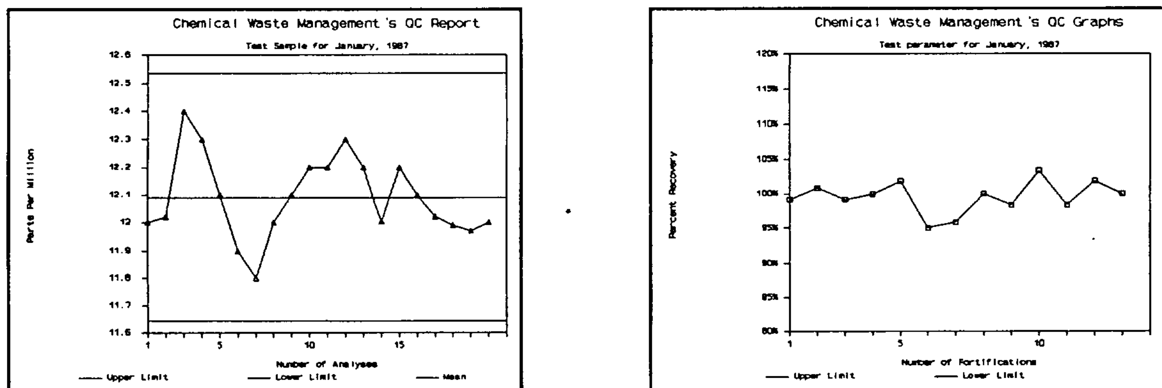


Figure 2: Example Graphs from QC Program

Extract Program: A Symphony[R] macro that extracts the summary report information from each QC program at a site laboratory. After the data has been extracted, the application dials the Technical Center and downloads the extracted data to the CWM Bulletin Board system. The Extract program is designed to require minimal user interface and is fully menu driven. If the site does not have the appropriate communication equipment, the Extract program will save the extracted data to a floppy disk. The disk is then mailed to the Technical Center for inclusion into the QA/QC database

QA/QC Database: The QA/QC database is a multi-user database in which the cumulative monthly site data, specific laboratory information, and other QA/QC data are stored and archived.

The QA/QC database is partitioned into several modules, designed to meet each specific Quality Assurance objective. The database application is menu driven with customized data entry screens to facilitate data input and customized reports to provide structure for frequently used queries. The collection of customized features is organized and tailored with the R:base[R] programming language. Ad Hoc queries can be applied to the database when special queries are required. The database modules are described below.

Monthly Report: The monthly QC data is downloaded from participating sites. This data array contains information pertaining to the analytical activity at CWM labs for any one particular month. The primary purpose of this module is to provide a statistical report of QC data for each individual laboratory for audit purposes and to provide historical information on QC analyses over a period of time.

Round Robin System: Round Robin analyses are conducted quarterly. All CWM labs and contract labs must participate in order to stay in compliance with the CWM Quality Assurance program. A set of prepared samples are submitted to all participants for analysis. These parameters represent the analyses conducted by that lab during the previous quarter. Round Robin data is entered manually into the QA/QC database for storage as results are received. The data is later exported to Symphony[R] where statistical analyses are performed by macros. The results of all laboratories within the system can then be graphed(Figure 3). Laboratories whose results digress from the control limits established by the majority of labs are then investigated and corrective actions are recommended.

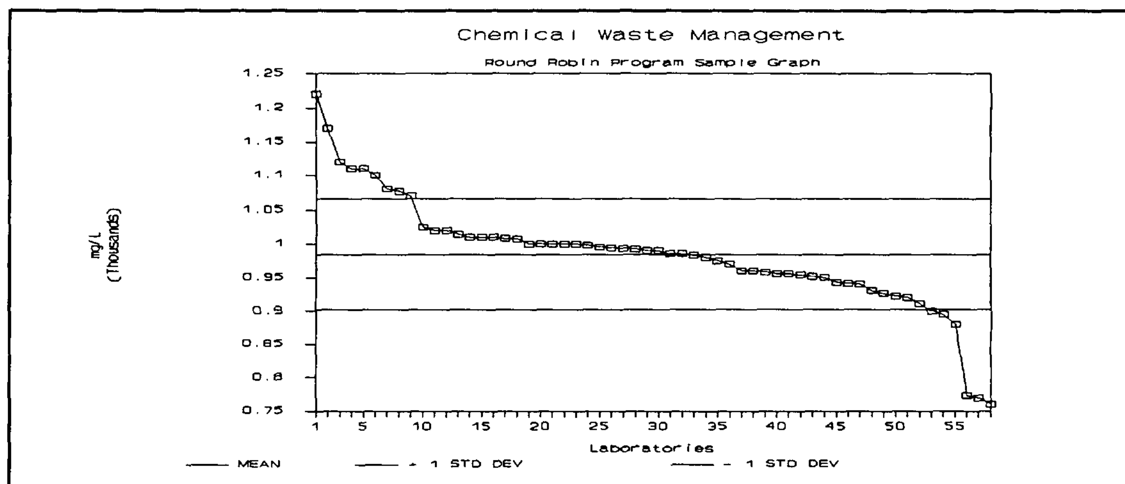


Figure 3: Example of Round Robin Graph.

Parallel System (Reference Laboratory Evaluation): A sample first analyzed by a CWM site laboratory and then by the Technical Center Laboratory is tracked by the QA/QC unit. The sample analysis turnaround time as well as the site responses to discrepancies are tracked. Another important function of the parallel analysis is as a means to evaluate method consistency and result precision between the site and the Technical Center laboratory.

Audit Performance Module: Laboratory audits are performed on a trimester basis. Each audit is partitioned to cover a portion of the lab's analytical/management performance. The combination of all three audits covers all phases of the lab's operation. The audit data is subdivided into categories for ease of retrieval. This organization allows the comparison of a lab's performance in specific areas from one year to the next.

Contract lab: The main function of this module is to track contract lab performance and their potential for use by CWM facilities. General business information regarding the contract laboratories, and the type of analyses performed are examples of the types of data stored.

DISCUSSION

Computerized information management techniques are critical to analytical laboratories. New methods, advances in instrumentation, and requirements for analysis of new materials have created a explosion in the amount of information processed annually by an analytical laboratory. This information explosion has had a corresponding effect on the Quality Assurance programs which monitor laboratory performance. New methods and more sophisticated analytical methodology require that the existing auditing criteria be continually evaluated to ensure that they are appropriate. If not, new ways to measure performance must be developed to assess data quality. However, at the same time the existing quality data must be processed, evaluated and acted on.

The QA/QC Data Management System is our approach at managing this volume of data. Prior to its implementation, QA Auditors had to sift through thousands of sheets of paper to determine if a lab conformed to our Quality Assurance Program. For example, the QC program generates 4 graphs and 1 summary report and a typical CWM lab uses 25 methods, each lab would send a monthly 125 page report. Since there are 26 CWM labs in the program, the auditors would have had to review 3250 pages of QC data per month. The QA/QC DMS has allowed our auditors to spend time evaluating laboratory compliance, instead of searching for pertinent data.

The QA/QC DMS has had a positive effect on the Quality Assurance Program. A major benefit is the ability for the auditors to review the qc data prior to a site audit. The auditor can spend more time preparing for a audit because of the ease of data retrieval. They can query the database for the lab's performance on qc samples, round robins, parallel analyses as well as reviewing the action items from the last audit. This enables the auditor to target areas which may require more thorough investigation prior to visiting the site.

The database also assists the Quality Assurance department in optimizing their travel schedules. Chemical Waste Management sites and contract labs are located throughout the country. The database can be queried to determine the timing and location of audits thereby minimizing travel time,associated costs and maximizing our quality assurance efforts. Miscellaneous support functions have also been developed which decrease the paperwork associated with CWM's large quality assurance effort. The database is used to create mailing labels, and mail merge lists which are used to send samples, audit results, and general correspondence to QA participants.

SUMMARY

The QA/QC Data Management System has proven to be a valuable tool in evaluating specific laboratory performance, as well as the performance of all CWM laboratories as a whole. Future enhancements are planned to automate the site audit, to expand the functionality of the Bulletin Board, and to interface with the Technical Center's Laboratory Information Management System.

ASSESSMENT OF ROUTINE LABORATORY PERFORMANCE IN THE CONTRACT LABORATORY PROGRAM: A PILOT STUDY

EVA J. HOFFMAN, CLP-DPO, BARBARA NIEBAUER, AO, U.S. Environmental Protection Agency, Region VIII, QAMS, P.O. Box 25366, Denver, Colorado, 80225; REGINA PREVOSTO REHM, ESAT Region VIII QA Coordinator, ICF Technology, P.O. Box 280041, Lakewood, Colorado, 80228

ABSTRACT

At present, laboratory performance in the EPA Superfund Contract Laboratory Program (CLP) is evaluated through analyses of quarterly blind samples and results of Contract Compliance Screening (CCS). Another tool for the evaluation of laboratory performance is the use of information contained in the data validation summary reports prepared by every region for sample data packages produced by CLP laboratories. Comparison of a group of data validation summary reports indicates there are both routine method specific problems and laboratory specific problems. Region VIII has developed a computer program that compiles the information present in the data validation summary reports and generates reports that identify various Quality Control(QC)-related problems.

Nine months of inorganic data validation summary report information has been entered into the Region VIII database and numerous reports generated. The results reflected the similarities and the differences between the three Region VIII inorganic CLP laboratories. In general, the soil sample matrix presented problems for every laboratory, and the most common QC problem was the matrix spike sample analysis result(s). The extent of the QC problems varied as a function of sample matrix, analyte and laboratory. Laboratory performance as estimated by the Region VIII program did not compare well with other traditional indicators of performance, such as quarterly blind sample analysis results or CCS results. The Region VIII program judges the laboratories' performance based on actual sample data, providing a more typical and reliable approach to evaluation of laboratory performance.

Notice: This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute recommendation for use.

INTRODUCTION

The Contract Laboratory Program (CLP) has developed a number of procedures to monitor CLP laboratory performance. Intermittent checks of performance are accomplished through the use of Quarterly Blind Sample analyses and laboratory audits. Routine performance checks are accomplished through Contract Compliance Screening (CCS) reports and the limited use of the data validation summary reports provided by regional data reviewers.

Both the organic and inorganic CLP statements of work were developed to provide the analysis of a large number of target analytes in a consistent, cost effective manner. While specialized analysis methods do exist which can resolve matrix or detection limit problems, the CLP analytical methods were not designed to address these unique situations. Consequently, under routine CLP analysis conditions, some compounds are more troublesome than others. The Deputy Project Officer must be able to identify which analytes present problems for the chosen method and which are indicative of an individual laboratory's performance. Each EPA region has a Contract Laboratory Program Deputy Project Officer (CLP-DPO) who must oversee the performance of the laboratories located in his/her region.

The Regional data validation summary reports are sent by the data reviewers to the Quality Assurance Section of the National Program Office (NPO), the Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV), the CLP laboratory's Deputy Project Officer (DPO), and the data user. The NPO has an overall quality summary checklist form whereby the EPA regions can indicate if there are major problems with the numerous quality control checks. The inorganic summary checklist indicates, for example, if there are matrix spike problems in the ICP analyses, Graphite Furnace (GFAA) analyses or cyanide determinations. Organic summary checklists show, for example, whether there have been calibration precision problems with volatile, semi-volatile, or pesticide analyses.

The CLP-DPOs can use these data validation summary reports in a variety of ways. CLP-DPOs take representative data validation summary reports along on laboratory audits. Problems which have been identified in the data validation process can be discussed with the laboratory personnel. Originally, the Region VIII CLP-DPO brought all the data validation summary reports for the previous six months to each audit to show the laboratory the data reviewers' evaluation of the laboratory's analytical results. Interestingly, several of the laboratories were unaware of the existence of these reviews and expressed a desire to read the contents thoroughly to determine what the data reviewers thought were the laboratory's strengths and weaknesses. In later audits, the volume of summaries became too large to carry in a briefcase. The Region VIII DPO then developed a manual spreadsheet on which problems were summarized on a case by case basis. This manual spreadsheet served the same purpose as the individual reviews. The DPO was able to quickly and easily identify the cases which should be discussed thoroughly with the laboratory.

This approach resulted in positive comments from the Region VIII laboratories and provided the laboratories with a new feedback mechanism. Region VIII has now designed and implemented a computerized spreadsheet program in which the data validation summary report information can be entered upon receipt. The primary objective of this program is to aid the CLP-DPO in monitoring routine laboratory performance. It is obvious that data reviewers consistently find both technical and contractual deficiencies in laboratory performance. This is even true for laboratories who routinely score 90-100% on performance evaluation sample analyses. The computerized tracking system provides a mechanism by which the CLP-DPO can see changes in laboratory performance that require immediate attention. In the process of designing such a system, it is apparent that other uses can be made of this information. These secondary objectives include: (1) evaluation of the technical sufficiency of the CLP Statement of Work(SOW), (2) identification of problem areas for individual laboratories and for the analytical method as a whole, (3) evaluation of the suitability of the method as a function of sample matrix, (4) comparison of technical problems with contractual problems, and (5) evaluation of potential new contractual requirements and their impact on the data.

This paper describes the case-by-case, element-by-element, problem-by-problem, laboratory-by-laboratory tracking system developed in Region VIII. Data were extracted from the data validation summary reports prepared for data packages resulting from the analyses of samples by Region VIII participants in the CLP. This system is a pilot project to demonstrate the utility of the concept using a small number of laboratories and a subset (i.e., a 9 month period) of the data validation summary reports for the Region VIII CLP laboratories. The maximum impact of such a system can be achieved through nationwide input and implementation. Region VIII's system currently involves summarization of the information contained in the data validation summary reports on standardized encoding sheets and entry into the computerized database program. In the future, with the advent of automated data review, the more labor intensive steps will be eliminated and a nationwide system could become much more feasible. This paper will describe the concept, the results, and the implication of such a system on a small scale, in the hope that an extensive evaluation can be made on a national basis.

METHODS

The 'R8LAB' database program was designed to track CLP laboratory performance of Routine Analytical Services (RAS) analyses and Special Analytical Services (SAS) analyses for inorganic, volatile, semi-volatile, and pesticide/PCBs.

The computer program was developed utilizing dBase language (i.e., DBXL, Quicksilver, and dBaseIII+). The dBase languages were chosen for their

flexibility, memory capability, and report generation potential. As a complied program, 'R8LAB' can be used as a stand alone application program on any IBM compatible computer.

The program is designed with numerous help screens and prompts. This allows non-technical clerical personnel access to data entry assistance. A standardized encoding process was developed for the 'R8LAB' database . Key codes have been developed to reduce the number of keystrokes required for data entry, thereby helping to reduce the number of clerical errors and minimizing data input time requirements. Keycodes include: inorganic element symbols, alpha-numeric codes for organic compounds, numeric codes for QC problems, alpha codes for sample matrices.

Encoding forms are designed to include each element or compound found in the RAS menu for inorganics, volatile, semi-volatile, and pesticide/PCBs, as well as, the organic surrogate compounds. A field for all possible QC problems, including field QC (blank, duplicate, blind standard) is provided.

Values (where possible) or alpha codes (i.e., H = high, L = low, OOC = out of control), are transferred onto the encoding sheets when problems are reported. The actual encoding task is performed by chemists, to reduce the possibility of overlooking relevant information.

There is substantial variability in the data validation summary reports formats for each region and data reviewers' styles. Since format styles range from narrative to table setups, it was difficult for non-technical personnel to enter data directly from the data validation summary reports. Although it was necessary to use technical personnel to transfer the information into a spreadsheet format, standardization of the data validation summary report formats between the regions could make this unnecessary in the future.

Time requirement for encoding may vary considerably and is dependent on the analysis type (i.e., inorganic versus organic), overall laboratory performance (i.e., as determined by the number of problems), and data validation summary report format. For example, a 20 sample RAS inorganic data package with minimal problems takes approximately 4 minutes to encode. A similar data package with numerous problems might take 10 minutes. Organic data packages, naturally take significantly more time due to the increased number of compounds of interest, and the nature of the analyses. As compared to inorganic data validation summary reports, more problems are generally reported for organic analyses. This is especially true for calibration data. An organic data package with few problems might take 15 minutes to encode. However, an organic data package with numerous problems could take 20 minutes or more to encode.

The cost for utilizing this system can be determined on a package by package basis, or by considering the overall cost per case per laboratory.

Considerations include technical personnel time, clerical data entry time, and computer time.

The program also checks for unique identifiers to prevent duplicate entry of data. The program has been designed to consider the laboratory name and the Sample Data Group (SDG) or QC Report numbers together as unique identifiers. This has been successful in most instances. The few exceptions that Region VIII has noted come from cases where the laboratory runs two complete RAS analyses on the same sample set and gives both RAS analysis data packages the same SDG number, (e.g.,, total and dissolved metals).

Data entry time/cost considerations are quite reasonable. Inorganic data entry can take between 3 - 10 minutes per encoding sheet for an average quality data or even less if there are few or no problems. Organic data entry does require more time due to the nature of the analyses and the larger number of analytes. In general, organic data entry requires 10 - 15 minutes per data package.

One of the most outstanding features of dBase files from a data user's perspective is the virtually unlimited number of reports that can be generated. Multi-user needs can readily be met. Selective use of data is also possible through these reports. Some reports which have been generated using the 'R8LAB' database are described below.

1. Summary of Database Content - number of cases, samples (by matrix), and problems/case with a regional breakdown for both inorganic and organic analyses.

2. Compound specific problem analysis - compounds with QC problems reported in descending order of number of problems per case.

3. Sample matrix related problems - problems for specific elements are reported by matrix.

4. Comparison of CCS Performance Check Compounds to all other organic compounds of interest.

5. Laboratory Related Analytical Problems - problems are reported as overall problems per case and for each specific laboratory.

RESULTS AND DISCUSSION

The contents of the inorganic portion of the Region VIII Laboratory Performance Tracking Database are summarized by media in Table 1.

TABLE 1

Summary of Laboratory Performance Tracking Database

	SOIL	WATER	TOTAL
NUMBER OF CASES (SDGS, QC REPORTS)	160	169	329
NUMBER OF SAMPLES	1892	1844	3736

REGIONAL BREAKDOWN

	CASES	PROBLEMS	PROBLEMS/CASE
REGION I	28	174	6
REGION II	20	110	6
REGION III	44	354	8
REGION IV	30	212	7
REGION V	153	1026	7
REGION VI	5	42	8
REGION VII	4	70	18
REGION VIII	30	157	5
REGION IX	13	49	4
REGION X	2	7	4
TOTAL	319	2201	7

There are three inorganic Contract Laboratory Program (CLP) laboratories in EPA Region VIII. Information from data validation summary reports forwarded to the Region VIII DPO by her counterparts in other regions between the period of July 1988 and April 1989 were included in the pilot study. The average number of QC problems (resulting in data being qualified) was seven problems per case, although the range over the different regions was from four to eighteen problems per case. Since this is only a subset of the entire CLP universe, these data are not particularly useful in assessing differences in regional data review practices.

The number of problems found was strongly influenced by the nature of the element being analyzed. Table 2 gives a list of elements and the number of problems found per case.

Table 2

Problems as a Function of Element

ELEMENT	PROBLEMS/CASE	ELEMENT	PROBLEMS/CASE	ELEMENT	PROBLEMS/CASE
Zn	0.418	Mn	0.226	Hg	0.097
Se(F)	0.396	Ag(P)	0.198	K	0.085
Tl(F)	0.371	Se(P)	0.195	Na	0.079
Sb(P)	0.340	CN	0.176	Ni	0.079
Pb(F)	0.308	As(P)	0.167	Sb(F)	0.063
Fe	0.267	Cd(P)	0.164	V	0.063
As(F)	0.261	Mg	0.157	Co	0.031
Cu	0.255	Cr(P)	0.154	Ag	0.016
Al	0.248	Tl(P)	0.148	Cd(F)	0.006
Pb(P)	0.242	Ba	0.123	Cr(F)	0.006
Ca	0.236	Be(P)	0.104		

(P) = ICP (F) = GFAA

The average number of problems per case per element is 0.177. But, zinc (Zn) has problems reported at 2.3 times more frequently than the average and chromium (Cr) by GFAA has only 1/30 of the average problems. A significance test based on the number of samples entered into the data base has not yet been run to determine the significance of these results, since the current objective of the data base is to determine if trends were observable utilizing this spreadsheet concept. Statistical evaluation of the results is planned as a future effort. ICP analyses do not appear have fewer problems overall than GFAA. Elements analyzed by both instrumental techniques are among the best and worst performers as judged from the number of problems reported.

The main utility of the data validation summary is in the evaluation of the types of problems resulting from use of CLP protocols. The frequency and types of problems found in the reviews are shown in Figure 1. For all the elements, matrix spike problems represented 30% of all the deficiencies noted by the data reviewers. The second most frequent problem identified was laboratory blank contamination. However, the problems found are not the same for all the elements. Six elements with the most frequent problems are given as an example of how the type of problem varies as a function of element. All of the GFAA elements (i.e., Selenium (Se), Thallium (Tl), Lead (Pb) and arsenic (As)) illustrated in Figure 1 have post-digestion spike recoveries as their most frequently cited problem, followed by matrix spike recoveries. The percentages for other problems are also similar to each other except that Pb has more laboratory blank problems reported than the other GFAA elements. The ICP elements illustrated in Figure 1 showed blank contamination as their most frequent problem. Serial dilution was also a problem for Zn and duplicate sample analyses were a problem for aluminum (Al). So, although there are

some patterns of problems as a function of analysis technique, each element can have a unique set of problems. This does not come as a startling revelation, because some elements are more prone to matrix interferences and some elements are notorious contributors to blank contamination.

It is also possible to compare overall laboratory performance between the three inorganic laboratories in Region VIII. The data validation problems found as a function of laboratory are given in Table 3, as well as, the more traditional performance measures used in the CLP.

Table 3

Comparison of Laboratory Performance Evaluation Techniques

	Lab 1	Lab 2	Lab 3
Problems/case in data validation summary reports	5.22	6.29	7.58
Average of last 4 Quarterly Blind Scores	88.6	84.0	95.0
Percent of price paid after CCS deductions	71.9	96.6	84.2

The three measures of laboratory performance do not correlate well within Region VIII. Lab 1 has the best performance based on the lowest number of problems in the data validation summary reports. Lab 2 has the best performance based on Contract Compliance Screening. Lab 3 has the best results on Quarterly Blinds. It is possible that these measures would correlate stronger using a national data base, but the data in this data base suggests that total reliance on the traditional indicators may not provide sufficient markers of routine analytical performance.

One of the main laboratory follow-up problems is distinguishing between method specific problems and laboratory specific problems. Figure 2 illustrates the types of problems as a function of the individual laboratory. This presentation clearly shows that Lab 2's problems are different than those of the other two laboratories. Lab 2 has nearly double the number duplicate problems as experienced by the other laboratories (i.e., Lab 2 duplicates = 1.62 problems per case; Lab 1 and Lab 3 duplicates = 0.82 problems per case). However, Lab 2 appears to do better overall with matrix spikes.

Since both the number and type of problems vary from laboratory to laboratory, Region VIII theorized that the laboratories might have varying success with the different elements. The data base evaluation showed that there was not a strong correlation between laboratory performance and specific elements analyzed, as shown in Table 4.

Table 4

Examples of Consistent Laboratory Performance

Combined Laboratory Performance	Elements
Good	V, Sb(F), Ni, Cr(F), Co, Cd(F)
Poor	Al, Fe, Mn, Pb(P), Sb(P)

(P) = ICP (F) = GFAA

However, inconsistent results were found for the remaining other elements. An example of several elements which reflect laboratory specific performance results is given in Figure 3. The graph shows that Lab 3 seems to have more problems than the other laboratories with Zn, Se(F), and Tl(F). However, Lab 2 has more problems with Se(P), and Lab 1 has more problems with iron (Fe). Further review shows that for Zn, Lab 3 had unusually high incidents of laboratory blank contamination and serial dilution problems. For Se(F) and Tl(F), Lab 3 also had an unusually large number of problems with post-digestion spikes and matrix spikes. These laboratory specific problems can be brought to the laboratory's attention during audits or visits with the CLP-DPO.

To this point, all of the calculations were performed on an elemental basis, a laboratory basis, or a type of problem basis. The program also has the capability of segregating the data by sample matrix. The type of sample matrix (i.e., soil or water) influences the number of problems found in each case. Table 5 presents data on the number of problems found per case as a function of sample matrix.

Table 5

Sample Matrix Specific Problems per Case

Matrix	All Region VIII Labs	Lab 1	Lab 2	Lab 3
Water	6.12	4.51	3.56	7.00
Soil	7.29	6.23	6.25	7.72

All laboratories had fewer problems overall with water samples than with soil samples. The sample matrix had a profound effect on the nature of the problems. Figure 4 gives a comparison of the types of problems found in the overall data base as a function of sample matrix and gives an illustration of the differences that sample matrix produces with two selected elements. On an overall inorganic analysis basis, soils produce twice the number, and twice the percentage of matrix spike problems;

whereas, the water matrix is more prone to laboratory blank contamination problems. Again, the individual elements each have their own set of problems in water and soil. For example, for Pb by GFAA, soils have a high incidence of matrix spike problems, whereas for Zn, soils have a high incidence of serial dilution problems. Both are indicative of matrix interferences, but they show up differently. In waters, Pb by GFAA has problems with post-digestion spikes and standard addition but Zn in water is prone to blank contamination in the laboratory and in the field.

Region VIII designed the program and the report formats to serve the needs of regional CLP-DPOs and aid in their laboratory oversight duties. The program has shown the potential of specifically identifying laboratory problems and with sufficient data, can aid in determining whether these problems are laboratory specific or whether all the laboratories in the region are having difficulty or an indication of an analysis method/field collection related problems. A flow chart of the current process is shown is shown in Figure 5, along with a flow-chart for the process that will be possible in the future. The current chart indicates that the investment of time is small relative to the time spent in data validation and that the investment of time is small relative to the benefits. The soon to be available automated data review program should eliminate the manual preparation of the encoding sheets, which could then be produced as a part of the data validation summary reports.

Region VIII currently has no performance-related monitoring system for non-CLP laboratories performing Superfund analyses. The QC system presented here can also be used regionally in evaluating the performance of these non-CLP laboratories in conjunction with performance samples to be included with each sample set sent to such laboratories. Users of these laboratories could independently evaluate whether to continue to solicit bids from laboratories which perform badly by both criteria.

For the CLP, the full capabilities of this concept could be incorporated into the National QA program with a little help from the regions. For example, the current checksheet required by the National Program Office (NPO) could be replaced with an encoding form and delivered either in hard copy or by diskettes. It would allow a comparison of ongoing laboratory performance on a nationwide basis, and could provide reports to the regions on a quarterly basis. The advantages of this system are (1) the NPO would have data which could rapidly identify method/field-related problems that could be targeted for methods research; and (2) the NPO could identify laboratories which seem to perform better with a particular method than others. These laboratories with better performance would be invited to make presentations at caucuses where they could be recognized for their success and share the secrets of their success with other CLP participants.

CONCLUSIONS AND RECOMMENDATIONS

For only a small investment of time, Region VIII has developed a technique to evaluate on-going laboratory performance in the Contract Laboratory Program. The results of the method have already proven to be quite useful to the Region VIII CLP-DPO in carrying out the duties of monitoring ongoing laboratory performance and have yielded preliminary information concerning analytical method performance. The full utility of the concept and the method could be achieved by adoption of this system on a nationwide basis. Moreover, since this represents only an improvement to the current QA services provided by the NPO, implementation should be straight-forward. Region VIII recommends this approach as a starting point for long-term evaluation of laboratory performance.

ACKNOWLEDGEMENTS

This work would not have been possible without the inputs and contributions of a large team. We particularly thank Tammy Kozak (EPA) for evaluating and testing out a number of programming options. We thank Deanna Peterson (EPA), Denise Link (EPA), and Robert Taylor (ICF) for aiding in the transfer of data review information onto the encoding sheets, and Tammy Kozak (EPA) and Michelle Rehm (ICF) for data entry. We also thank Deanna Peterson (EPA), Denise Link (EPA), and Eileen Simmons (ICF) for their thoughtful review of this manuscript.

Figure Captions:

Figure 1: QC Problems - Function of Element; key is found on top graph

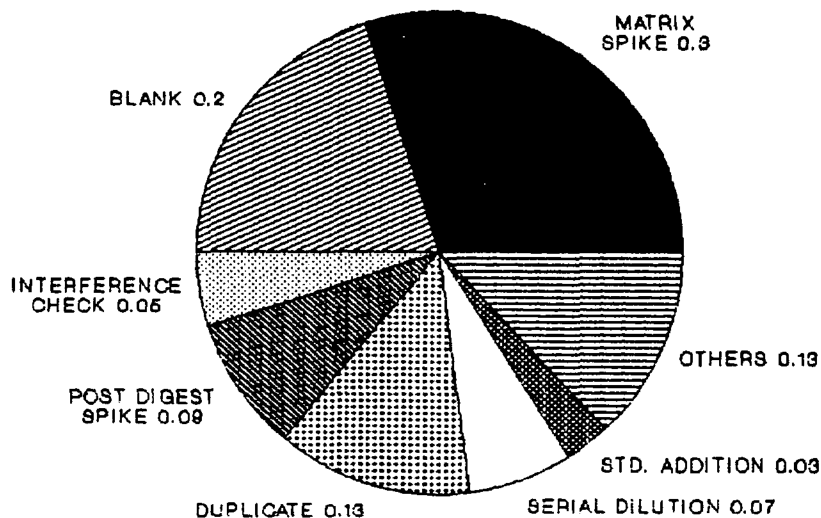
Figure 2: QC Problems - Function of Lab; key is found on top graph

Figure 3: Problem Elements - Lab Specific; key is found at bottom of page

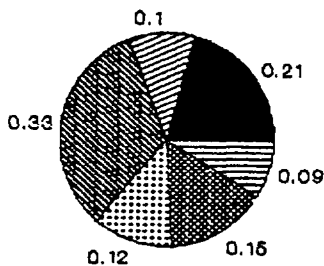
Figure 4: QC Problems - Function of Matrix; key is found on top graph

Figure 5: Lab Performance - Evaluation Process

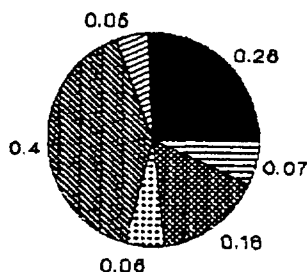
QC Problems
Function of Element



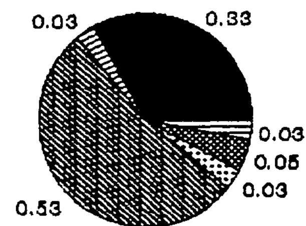
All Elements



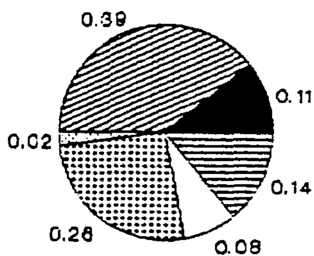
Pb(F)



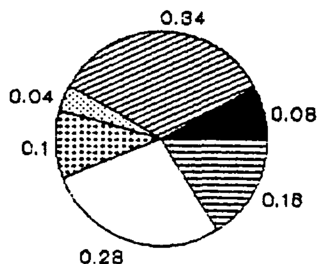
As(F)



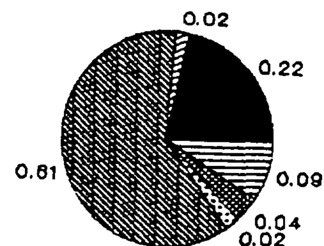
Se(F)



Al

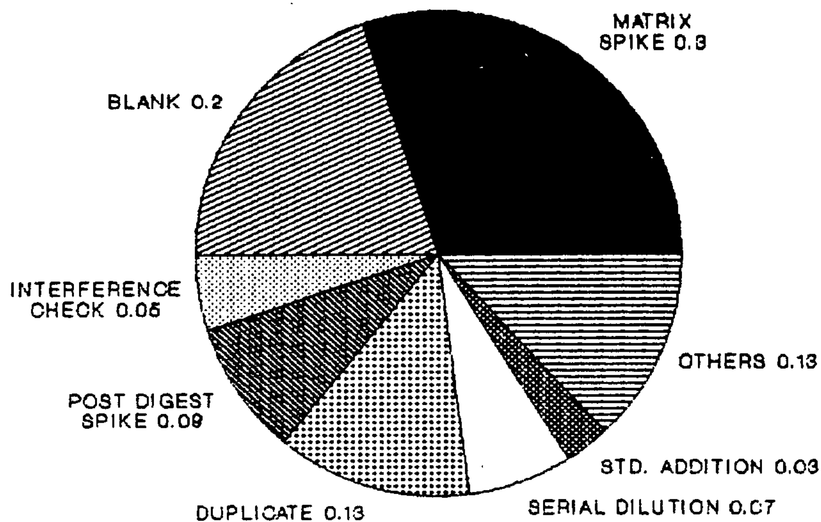


Zn

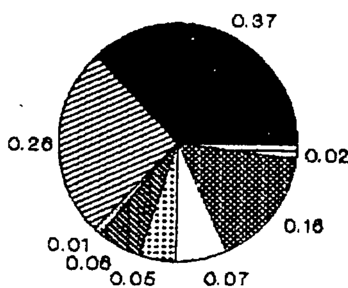


Tl(F)

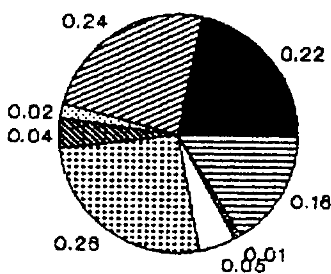
QC Problems
Function of Lab



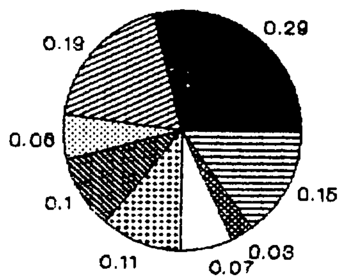
All Labs



Lab 1

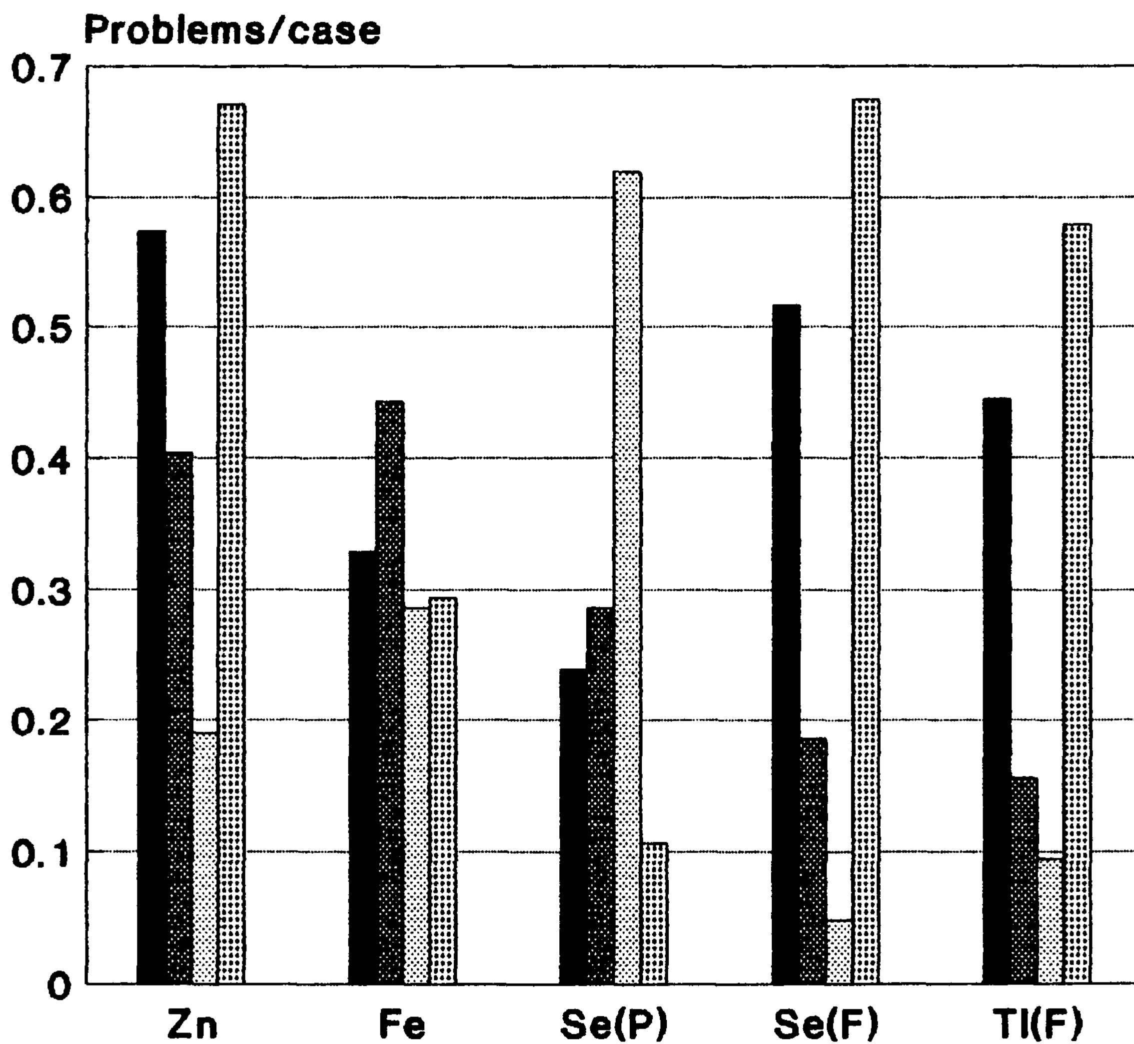


Lab 2

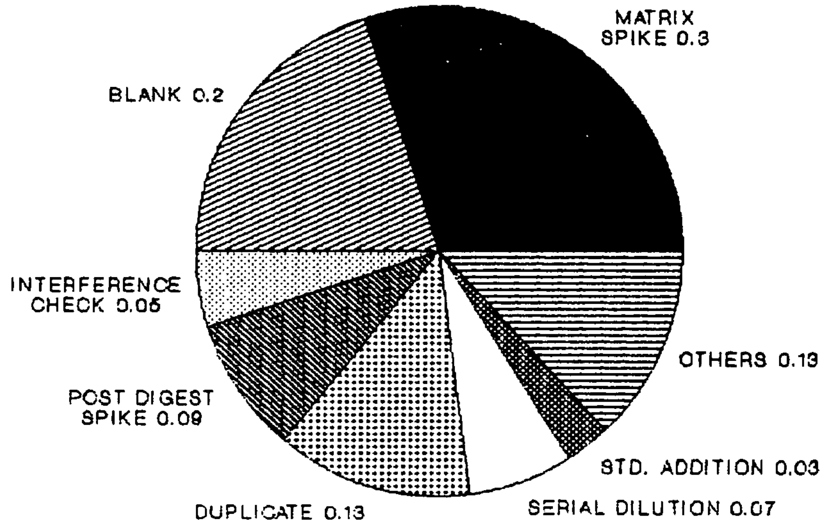


Lab 3

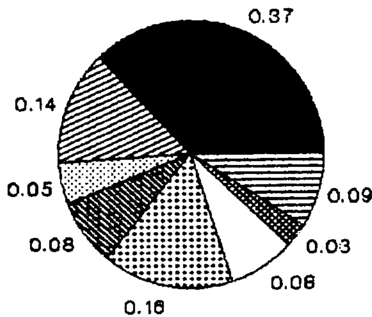
Problem Elements
Lab Specific



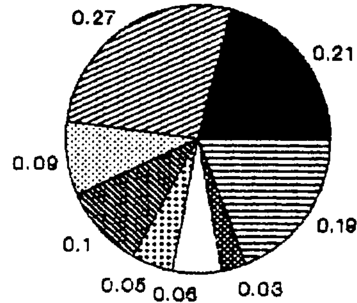
QC Problems
Function of Matrix



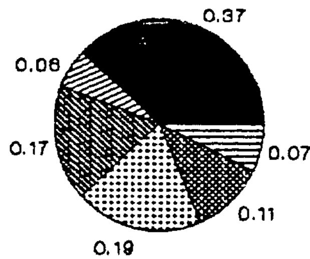
All Matrices - All Elements



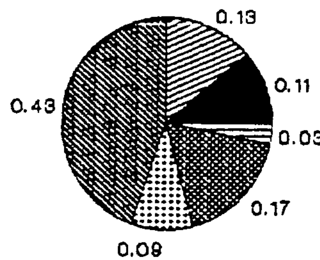
Soil - All Elements



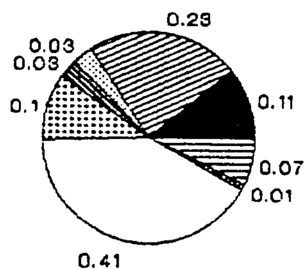
Water - All Elements



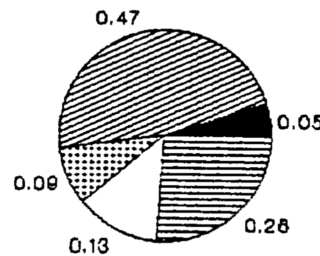
Pb - Soil



Pb - Water



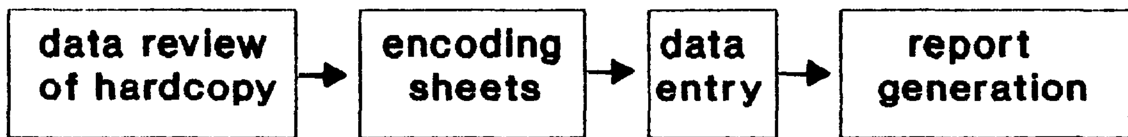
Zn - Soil



Zn - Water

Lab Performance
Evaluation Process

TODAY



Inorganic	15hrs	4 min	3 min	2 min
Organic	30 hrs	15 min	6 min	2 min

FUTURE

Inorganic	8 hrs	2 min
Organic	15 hrs	2 min

THE USE OF INTERNAL STANDARD AREA RESPONSE AS A QA/QC MEASURE IN THE CONTRACT LABORATORY PROGRAM

GARY ROBERTSON AND MARILEW BARTLING, LOCKHEED ENGINEERING AND SCIENCES CO. 1050 E. FLAMINGO ROAD, LAS VEGAS, NV 89119;

E.J. KANTOR, U.S.E.P.A., ENVIRONMENTAL MONITORING SYSTEMS LABORATORY, P.O. BOX 93478, LAS VEGAS, NV 89193-3478.

ABSTRACT: One of the Quality Assurance (QA) measures monitored by the USEPA Contract Laboratory Program (CLP) during analysis for volatile and semivolatile organic compounds is the area response of the internal standards. A contractual criteria is set that the laboratory must meet to produce acceptable data. The criteria is the internal standard areas in each sample and blank must be within a factor of two of the area of that internal standard in the current calibration. A large data base of CLP data has recently become available which allows the examination of internal standard data on a method and laboratory basis in addition to the individual sample criteria.

The presentation will discuss method and laboratory performance information obtained from the internal standard area data base. Day-to-day and within-day instrument trends, relationships between the different internal standards, and the effects of different matrices (soil and water) on internal standard performance will be covered.

METHOD DETECTION LIMITS

Robert D. Gibbons, Associate Professor of Biostatistics, University of Illinois at Chicago, 1601 W. Taylor, Chicago Il. 60612; Frank H. Jarke, Manager of Quality Programs, Kenneth P. Stoub, Director, WMI Environmental Monitoring Laboratories, 2100 Cleanwater Drive, Geneva Il. 60134

ABSTRACT

Experimental and statistical aspects of several method detection limit (MDL) procedures are examined in detail and contrasted. Significant conceptual errors as well as problems with experimental and statistical derivations are noted. It is shown that the statistical form of the MDL is dependent on the number of detection decisions to be made prior to re-estimating the MDL. The four possibilities relate to detection decisions for (1) the next single measurement, (2) the next r measurements, (3) the average of m measurements, and (4) all future measurements regardless of laboratory, machine or analyst (*i.e.*, a regulatory threshold). To accommodate the latter case, a new method is derived, based on a tolerance region for the linear regression of response signal on target concentration. The new method produces estimates of the critical level (L_C) and detection level (L_D) described by Currie (1968) and generalized to linear regression by Hubaux and Vos (1970). A generalization of the method due to Clayton *et al.*, (1987) to the case of MDLs with specified assurance probabilities for $P(100)\%$ of all future determinations is also provided. Guidelines for unbiased MDL experiments are also set forth. The methods are then compared and contrasted using analytical data for 10 volatile organic compounds (USEPA method 624). Complete computational details are provided.

1 INTRODUCTION

With the increased use of non-endogenous compounds, such as priority pollutant volatile organics, base neutrals and acids, as indicators of contamination at hazardous waste disposal facilities, the question of whether such compounds are actually detected in a ground-water sample becomes paramount. Often, if one out of 100 or more of these compounds is reported above an established method detection limit (MDL) the inference drawn is that the facility is impacting ground-water. If this practice is to continue, the validity of these published MDLs and their relevance to practical application in ground-water monitoring must be rigorously established. Our review of this literature suggests that, to varying degrees, most existing MDL strategies lack validity both from statistical and experimental perspectives.

The purpose of this paper is to provide a critical overview of several approaches to

the problem of estimating method detection limits and to illustrate their connection to the statistical theory of interval estimation and hypothesis testing. With possibly a single notable exception (Clayton *et al.*, , 1987), all existing method detection limit strategies are based on the concept of interval estimation. However, in most cases, when the population mean and variance are unknown (which is almost certainly the case in practice), the form commonly chosen for the interval is questionable. To expand on this point, we begin by providing a review of statistical interval estimation.

2 STATISTICAL INTERVAL ESTIMATES

2.1 The Basic Idea

Let us assume that we have obtained a random sample of n measurements denoted $\boldsymbol{X} = [X_1, \ldots, X_n]$, drawn from a normal probability distribution with mean μ and variance σ^2 (*i.e.*, $\mathcal{N}(\mu, \sigma^2)$).

If μ and σ^2 are known, we may construct an interval for the population distribution that will contain a certain proportion of all possible measurements. This interval is obtained by simply referring to the probability points of the normal distribution. For example, 95% of the total population will lie within the interval

$$\mu \pm 1.96\,\sigma$$

Alternatively, if we are only interested in the possible values that exceed μ, we may construct the one-tailed limit

$$\mu + 1.65\,\sigma$$

Let us now change the problem in a small but very significant way. Assume that we know the population variance, σ^2, but only have the estimate $\bar{X}$ of the population mean derived from a random sample of n measurements as $\sum_{i=1}^{n} X_i/n$. In this case, we might construct an interval around our estimate $\bar{X}$ to reflect our uncertainty regarding the true population mean μ.

Assuming that with repeated sampling, the distribution of our estimate $\bar{X}$ is normal with mean μ and standard deviation $\sigma/\sqrt{n}$, our interval becomes

$$\bar{X} \pm 1.96\,\sigma/\sqrt{n}$$

or in the one-tailed case,

$$\bar{X} + 1.65\,\sigma/\sqrt{n}$$

The important distinction between these two examples is that in the first case, we are concerned with the problem of limits for possible individual observations sampled from a specific population, whereas in the second case, we are concerned with setting limits for a parameter that was estimated from a random sample obtained from the population. The distribution of sample means $\mathcal{N}(\mu, \sigma^2/n)$ is clearly quite

different from the distribution of individual observations $\mathcal{N}(\mu, \sigma^2)$. The former may be described as a "confidence interval" whereas the latter is termed a "tolerance" or "coverage" interval.

The choice between these two approaches to interval estimation is clearly not a trivial one and is completely dependent on the nature of the specific problem. In addition, the form of these intervals is highly dependent on whether μ and σ^2 are known or whether one or both must be estimated from a random sample of data. Similarly, the form of the interval changes depending on what we want to use it for. For example, if we want to determine if a *single* new observation was drawn from a particular population from which we have computed sample based estimates $\bar{X}$ and s^2 for μ and σ^2, the interval will be smaller, and has a quite different form, than if we want to construct an interval for a proportion of *all future measurements.*

Finally, the form of the interval is also dependent on whether we are drawing inference from a single random sample, for example, response signals from n blanks, or whether the MDL is to be determined from a calibration design in which a variety of "spiked" concentrations are considered. In the latter case, uncertainty in the estimated parameters of the calibration function that relate response signals to concentrations must also be considered in constructing interval estimates.

Although there are numerous other statistical considerations that are involved in computing MDLs, such as the validity of assuming normality or the possible lack of independence between concentration level and variability, we will proceed further by exploring the variety of statistical interval estimates for normal distributions and their relevance to the problem of estimating method detection limits.

2.2 Case 1: Constant Concentration Designs

In the following discussion, we assume that a set of random samples, of perhaps, n blank samples, n paired samples (*i.e.*, the difference between spiked and blank response signals) or n spiked samples are to be used in deriving the MDL. In this section we consider concentration to be fixed at a single level, possibly zero as in the case of a "blank". The validity of these three experimental approaches to the MDL problem are beyond the scope of this paper and the interested reader is referred to Currie (1988) for a detailed review. In the following, we assume that the response signals are normally distributed or can be transformed to approximate normality (*e.g.*, square root transformation for ion counting data). Furthermore, we assume that variability of the response signal (*i.e.*, σ^2) is constant in the range of the blank to the MDL.

2.2.1 Confidence Intervals

As previously shown, when σ^2 is known, variability in the mean $\bar{X}$, with repeated sampling is σ^2/n; therefore the $(1-\alpha)100\%$ confidence interval for $\bar{X}$ is

$$\bar{X} \pm z_{1-\alpha/2}\, \sigma/\sqrt{n}$$

where $1-\alpha$ is the desired confidence probability (*e.g.*, .95), and $z_{1-\alpha/2}$ is a value from the cumulative normal distribution that contains probability P between $z_{\alpha/2}$ and $z_{1-\alpha/2}$.

When σ is unknown, and is replaced by its sample based estimate

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

the ratio

$$\frac{\bar{X}-\mu}{s/\sqrt{n}}$$

follows Student's t-distribution with $n-1$ degrees of freedom; therefore, the required confidence interval is

$$\bar{X} \pm t_{[1-\alpha/2,\,n-1]}\, s/\sqrt{n}$$

and the upper confidence limit is

$$\bar{X} + t_{[1-\alpha,\,n-1]}\, s/\sqrt{n}$$

In the present context, the confidence interval tells us what we have learned about the population mean once we have the results for a series of analytical measurements. If we were to repeat our MDL study 100 times, we would expect that $(1-\alpha)100\%$ of the time the average response signal would lie within the confidence interval. Since the objective of an MDL is to determine if the analyte is present in a single new measurement or collection of new measurements, it is hard to imagine what confidence limits have to do with MDL calculations. Nevertheless, "method detection limits" and "confidence limits" are used synonymously by many prominent authors (Currie, 1968, page 586; Kaiser 1973, page 58; Hubaux and Vos, 1970, page 850; Ingle, 1974, page 104).

2.2.2 Tolerance Intervals

When μ and σ are known, and the measurements are independent and normally distributed, 95% of the distribution of measurements will be contained in the interval

$$\mu \pm 1.96\,\sigma$$

Alternatively, if we are only concerned with that portion of the distribution that is greater than μ for example when $\mu = 0$, the one-tailed 95% tolerance limit is

$$\mu + 1.65\,\sigma$$

From this definition, the tolerance interval is a coverage interval, that is, the interval can be expected to contain a proportion of all possible measurements from the population. When μ and σ^2 are unknown, however, computation of tolerance intervals becomes far more complex, since we must also incorporate our uncertainty in our sample based estimates $\bar{X}$ and s^2.

It is, however, possible to compute a constant k, such that one can assert with a certain degree of confidence, say 95%, that the proportion of the population contained between

$$\bar{X} \pm k_{[1-\alpha\,,P]}\; s$$

is at least P, say 99%. Values of $k_{[1-\alpha\,,P]}$ for constructing two sided intervals from random samples from normal distributions are given in Table 1 for $P = .95$ and $.99$ and confidence $1 - \alpha = .95$ and $.99$, and selected values of n from 6 to 50. Corresponding values for k for constructing one-sided tolerance limits are given in Table 2. The interested reader is referred to the original work conducted by Wald and Wolfowitz (1946) for the details of the derivation.

To avoid confusion, it is important to reiterate the distinction between confidence intervals and tolerance intervals. Confidence intervals are used to describe our uncertainty in an estimate of a parameter of a population, whereas tolerance intervals are used to indicate between what limits we can expect to find a certain proportion of the population. The distinction is emphasized by the fact that as n becomes large, the length of the confidence interval approaches zero, whereas, the tolerance interval will approach the corresponding values for the population (*e.g.*, $P = .95, k \rightarrow 1.96$).

2.2.3 Prediction Intervals

Let us now suppose that instead of constructing an interval that will contain a specified proportion of all future measurements, we are instead concerned with constructing an interval that will have a specified probability of containing the next *single* measurement. In the context, of MDL estimation, this is a natural case when we attempt to determine if the response for a particular compound, say benzene, in a single new ground-water sample, exceeds the response signal obtained from n blank samples with a certain level of confidence, say 99%. A similar argument can, of course, be made for estimates of variability obtained from a series of n analyte containing samples with fixed spiking concentration. For a random collection of measurements drawn from a normal distribution with μ and σ unknown (*e.g.*, n blank determinations distributed $\mathcal{N}(\bar{X}, s)$), the $(1-\alpha)100\%$ two-sided prediction interval is:

$$\bar{X} \pm t_{[1-\alpha/2\,,n-1]}\; s\sqrt{1+\frac{1}{n}}$$

and the corresponding one sided limit is

$$\bar{X} + t_{[1-\alpha\,,n-1]}\; s\sqrt{1+\frac{1}{n}}$$

The interested reader is referred to the work of Aitchison and Sculthorpe (1965) for a theoretical derivation from both Bayesian and frequentist perspectives and to Hahn (1969, 1970) for computational results.

In many cases, however, we may use a single collection of n background measurements (*i.e.*, blanks or fixed analyte containing samples), to determine if a particular compound is detected in several different environmental samples. This situation might occur if the mean and variance of the response signal in n spiked samples were determined in the morning, and all test samples for the remainder of the day were compared to the MDL derived earlier that day. In this case, the problem of statistical prediction is not for the next single measurement, but rather for the next r determinations. A simple approximation to this more general case can be obtained from the Bonferonni inequality as

$$\bar{X} \pm t_{[1-\alpha/2r\,,\,n-1]}\, s\sqrt{1+\frac{1}{n}}$$

and has been shown to be sufficiently accurate for practical purposes by Hahn (1969). The one-sided limit for the next r measurements is

$$\bar{X} + t_{[1-\alpha/r\,,\,n-1]}\, s\sqrt{1+\frac{1}{n}}$$

Again, to avoid confusion, let us highlight the distinction between tolerance intervals and prediction intervals. The tolerance interval is appropriate for cases in which the exact number of future measurements, or in our case test samples, is large and generally unknown, such that we must rely on an interval that will cover a fixed proportion of all future measurements with a given level of confidence. In contrast, the prediction limit applies to cases in which the number of test samples to be determined is known exactly, and is small, perhaps even only a single test sample. In the context of MDL estimation, a prediction limit would be the method of choice when the individual lab determines its own MDL daily (*i.e.*, $r < 20$) or with each test sample determination (*i.e.*, $r = 1$). Conversely, if MDLs are to be used for a large and/or potentially unknown number of future determinations, or established as regulatory thresholds, such that all laboratories must compare derived test sample concentrations to a fixed MDL determined by a government agency, then clearly the tolerance limit is the method of choice.

A final generalization that may be of some interest in the context of MDL estimates is the comparison of the average of m test sample determinations to the MDL estimated from the mean and variance of n background samples (*e.g.*, n spiked samples). In this case, the prediction limit takes the form:

$$\bar{X} \pm t_{[1-\alpha/2\,,\,n-1]}\, s\sqrt{\frac{1}{m}+\frac{1}{n}}$$

2.3 Case 2: Calibration Samples

An alternative method for estimating MDLs is to use a calibration design. In this case, a series of samples are spiked at known concentrations in the range of the hypothesized MDL, and variability is determined by examining the deviations of the actual response signals from the fitted regression line of response signal on known concentration. In these designs, it is generally assumed that the distribution of these deviations from the fitted regression line are normally distributed with constant variance across the range of concentrations used in the study. Again, the concepts of confidence limits, tolerance limits and prediction limits apply, and again, there appears to be some confusion regarding the choice of the appropriate interval and in some cases, discrepancies between what is computed and what it is called (Hubaux and Vos, 1970). In the following, a brief description of these three statistical interval estimates in the calibration setting is presented.

As preparation for the following discussion, we generally conceive of the relationship between response signal (Y) and spiking concentration (X) in the region of the MDL as a linear function of the form:

$$Y = \alpha + \beta(X - \bar{X}) + \varepsilon \quad = \quad \alpha + \beta x + \varepsilon$$

where ε is a random variable that describes the deviations from the regression line, which is distributed with mean 0 and constant variance $\sigma^2_{Y \cdot X}$.
The sample regression coefficient

$$b = \frac{\sum x_i y_i}{\sum x_i^2}$$

provides an estimate of the population parameter β, where x_i and y_i denote deviations from the mean concentration and response signal respectively (*i.e.*, $x_i = X_i - \bar{X}$ and $y_i = Y_i - \bar{Y}$. The sample intercept

$$a = \bar{Y}$$

provides an estimate of the population parameter α. An unbiased sample estimate of $\sigma^2_{Y \cdot X}$ (*i.e.*, the variance of deviations from the population regression line) is given by:

$$s^2_{Y \cdot X} = \sum_{i=1}^{n} (Y_i - \hat{Y}_i)^2 / (n-2)$$

where $\hat{Y}_i = \bar{Y} + b(X_i - \bar{X}) = \bar{Y} + bx_i$.

2.3.1 Confidence Intervals for Calibration lines

A $(1-\alpha)100\%$ confidence interval for the population calibration line is given by

$$\bar{Y} + bx \pm \sqrt{2F}\, s_{Y \cdot X}$$

where F is the "variance ratio" extracted from a table of the F-distribution with 2 and $n-2$ degrees of freedom. As X covers the range of spiking concentrations, the confidence bands form smooth curves that are two branches of a hyperbola.

Confidence bands define a region within which the true population regression line may be found with a certain level of confidence (*e.g.*, 95% confidence). However, the precision with which the sample regression line approximates the population regression line has little to do with the problem of determining MDLs. In the context of the calibration design, we are concerned with establishing concentration limits, which we can have a certain level of confidence that the concentration of the analyte in the solution is not zero. This problem is only indirectly related to the confidence limit problem in that they both require an estimate of $\sigma^2_{Y \cdot X}$.

2.3.2 Tolerance Intervals for Calibration Lines

The notion of a tolerance interval for a random sample of measurements can also be extended to the regression setting in which the intervals are simultaneous in each possible value of the independent variable X (*e.g.*, spiking concentration levels). Lieberman and Miller give four techniques for deriving such intervals, the simplest and most robust is based on the Bonferonni inequality.

For the predicted response signal $\hat{Y}$ at concentration X, the interval is

$$\hat{Y}_X \pm s_{Y \cdot X} \left\{ (2F^{1-\alpha/2}_{2,n-2})^{1/2} \left[\frac{1}{n} + \frac{x_i^2}{\sum_{i=1}^{n} x_i^2} \right]^{1/2} + \Phi(P) \left(\frac{n-2}{{}^{\alpha/2}\chi^2_{n-2}} \right)^{1/2} \right\}$$

where $F^{1-\alpha/2}_{2,n-2}$ is the upper $(1-\alpha/2)$ percentile point of the F distribution on 2 and $n-2$ degrees of freedom.

${}^{\alpha/2}\chi^2_{n-2}$ is the lower $\alpha/2$ percentile point of the χ^2 distribution with $n-2$ df.

and $\Phi(P)$ is the two-sided P percentile point of the unit normal distribution.

For the case of $X = 0$, the upper tolerance limit is:

$$Y_C = \bar{Y} - b\bar{X} + s_{Y \cdot X} \left\{ (2F^{1-\alpha/2}_{2,n-2})^{1/2} \left[\frac{1}{n} + \frac{\bar{X}^2}{\sum_{i=1}^{n} x_i^2} \right]^{1/2} + \Phi(P) \left(\frac{n-2}{{}^{\alpha/2}\chi^2_{n-2}} \right)^{1/2} \right\}$$

The value Y_c in the previous equation specifies a proportion P of the population of response signals that are possible when the true concentration is 0, given a $(1-\alpha)100\%$ confidence level. This interval estimate corresponds to the concept of a "critical level" defined by Currie (1968), for the case in which the data arise from a calibration experiment, μ and σ at $X = 0$ are unknown and we wish to provide coverage of a proportion of the population of possible test samples and not just the next single test sample. Again, this approach is well suited to the case of MDLs as regulatory thresholds, or when they are to be applied to a large and/or potentially unknown number of future sample determinations, but not for the case in which MDLs are *continuously* re-evaluated in the laboratory.

2.3.3 Prediction Limits For Calibration Lines

In the regression case, prediction limits for a single new measurement parallel those for the case of a fixed concentration design. In this case the estimated standard error of the prediction $\hat{Y}_X$ for a new value of Y at point X is

$$s(\hat{Y}_X) = s_{Y \cdot X}\sqrt{1 + \frac{1}{n} + x^2 / \sum_{i=1}^{n}(x_i)^2}$$

The prediction interval for a response signal obtained from a new test sample given a concentration X (*e.g.*, $X = 0$), is therefore;

$$\bar{Y} + bx \pm t_{[1-\alpha/2, n-2]}\, s(\hat{Y}_X)$$

For example, at a concentration of $X = 0$, $x = 0 - \bar{X} = -\bar{X}$, and the prediction limit is

$$\bar{Y} - b\bar{X} \pm t_{[1-\alpha/2, n-2]}\, s(\hat{Y}_X)$$

As in the previous examples, the one-sided limit can be obtained by substituting α for $\alpha/2$. Similarly, prediction limits for r future test samples can be obtained via the Bonferonni inequality by substituting $\alpha/2r$ for $\alpha/2$. Finally, prediction limits for the average of m test sample determinations may be obtained by replacing the previous standard error of the prediction with:

$$s(\hat{Y}_X) = s_{Y \cdot X}\sqrt{\frac{1}{m} + \frac{1}{n} + x^2 / \sum_{i=1}^{n} x_i^2}$$

As a summary, let us illustrate the distinction between the three types of statistical intervals using the example of the typical astronaut's problem (Hahn, 1970).

> An astronaut who has been assigned a limited number of space flights is not very interested in what will happen on the average in the population of all space flights, of which his happens to be a random sample (a confidence limit), or even in what will happen in 99 percent of the population of such space flights (a tolerance limit). His main interest is in the worst that my happen in the one, or three, or five flights in which he will be personally involved (a prediction limit).

3 METHOD DETECTION LIMITS

The most common definition of the method detection limit, is the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analytic concentration is greater than zero (Kaiser, 1965). In the following sections, we describe several strategies that have been proposed for the estimation of MDLs from blank samples, spiked samples (fixed concentration) and calibration samples (variable concentrations).

3.1 Kaiser-Currie Method

Based on developments due to Kaiser (1956, 1965, 1966), Currie (1968) described a two-stage procedure for calculating the MDL. At the first level of analysis, Currie defined the critical level L_C. The critical level is the concentration at which the binary decision of detection can be made with a specified level of confidence. Statistically, Currie defined the critical level as:

$$L_C = z_{1-\alpha}\sigma_0$$

where σ_0 is the population standard deviation of the response signal when the true concentration (C) is zero (*i.e.*, the standard deviation of the net signal found in the population of blank samples),

and $z_{1-\alpha}$ is a multiplication factor based on the $(1-\alpha)100$ percentage point of the standardized normal distribution.

For example, the one-sided 99% point of the normal distribution is 2.33; therefore, the critical value is defined as:

$$L_C = z_{1-\alpha}\sigma_0 \;=\; 2.33\sigma_0$$

Although the critical level places a restriction on the Type I error rate (*i.e.*, false positives), no such restriction is placed on Type II error rates (*i.e.*, false negative rates). When σ_0 and σ_D are known, the Type II error rate for the critical level is 50%. That is, we have a 50% chance of declaring that the analyte is not present when it, in fact, is present. In order to provide an acceptable Type II error rate, Currie defines the detection limit (L_D) as

$$L_D = L_C + z_{1-\beta}\sigma_D$$

where σ_D is the population standard deviation of the response signal at L_D (or net response signal after subtracting the background signal),

and β is the acceptable type II error rate (*i.e.*, false negative rate).

Currie points out that if we make the simplifying assumption that $\sigma_0 = \sigma_D$ (*i.e.*, the variability of the signal is constant in the range of L_C to L_D) and that the risk of false positive and false negative rates are equivalent (*i.e.*, $z_{1-\alpha} = z_{1-\beta} = z$) then the MDL is simply:

$$L_D = L_C + z_\beta \sigma_D \ = \ z(\sigma_0 + \sigma_D) \ = \ 2L_C$$

or twice the critical level. For $\alpha = \beta = .01$, the MDL is therefore $4.66\sigma_0$.

In reviewing Currie's method it is critically important to note that he only considers the case in which the population values σ_0 and σ_D are known. In practice, however, σ_0 and σ_D may be equal but they are rarely if ever known. In this case, σ_0 must be replaced with its estimate s_0 obtained from a sample of n_1 blank measurements (*i.e.*, s_0) and σ_D must be replaced with its estimate s_D obtained from a series of n_2 spiked samples in the region of the MDL (*i.e.*, s_D). Alternatively, we may assume that $s_D = s_0$, if there is evidence to suggest that such an assumption is reasonable. In this case, the general consensus (Currie, 1988, page 28) appears to be to replace $z_{1-\alpha}$ and $z_{1-\beta}$ with the corresponding values from Student's t-distribution yielding:

$$L_D = 2t_{[1-\alpha\,,\,n-1]}\, s_0$$

or in the procedure adopted by the USEPA (Glaser *et al.*, 1981),

$$MDL = t_{[.01\,,\,6]}\, s_D$$

where s_D is the standard deviation of 7 samples in which the analyte was spiked at a concentration of 2-5 times the suspected MDL.

There are two fundamental problems with this approach. First, the interval proposed by Currie for the case in which σ is known, is clearly a tolerance or coverage interval. When σ is unknown and replaced by its sample based estimate s, we cannot simply substitute $t_{1-\alpha}$ for $z_{1-\alpha}$. In this case, we must equate the critical level to the corresponding tolerance limit:

$$L_C = k_{[1-\alpha\,,\,P]}\, s$$

where $k_{[1-\alpha\,,\,P]}$ is the appropriate multiplier extracted from Table 2 depending on the desired coverage proportion P, confidence level $1 - \alpha$ and number of background samples (possibly blanks) used to establish s. Alternatively, if we only intend to use the critical level and corresponding detection limit for determining whether the analyte in question is present in a single test sample, the critical limit becomes a prediction limit of the form

$$L_C = t_{[1-\alpha\,,\,n-1]}\, s\sqrt{1 + \frac{1}{n}}$$

Of course, if the L_C and L_D are to be used for the next r determinations, where, for example, r is the number of test samples to be analyzed on that particular day, the critical level becomes

$$L_C = t_{[1-\alpha/r\,,n-1]}\, s\sqrt{1+\frac{1}{n}}$$

Finally, if we seek to determine if the analyte was detected based on the average signal obtained from m test samples, the appropriate value of L_C is given by

$$L_C = t_{[1-\alpha\,,n-1]}\, s\sqrt{\frac{1}{m}+\frac{1}{n}}$$

The choice of how to compute L_C when σ is unknown is clearly tied to the specific application. Simple substitution of $t_{1-\alpha}$ for $z_{1-\alpha}$ does not provide a statistically rigorous solution to any of these cases.

The second problem encountered when σ is unknown, involves the conversion of the critical level (L_C) to the detection limit (L_D). For prediction limits, the false positive rate is described by Student's t-distribution, however the false negative rate is governed by the non-central t-distribution. For this reason, Clayton *et al.*, (1987), have proposed that the detection limit be computed as

$$L_D = \phi\, s\sqrt{1+\frac{1}{n}}$$

where ϕ is the noncentrality parameter of the noncentral t-distribution with $n-1$ degrees of freedom and specified Type I and II error rates (*e.g.*, $\alpha = \beta = .01$). This formulation has identical properties to the prediction limit strategy, with the additional advantage of simultaneously controlling both false positive and false negative rates. To date, it is the only MDL calculation that correctly specifies both false positive and false negative rates when σ is unknown.

Unlike prediction intervals for which the distribution under the alternative hypothesis can be specified (*i.e.*, the noncentral t-distribution), no such alternative distribution is available for tolerance intervals. In this case, the detection limit can be approximated as:

$$L_D = k_{[1-\alpha\,,P]}s_0 + k_{[1-\beta\,,P]}s_D \;=\; L_C + k_{[1-\beta\,,P]}s_D$$

Of course, if it is reasonable to assume that the variability is constant in the range of L_C to L_D (*i.e.*, $s_0 = s_D = s$) and that the risk of false positive and false negative results is the same (*i.e.*, $\alpha = \beta$), then the detection limit is simply:

$$L_D = 2k_{[1-\alpha\,,P]}s$$

Fortunately, an exact solution for a detection limit based on tolerance limits is possible. Guttman (1970) has explored the relationship between prediction intervals (in his terms tolerance intervals of β-expectation) and tolerance intervals (tolerance intervals of β-content). For example, he demonstrates that for $n = 100$, the probability that a 99% prediction limit for the next single observation will actually cover 99% of the entire population of measurements is only .5861; that is, we can only have 59% confidence that the prediction limit will cover 99% of all future measurements. We can also determine the confidence level α^* for a prediction interval that corresponds to a tolerance interval for coverage P and confidence $1-\alpha$. This relation is

$$t_{[1-\alpha^*, n-1]} = k/\sqrt{1+\frac{1}{n}}$$

(see Guttman, 1970, page 89, equation 4.42). Substitution of α^* for α in the detection limit formulation based on the noncentral t-distribution due to Clayton *et al.*, (1987), will provide a detection limit that can be applied to a large and potentially unknown number of future sample determinations.

To illustrate these three approaches, let us consider the cases in which (1) σ is known and $\sigma_0 = \sigma_D = \sigma$ and $\alpha = \beta = .01$ (2) σ is unknown and $s_0 = s_D = s$, is estimated from $n = 7$ blank samples or fixed concentration samples, $\alpha = \beta = .01$ and we wish to construct a detection limit for the purpose of deciding whether the analyte is present in the next single test sample and (3) σ is unknown $s_0 = s_D = s$, $\alpha = \beta = .01$ and we wish to construct our detection limit not to be exceeded by 99% of all future test samples in which the true concentration of the analyte is zero.

With respect to case 1, the detection limit is

$$L_D = 2(2.33)\sigma = 4.66\sigma$$

For case 2, the detection limit based on the noncentral t-distribution prediction limit is

$$L_D = 6.21s\sqrt{1+\frac{1}{7}} = 6.64s$$

For case 3, the tolerance limit can be expressed as a prediction limit and the detection limit can be estimated using the method described in case 2, substituting α^* for α. In the present example, the value of k for a one-sided interval based on $n = 7, P = .99$ and $\alpha = .01$, is $k = 6.411$ (see Table 1). Solving for α^* yields:

$$t_{[1-\alpha^*, 6]} = \frac{6.411}{\sqrt{1+1/7}} = 5.997$$

therefore, $\alpha^* = .0005$. In light of this result, the prediction limit is $t_{[.9995, 6]}\sqrt{1+1/7}s$; that is a limit which will include the next single measurement with .9995 confidence, will also provide 99% coverage of all future measurements from the population with 99% confidence.

We can verify this result by computing the probability γ, that the $(1-\alpha^*)100\%$ expectation interval, has coverage $c \geq 1-\beta$. Guttman (1970, page 89) shows that this probability is given by:

$$\gamma = \Pr(c \geq 1-\beta) = \Pr\left[T^*_{n-1}(\sqrt{n}\, z_{1-\beta}) \leq \sqrt{n+1}\, t_{[1-\alpha^*, n-1]}\right]$$

This probability can be approximated (see Winer, 1971, page 35) as $\Phi(z_\gamma)$ where

$$z_\gamma = \frac{\sqrt{n+1}\, t_{[1-\alpha^*, n-1]} - \sqrt{n}\, z_{1-\beta}}{\sqrt{1+\left[\left(\sqrt{n+1}\, t_{[1-\alpha, n-1]}\right)^2 / 2(n-1)\right]}}$$

In the present example,

$$\begin{aligned} \sqrt{n}\, z_{1-\beta} &= \sqrt{7}\, 2.326 = 6.15 \\ \sqrt{n+1}\, t_{[1-\alpha^*, n-1]} &= \sqrt{8}\, 5.997 = 16.96 \end{aligned}$$

Therefore,

$$\Phi(z_\gamma) = \Phi\left(\frac{16.96 - 6.15}{\sqrt{1 + (16.96)^2/12}}\right) = \Phi(2.16) = .985$$

This value falls slightly short of the required value of $\Phi(2.33) = .990$; however, it appears to be more than adequate for practical purposes.

Given this equivalence, we can specify a detection limit L_D that properly balances false positive and false negative rates by refering to the noncentral t-distribution with α^*, β and $n-1$ degrees of freedom. The noncentrality parameter of the noncentral t-distribution can also be approximated as:

$$\phi = -z_\beta \sqrt{1 + \left[t^2_{[1-\alpha^*, n-1]}/2(n-1)\right]} + t_{[1-\alpha^*, n-1]}$$

where z_β is the lower $\beta(100)\%$ point of the unit normal distribution, and $t_{[1-\alpha^*, n-1]}$ is the upper $(1-\alpha^*)100\%$ point of Student's t-distribution. In the present example, $z_{.01} = -2.326$ and $t_{[.9995, 6]} = 5.997$; therefore the noncentrality parameter $\phi(\alpha^*, \beta)$ is approximately:

$$\phi = -(-2.326)\sqrt{1 + (5.997)^2/12} + 5.997 = 10.647$$

Values of $\phi(\alpha^*, \beta)$ for $\alpha = \beta = .05$ and $\alpha = \beta = .01$ and 95% and 99% coverage are given in Table 3 for $df = n - 1$ ranging from 5 to 49.

The detection limit is therefore

$$L_D = 10.647 s \sqrt{1 + \frac{1}{7}} = 11.382 s$$

This interval will cover 99% of all future values (for $x = 0$) with corresponding false positive and false negative rates of 1%. If the same conditions applied to an experiment with $n = 30$, as opposed to $n = 7$, the detection limits would be $2(3.446)\, s = 6.892\, s$ and $5.936\, s\, \sqrt{1 + 1/30} = 6.034\, s$. The method described by Clayton *et al.*, provides the same level of assurance, but only for the next single observation. In the present example, of $\alpha = .01, \beta = .01$ and $n = 7$, the method of Clayton *et al.*, will only provide .8264 confidence that 99% of the population of future measurements will be covered (see Guttman, 1970, Table 4.7). The Clayton *et al.*, MDL for $n = 7$, is $6.642\, s$ and for $n = 30$, the MDL is $4.969\, s$.

The reader may wonder why we can have a confidence level of 83% for $n = 7, \alpha = .01$ and $\beta = .01$, and only 59% confidence for $n = 100$, since intuitively, we would

expect the opposite. The answer is two-fold. First, values of the t-distribution are far more extreme for small degrees of freedom, which of course produces *greater* coverage. Second, the factor $\sqrt{1+1/n}$ is equal to 1.069 for $n = 7$, but only 1.005 for $n = 100$. The larger the multiplier, the larger the interval and of course, the greater the coverage.

These results also shed light on the question of, what is a large number of samples? In the present example, we find that a prediction interval with $\alpha^* = .0005$ provides the required coverage of 99% with 99% confidence. Based on the Bonferonni inequality, the overall experimentwise type I error rate will be $\alpha = .01$ given an individual comparison type I error rate of $\alpha^* = .0005$, when the experiment consists of $j = 20$ test sample comparisons; that is

$$\alpha = 1 - (1 - \alpha^*)^j \;=\; 1 - (1 - .0005)^{20} \;=\; .01$$

In light of this result, as the number of test samples increases beyond 20, and the number of background samples used in establishing the MDL is small, say $n \leq 10$, method detection limits should be based on tolerance limits. Exact values of j could of course, be computed for varying levels of α, β and n.

These illustrations should make it clear that we pay a very large price for replacing σ with its sample based estimate s, particularly when n is small (*e.g.*, $n = 7$ as suggested by USEPA). Furthermore, if MDLs are to be used as regulatory thresholds, then the size of the detection limit must increase even further in order to provide the same overall protection from false positive and false negative rates.

3.2 USEPA - Glaser *et al.*, method

Glaser *et al.*, (1981) constructed a model for the MDL by assuming that the variability is a linear function of concentration, such that for a limited number of analyses

$$s_C = b_0 + b_1 C + e_C$$

where s_C is the standard deviation of n replicate analyses at concentration C
b_0 and b_1 are the intercept and the slope of the linear regression
and e_C is a random error associated with concentration C distributed $\mathcal{N}(0,1)$ over concentrations.

To avoid a negative variance estimate at $C = 0$, Glaser *et al.*, divided through by C and obtained a new regression equation:

$$\frac{s_C}{C} = \frac{b_0}{C} + b_1$$

The slope of the new regression is now b_0 and the intercept is b_1, estimates for which can be obtained by regressing $1/C$ on s_C/C.

Let us now define:

$$t_C = \frac{C}{s_C/\sqrt{n}}$$

which is the t-value for a test of significance of the ratio of the concentration to its standard error of measurement. The regression equation can now be written as:

$$\frac{\sqrt{n}}{t_C} = \frac{s_C}{C} = \frac{b_0}{C} + b_1$$

If we set t_C to equal its critical value of $t_{[0.01,n-1]}$ and solve for C, we find that:

$$\text{MDL} = C = \frac{t_{[0.01,n-1]}b_0}{\sqrt{n} - b_1 t_{[0.01,n-1]}}$$

At this point Glaser *et al.*, made two simplifying assumptions. First, they set b_1 to zero, therefore

$$\text{MDL} = \frac{t_{[0.01,n-1]}b_0}{\sqrt{n}}$$

Second, they assume that $s_C = b_0/\sqrt{n}$, therefore

$$\text{MDL} = t_{[0.01,n-1]}s_C$$

where they define s_C as the standard deviation of n analytical replicates. However, this equation is not a confidence interval or any other usual statistical interval estimate (*i.e.*, a prediction or tolerance interval). Returning to their original regression equation:

$$\frac{s_C}{C} = \frac{b_0}{C} + b_1$$

if we set $b_1 = 0$, then $s_C = b_0$ and not $b_0/\sqrt{n}$. In light of this, the correct equation should be

$$\text{MDL} = t_{[0.01,n-1]}s_C/\sqrt{n}$$

which is, in fact, a 99% confidence limit estimate, assuming that the mean of the 7 replicate samples is zero.

Glaser *et al.*, appear to be interchanging the concepts of the standard error $s_C/\sqrt{n}$ with the standard deviation s_C of n replicate determinations of a fixed concentration. The only case in which these two estimators are the same is for $n = 1$; however, if $n = 1$ how can we possibly estimate s_C?

In addition, the Glaser *et al.*, method will underestimate the MDL as defined by Currie and others, because they assume that $L_C = 0$; that is, they have 99% confidence that any signal greater than zero can be detected (*i.e.*, present or absent). This assumption highlights a major distinction between this and the other methods reviewed here, and is, of course, demonstrably false in practice.

3.3 Hubaux and Vos method

Hubaux and Vos (1970) were the first to apply the theory of statistical prediction to the problem of MDL estimation. Beginning from a calibration design in which response signals are determined for analyte containing samples with concentrations throughout the range of L_C to L_D, they constructed a 99% prediction interval for the calibration regression line. (See Figure 1). The prediction limit is exactly of the form given in the second equation in section 2.3.3 and the critical level is defined as the value of the prediction limit for zero concentration (*i.e.*, X = 0) which is given in the third equation in section 2.33 (See L_C in Figure 1). The limit of detection is defined as the point at which we can have 99% confidence that the response signal is not L_C; therefore, Hubaux and Vos suggest that it be obtained graphically by locating the abscissa corresponding to L_C on the lower prediction limit (see L_D in Figure 1). A somewhat more direct solution for L_D is obtained by solving a quadratic equation in X for given Y, in our case L_C. We begin by expressing $x_i = X_i - \bar{X}$ (*i.e.*, a deviation from the average concentration); then, the most computationally tractable solution is:

$$x_D = \frac{\hat{x} + (t_{[1-\alpha,n-2]} s_{Y \cdot X}/b)\sqrt{[(n+1)/n](1-c^2) + \hat{x}^2/\sum x^2}}{1-c^2}$$

where

$$c^2 = t^2 s_b^2 / b^2 = (1/\sum x^2)\left(\frac{t s_{Y \cdot X}}{b}\right)^2$$

and

$$\hat{x} = (Y_C - \bar{Y})/b$$

The quantity $c = ts_b/b$ is related to the significant test for b. In the present context, b will be highly significant. As such, c will be small, c^2 will become negligible and the prediction limit becomes

$$x_D = \hat{x} + (t s_{Y \cdot X}/b)\sqrt{1 + 1/n + \hat{x}^2/\sum x^2}$$

To transform the limit back into the original metric, simply add in the mean of the actual concentrations $\bar{X}$ to the computed limit value.

As previously mentioned, this method assumes that variability is constant throughout the range of concentrations used in the calibration design. If this assumption is violated, then a variance stabilizing transformation, such as the square root transformation might be applied and the assumption of constant variance may be re-evaluated. The choice of the square root transformation is not at all arbitrary. Since the response signals are essentially sums of ion counts, the Poisson distribution may apply, and is, of course, consistent with the observation that concentration and variability are proportional (*i.e.*, the Poisson mean and variance are identical). The

square root transformation is used to bring about normality for data arising from a Poisson process.

3.4 The Procedure Due to Clayton and Co-Workers

Clayton *et al.*, (1987) point out that the method due to Hubaux and Vos is appropriate for establishing the critical level (L_C) but not the detection limit (L_D). Their argument is that under the null hypothesis (*i.e.*, $X = 0$) Student's t-distribution applies to case in which σ is replaced by its sample based estimate s and the errors of measurement are normally distributed; however, under the alternative hypothesis (*i.e.*, $X > 0$) the appropriate distribution is the noncentral t-distribution. In light of this, they point out that the only viable method for simultaneously controlling both false positive and false negative rates at nominal levels is to derive detection limits as functions of the noncentrality parameter of the noncentral t-distribution with $n-2$ degrees of freedom and specified values of α and β. The estimate of L_D may be found directly as:

$$L_D = (\phi \, s_{Y \cdot X} \; / \; b) \sqrt{1 + \frac{1}{n} + \bar{X}^2 / \sum_{i=1}^{n} x_i^2}$$

where ϕ is the noncentrality parameter from the noncentral t-distribution with $n-2$ degrees of freedom and specified Type I and II error rates (*e.g.*, $\alpha = \beta = .01$). As in the case of the Hubaux and Vos method, this approach also assumes constant variance throughout the range of the calibration. As illustrated in section 3.1, this idea can also be extended to non-calibration designs.

3.5 Tolerance Intervals For the Calibration Line

The previous two methods solve the problem of predicting an interval that will contain a single future measurement with specified Type I and Type II error rates. Ideally, a calibration of this type would be performed, and corresponding MDL estimated, each time a new test sample is to be evaluated. This, however, is rarely if ever the case. For example, in the context of ground-water monitoring, the USEPA has experimentally determined the MDLs for a variety of classes of compounds (see Federal Register, Vol. 29, No. 209), and these "regulatory limits" (computed using the method of Glaser *et al.*, 1981), are, at least in practice, used regardless of the true limit for a particular laboratory on a particular occasion. As such, the detection decision for enormous numbers of test samples are being made on the basis of results obtained from a single analytical study in a single laboratory using single analyst and single instrument. Furthermore, the detection limits reported were computed assuming the task was to make a detection decision in a single future sample. If this practice is to continue, the method by which the detection limit is computed must be commensurate with the actual way in which the resulting limit is to be applied. When the number of future test samples is large , say greater than 20, and the exact number may even be unknown, the best we can do, is to produce an interval that

will cover a certain proportion P of the total population of measurements with a specified level of assurance $(1-\alpha)100\%$.

As previously shown in section 2.3.2, a simultaneous tolerance interval with $P\%$ coverage and $(1-\alpha)100\%$ confidence can be constructed for the entire calibration line using the method described by Lieberman and Miller (1963). The second equation in section 2.3.2 demonstrates the special case of computing the upper tolerance limit when $X = 0$ (*i.e.*, the test sample does not contain the analyte in question). The solution of this equation corresponds to Currie's notion of the critical level L_C. Again, solving the quadratic equation in $x = X - \bar{X}$ for $Y = L_C$ yields the detection limit:

$$x_D = \frac{c + \frac{s_{Y\cdot X}(2F^{1-\alpha/2}_{2,n-2})^{1/2}}{b\sqrt{\sum x^2}}\sqrt{c^2 + \frac{b^2\sum x^2 - s^2_{Y\cdot X}2F^{1-\alpha/2}_{2,n-2}}{nb^2}}}{\left(1 - \frac{s^2_{Y\cdot X}2F^{1-\alpha/2}_{2,n-2}}{b^2\sum x^2}\right)}$$

where

$$c = \hat{x} + \frac{s_{Y\cdot X}}{b}\Phi(P)\left(\frac{n-2}{{}^{\alpha/2}\chi^2_{n-2}}\right)^{1/2}$$

and

$$\hat{x} = (Y_C - \bar{Y})/b$$

In order to express the detection limit in its original metric, we simply add the average absolute concentration $\bar{X}$ to the computed value of x_D.

For example, if $P = .95$ and $\alpha = .01$, we will have 99% confidence that 95% of the population of future measurements that do not contain the analyte in the question, will be below the MDL.

The objection raised by Clayton *et al.*, (1987) regarding use of the central t-distribution for characterizing both false positive and false negative rates, also applies to the tolerance intervals just described. As previously shown, one solution to this problem is to compute the required type I error rate α^*, necessary for the expectation interval to have coverage $1-\beta$, for example 99%. This solution proceeds along the lines previously described in section 3.1. Estimates of the noncentrality parameter $\phi(\alpha^*, \beta)$, can then be substituted for $\phi(\alpha, \beta)$ and a tolerance interval based MDL can be obtained using the equation in section 3.4. In the regression framework, the degrees of freedom are now $n-2$. Table 3 presents values of $\phi(\alpha^*, \beta)$ for a selection of degrees of freedom ranging from 5 to 48, and combinations of $\alpha = \beta = .05$ and .01 and coverage of 95% and 99%.

3.6 Experimental Design of Detection Limit Studies

A detailed review of the principles of experimental design of method detection limit studies would easily require a paper unto itself and is clearly beyond the scope of the present work and has been reviewed in some detail by others (see Liteanu and Rica, 1980). There are, however, several guiding concepts that are critical for producing unbiased detection limit estimates of practical relevance.

First, in analyte present studies, the analysts must be blind to both the number of compounds in the sample as well as their spiking concentrations. To achieve this goal, the number of compounds must vary, perhaps randomly, from sample to sample. Similarly, the concentration of each constituent should also vary both within and across samples. Without insuring that the analyst is blind to both presence and concentration of the analyte under study, the resulting detection limit simply cannot be applied to routine practice where such uncertainty must always exist.

Second, two or more instruments and analysts must be used and the assignment of samples to analysts and instruments must also be random. Since in large production laboratories, any one of a number of analysts and/or instruments may be called upon to analyze a test sample, this same component of variability must be included in determining the detection limit.

Third, whenever possible, the entire detection limit study should be replicated in two or more different laboratories.

Fourth, the number of samples selected should be based on statistical power criteria, such that a reasonable balance of false positive and false negative rates is achieved. For example, if we estimate σ by computing s on 7 samples, our uncertainty in σ will be extremely large and our resulting detection limit estimate L_D will also be quite large. By increasing the number of samples to, say 25, we achieve a much more reasonable estimate of σ, and resulting L_D are greatly reduced. The cost of running a few additional samples, far outweighs the drawbacks of having detection limits that are incapable of detecting anything but the largest signals.

An additional note regarding analyte absent experiments (*i.e.*, blank samples). Rather than running a series of blank samples at once, they should be randomly entered into the analysts work load throughout the course of the day. Again, the purpose of this approach is to insure that the analysts is blind to sample composition. The broader question, of course, is whether analyte absent experiments are relevant to establishing MDLs. It can certainly be argued that the properties of the *method* can only be evaluated when the analyte is present, at least in some of the samples. The answer to this question is clearly beyond the scope of this paper; however, our general recommendation of calibration designs over fixed concentration designs allows for a mixture of samples in which the analyte is present and absent.

There are several experimental designs that can fulfill the preceding requirements. When the number of samples is large, say $n = 30$, one possibility is to give each compound in the study a .5 probability of being in any given sample, and once selected, its concentration could also be randomly selected from a uniform distribution covering the range of 0 to $2L'_D$, where L'_D is the presumed detection limit. This

design is perhaps optimal for insuring blindness, but not necessarily for maximizing the signal to noise ratio which, of course, increases the amount of information that can be gained in such a study. For example, Hubaux and Vos (1970) suggest a "three values repartition", in which n_1 replicate samples with concentrations at the lowest "permissible content" (X_1) are selected, $n_2 = N - n_1 - 1$ samples at the highest "permissible content" (X_2) and a single sample at $(X_1 + X_2)/2$. In their work, they find that this design minimizes the number of required standards for a fixed level of sensitivity.

Liteanu and Rica (1980), review a wide variety of sampling designs for detection limit studies, including, response surface designs, fractional factorial designs and rotatable designs. Youden pair type designs are also excellent candidates for maintaining blind and unbiased detection limit studies.

4 ILLUSTRATION

To illustrate the various approaches to estimating the MDL, we conducted the following study of 10 volatile organic priority pollutant compounds from the USEPA method 624 list. The compounds were:

1. methylene chloride
2. chloroform
3. trichloroethylene
4. tetrachloroethylene
5. trans-1,2-dichloroethene
6. benzene
7. chlorobenzene
8. carbon tetrachloride
9. 1,1-dichloroethane
10. chloromethane

Thirty five samples were prepared. For each sample, each compound was given a .5 probability of being selected by drawing 10 random numbers from a uniform random number generator on the interval of 0 to 1. Those compounds with random numbers above .5, were selected for that particular sample; therefore, on average, there were 5 compounds present in each sample. Once a compound was randomly selected for a particular sample, its spiking concentration was determined by selecting a random number from a uniform random number generator on the interval of 0 to 50. The integer value of this random number was used as the spiking concentration in $\mu g/l$.

The 35 samples were then sent to a major analytical laboratory and USEPA method 624 analyses were requested for each. By design, the samples were split between two different analysts and two different instruments.

For the purpose of our analysis, the data were recorded as peak areas for each compound and a corresponding internal standard. To help provide homogeneous variation throughout the calibration line, the data were expressed as:

$$\text{response} = \sqrt{\frac{\text{peak area for compound}}{\text{peak area for internal standard}}} \tag{1}$$

that is the square root of the ratio of peak areas for the compound to the internal standard. As an example, Figure 1 displays a scatter plot of the relationship between actual concentration and instrument response for tetrachloroethylene. Inspection of Figure 1, reveals that the deviations from the fitted regression line are modest and relatively homogeneous throughout the calibration range. Furthermore, the relationship appears to be linear. For the linear regression model, $r^2 = .96$ indicating that 96% of the variation in instrument response was accounted for by a linear function of actual concentration. In all cases, the value of r^2 exceeded .9 suggesting that the linear model is reasonable for these 10 compounds.

Returning to Figure 1, the result of the Hubaux-Vos calculation produced an MDL of 15.493 $\mu g/l$. In contrast, the MDL based on a 99% confidence 99% coverage tolerance interval was 28.941 $\mu g/l$ (see Figure 2). As pointed out by Clayton and co-workers, neither of these approaches are statistically correct, since the limiting distribution assumed under both the null and alternative hypotheses is the same. The MDL based on the method due to Clayton *et al.*, (1987) is computed for tetrachloroethylene as:

$$\begin{aligned} MDL &= (\phi s_{Y.X}/b)\sqrt{1+\frac{1}{n}+\frac{\bar{X}^2}{\sum_{i=1}^{n} x_i^2}} \\ &= (5.08(.0442)/.0174)\sqrt{1+\frac{1}{19}+\frac{24.7842^2}{4944.1853}} \\ &= 14.01 \mu g/l \end{aligned}$$

This MDL balances false positive and false negative rates at 1% for the next single determination. Using the method described in sections 3.1 and 3.5, we can extend this MDL to provide false positive and false negative rates of 1% for 99% of all future determinations, by substituting $\phi = 6.57$ for $\phi = 5.08$, in the previous equation (see Table 4, $\alpha = \beta = .01$, coverage = 99%; and df = 17). The resulting MDL is 18.12 $\mu g/l$. As expected, these two MDL's are more conservative than the their corresponding interval estimates. As previously shown in Section 3.1, if the computed MDL is to be used for a single determination, the Clayton *et al.*, method should be used. If the MDL is to be used for 20 or more determinations, the latter

method based on tolerance limits should be used. For cases in between, the tolerance limit procedure is reasonable; however, a more conservative solution can be obtained by using a slight modification of the Clayton et. al. procedure where $\alpha^* = \alpha/r$ and r is the number of determinations. For example, if $r = 10$, and $\alpha = .01$, then $\alpha^* = .01/10 = .001$. Computed MDLs for both procedures for the 10 compounds are displayed in Table 5.

5 CONCLUSION

Method detection limits test the null hypothesis that the concentration of an analyte in solution is zero. For tests of this kind, both false positive and false negative results are possible and control of both of these rates at nominal levels can and should be provided. When the same MDL is applied to more than a single determination decision, these error rates are no longer valid; that is, they do not achieve their nominal levels. When the number of future determinations is small (*i.e.*, less than 20) the inflation in error rates may be controlled using the Bonferonni inequality; which in this context, amounts to nothing more than substituting $\phi_{(n-2,\alpha^*,\beta)}$ for $\phi_{(n-2,\alpha,\beta)}$ into the equation derived by Clayton and co-workers, where $\alpha^* = \alpha/r$ and r is the number of future determinations. In this way, the probability that any one of the next r determinations will result in a detection when the true concentration is zero, will be α.

When the number of future determinations exceeds 20, or is large and potentially unknown, a more conservative approach is to construct an MDL that will include a proportion of all future measurements with specified assurance probabilities. Although the computation is somewhat more complex, tabled values of the appropriate noncentrality parameters are provided here, so that routine application is straightforward.

It is of considerable interest to note that the results of our limited experimental study produced MDL's that are 2 to 10 times the values of the published MDLs based on the method due to Glaser and co-workers. Although we have identified several problems with their statistical procedure and derivation, we strongly feel that the majority of the difference is due to the fact that the analysts were blind to presence and concentration in our study but not in the USEPA study. Given that in practice, analysts do not know what is in a sample or its concentration, we conclude that the limits presented here reflect the level of precision that is attainable in the routine application of this analytical procedure.

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Table 1

Factors (k) for Constructing Two-Sided Normal Tolerance Limits

	95% Confidence Coverage		99% Confidence Coverage	
N	95%	99%	95%	99%
6	4.414	5.775	6.345	8.301
7	4.007	5.248	5.448	7.187
8	3.732	4.891	4.936	6.468
9	3.532	4.631	4.550	5.966
10	3.379	4.433	4.265	5.594
11	3.259	4.277	4.045	5.308
12	3.169	4.150	3.870	5.079
13	3.081	4.044	3.727	4.893
14	3.012	3.955	3.608	4.737
15	2.954	3.878	3.507	4.605
16	2.903	3.812	3.421	4.492
17	2.858	3.754	3.345	4.393
18	2.819	3.702	3.279	4.307
19	2.784	3.656	3.221	4.230
20	2.752	3.615	3.168	4.161
21	2.723	3.577	3.121	4.100
22	2.697	3.543	3.078	4.044
23	2.673	3.512	3.040	3.993
24	2.651	3.483	3.004	3.947
25	2.631	3.457	2.972	3.904
30	2.549	3.350	2.841	3.733
35	2.490	3.272	2.748	3.611
40	2.445	3.212	2.677	3.518
50	2.379	3.126	2.576	3.385

Table 2

Factors (k) for Constructing One-Sided Normal Tolerance Limits

	95% Confidence Coverage		99% Confidence Coverage	
N	95%	99%	95%	99%
6	3.707	5.062	5.409	7.334
7	3.399	4.641	4.730	6.411
8	3.188	4.353	4.287	5.811
9	3.031	4.143	3.971	5.389
10	2.911	3.981	3.739	5.075
11	2.815	3.852	3.557	4.828
12	2.736	3.747	3.410	4.633
13	2.670	3.659	3.290	4.472
14	2.614	3.585	3.189	4.336
15	2.566	3.520	3.102	4.224
16	2.523	3.463	3.028	4.124
17	2.486	3.415	2.962	4.038
18	2.453	3.370	2.906	3.961
19	2.423	3.331	2.855	3.893
20	2.396	3.295	2.807	3.832
21	2.371	3.262	2.768	3.776
22	2.350	3.233	2.729	3.727
23	2.329	3.206	2.693	3.680
24	2.309	3.181	2.663	3.638
25	2.292	3.158	2.632	3.601
30	2.220	3.064	2.516	3.446
35	2.166	2.994	2.431	3.334
40	2.126	2.941	2.365	3.250
50	2.065	2.863	2.296	3.124

Table 3

Values of $\phi(\alpha^*, \beta)$ for Computing MDLs based on Normal Tolerance Limits for Fixed Concentration Designs - $df = n - 1$

	$\alpha = \beta = .05$ Coverage		$\alpha = \beta = .01$ Coverage	
df	95%	99%	95%	99%
5	5.860	8.845	8.089	12.299
6	5.412	8.071	7.093	10.647
7	5.116	7.556	6.463	9.603
8	4.901	7.191	6.027	8.887
9	4.741	6.917	5.714	8.367
10	4.616	6.703	5.473	7.968
11	4.514	6.532	5.283	7.658
12	4.431	6.392	5.130	7.407
13	4.361	6.275	5.003	7.199
14	4.302	6.175	4.895	7.030
15	4.249	6.088	4.804	6.881
16	4.205	6.016	4.724	6.755
17	4.165	5.949	4.657	6.644
18	4.129	5.891	4.596	6.547
19	4.098	5.839	4.539	6.460
20	4.068	5.792	4.493	6.382
21	4.044	5.750	4.448	6.314
22	4.019	5.712	4.406	6.249
23	3.996	5.677	4.372	6.192
24	3.977	5.644	4.336	6.142
29	3.895	5.516	4.205	5.936
34	3.835	5.423	4.110	5.791
39	3.791	5.354	4.038	5.685
49	3.724	5.254	3.962	5.530

Table 4

Values of $\phi(\alpha^*, \beta)$ for Computing MDLs based on Normal Tolerance Limits for Calibration Designs - $df = n - 2$

	$\alpha = \beta = .05$ Coverage		$\alpha = \beta = .01$ Coverage	
df	95%	99%	95%	99%
5	5.512	8.292	7.254	10.984
6	5.184	7.710	6.570	9.831
7	4.950	7.304	6.102	9.051
8	4.778	7.002	5.769	8.490
9	4.644	6.770	5.515	8.062
10	4.537	6.586	5.315	7.733
11	4.449	6.436	5.156	7.468
12	4.376	6.312	5.024	7.249
13	4.314	6.206	4.913	7.072
14	4.260	6.115	4.819	6.917
15	4.214	6.038	4.737	6.786
16	4.173	5.969	4.668	6.670
17	4.136	5.909	4.605	6.570
18	4.104	5.855	4.548	6.480
19	4.074	5.805	4.501	6.400
20	4.049	5.762	4.454	6.330
21	4.024	5.723	4.412	6.264
22	4.000	5.687	4.377	6.205
23	3.980	5.654	4.341	6.153
28	3.898	5.522	4.208	5.943
33	3.837	5.427	4.112	5.797
38	3.792	5.357	4.039	5.689
48	3.725	5.256	3.963	5.532

PERFORMANCE EVALUATION OF THE ORGANIC METHODS USED IN THE CONTRACT LABORATORY PROGRAM

JACK BERGES AND RICHARD FLOTARD, PhD, LOCKHEED ENGINEERING AND SCIENCES CO., 1050 E. FLAMINGO ROAD, LAS VEGAS, NV 89119, E. J. KANTOR AND L. C. BUTLER, PhD, U.S.E.P.A., ENVIRONMENTAL MONITORING SYSTEMS LABORATORY, P.O. BOX 93478, LAS VEGAS, NV 89193-3478.

ABSTRACT. Organic Method Validation Studies are regularly performed for the Contract Laboratory Program (CLP) by the Enviromental Monitoring Systems Laboratory in Las Vegas (EMSL-LV). These studies utilize Quality Control (QC) data submitted during the previous year by laboratories participating in the organic CLP. Statistical surrogate and matrix spike recovery windows are determined for the three methods used in the organic CLP. The validation studies can be used to monitor and update QC windows used in the program and to determine whether the methods are meeting user needs.

The study which will be presented was obtained by analysis of FY 87 Quarterly Blind (QB) and Pre-Award (PA) performance evaluation sample results. Precision and accuracy results obtained for the CLP Volatile organic (VOA), Semi-volatile (SVOA), and Pesticide methods will be reported. Some of the samples used in the study include analytes spiked at near the CLP Contract Required Detection Limits (CRQLs).

MINIMAL QA/QC CRITERIA FOR FIELD AND LABORATORY ORGANIZATIONS GENERATING ENVIRONMENTAL DATA[1]

Kathleen A. Carlberg, QA Director, Enseco Incorporated, 2200 Cottontail Lane, Somerset, New Jersey 08873; Mitzi S. Miller, Program Manager, Henry Beiro, Project Manager, Dennis Forsberg, Project Manager, Analytical Environmental Support Group, Martin Marietta Energy Systems, Inc., P.O. Box 2003, Oak Ridge, Tennessee 37831-7440; S. Reid Tait, Research Associate, Dow Chemical U.S.A., Environmental Services, Building 1261, Midland, Michigan 48667

ABSTRACT

A group of environmental professionals from industry, government agencies, and engineering firms have met over the past year under the auspices of ASTM Committee D34.02.10 to identify the elements of field and laboratory quality assurance essential to generating quality environmental data. The result of their effort is an ASTM draft document entitled "Standard Practice for Generation of Environmental Data Related to Waste Management Activities."

This practice defines minimal QA/QC criteria for field and laboratory organizations generating environmental data. It also identifies other QA/QC practices which may be required based on the Data Quality Objectives of the data collection effort. The minimal criteria and recommended practices are described in terms of human and physical resources, QA/QC procedures, and documentation requirements.

INTRODUCTION

In July of 1988 a group of chemists, geologists, and environmental specialists met to establish minimal requirements for generation of environmental data. This was done through ASTM in cooperation with EPA. The results of their effort is an ASTM document, currently in draft form, entitled "Standard Practice for Generation of Environmental Data Related to Waste Management Activities". The practice outlines the critical elements in the data generation process. These elements consist of: establishment of Data Quality Objectives (DQOs), design and implementation of field and laboratory programs, and performing data quality assessment. The practice primarily addresses two of the four parts: the design and implementation of the sampling and analysis aspect of the environmental data generation activities.

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ESTABLISHMENT OF DQOs

The standard emphasizes that DQOs be established prior to generation of data; that the project plan be designed to meet these objectives; and that the data be evaluated to determine whether these objectives have been met. The practice stresses the importance of communication among those involved in establishing Data Quality Objectives, planning and implementing the sampling and analysis aspect of environmental data generation activities and assessing data quality.

PROJECT DESIGN

The project plan, which is built around the DQOs, should define project objectives, project management, sampling requirements, analytical requirements and QA/QC requirements for both field and laboratory QC. The project documentation should contain all of these plans, and should specify document control requirements including those personnel having access to the documentation. The plans should also contain scheduling information.

PROJECT IMPLEMENTATION

The project plan should require that field and laboratory organizations performing the work incorporate certain minimal QA/QC procedures into the effort. The key elements for an effective QA Program include demonstration of the qualifications to do the work, controlling the operations to ensure continuous quality, and documenting and reporting the appropriate information. The document outlines the minimal requirements for the field and lab QA programs. Table 1 outlines the areas covered by the field and lab QA programs. The field and lab QA programs are comparable. Both the laboratory and field organizations must establish organizational, operational, health and safety, and QA policies. The QA functions must be clearly defined and must be independent from the personnel engaged in the work. Any subcontractors must also comply with QA requirements applicable to the tasks performed. The organization must demonstrate that personnel are qualified by education, experience, and training or some combination thereof, to perform their function.

Table 1
Comparability Between Field and Lab QA Programs

Field	Lab
Organization	Organization
Field Logistics	Facility Requirements
Equipment/Instrumentation	Equipment/Instrumentation
SOPs	SOPs
Field QA/QC Requirements	Lab QA/QC Requirements
QA Review	QA Review
Field Records	Lab Records
Document Storage	Document Storage

The field logistics are comparable to the lab facility requirements. In the field, the area of sampling must be examined to ensure that trucks, drilling equipment, and personnel have site access. Plans must address areas to perform field measurements such as pH. These field plans must address ventilation, protection from extreme weather and temperature changes, access to stable power, and provision for water and gases of required purity. The laboratory must have adequate space, ventilation, be free of dust and drafts, be protected from extreme temperatures, and have access to a stable source of power. Other logistics/facilities with specified requirements include 1) sample handling and storage areas, 2) chemical storage area, 3) decontamination or lab operations area, 4) waste storage area, and 5) data storage area.

Requirements for equipment and instrumentation must also be specified. For both the field and the lab, the equipment, instrumentation, and supplies must be appropriate to the task and must be specified in the planning documents. The equipment must be maintained and calibrated. Procedures or manuals must discuss how this is done. The personnel performing maintenance must be identified and maintenance records to be kept must be specified.

A crucial area which is often ignored is the availability of current Standard Operating Procedures (SOPs). The organization shall have written SOPs for all procedures routinely performed that affect data quality. The practice describes areas which require SOPs and the minimum information needed in each. Table 2 outlines the areas for which SOPs must be available.

Table 2
Standard Operating Procedures (SOPs)

Field	Lab
Sample Management	Sample Management
Reagent/Standard Preparation	Reagent/Standard Preparation
Decontamination	General Lab Techniques
Sample Collection	Analytical Procedures
Equipment Calibration and Maintenance	Equipment Calibration and Maintenance
Field Measurements	QC Data
Corrective Action	Corrective Action
Data Reduction and Validation	Data Reduction and Validation
Reporting	Reporting
Records Management	Records Management
Waste Disposal	Waste Disposal
Health & Safety	Health & Safety

Sample management SOPs from the field include those describing the sample numbering and labeling system, chain-of-custody procedures, and tracking of sample from collection to relinquishment to the laboratory. Specifics to be covered include shipping, holding times, volume of sample required, and

preservatives required. In the laboratory, SOPs describing scheduling, storage, and sample receipt and handling procedures are required. The reagent/standard preparation SOP includes the procedures for preparing, storing, determining the grade and purity of materials, and disposing of these materials.

The decontamination SOPs should describe the cleaning materials used in the field, the order of washing and rinsing, equipment protection requirements, and procedures for disposing of cleaning materials. The laboratory must have SOPs for general lab techniques such as glassware cleaning and use of balances.

The SOPs for field procedures related to sample collection shall specify how the samples are actually collected and not be a simple reference to methods, unless a procedures is performed exactly as described in the method. The same shall be true of the laboratory. The laboratory SOPs for analytical methods shall include preparation and analysis information with holding time requirements, dilution information, instrument standardization, raw data recording requirements, and detection and reporting limits.

Field and laboratory organizations must also have SOPs which outline equipment calibration and maintenance procedures including schedules, logs, service contracts and spare parts available in-house. These procedures should be in compliance with the manufacturer's recommended practices.

The Field Measurement SOPs must include procedures for methods used in the field to determine a chemical or physical parameter. Any analysis procedures performed in the field must meet the applicable laboratory requirements outlined in the document.

The QC data generated by the lab shall be outlined in an SOP which details the type, purpose, and frequency of QC samples. The lab should include the applicability of the QC sample to the process, statistical treatment of the data, and who is responsible for performing and evaluating the QC samples.

The practice requires that SOPs describe corrective action procedures which identify and correct deficiencies in the sample collection and analyses process. The person responsible for the action, the corrective action taken, samples affected, and the outcomes shall be documented.

An SOP for data reduction and validation shall be provided and shall describe how to compute results and how to review and validate these data. The SOPs for reporting and records management shall describe who reports data and how the records are handled. They should describe policies for record retention, including type, time, security and retrieval and disposal authorities. Since field records may be transported, special care must be taken with field records in assuring that these are complete and readily available.

SOPs for waste disposal should describe policies and procedures pertaining to waste resulting from field and laboratory operations, including reagents and sample remains. These should conform to Federal, State and local regulations. Health and safety procedures required of those working in field and lab areas shall be described in SOPs. These procedures shall comply with Federal and State regulations.

The minimum requirements for field QA/QC procedures is a major section of the practice. Included in this section are requirements for QA Program Plans, QA Project Plans, identification and definition of control samples, procedures for establishing acceptance criteria, and requirements for corrective actions. The field section also defines procedures for documenting a deviation from the SOP or project plan. These deviations may not cause a quality problem but may be necessitated by occurrences such as weather or equipment operation.

The comparable section in the laboratory adds items to those listed in the field QA/QC requirements such as method proficiency and requires specific control samples, and defines their purpose. These control samples include method blanks and laboratory control samples. In addition, the use of matrix spikes and matrix spike duplicates to meet specific DQOs is described. The QA/QC procedures also include data handling procedures for data reduction, data review and reporting.

QA review requirements include requirements for internal and external assessments of the organization to ensure that QA/QC procedures are in place and to assure that laboratory and field staff conform to the procedures. The project planning documents must specify the frequency and documentation of these assessments. The assessments may include on-site evaluations or audits.

QA review also includes data review. The evaluation of field records shall include verification of completeness, identification of valid sample data, and correlation of measurements obtained by more than one method. In reviewing field data, anomalous field results should be identified. The QA review of laboratory data or data from field analyses such as soil gas includes the above items as well as evaluation of the data with respect to detection limits, control limits and holding times. Any performance evaluation sample results associated with the samples shall also be reviewed.

In order to correct and improve the quality of the sample collection process, management must be kept informed of the quality of the work being performed. Reports to management must include an assessment of the QC data, a summary of any internal or external on-site evaluations, measures which are being taken to improve the quality of the data, a summary of quality related issues from clients or agencies, QA organizational changes, and notice of SOPs issued.

Documentation is an important part of the data collection process. Records shall include personnel training and qualifications, SOPs, QA Plan(s), equipment maintenance logs, method proficiency data, calibration data, sample management records, sample and QC data, and final reports from projects. Any corrections or deviations to procedures or data shall also be documented. All documentation errors shall be corrected by drawing a single line through the error. The change shall be initialled and dated by the responsible individual. These records must be legible, identifiable, and retrievable and protected against damage, deterioration or loss.

The documents described above must be stored for a time specified in project planning documents. The procedures must specify how the archiving process will be maintained, the storage time required and the filing system to be used. Personnel who have access to the records and a method for controlling access shall be specified.

DATA ASSESSMENT

Once the above process is completed, the data must be assessed. Data assessment occurs in two stages. The first includes summarizing the information contained in the field records and evaluating the results from the review of the field and laboratory data. This information is used to clearly identify data that are not representative of environmental conditions or that were generated using poor practices.

The second phase of assessment is to evaluate whether the DQOs were met. While this Standard Practice is not intended to detail the assessment of data versus DQOs, a general list of items to be considered in the process is presented. The representativeness, completeness, precision, bias, and defensibility should be assessed against the project goals. The comparison of all field blanks, trip blanks, and equipment rinsates with the actual sample data should be made. Matrix effects should be examined. The laboratory data should be integrated with geological, hydrogeological and meteorological data to determine the extent of contamination.

SUMMARY

This Standard Practice is designed to provide information concerning minimal QA/QC criteria which should be incorporated into the design and implementation of environmental generation activities. It is foreseen that future practices from ASTM D34.02.10 will include details concerning establishment of DQOs and procedures to be used in assessing data quality.

SURVEY OF LABORATORY APPROVAL PROGRAMS

Ann G. Miller, QA Manager, Dynamac Corporation, 11140 Rockville Pike, Rockville, Maryland 20852

ABSTRACT

Numerous State, Federal, and private laboratory accreditation/certification/approval programs have been developed. Differences in quality assurance programs raise a number of questions about the accuracy, defensibility, and cost of data generated under the various program types. Dynamac has designed a three-dimensional matrix approach for comparing these programs. The approach consists of the following:

Scope: What matrices, analytes, and methods are covered?

Elements of Quality Assurance: What items (e.g., audits, performance evaluation samples) are included in the quality assurance program?

Standards: What are the requirements (e.g., two audits per year, less than 10% error in performance evaluation quantitation) for each element of quality assurance?

We have applied this approach to compare several widely used programs, and we present our results.

We discuss the possibilities for creating a "master matrix," which covers the entire scope of all existing programs, containing all the elements and adequate standards of any program. This master matrix would serve as the technical basis for a national, universal laboratory accreditation/certification/approval program.

INTRODUCTION

In December 1987, Dynamac Corporation of Rockville, Maryland (as a subcontractor to Touche Ross & Co. of New York, New York) was selected to assess the reasonableness, adequacy, and equity of the New York Department of Health Environmental Laboratory Approval Program (ELAP).

The objectives of the study mirror the issues surrounding all laboratory certification procedures and fee-setting policies, which have been raised by interested laboratories and the legislature. Specifically, this study was intended to accomplish the following:

- o Review and assess whether the present ELAP procedures, standards, and costs are necessary and appropriate in light of New York environmental quality goals;

- o Compare the New York ELAP with similar Federal and State programs in terms of program costs and intended benefits or quality standards; and

- o Evaluate alternative fee structures according to expected ability to recover the cost of ELAP equitably and reasonably.

This report served as the basis for an overall survey of the environmental laboratory certification/approval QA programs considered to be the most prominent. This paper does not discuss the results of the ELAP study and is not intended to focus on ELAP. Dynamac does not own or operate a chemical laboratory, but has a number of well known laboratories under subcontract; it is in Dynamac's interest that they perform well and meet the highest standards of quality assurance and quality control.

FRAMEWORK FOR ANALYSIS AND COMPARISON OF QA PROGRAMS

Most of the information summarized in this paper was gathered via telephone conversations or personal interviews. Some was collected through written surveys, and some was gleaned from reports and manuals. It is not possible to verify all documentation because a number of contacts insisted that they not be named or quoted in the report. Dynamac has maintained a confidential file of memoranda of conversations and surveys that were used in compiling the report.

Laboratory approval programs may include various types of testing: chemical, bacteriological, physical properties, and radioactivity. Even though many laboratories certified by the various programs are oriented toward routine water testing for bacteriological or gross characteristics, the program fees are primarily based on chemical analyses. Often, this is because fees are calculated on a per category or per analyte basis, and numerous analytes are sought in most chemical testing.

Chemical analyses include the following generic characteristics (Figure 1):

- o Sample collection (which is generally not part of most approval processes),

- o Sample extraction/digestion,

- o Extract cleanup (if applicable), and
- o Analyte identification/detection and quantitation.

Although a generic scheme for chemical analyses is available and attempts are being made to standardize current analytical methodologies, the evaluation criteria for existing laboratory approval programs continue to differ. A result of this approval program survey is the description of a generic laboratory approval program. It is noted that the basic objectives of an approval program can be achieved by various means, and it is not essential for all aspects of laboratory approval programs to have exactly the same elements or to be implemented in exactly the same way.

Figure 2 summarizes the elements and relationships involved in a chemical analysis. If the elements are in place and are being performed appropriately, the analysis theoretically should meet its intended objective(s). Quality assurance and quality control are elements of laboratory approval processes that (1) encourage the proper execution of the test protocol, (2) provide documentation that the tests were properly conducted, and (3) allow elimination of tests that either were not conducted properly or were not documented properly. Most QA programs have a built-in redundancy at least between implicit and explicit elements of QA, and often redundancy exists among the explicit elements of QA themselves. This redundancy normally includes overlap both in the information gathered by entirely different elements of the program and in simple repetition of the same elements.

IMPLICIT AND EXPLICIT ELEMENTS OF QUALITY ASSURANCE

If a quality assurance program certifies that all of the essential elements of a chemical analysis are present and functioning, there is implicit assurance that the results will be correct. Implicit elements of quality assurance include personnel and organization, facilities, equipment, methodologies, time, sample type (within scope of method), and results (reporting standards). If all implicit elements of quality assurance are present, the test should conform to quality standards. However, few organizations are willing to accept the implicit elements alone. Because most testing is conducted for profit and/or regulatory purposes and not for research, the testing must stand on its own and must be completely documented. These needs can be partially met by implementing implicit procedures. However, experience has shown that explicit quality control actions are generally more effective.

The explicit elements of quality assurance generally consist of the procedures the laboratory considers to be quality

control. These elements include sample control, tests for background contamination, tests for detection limits, tests for false positives, determination of quantitative accuracy, and determination of quantitative precision.

The implicit and explicit elements of quality assurance may be integrated in a variety of ways to produce workable quality assurance programs. The efficiency (i.e., cost) of each program will be determined by the way the elements are implemented, the standards that are set, and the degree of documentation that is required. Because various testing programs have different needs and objectives, no single quality assurance program will be most efficient for all cases.

The types of quality assurance activities presented in Figure 3 are typical of many programs. The activities are often an integration of some implicit and explicit elements of quality assurance. The activity may in some cases be applied in a redundant fashion to ensure continuity in a program. Likewise, some activities may overlap with subparts of other activities providing partial redundancy.

Three obvious levels of potential redundancy may be identified in the quality assurance/control procedures shown in Figure 3. Implicit quality assurance tends to provide a "safety net" ensuring that the tests are in competent, responsible hands. When other elements break down or provide ambiguous results, the existence of the implicit level of quality assurance can give confidence that the system can be made to work or was working despite inadequate documentation.

Typical elements included in an integrated program are personnel approval; organizational approval; facilities and equipment approval; method approval; time approval; sample control; use of blanks, spikes, and duplicates; calibration control charts; performance evaluation samples; onsite audits; and documentation. These elements provide a basis for comparison of QA programs. They are useful to evaluate the general coverage and emphasis of various programs, but we have not been able to provide a quantitative comparison of laboratory approval QA programs. The programs are too diverse to allow simple comparisons.

For example, with respect to personnel qualifications, one program may require that the laboratory director have a Ph.D. degree and may have no requirements for the instrument operators. Another program may not have any requirements for the laboratory director but may require that each laboratory technician have a B.S. degree and 2 years of experience. We believe that it is not realistic to apply quantitative standards to compare the two programs on this basis, and that no one can realistically claim that one program is "better" than the other

on this basis. We believe that both programs demonstrate concern about the knowledge of the personnel performing the analyses and that either program may produce correct results.

As a corollary, we believe it would be unrealistic to escalate the standards for a program beyond the level normally expected to be sufficient just to increase the rigor of the program. For example, a requirement that all the workers in a laboratory have Ph.D. degrees to conduct routine analyses is not cost effective.

Thus, we have not be able to create a yardstick to measure entire programs quantitatively, and we do not believe that a strict ranking of programs would be particularly informative. Nonetheless, some narrow aspects of programs can be addressed quantitatively in terms of rigor, difficulty, scope, number, frequency, etc. We do not advocate translating these terms into assessments that a program is "good" or "bad," but it is fair to point out that some QA programs have exceptionally strong/weak requirements in various areas.

With this discussion in mind, we have prepared a summary chart (Table 1) that summarizes some of the most prominent, widely used programs. Because most states have assumed primacy in implementing the Safe Drinking Water Act and the National Interim Primary Drinking Water Regulations, the Clean Water Act, and the National Pollution Discharge Elimination System, the EPA Drinking Water Programs have not been included in Table 1. When a state assumes primacy, it usually codifies the national program, with minor variations, into state law.

SUMMARY

Appropriate quality assurance programs are essential to the implementation and enforcement of State and Federal regulatory programs. Commercial interstate laboratories are subject to the laws, rules, and contract requirements of numerous State and Federal programs. It is clear that many of these programs address the same analytes, methods, subcategories, or categories of analyses. It is feasible from a technical standpoint and desirable from a cost standpoint to eliminate all unnecessary redundancies in QA programs. We are currently examining all major programs in depth to create a master matrix that would cover the entire scope of each program. From this matrix, the most important elements of each program will be identified. By using the implicit and explicit elements of a quality assurance program as a guide and combining them with the appropriate Federal and State program requirements, a technical basis for a national laboratory accreditation program will be established.

NOTE:

Although the Contract Laboratory Program is not a true environmental laboratory certification program, its rigorous QA program merits inclusion in this study.

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FIGURE 1.

GENERIC METHOD SUMMARY

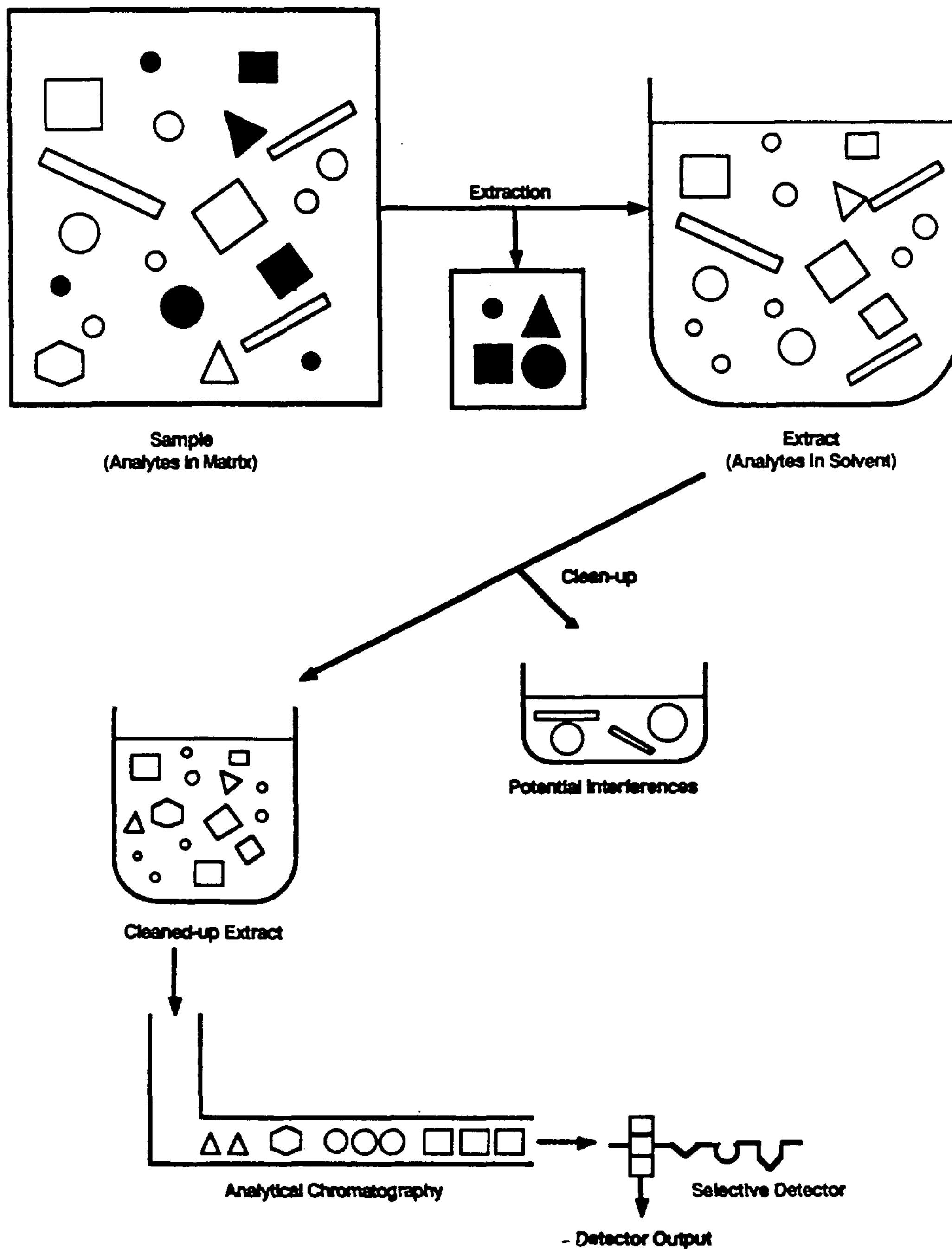

FIGURE 2.

ELEMENTS OF ANALYSES

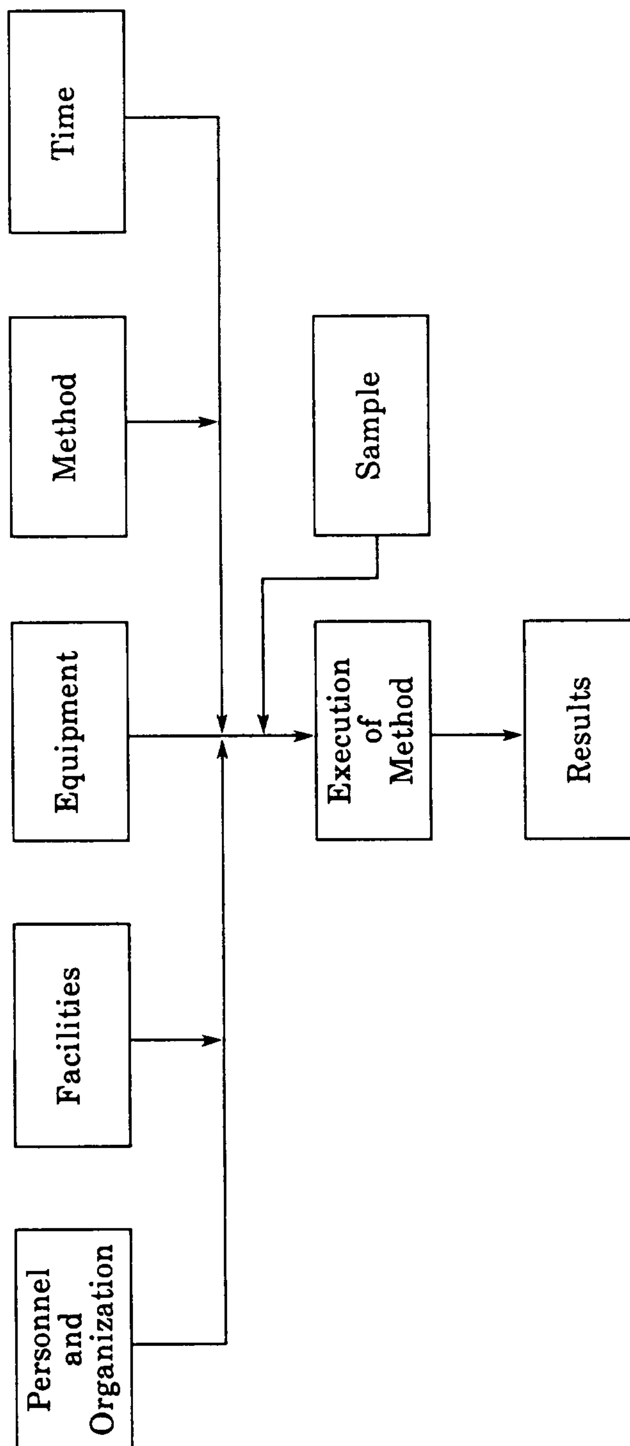

FIGURE 3.

LEVELS OF QUALITY ASSURANCE

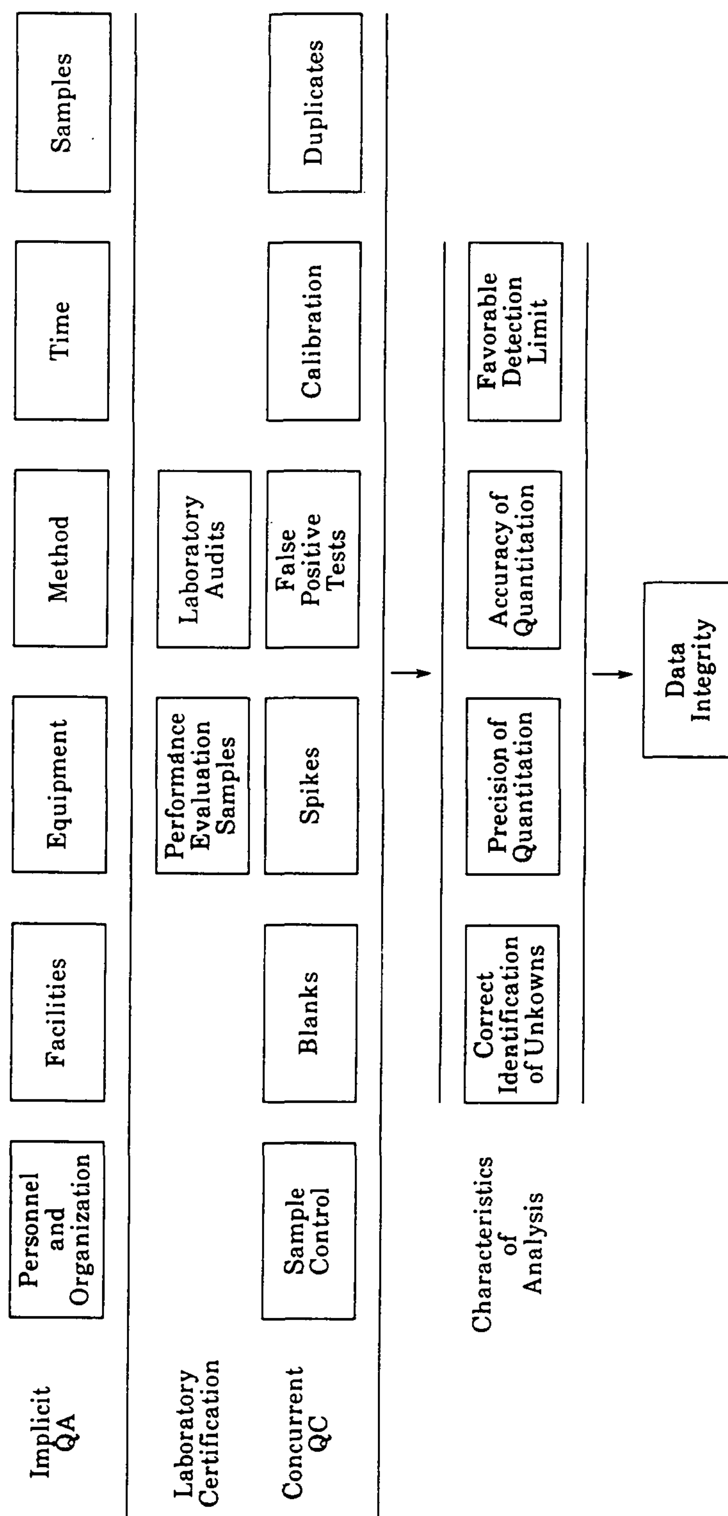

TABLE 1.
SUMMARY COMPARISON OF QUALITY ASSURANCE PROGRAMS[a]

Item	Implementation	CLP[b]	USATHAMA	EMSL/state NJ	EMSL/state WI	EMSL/state FL	NY	CA
Personnel approval	Resume review	+	0	+	0	+	+	+
	Training record review	+	0	0	0	+	+	+
Organizational approval	Review of organization chart	0	0	0	0	+	0	0
	Review of QA plan	+	0	?	?	+	+	+
	Review of QA policy statement	+	0	0	0	0	+	0
	Review of SOP	+	+	?	?	+	+	+
Facilities approval	Inspection of building and laboratories	+	+	+	+	+	+	+
	Review of floor plans	+	+	+	+	+	+	+
	Location	0	0	0	0	0	+	0
Equipment approval	Inspection of equipment	+	+	+	+	+	+	+
	Review of manufacturer's specifications	+	+	+	+	+	+	+
	Review of maintenance and calibration records	+	+	+	+	+	+	+
Method approval	Review of results of new method	0	+	0	+	0	0	0
	Review of recognized method	+	+	+	+	+	+	+
Time approval	Inspection of workload	0	0	0	0	0	0	0
	Review of productivity reports	0	0	0	0	0	0	0
	Review of laboratory staff	+	0	0	0	0	+	0
Sample control	Audit of sample logs	+	+	+	+	+	+	+
	Inspect sample flow	+	+	+	+	+	+	+
	Audit chain of custody logs/tags	+	+	+	+	+	+	+

TABLE 1.
(continued)

Item	Implementation	CLP[b]	USATHAMA	EMSL/state NJ	EMSL/state WI	EMSL/state FL	NY	CA
Blanks	Audit blank results	+	+	0	0	0	+	0
Spikes (including PE samples)	Audit analytical results for actual matrix spike	*	+ (No PE)	+	+	+	+	+
	Audit analytical results for standard matrix spike (or PE sample)	*	+ (No PE)	+	+	+	+	+
False positive test	Audit analytical results	+	0	0	0	0	0	?
Calibration	Compare analytical result to known value	+	+	+	+	+	+	+
Duplicates	Compare results for two or more identical samples	+	+	+	+	+	+	+
Documentation	Laboratory notebook inspection	+	+	+	+	+	+	+
	Sample log inspection	*	+	+	+	+	+	+
	Computerized data base inspection	*	+	0	0	0	0	0
	Chromatogram and spectrum file inspection	*	0	0	0	0	0	0

[a]0 = Not addressed by program
+ = Basic requirements, standards, etc.
* = Special rigor in requirements

Each QA program is identified by an abbreviation as follows:

Abbreviation	Program
ELAP	NY Environmental Laboratory Approval Program
CLP	U.S. EPA Contract Laboratory Program
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency Program
EMSL/state	U.S. EPA PE samples with state program (e.g., FL, WI, NJ)
CA	California Program
NY	New York Environmental Laboratory Approval Program

[b]Although the CLP is not an actual laboratory certification program, its rigorous quality assurance criteria merit inclusion in the discussion of QA/QC practices.

QUALITY CONTROL IN FIELD SAMPLING METHODS

Karen N. Kontopanos, Senior Staff Geologist, Geoenvironmental Services, Virginia Geotechnical Services, P.C., 8211 Hermitage Road, Richmond, Virginia 23228; Eileen Sullivan Williams, Environmental Program Analyst, Division of Special Programs, Virginia Department of Waste Management, 18th Floor Monroe Building, 101 North 14th Street, Richmond, Virginia 23219.

ABSTRACT

Maintaining quality control in field sampling involves preparation in three stages: 1) Pre-sampling preparation of sampling and safety plans, sampling equipment and sampling containers; 2) On-site collection of site specific and quality control samples; 3) Post sampling preparation of laboratory and chain-of-custody forms as well as preparation of samples for shipment.

Sampling begins with the development of site sampling and safety plans. The sampling plan is used to determine the location, type and number of samples to be collected. The safety plan is used to establish levels of protection required for specific activities and any other emergency information necessary. Once these determinations are made, field equipment (which includes both sampling supplies and personal protective clothing) can be prepared. For each sample collected, a lab specified volume of aqueous or solid material must be supplied to ensure an adequate volume of sample for analysis. Samples are collected in specified types of jars so that the container itself does not influence sample results. When packing sampling equipment, care is given to each item so that samples will not be contaminated with off-site material.

On the site, the sampling plan may be adjusted to reflect field conditions. Quality control samples are collected to assure reliable analytical results. These quality control samples include: a trip blank, used to determine previously existing container or deionized water contamination and contamination which may result from transport or site activities; a field blank, used to determine previously existing container contamination and contamination which may result from ambient on-site conditions; an equipment blank, used to determine previously existing equipment contamination; a matrix spike/matrix spike duplicate sample, used by the laboratory to determine spike recoveries for analysis of matrix effects and laboratory data accuracy; unidentified ("blind") duplicate samples, used to check laboratory

precision; and background samples, used for comparison when determining the type and amount of contamination present. Quality control begins with the sampling event. Preserve aqueous inorganic samples in the field. Decontaminate all field equipment to prevent cross-contamination of samples collected.

After sampling, complete all required laboratory forms. Maintain chain-of-custody on samples at all times. Pack jars in individual plastic bags to reduce cross-contamination if breakage occurs. Wrap jars individually with bubble plastic and place in coolers with ice for shipment. Ship samples for overnight delivery.

INTRODUCTION

Sampling methods and techniques included in this paper are based on sampling protocols for Pre-Remedial Site Investigations in the Superfund Program. The methods and techniques discussed are intentionally biased toward identifying releases of hazardous substances from a facility rather than general site characterization or definition of off-site sources. As a result samples should be representative of on-site contamination and of contaminant migration pathways rather than the site as a whole. To maintain quality control in field sampling methods any team performing sampling should have written Standard Operating Procedures included in a Field Procedures Guide. These procedures should be followed consistently by all field personnel to assure quality control in field operations, uniformity between different field personnel, and a means to trace possible causes of error in analytical results. There are presently numerous accepted methods for collecting environmental samples. The American Society for Testing Materials (ASTM), Association of Official Analytical Chemists (AOAC), American Conference of Governmental Industrial Hygienists (ACGIH) and the National Bureau of Standards (NBS) (Cheremisinoff, 1987), and the Environmental Protection Agency (EPA) are a few of the organizations which specify field sampling methods.

Quality control in field sampling involves three stages of sampling preparation. Pre-sampling preparation includes the preparation of site specific sampling and safety plans and the organization of sampling equipment. On-site activities include the collection of site specific and quality control samples. Post-sampling activities include the preparation of laboratory and chain-of-custody forms as well as the preparation of samples for shipment to the laboratory.

PRE-SAMPLING PREPARATION

Pre-sampling preparation begins with the assignment of a site specific project officer. The project officer is responsible for all activities associated with the site to be sampled. The project officer establishes a sampling team based on number and expertise of team members needed to efficiently and safely sample the site. Sampling begins with the development of a site specific sampling plan. The site should have been visited by at least one member of the sampling team, preferably the project officer, prior to writing a sampling plan. Otherwise, time should be allotted for a pre-sampling site reconnaissance to aid in the selection of appropriate sampling locations. The sampling plan is used to determine the location, type and number of samples to be collected and should include justification for each sample point selected. Sample matrices, locations and numbers should be selected so that the resulting data may be utilized in determining any hazard posed by the facility to human health and the environment. Sample locations should also be chosen so that the resulting data may be used to determine whether contamination found may be attributed to the site or to an off-site location. Data is primarily used to determine the types and concentrations of uncontrolled hazardous substances present at a facility.

After the sampling and safety plans have been written and prior to on-site activities, the project officer must hold a meeting for all personnel who will be involved in on-site activities. The purpose of the meeting is to establish team understanding of the site and the sampling plan as well as objectives of sampling and safety concerns. At the time of the meeting the sampling team will be divided into smaller subteams for specific on-site assignments. The project officer will establish a "clean" team member who will remain at the staging area and be responsible for all paper work and organization of sample containers and equipment.

Samples need to be collected from all areas and matrices of potential contamination if a site characterization is to be established. Known contaminated areas such as disposal areas or areas with a history of contamination or dumping should be sampled. Samples should be obtained from areas of visible contamination such as soil staining, leachate seeps and oil sheens. Drainage and/or runoff pathways may not be obvious but may provide routes of contaminant transport within the site boundaries or off-site, and should be sampled for surface water if available and sediment or soil. Locations of

potential contamination should be sampled, such as areas where odors are noted or areas of alleged dumping or contamination. Ground water wells within an area which may be influenced by the site both upgradient and downgradient should be sampled. These wells may include domestic, commercial, industrial or monitoring wells. Any affected or potentially affected surface waters should be sampled at an upstream location for background data, at any site discharge points or suspected discharge points, and downstream of the site so that a profile of the site's impact on surface waters can be obtained. Sediment samples should also be taken from surface water sample locations. Background samples need to be taken from undisturbed areas or areas not affected by the site.

On the site, the sampling plan may be adjusted according to field conditions. The sampling plan must be treated as a living document. If the sampling plan needs to be modified because of changed on-site conditions then the sampling plan should be considered flawed. Strict adherence to a flawed plan will not result in quality data. A flawed plan is not, however, a statement of failure for whoever was responsible for its development. On-site conditions may have changed since a previous site visit or additional visible contamination may be noted by sampling team members. These areas should be evaluated in the field for sampling potential. Drainage or runoff pathways which contained water may now be dry, or dry pathways may now contain water, surface water and/or sediment samples should be taken whenever possible from these locations. Streams may be flowing or dry; therefore the sampling team should be prepared to collect whatever sample media is available. Samples taken in surface water areas such as streams and drainageways should include both water and sediment when available. If either water or sediment is not available obtain a sample of whichever matrix (water or sediment) may be obtained in sufficient quantities for analytical needs. The sampling plan should include contingencies for collecting more samples than originally estimated.

If sampling conditions have changed dramatically and the site cannot be adequately sampled, the sampling event should be postponed until conditions are conducive to proper and appropriate sampling. If the sampling event is not postponed and samples are collected in conditions which do not meet sampling quality control criteria, analytical results may not be valid. In this case the site may need to be resampled at additional cost and time delay. Once samples have been collected subsequent analysis and data validation will typically take 3-4 months (6-8 months if using CLP through

EPA's Sample Management Office). If the validation procedure indicates resampling is necessary an additional delay of 4-6 weeks or more will be necessary for rescheduling. If the sampling event is postponed when on-site conditions are observed to be inappropriate for sampling, the delay will most likely be minimal (2-3 weeks). If sampling equipment is found to be inappropriate or grossly inefficient, sampling should be postponed until appropriate equipment is obtained for the proper collection of samples and protection of workers. Conditions which may hinder adequate sampling include: drought, flooding, extreme cold, extreme heat, and inappropriate sampling equipment. Drought precludes the collection of necessary surface water and leachate samples. Flooding may restrict access to important areas or may cause dilution of contaminated areas. Extreme cold may interfere with proper decontamination of equipment as well as cause hazardous conditions for workers. Extreme heat may cause heat stroke, heat stress and/or dehydration of workers, especially those suited in impermeable protective clothing.

Sampling equipment should be inventoried, collected and organized prior to arrival at the site to ensure that the appropriate types, sizes and numbers of equipment and supplies are available for the sampling event. Sampling equipment includes both sampling supplies and personal protective clothing. Basic laboratory information such as laboratory name and address and basic site information such as site name and case number should be completed on chain-of-custody forms and tracking forms before reaching the field. Completing basic information on forms helps improve time efficiency in the field and helps prevent the confusion that results when all information must be filled out at one time. These forms should be taken in the field during sampling and completed as the samples are collected.

Equipment should be packed so that exposure to potential off-site contamination from storage and transportation is avoided. Place supplies, such as bailers, reels and tape measures, in clean plastic bags for storage and transport to prevent contamination. Other equipment, such as filters for inorganic samples and pH and conductivity meters, should be stored in their respective cleaned containers.

Packing sample jars in the coolers in which they will be shipped enables the project officer to estimate cooler needs for shipping after sampling and helps prevent breakage. Jars should be wrapped in bubble plastic for protection. Quantities of sample jars taken into the field should be based on the sampling plan and should include containers for quality

control samples such as matrix spike and blanks. Additional sample jars should be taken in the field to replace any broken jars or in the event additional samples need to be collected based on sampling plan contingencies. Jar lids should be checked to see they are securely tightened prior to storage and transport. Containers should always be stored in a clean environment.

For each sample collected, a specified quantity of aqueous or solid material must be supplied to the laboratory. The project officer should verify the quantities and sample container requirements with the laboratory. When using EPA's Contract Laboratory Program (CLP), quantities are specified by the Program (See User's Guide to the CLP). Samples should also be collected in specified types of jars to ensure an adequate volume of sample and to minimize the potential for interferences from the container.

Use of proper sampling containers is important for quality control. Low-level environmental samples should be collected in the following types of sample containers. Samples collected for volatile organic analysis (VOAs) should be taken in 40 ml glass vials with teflon-lined silicon septa and black phenolic caps. Volatile organic compounds may adsorb onto the surface of a plastic container (Cheremisinoff, 1987) and/or plastics may contain volatile organic constituents which may leach into the sample. Several VOA vials for each sample should be collected in the event that one is broken or contains air space not observed in the field. Base neutral acid extractable, pesticide and polychlorinated biphenyl (BNA/Pest/PCB) samples should be taken in amber glass jars with teflon-lined black phenolic caps to lessen photodegradation. Phthalates may be leached from a plastic container into BNA samples. Inorganic soil samples should be taken in borosilicate glass jars and inorganic aqueous samples should be taken in polyethylene jars to prevent leaching of metals, such as lead from amber glass, from the sample container. Samples collected with inappropriate types of containers or in insufficient volume cannot produce high quality analytical results.

ON-SITE ACTIVITIES

The first priority after arrival at the site is establishing a staging area upwind of the facility in an uncontaminated area. Sampling team members should don protective equipment if required and set up sampling equipment and a decontamination line.

Reusable equipment such as tape measures, tools, bailers, and filters should be carefully decontaminated before and after use. Sampling equipment should be decontaminated immediately before being used for sampling. Decontamination of reusable sampling equipment is performed before each sample to prevent cross-contamination of samples collected. Equipment should be decontaminated using clean gloves and finally rinsed with distilled and/or deionized water. Personal protective equipment should be kept clean and decontaminated when necessary or at the end of a sampling day. Personal protective equipment such as outer gloves cannot be successfully cleaned and must be changed between samples to avoid cross-contamination of samples. Equipment used and purchased for use should be made from easily decontaminated materials (such as teflon and stainless steel), without grooves or crevices and should not contain materials (such as wood or leather) that may easily absorb contaminants. In some cases disposable equipment affords higher quality control in sampling situations where adequate decontamination may be difficult or impossible to achieve. Use biodegradable cleaners (Liquinox) which are easy to rinse and contain no phosphates.

Bound field books with numbered pages are utilized during field activities to record samples taken, sample times, locations, description of samples, and any other pertinent information or unusual circumstance encountered (such as "dog stepped in sample") during sampling or field activities. Field book entries should each be signed and dated by the person making the entry. Field books become an integral part of the permanent project records. Unbound, unsigned log books are generally not admissable as evidence in court. Field book documentation is critical. Good field notes can be used at any time to reconstruct a precise sequence of events which occurred during sampling. Poor field notes do not contain information needed to resolve apparent aberrant analytical results.

All samples including quality control samples, should be collected with clean gloves and in clean jars. Jars should be handled carefully to prevent on-site contamination. Jar lids must be kept clean at all times during sample collection and must not come in contact with any potentially contaminated surfaces. One member of the sampling team should hold the jar lid while another collects the sample whenever possible. Jar lids cannot be effectively decontaminated in the field and should generally be replaced if they are inadvertently dropped or otherwise contaminated. Any incidents which may compromise the integrity of the sample must be noted in the Field Book.

This information can then be used during data analysis for evaluation of the causes of unanticipated analytical results.

Samples should be collected in order of decreasing volatilization. During sampling all sample jars should be labeled with site name, sample location, time, analysis to be performed and preservative, if any. Conductivity and pH readings should be taken for all aqueous samples. Readings and measurement times should be accurately recorded in the Field Book. All aqueous inorganic samples, including quality control samples, are preserved in the field to keep analytes in solution. Aqueous inorganic samples are preserved with nitric acid to a pH below 2. Aqueous cyanide samples are preserved with sodium hydroxide to a pH above 12. Jars provided by laboratories with preservatives already added are dangerous in unknown sampling situations. The preservatives may react violently with sample constituents, overfilling of acidified jars can expose personnel to concentrated acid, and sample jar breakage in transit can contaminate the other jars and shipping containers. Pre-preserved containers cannot be relied upon to meet the preservation goal and may need additional preservative in the field. Some naturally buffered samples require considerably more preservative than the standard "cookbook" amounts. After addition of standard preservative amounts the pH of an aqueous inorganic samples must be verified with field measurements and adjusted if not at the required pH. If preserving more than one sample at a time avoid cross contamination by decontaminating the pH and conductivity probes between each sample. If a pipet is used to transfer preservative from the stock solution to the sample jar, do not to allow the pipet to contact the sample container or sample. If contact occurs decontaminate the pipet or dispose of it and use a clean pipet to avoid cross-contamination of samples during preservation and to avoid contamination of the stock preservative solution.

Sample jars are typically laboratory cleaned in designated lots. Requesting and using jars from a minimum number of lots will minimize potential for undetected container contamination effects on the samples. The cleanliness of jars from one lot can be characterized more readily than the cleanliness of jars from many different lots. Whenever possible samples should be taken in jars cleaned in the same lot or obtained from the same lab to ensure applicability of blank data. To maintain consistency in blank data deionized water from one source must be used for all blanks.

Quality control samples are collected with the same sampling protocols as target samples to aid in the evaluation of analytical results and in the evaluation of field methods.

Trip blanks are used to determine previously existing container and/or deionized water contamination or any contamination which may have occurred during transport. Trip blanks are prefilled sample jars carried into the field. These blanks remain unopened and are sent to the laboratory after the sampling event along with the samples. Trip blanks should be supplied by the laboratory, if the laboratory is supplying deionized water for the blanks and the sample jars. If jars are supplied separately from the water, trip blanks should be prepared by the sampling team prior to leaving the office.

Field blanks are used to determine previously existing container contamination and/or contamination which may have resulted from existing field conditions when the samples were actually collected. These samples are taken in the field. Deionized water is poured while on-site from the initial containers into sample jars. The field blank should be collected, preserved and labeled as an aqueous sample.

Equipment blanks are used to determine previously existing equipment contamination and/or contamination which may have resulted from existing field conditions when the samples were actually taken. These blanks should be taken after the equipment has been decontaminated on-site in order to closely match conditions of actual sample collection. Deionized water should be poured through or over any equipment which may come in contact with the samples. For example, when sampling monitoring wells with a bailer, an equipment blank should be taken by pouring deionized water into the bailer and then into the jars for organic and inorganic samples, and should be poured into the bailer and then into the filter and filtered for filtered inorganic sample blanks.

Duplicate samples are used to check laboratory precision and should not be identified to the laboratory as a duplicate. Duplicate samples normally require one extra volume of sample. They should be taken in an area of suspected or known contamination and given a unique sample number. Duplicate samples must be collected at the same time, from exactly the same location, using the same sampling equipment. These samples should be collected by first collecting VOAs for both the sample and the duplicate, collecting the BNA/Pest/PCB aliquots for the sample and the duplicate, and finally by collecting the inorganic portions for both the sample and the

duplicate. By collecting the samples in the above manner the sample and duplicate are as similar as possible. Variability is expected in duplicate samples due to nonhomogeneous sample media and laboratory techniques.

Matrix spike samples are used by the laboratory to determine the effects of the sample matrix on the accuracy of analytical results. Matrix spike samples typically require 2 to 3 additional volumes of sample. For best analytical results, an uncontaminated background location is required. Matrix spike percent recoveries are used to judge the accuracy of sample results only if the indigenous sample levels are low enough so that they do not interfere with spike recovery results. Additional volumes should be collected for all matrices sampled.

Background samples are collected for all matrices sampled to determine those parameters indigenous to the area. They are then used for comparative purposes when determining the type, amount and extent of contamination present and attributable to the site. In order to attribute contamination to the site, background samples need to be collected from undisturbed areas but should include off-site influences. Avoid taking background samples near railroads and fence lines, roadways and driveways, near telephone poles or in active areas of the site if possible. Railroad right-of-ways and fencelines may be treated with herbicides; roadways and driveways may have above background levels of lead and petroleum hydrocarbons; and treated telephone poles may leach preservatives such as CCA, pentachlorophenol, creosote or polynuclear aromatic hydrocarbons; transformers mounted on electrical poles may provide a source of PCB contamination in "background" samples.

Site specific sample collecting methods and techniques are based on sampling protocols for Pre-Remedial Site Investigations in the Superfund Program. The methods and techniques discussed are intentionally biased toward identifying releases of hazardous substances from a facility. As a result samples should be representative of on-site contamination and of contaminant migration pathways rather than the site as a whole.

Ground water samples may be taken from domestic, commercial, industrial or monitoring wells. Information should be collected and recorded in the Field Book on each of the wells indicating well age, well depth, depth to ground water, well construction data, location, any odor or color, existence and size of in-line pressure tanks, existence and type of in-line water treatment, well driller, knowledge of

taste/odor/corrosion problems in the area, type and age of piping, past land uses in the area, existence of any other wells, buried tanks, or former buried tanks, location of nearby septic system, and flow rate. Select a faucet for sampling in as direct a line to the well as possible in order to obtain a sample most characteristic of ground water without loss of VOAs or addition of materials such as lead from pipes. Do not choose a faucet following any type of water treatment. Domestic wells should be purged for approximately five minutes or long enough to drain the pressure tank and piping, whichever is shortest. Purging is used to achieve fresh water flow from the aquifer into the well for sampling. Do not completely cut off water flow until all samples have been taken to prevent water standing in pipes and potentially losing VOAs and adding materials which may be in the pipes or solder, such as lead. VOA samples should be obtained from non-turbulent flow in order to minimize volatilization of VOA constituents.

Monitoring well samples should be taken after three volumes of water have been removed from the well or until fresh ground water movement from the aquifer is confirmed by consistent pH and conductivity readings. Monitoring well depth, diameter, screened interval, depth to water and any other pertinent information should be recorded in the Field Book. EPA requires monitoring well inorganic samples to be filtered for analysis of dissolved metals. Unfiltered and filtered inorganic samples may be taken for analysis of total and dissolved metals.

Any affected or potentially affected surface waters should be sampled at an upstream location for background data, at any site discharge points or suspected discharge points, and downstream of the site. Downstream samples should be obtained first. If initial samples are collected upstream, the disturbance created by the upstream sample collection may affect the downstream samples. Channel depth, width, configuration, and flow should be recorded in the Field Book, along with color, odor, any sheen or organic material noted. Stream channel information will provide insight into analytical results. Samples taken along the edges of a stream where flow is substantially slower and less turbulent than in midstream may contain higher levels of VOAs. If several streams are to be sampled, a background sample should be obtained for each stream. In some cases a site may be located at or on the origin of a stream. In this case a background sample may be obtained from a nearby stream after careful consideration of effectiveness of this type of background sample based on any other influences on the potential

background location. All surface water samples should be taken upstream of where the sampler is standing to avoid any influence from the sampler disturbing the stream bed. The mouth of the sample container should be oriented so that it faces upstream during sample collection.

Sediment samples should be taken at all surface water sample locations if possible. Sediment samples will indicate whether contaminants are concentrating along stream bottoms, creating hot spots which may have high concentrations of heavy metals, pesticides, or low solubility heavy organic matter. Sediment VOA samples should be obtained with as little disturbance of the sediments as possible. A description of the sediments, odor and color should be recorded along with other sediment sample data in the Field Book. Sediment samples should be collected following aqueous samples at the same location because the sediment sampling process suspends particulates in the water column which could influence aqueous sample analytical results.

Surface or subsurface soil samples may be taken depending on site conditions. Surface soil samples should be taken after vegetation has been cleared. Stainless steel or disposable plastic scoops may be utilized. Subsurface soil samples are generally obtained using a decontaminated steel hand auger. Obtain subsurface soil samples from obviously contaminated zones. Record in the Field Book soil descriptions, depth of sample, color, consistency, identifiable constituents, moisture content, odors, stained intervals and any other relevant information.

POST-SAMPLING ACTIVITIES

All samples should be returned to the staging area after collection to be prepared for shipment. Sample jars should be decontaminated if necessary and handled with clean gloves. All sample jars should be checked for complete label information and Field Books should be checked for complete information and any information which may not be available once the samples are shipped. All samples must be preserved as required as soon as possible after returning to the staging area.

After sampling, all laboratory, tracking and chain-of-custody forms must be completed. Completing information on chain-of-custody and tracking forms for specific samples as the samples are returned to the staging area prevents confusion and minimizes the chance of losing data or incorrectly recording data. The team member in charge should check and

verify sample information recorded on sample jars before they are packed in the coolers.

Chain-of-custody is maintained by constant surveillance of samples at all times. Jars are packed in individual plastic bags and wrapped in bubble plastic to prevent breakage and reduce cross contamination if breakage occurs. The sample jars are placed in coolers with ice in ziplock bags to prevent water standing in the cooler which may contaminate samples or cause labels to become illegible. Blue ice is inconvenient to use unless a freezer is available. All samples must be maintained at a maximum temperature of 4°C. Jars are packed in the coolers with styrofoam packing material. Packaging of samples is very important because proper packaging prevents: cross-contamination of samples, contamination of coolers and/or shipping facilities, and prevents the sampling team from having to recollect any broken samples. The shipping container (cooler) is sealed with signed chain-of-custody seals to prevent tampering and shipped for overnight delivery with constant surveillance to maintain chain-of-custody. Samples are preferably shipped on the same day as they were collected to aid the laboratory in meeting holding times.

SUMMARY

Pre-sampling preparation of a well designed, flexible sampling plan is crucial to collection of quality samples. The sampling plan must be flexible to allow for changed conditions and the exercise of some professional judgement in the field. Proper organization of field equipment during this phase will lead to a cost effective and efficient sampling event.

During on-site activities consistent field procedures must be used by all members of the sampling team. Complete documentation of all activities carried out during sampling is a critical element of quality control. Proper documentation can be used to resolve many subsequent questions concerning analytical results and help evaluate the overall quality of the project.

Laboratory, tracking and chain-of-custody forms must be properly completed as the samples are collected to avoid confusion and lost information. Proper packing of samples will minimize the risk of breakage and cross-contamination during shipment. Properly packaged samples will arrive safely at the laboratory and provide a successful completion of the sampling event.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to W. Jerrold Samford, Geoenvironmental Manager, Virginia Geotechnical Services, without whose patient review and great suggestions this paper would never have been finished in time - Thanks.

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QUALITY ASSURANCE AS VIEWED BY A DATA USER

Richard D. Brown, Lead Scientist, System Planning and Analysis Department, and David E. Egan and George Marinenko, Members of the Technical Staff, Hazardous Waste Systems Department, Energy, Resource and Environmental Systems Division, The MITRE Corporation, McLean, Virginia 22102-3481

ABSTRACT

Although considerable attention is given to the concept of quality assurance during the sample collection, laboratory analysis, and data confirmation stages associated with the production of environmental data, few quality assurance concepts have been incorporated into the use of such data in decision-making. This paper presents information feedback from individuals involved in using environmental data for the purpose of evaluating uncontrolled hazardous waste sites. The paper discusses the principles of quality assurance when using data for evaluation purposes. The few data left for decision-making after data winnowing, possible use of qualified data, the need for awareness of background variability, and the dependence on thorough documentation are discussed. A case example is provided.

INTRODUCTION

After environmental field and laboratory data are produced, reviewed, and submitted for use in decision-making, certain elements critical to the outcome of the data evaluation are often overlooked in terms of importance placed on thoroughness and discipline. These elements include an understanding of the "softness" or "hardness" of the values with respect to quantitation, uncertainty introduced during sample collection, representativeness of actual site and background conditions in light of natural variability, the context in which the samples were collected, and the history of the site and surrounding properties. Attention to these elements is crucial in evaluating hazardous waste sites where the evaluation of results from initial screening studies can determine whether hundreds of thousands of dollars will or will not be spent to identify the extent of environmental contamination and possible remedial actions. The designation of a site as warranting further study could adversely affect bond ratings of local communities, financial status of site owners, real estate values, and emotional stress on individuals living nearby. Yet, further study and corrective actions (if needed) could substantially diminish a level of threat to human health and the environment.

Characteristic of screening surveys is the fact that the amount of information to be collected must be balanced against the cost and time required to obtain that information. When thousands of sites, such as uncontrolled hazardous waste (Superfund) sites, must be evaluated, it is financially and logistically prohibitive to examine each by means of a detailed and comprehensive risk assessment in a timely manner. A

model has been developed to screen such potential sites (1). Should the screening process indicate that a remedial investigation ought to be undertaken, subsequent remedial corrective actions may not be implemented if the detailed investigation discloses the hazard to be less significant than originally thought. Thus, quality assurance, as a concept, is highly important in environmental evaluations which screen sites in relation to their potential hazard.

QUALITY ASSURANCE

Monitoring efforts are expended needlessly if the data obtained are of poor or unknown quality. Most analytical data, especially those produced under the U.S. Environmental Protection Agency's Contract Laboratory Program (CLP) are well documented and are of known quality. However, beyond the analytical laboratory, not the quality, but the usefulness, of data is affected by nearly every step in the process of setting up and implementing a sampling program, the transport and storage of samples, chain of custody documentation, the planning and executing of a program to maintain data archives, and the evaluation of the data.

From the viewpoint of a data user, one asks "What makes me think the data are reliable?" and "How reliable are they?" These questions are germane to decision-making, no matter how sophisticated or precise is the sampling or measurement protocol. The data user looks at all aspects of quality, especially the representativeness of the data, not only the level of quality control exercised in analysis. For example, one asks "How quantitative are the values; i.e., are they above the Limit of Quantitation?", "Were the soil samples collected from the same soil horizon?", and "How do I know that the background samples account for natural variability?"

Quality assurance with respect to decision-making translates into the deliberate and disciplined comparison of information. Just because one value produced by an analytical laboratory is higher than another doesn't mean that the two values are significantly different. A data user cannot take data on their face value. A data user must have an awareness and understanding of the precision of a laboratory's analytical method, the accuracy of data, representativeness of samples, comparability of data, etc. This self-disciplined approach to data evaluation is a responsibility of a data user and embodies the concepts and philosophy inherent in quality assurance.

DATA REDUCTION

As many as a thousand values can be produced from a one or two day preliminary site investigation, including various blanks, duplicate samples, spike samples, and organic (volatile, semivolatile, pesticide) and inorganic, air, surface water, ground water, sediment, and soil samples. Often, when evaluating the threat posed by a site to human health and the environment, the most desirable data were not obtained.

Therefore, many sets of data do not exist for comparison of natural background levels to equivalent data associated with the site. And, many data which are available are not pertinent for such comparison (e.g., acidity, alkalinity, BOD, cloride, COD, dissolved oxygen, hardness, oil and grease, turbidity, etc.; Figure 1). Frequently, data are not useful for quantitative comparison because they were obtained under conditions not conforming to quality control criteria, resulting in the values being estimates rather than connoting a high level of certainty. Some data are not suitable because the contaminants, represented by the data, cannot be attributed to disposal activities at the site. Comparisons of other data lack significant differences between background and site values. For a typical site, the ramification of such data winnowing is that only about one percent of data can be used to demonstrate that a site has released hazardous substances to the environment (Figure 1).

QUALIFIED DATA

Data qualifiers are used to properly define analytical results. Often they accompany data in the form of codes, specific flags, and footnotes. They usually indicate when a value is not reliable for a variety of reasons or that a value is unknown but is less than or greater than the detection limit. Data qualification signals that quality control criteria probably were not attained, most often because excessive sample dilution was required, sample holding times were exceeded, spike recoveries were outside of limits (e.g., 75 to 125 percent), calibrations were outside of control limits, or unacceptable blank contamination was present. When data are accompanied by such qualifiers, they usually are considered to be estimated values, inferring a lack of certainty in quantification. While such data are estimates (i.e., lacking a high level of credibility and may not be defensible during litigation), they are useful in understanding the overall pattern of environmental contamination around a site. If, under certain circumstances, qualified data could be used for decision-making, the decision-making process would be enhanced dramatically. The case example, contained in this paper, examines this issue.

A laboratory or method blank is used to detect bias resulting from inadvertent and often unavoidable contamination. The presence of blank contamination does not, by itself, serve as an indication of careless or inappropriate performance of analyses. Laboratories which process thousands of samples on a routine basis also use a multitude of solvents, cleaning solutions, reagents, and other chemicals. Although stringent housekeeping practices are employed, a certain level of background contamination within a laboratory is inevitable. When measurement accuracy focuses on the order of parts per billion, a seemingly trivial amount of condensate from laboratory air deposited on a glassware or sample surface can represent a substantial source of blank and sample contamination (Table 1). A key quality assurance goal to deal with laboratory contamination is to know and to continually monitor its level. When precision in its measurement can be

established and its pattern, level, and trend is characterized, it can become a known factor in analysis, in effect, enhancing the credibility of analytical results.

DOCUMENTATION

Documentation is essential to the process of decision-making. Frequently, the results of a site investigation are evaluated many months and sometimes many years (given time required for public review of prepared reports) after samples are collected. The office where the data are reviewed usually is far removed from the site or analytical laboratory. Many times, the individuals who collected the samples no longer are employed by the same company, cannot be located, or have forgotten details related to the site.

Detailed notes taken during the sampling process often are invaluable to the data user and can make the difference of whether or not site data can be interpreted in a particular way. For example, when a field technician bends down to collect a sample beside a dried-up waste disposal lagoon, it could be very important to have notes indicating whether the collected sample was a sediment sample or a soil sample and the basis for such a determination. Depending on the type of sample, different analytical procedures may be utilized and different conclusions may be drawn.

SOLID MATRIX REFERENCE MATERIALS

Analytical measurement invariably involves comparisons of quantities. In environmental sample analysis, measurement may involve comparing the magnitudes of signals from the samples of concern with signals obtained from the uncontaminated background samples. While these differences may readily be observable qualitatively, to quantify them requires a means for scaling these quantities. Generally, scaling involves calibration of the measurement system with known, preferably certified, standards which simulate, as closely as possible, the actual samples under investigation.

For calibration of systems used in the analysis of water samples, standard reference solutions can either be obtained commercially, or be carefully prepared in the laboratory. Water samples also can be "spiked" with the constituents of interest. In this latter method of calibration, the difference between the original magnitude of the signal and its magnitude after the spike addition is attributed to the spike value.

The above calibration techniques are possible because solutions easily can be made to be homogeneous, where every fraction of the solution is compositionally representative of the entire solution. Thus, solution reference materials provide measurement benchmarks for water analysis.

For analysis of solid and semisolid samples (soils, cores, sludges, heavy sediments, etc.) the problem of obtaining reference materials, containing known and certified concentrations of common contaminants, is more difficult. Furthermore, the introduction of a spike homogeneously throughout a solid matrix, even under ideal conditions, is more challenging. Therefore, judgments relating to the quality of solid sample analyses often are based on calibration of the measurement system using standard aqueous solutions. While in many cases this may be satisfactory, sometimes the attenuation of the signal is matrix dependent. Therefore, to simulate the conditions under which the signal from a solid sample is measured, the contaminant of interest in the reference material should be incorporated into the solid matrix in the same manner as it exists in the unknown sample.

To minimize possible measurement biases due to matrix effects, to facilitate the efforts of analysts, and to provide a tangible means for assuring the accuracy of analyses of solid samples, a spectrum of standard solid matrix reference materials is desirable. These reference materials should represent solid matrices commonly found at hazardous waste sites. If available, these solid reference materials should be incorporated into the quality assurance protocols for the appropriate analyses. This approach would not only provide the analyst with a better means for quality control in the measurement process but also would help improve reliance on analytical data from the standpoint of the data user.

BACKGROUND VARIABILITY

Having an awareness of, and a confidence gained from experience (i.e., "feeling"), for natural background variability is an essential attribute for the user of environmental data. Natural variability can account for many values. For example, surface soils in western states (e.g., Powder River Basin in southeast Montana and northeast Wyoming) contain lower levels of environmentally objectionable trace elements than do eastern states. However, the highest levels of arsenic, antimony, beryllium, cadmium, and selenium generally are in the West. Lead, mercury, and zinc levels are higher in several eastern states.

Background concentrations of contaminants in surface water and ground water concentrations can be misinterpreted without an awareness of natural background conditions. For example, in the West, excessive amounts of alkaline calcite and dolomite in overburden material, coupled with sulfides, result in high levels of dissolved solids in surface and ground waters. While higher pH values decrease the mobility of most metal species , they also enhance the transport of molybdenum, boron, arsenic, and selenium. This mobility of contaminants under alkaline conditions is not normally apparent to those accustomed to interpreting data relating to the transport of metals under the acid mine drainage or overburden drainage conditions often occurring in the East.

A data user also has to be mindful that the primary influence on soil composition is its parent material. Because in many locations the degree of variability in parent material is high, the degree of variability both between and also within soil types can be high. For given percolation patterns, variability influenced by lateral heterogeneity, horizon, and grain size can yield significant variability of chemical substances within a single soil type. The tendency of such variability to confound data interpretation can be minimized by restricting soil sampling to the same soil horizon.

CASE EXAMPLE

The following case example is presented to illustrate the considerations that typically arise in the interpretation of analytical data from an uncontrolled hazardous waste site. This case study, while based on the experiences of the authors, is fictional.

The example site consists of an abandoned warehouse in a relatively rural setting. The warehouse was formerly used for a solvent recovery operation where wastes were disposed in two on-site trenches (Figure 2). In addition, wastes from other small shops in the area were periodically accepted for disposal in the trenches. The surrounding land is undeveloped, except for an active gas station located across the street.

An initial site assessment was conducted to identify contaminants present in the disposal trenches and to determine whether contaminants had been released from the trenches into ground water. During the site assessment, three soil samples and three ground water samples were collected. The sampling locations are shown in Figure 2. The samples were transmitted to an analytical laboratory for analysis of inorganic substances and volatile and semivolatile organic substances. A report summarizing a quality control (QC) review of the data was transmitted with the reported values.

Excerpts of the QC review are as follows.

Water Samples:

- Methylene chloride was detected in the laboratory blank at 12 ug/l; all positive values were flagged with a "B" (blank contamination, reported value represents questionable detection)

- Samples for cyanide were analyzed 16 to 19 days after sample collection. Since the QC limit of 14 days was exceeded, all positive results for cyanide were qualified with a "J" (estimated value because QC criteria were not met)

- Carbon tetrachloride was detected in sample W-2 above the stated instrument detection limit. Because mass spectral matching criteria could not be met for this compound, the positive result was flagged

with an "M" (confirmatory analysis on same sample exceeded control limits, value considered semi-quantitative).

Soil Samples:

- Methylene chloride was detected in the laboratory blank at 27 ug/kg. All positive results for this compound were flagged with a "B".

- The spike recovery for arsenic in the laboratory control sample was 67 percent (outside the QC limits). Although arsenic was reanalyzed by the Method of Standard Addition (MSA), the results generated by MSA were outside the QC limits for linearity. Thus, all positive values for arsenic were flagged with a "J".

- Samples for cyanide were analyzed 16 to 19 days after sample collection. Since the QC limit of 14 days was exceeded, all positive results for cyanide were flagged with a "J".

- The Relative Percent Difference (RPD) for chromium in the duplicate sample S-3 exceeded the QC limit of 35 percent. All positive results for chromium were flagged with a "J".

- The Average Relative Response Factor (ARRF) for acetone in the initial calibration was 0.2455 (less than the QC limit of 0.300). All positive values for acetone were flagged with a "J".

- The percent difference seen in the continuing calibration for chloroethane was 28.83 percent (exceeding the QC limit of 25 percent). All positive values for chloroethane were flagged with a "J".

The reported values for selected substances are presented in Tables 2 and 3. Table 2 presents the results of the ground water sample analyses. Table 3 presents the results of the soil sample analyses. Soil samples S-2 and S-3 are compared with S-1 to identify substances disposed in the trenches. Similarly, ground water samples W-2 and W-3 are compared with W-1 (along with substances identified in the trenches) to determine whether substances from the trenches were released to ground water.

For the purposes of this example, data interpretation is based on the following premises. First, unqualified values are accepted as quantifiable concentrations. Second, a five-fold increase above background levels (or three times the detection limit if substance not detected in background) is indicative of environmental contamination. Third, qualified values generally are not used either because the values are not likely to be defensible during litigation or because the influence of the qualifier on the context and relevance of the reported value is not understood by the data user. (Note that under certain circumstances, discussed later in this paper, qualified data may be used cautiously to substantiate a release.)

Examination of the soil analyses shows that only the results for lead, carbon tetrachloride, and cadmium are not qualified. For lead, the concentrations in either S-2 or S-3 are less than five times the concentrations detected in S-1. Therefore, lead is not considered to be associated with the trenches. For carbon tetrachloride, none was detected in S-1, and concentrations in either S-2 or S-3 are not greater than three times the detection limit. Thus, carbon tetrachloride is not associated with the trenches. For cadmium, the concentrations both in S-2 and S-3 are greater than five times the concentration in S-1. Thus, cadmium is associated with the trenches.

The remaining concentrations of substances reported in the soil analyses were qualified, in general, signifying that the concentrations are estimates. Initially, the qualified data is reviewed to determine whether the data, without the qualifiers, indicates that substances are significantly higher in the trench samples. For example, chloroethane was not detected in S-1 but was estimated at less than three times the detection limit in both S-2 and S-3. Since these values do not meet the criteria for significance above background, chloroethane is not considered further. In contrast, the estimates for arsenic, chromium, cyanide, methylene chloride, and acetone appear to be significantly greater in either S-2 or S-3, but are not reliable for decision-making.

For arsenic, chromium, cyanide, methylene chloride, and acetone, the reasons for which the data were qualified must be examined to determine their impacts on the estimated values. For example, because the spike recovery for arsenic and the ARRF for acetone were lower than QC limits, the reported values for both substances are probably lower than the actual concentrations. However, the fact that actual concentrations were probably greater is not, by itself, useful for determining significance above a background. If it were possible to assign ranges to these estimated values, then the criteria for significance could be applied to the ranges. For example, because the field-collected duplicate samples varied by 50 percent (for chromium), the assumption is made that the reported values for chromium are estimates of plus or minus 50 percent. Using this assumption, it could be determined that chromium is significantly higher in S-3 than S-1. However, these ranges need to be assigned by the analyst or the QC data reviewer to assure that some minimum standards are met and followed. Because no ranges are provided for the qualified data, criteria for significance above background cannot be applied. Consequently, the qualified data is not used to identify substances in the trenches.

Examination of the ground water samples shows that the results for ethyl benzene, xylene, toluene, iron, and aluminum are not qualified. Further, reported values for all five substances indicate that concentrations in either of the downgradient samples, W-2 or W-3, are significantly higher than in the upgradient sample, W-1. However, ethyl benzene, xylene and toluene were not detected in the trench samples. Also, these substances are constituents of gasoline, and

there is a gas station located across the street in an upgradient direction from W-3. Consequently, for purposes of evaluating releases in this case example, these contaminants are considered to originate from other sources, such as the gasoline station. Similarly, iron and aluminum were not reported in the trench samples and therefore cannot be identified as site contaminants. Relatively low levels of iron and aluminum in natural waters may not be considered substances of concern when evaluating threats to human health. (Concentrations at which health threats occur are very high, such that other parameters like taste and color would minimize ingestion by humans before harmful levels are reached.) For both reasons stated above, iron and aluminum are not considered further.

Values are also reported for methylene chloride, cyanide, and carbon tetrachloride, but these values are qualified. First, the qualifiers are ignored to determine whether or not it is possible that the results demonstrate significantly higher levels in the downgradient samples. Methylene chloride is reported in W-1, but it is not five times greater in W-2 or W-3. Carbon tetrachloride is not reported in W-1, but it also is reported at less than three times the detection limit in either W-2 or W-3. Therefore, these two substances are not considered further.

Cyanide, however, is not detected in W-1 but is present in W-3 at greater than three times the detection limit. The cyanide data are qualified because the holding times of the samples were exceeded by a few days. If the effect of this exceedence on the reported values could be estimated (e.g., plus or minus 25%), the cyanide values could be evaluated using the criteria for significance above a background. This is one example of how qualified data can be used under certain conditions. However, since the cyanide values are considered estimates and no ranges were provided, the data cannot be used at face value to determine whether or not contaminants are being released from the trenches.

The exceedence of cyanide holding time could only result in losses of cyanide (not gains). Therefore, the reported cyanide value may not be plus or minus 25 percent, but be lower by 25 percent (from the true concentration). Yet, if this lower value is above the limit of quantitation and is significantly higher than background (W-1), it could be used for demonstrating that a release has occurred (and therefore showing that substances at the site can escape). Even if cyanide were detected on-site and not in background (with values below the limit of quantitation), a release could be demonstrated.

A conservative quality assurance approach to the cyanide issue presented above would be to presume that no suitable estimate of the effect of the exceedence of sample holding time on cyanide data is presently known. Therefore, qualified data in this case cannot be used to establish that a release of cyanide to ground water has occurred.

On the other hand, an alternative, more logical, interpretive approach could be applied to this situation. Since spontaneous production of cyanide in the sample vial is highly unlikely, and a typical sample storage chamber (e.g., refrigerator) does not have any appreciable cyanide as background, the exceedence of holding time could only promote the normal fate of cyanide, namely gradual loss and decomposition. Thus, in this case the effect of storage time exceedence would only produce a decrease in cyanide concentration. Since the cyanide value (though possibly negatively biased) is still significantly higher than the background (W-1), an analytical result obtained within the specified holding time would exceed the observed background cyanide level even more. On the basis of this reasonable argument, the occurrence of a cyanide release to ground water could be demonstrated (thus demonstrating that other substances at the site can migrate).

It should be noted that cyanide is not a naturally occurring substance in water and, in this case, must be an introduced substance. The question at hand is "Is the site the source of the cyanide?".

In summary, of all the data produced, very few of the data actually were appropriate for evaluation of the site. Nine substances were detected in the soil samples. According to the criteria stipulated for this case study, only cadmium could be interpreted to be associated with the trenches. Further, of eight substances detected in the ground water samples, none of the values would be interpreted as demonstrating that the trenches had released contaminants to ground water.

SUMMARY

A decision-maker ultimately has to make a binary (yes or no) decision. To a large extent, environmental decisions depend on the quality and appropriateness of data. Fundamental to the decision process is a "feeling" or assurance by the data user that the data supporting a decision are representative of reality, with respect to conditions at a particular site.

The philosophical concepts of quality assurance are important components of decisions based on environmental data. It may not be sufficient to rely solely on values produced under good quality control procedures. The data exist and must be viewed within a context which establishes whether or not they are representative and defensible in court. The context encompasses reliance on the absoluteness of the values, their representativeness, and their suitability for comparisons. A decision-maker does not generate data or second-guess the laboratory chemist's decision. A wise data user uses data in a disciplined manner, drawing on advice from the lab chemist, field technician, and statistician as appropriate.

In the use of data, only about one percent of the few values derived from initial screening investigations are suitable for decision-making.

An important observation is that every value counts. It counts because of the substantial resources (time and money) needed to collect, analyze, and quality assure samples and values. This is especially true in light of the limited number of samples available and, even more, in light of the few data remaining after the data winnowing process.

Qualified data represent at least one-third of data available to a data user. Although useful in intuitive judgments, qualified data are not desirable in litigation. By understanding the limits wherein qualified data can be quantitative, a considerable amount of data can be made available for environmental decisions. The conditions under which qualified data can be used need to be examined and documented, together with the development of appropriate reference materials and procedures to define the limits of data confidence.

It is essential for the data user to have an environmental awareness. We must look "past the tree and barn door" in order to refamiliarize ourselves with world around us and its variability. We need to strive to rediscover the indispensable attributes of disciplined observation and comprehensive, detailed record keeping.

The bottom line of this paper is to inspire all of us involved in data evaluation to make sure we "know what we know" and to "know what we don't know".

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Table 1
Examples of Common Laboratory Contaminants

Substance	Use in Analytical Laboratory
1,2,4-Trichlorobenzene	Calibration compound, matrix spike
1,4-Dichlorobenzene	Calibration compound, matrix spike
2-Chlorophenol	Matrix spike compound
2,4-Dichlorophenol	Calibration check compound
2,4,6-Trichlorophenol	Calibration check compound
4-Bromofluorobenzene	Surrogate compound for VOA
4-Nitrophenol	Compound in matrix spiking solution
Acenaphthene	Calibration compound, matrix spike
Acetone	Extraction solvent
Aluminum	High level spike sample
Arsenic	High level spike sample
Benzene	Matrix spike compound
Benzo(a)pyrene	Calibration check compound
Chlorobenzene	Matrix spike compound
Chloroform	Extraction, sample preservation
Chromium	Digestion, cleaning solution
Copper	Sample preservation
Fluoranthene	Calibration check compound
Iron	High level spike sample
Mercury	Gas displacement/sample preservation
Methylene chloride	Extraction compound
Phenol	Calibration compound, matrix spike
Pentachlorophenol	Calibration compound, matrix spike
Pyrene	Compound in matrix spiking solution
Selenium	High level spike sample
Thallium	High level spike sample
Toluene	Extraction solvent, matrix spike
Trichloroethene	Matrix spike compound
Various phthalates	Inks, plasticizers, plastics
Xylene	General solvent, slide cleaning
Zinc	Sample preservation, hand cream

Table 2
Ground Water Sample Results For Selected Substances

Substance	W-1*	W-2*	W-3*
Aluminum	110	1,200	970
Carbon tetrachloride	5U	12M	5U
Cyanide	10U	10U	37J
Ethyl benzene	5U	5U	130
Iron	134	1,700	2,100
Methylene chloride	9B	47B	7B
Toluene	5U	5U	110
Xylene	5U	5U	410

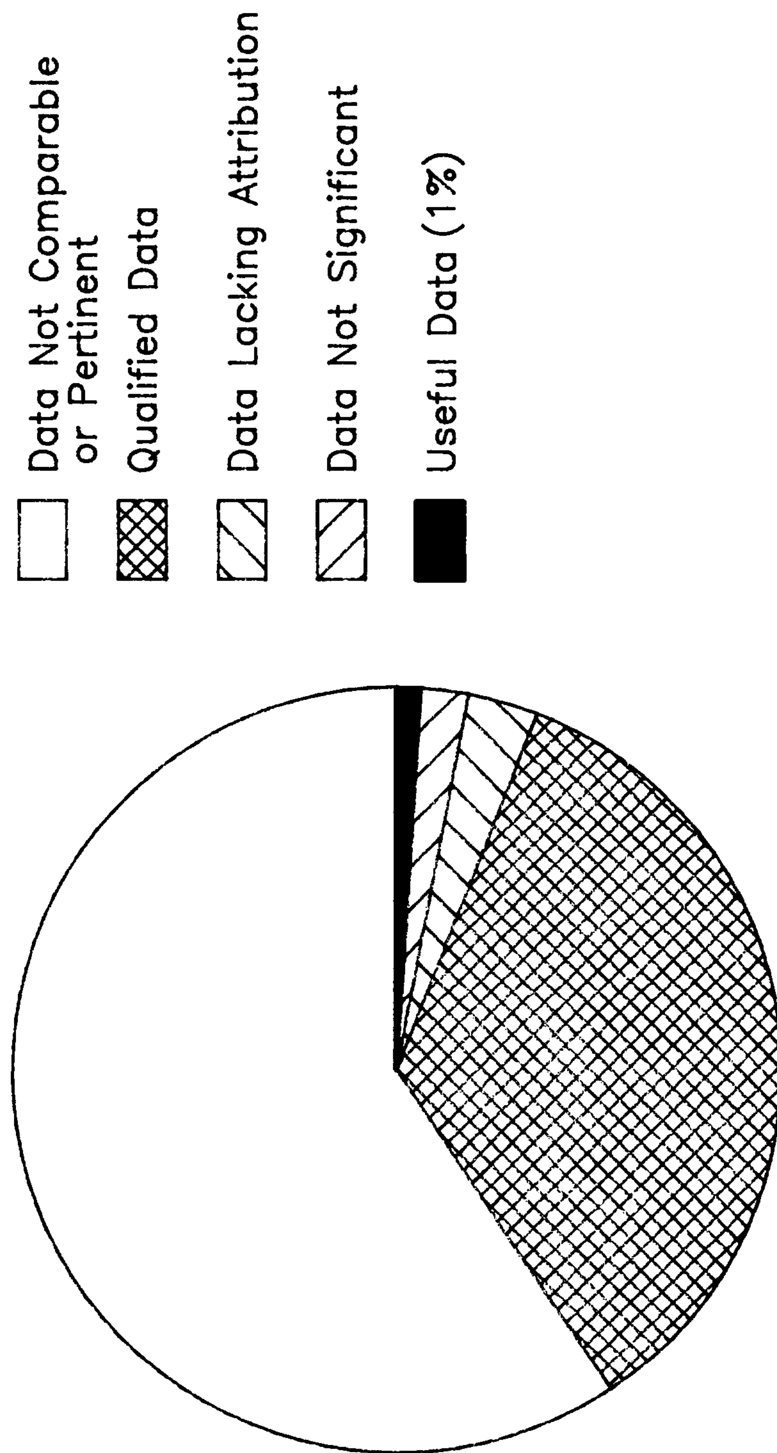
* All results reported in ug/l (ppb)
B - Substance detected in blank
J - Value is estimated
M - Identification could not be confirmed
U - Undetected, value represents required detection limit

Table 3
Soil Sample Results For Selected Substances

Substance	S-1	S-2	S-3
Acetone	10UJ (ug/kg)	39J (ug/kg)	43J (ug/kg)
Arsenic	1.4J (mg/kg)	16.5J (mg/kg)	14.2J (mg/kg)
Cadmium	4.3 (mg/kg)	51 (mg/kg)	64 (mg/kg)
Carbon tetrachloride	5U (ug/kg)	12 (ug/kg)	10 (ug/kg)
Chloroethane	10UJ (ug/kg)	27J (ug/kg)	19J (ug/kg)
Chromium*	17J (mg/kg)	140J (mg/kg)	163/244J (mg/kg)
Cyanide	.010UJ (mg/kg)	.056J (mg/kg)	.046J (mg/kg)
Methylene chloride	18B (ug/kg)	172B (ug/kg)	149B (ug/kg)
Lead	85 (mg/kg)	62 (mg/kg)	158 (mg/kg)

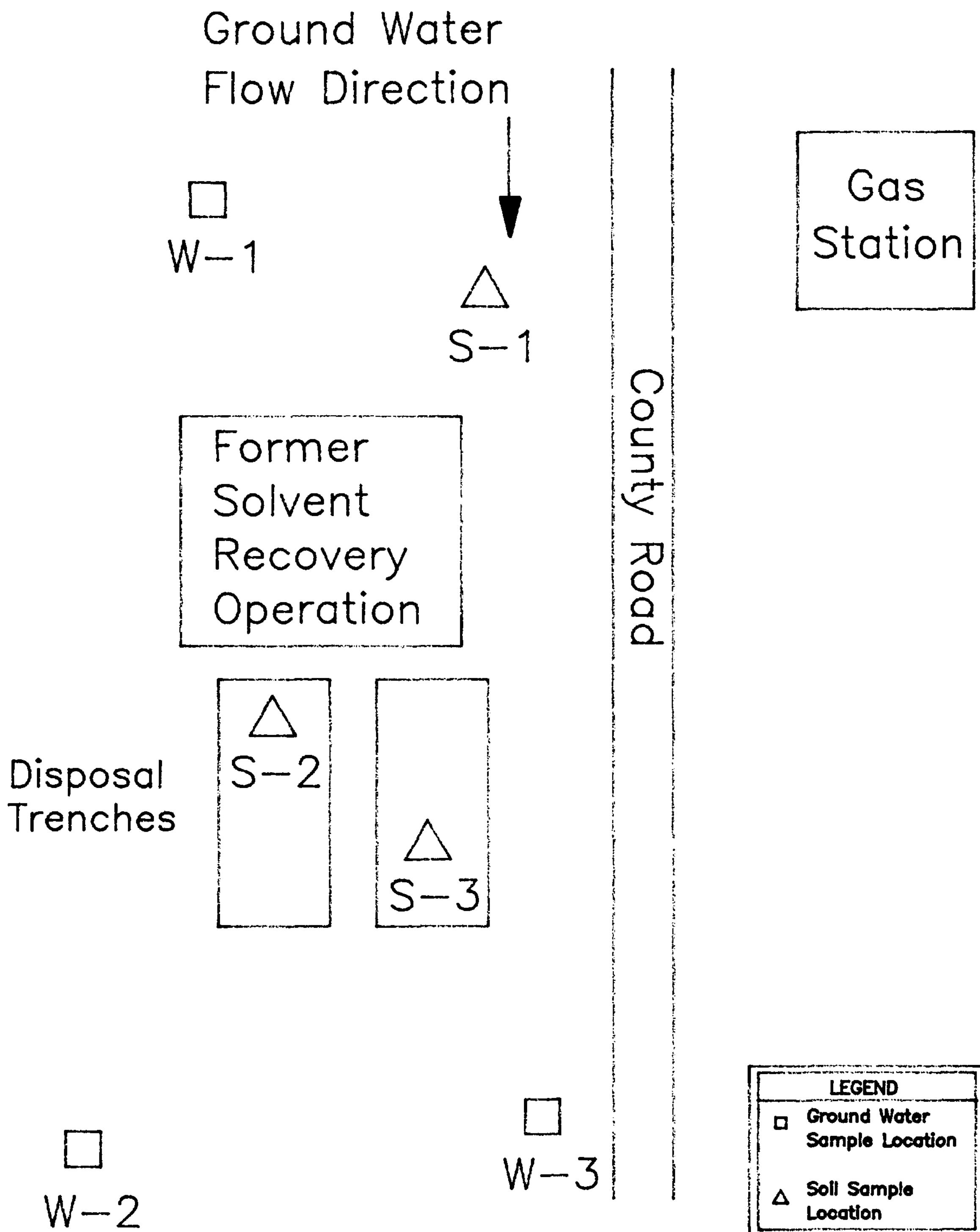
* S-3 values represent duplicate samples
B - Substance detected in blank
J - Value is estimated
U - Undetected, value represents required detection limit

Figure 1
FACTORS AFFECTING DATA REDUCTION



Relative Amount of Data
(Information Based on Experience of Authors)

Figure 2
Case Example Site Sketch



PERFORMANCE AUDIT RESULTS FOR POHC TESTING DURING RCRA TRIAL BURNS

D. J. von Lehmden
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

R. K. M. Jayanty
Research Triangle Institute
Research Triangle Park, NC 27709

INTRODUCTION

The determination of Principal Organic Hazardous Constituents (POHCs) at trace levels (<50 ppb levels) during hazardous waste trial burn tests requires sophisticated sampling and analysis systems. Agency personnel responsible for trial burn tests need to be concerned about the accuracy of POHC measurements. Accuracy of such measurements may be assessed by conducting a performance audit. A performance audit is a quantitative assessment of the accuracy of a measurement system. For volatile POHC, a performance audit consists of providing an "unknown" or "blind" cylinder gas to the organization being audited. The organization draws a sample from the cylinder gas through (VOST - Volatile Organic Sampling Train) or into (bag measurement) the POHC Sampling System and analyzes the collected sample. When a performance audit is conducted during or prior to a hazardous waste trial burn test, it provides an assessment of the measurement accuracy and indicates the presence of any bias for the combined sampling and analysis system. In addition, an audit conducted during the actual trial burn test provides documentation to agency personnel on the quality of POHC measurements.

When the VOST method was published in the 3rd Edition of the SW-846

Manual[1], the requirement to conduct a performance audit during the actual trial burn test was added.

EPA'S PERFORMANCE AUDIT PROGRAM

The EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) operates a program to develop organic gas audit materials and provide these audit gases to federal and state agencies or their contractors for use in performance audits during hazardous waste trial burn tests. The Research Triangle Institute (RTI), under contract to the EPA, is the principal organization for development of audit gases and coordinating subsequent audits using these gases. Currently five, six, seven, and nine component gas mixtures have been developed and are available for audits. A list of the gaseous volatile organic compounds and their concentrations are shown in Table I.

The gaseous organic compounds in Table I are purchased in compressed gas cylinders from commercial suppliers. These cylinders, along with an appropriate delivery system, are used directly without dilution in the performance audits. The compressed gas cylinders are especially suitable as an audit material for a number of reasons including simplicity, portability, stability, blind mode of operation (i.e., the user cannot readily ascertain the concentration levels), and ruggedness for interstate shipping.

Before being used as an audit standard, the contents of each cylinder undergoes a series of analyses by the RTI using gas standards for calibration and quality control prepared and analyzed by the National Institute of Standards

and Technology. The NIST gas standards are cylinder gases at the same nominal concentrations as the audit cylinder gases being analyzed.

Criteria Used for Selection of Organic Compounds

In 1983, EPA initiated a program to develop ppb cylinder gas standards containing hazardous organic compounds that could be used to audit volatile POHC measurement systems during trial burn tests. Through 1985, three mixtures of ppb cylinder gases were developed which are shown in Table I. The criteria used by EPA for selecting various organic compounds in the three mixtures (Groups I, II and III) are described in a separate publication.(2) Briefly, on the basis of experience of EPA's Air and Energy Engineering Research Laboratory with RCRA trial burn testing, five, nine, and seven compound gas standards were developed during 1983 to 1985. Several compounds were included in the same cylinder with the idea that the same gas cylinders could be used to audit more than one POHC during trial burn tests.

In 1986, a six-compound Group IV gas standard was developed. The selection of six organic compounds for Group IV was based on EPA health risk assessment studies plus input from a state agency.

Selection of Compound Concentrations for Audit Standards

The gas standards were initially developed at two concentration ranges to audit the two prevalent test methods for volatile POHC's. The 7-90 ppb and 90-430 ppb concentration ranges were selected for the Groups I, II, III and IV gas

standards to audit POHC measurements during RCRA trial burn tests; the lower range standard is used to audit VOST measurements, and the higher gas standard is used to audit bag sampling measurements. Later, Group I, and IV standards in the 430 to 10,000 ppL concentration range were added. These standards were added because the RCRA regulation requires a destruction removal efficiency (DRE) of at least 99.99 percent during the trial burn test but does not regulate a maximum emission rate for the POHCs. Therefore, some source testers have received approval to conduct the trial burn test in such a manner that POHC concentrations in stack emissions are about 1000 ppb. This reduces considerably the effect of atmospheric POHC contamination on the VOST measurement system, compared to trial burn tests where the POHC stack emissions are in the order to 10 to 50 ppb concentrations.

Stability of Audit Standards

To ensure that the concentration of each gas standard has not changed, each standard is periodically analyzed for stability. A two-tier stability assessment is conducted. In the first tier, on each standard, the commercial gas manufacturer conducts a minimum of two analyses that are separated by at least 30 days. The second tier stability assessment involves the periodic reanalysis by RTI. Once a gas standard is received from the commercial gas manufacturer, it is analyzed as soon as possible, then reanalyzed at 2, 6 and 12 months and annually thereafter to determine any change in the gas mixtures. The stability data obtained to date for all the ppb level organics are summarized and published in a separate Report.[3] An example of stability data for a Group I ppb gas standard is shown in Table 2. An examination of the stability data for many of

the organics in the ppb level cylinder gases show the results varied by less than 10 percent over the following period: four years for Groups I and II; two years for Groups III and IV. A gas standard is not available for auditing purposes until the 2-month RTI analysis is completed. If any compounds are not stable during that period, those compounds are not recommended for audits. It appears from the long term stability study, that all the organics tested (with the exception of ethylene oxide and propylene oxide at the 10-ppb level) are stable enough to be used as reliable audit materials.

RCRA TRIAL BURN AUDIT RESULTS

Distribution and Frequency of Trial Burn Audits

As of May 1989, 183 performance audits have been initiated using ppb audit gases. These audits have been initiated to assess the accuracy of measurement methods (VOST or bag measurement and GC/MS or GC with specific detector for analysis) during or prior to trial burn tests.

The distribution of trial burn audit requests by EPA Regions is shown in Table 3. The greatest requests for audits are from Region 4 (49 audits) and Region 6 (44 audits). Nine of the Region 4 audit requests were from EPA's AREAL during method validation studies of the VOST method.

The request for performance audits has increased since 1986. As stated previously, a performance audit requirement was added to the VOST method when the method was published in 1986 in the 3rd Edition of the SW-846 manual.[1] Figure 1 shows the frequency audits have been initiated since 1984.

POHC Audit Results

Of the 183 audits initiated, 151 are complete and the results are summarized in Table 4. The frequency each compound was selected for audits is shown. Ten compounds have been found to be more popular for auditing POHCs. These compounds are: carbon tetrachloride, chloroform, perchloroethylene, vinyl chloride, benzene, trichloroethylene, 1,2-dichloroethane, trichlorofluoromethane (F-11), toluene and chlorobenzene. All VOST audits employed GC/MS for analysis, while GC with a specific detector was used for all tedlar bag audits.

It is very interesting to note from the table that the auditee results for the VOST method are usually within the ± 50 percent accuracy limit stated in the method. Currently the VOST method has been validated by AREAL for carbon tetrachloride, chloroform, perchloroethylene, benzene, and trichlorofluoromethane (F-11).[4] The high frequency of VOST audit results within the ± 50 percent accuracy limit suggests that this method may be an effective means of measuring a large number of POHCs in addition to the five compounds validated.

It is equally interesting to note that 22 of 23 audit results of tedlar bag measurement were within ± 50 percent of the stated audit concentrations. This suggests that bag sampling and GC analysis may be a viable alternative to

the VOST method for some POHCs during RCRA trial burn tests. This is particularly interesting since for nine of 23 audits the audit gas concentration was in the same range (7 to 90 ppb) as that used for VOST audits. The remaining 14 audits were conducted with audit gases in the concentration range of 90 to 430 ppb.

Interpretation of Audit Results

As stated in the VOST method, the use of the method is expected to yield results that are within ± 50 percent of the source emission concentration. The VOST validation studies(4) and results of audits shown in Table 4 support this statement. Interpretation of audit results that fall outside the boundary of ± 50 percent requires the application of logic in deciding whether or not to accept the trial burn test results.

First, any negative audit bias must be looked on with concern by agency personnel. Since percent audit bias is calculated as shown in Equation 1, a negative bias means the auditee results are low. Therefore, it must be inferred that the auditee source test results are also low for the POHCs being audited. As seen from Equation 2, this means that the 99.99 percent DRE may be achieved partly because of fictitously low source test results. If the negative bias is greater than 50 percent, real agency concern exists. Remember that calculations by Equation 1 can never go higher than, 100 percent negative bias. At what point does the agency reject the source test results in the bias range of -50 to -100 percent? It is the authors' opinion that if after considering negative bias for audit results in the range of -50 to -100 percent, the 99.99 percent DRE is not

achieved and after ruling out all other possible sources of error (calculation error, etc.); the source test results should be rejected.

$$\text{auditee \% bias} = \frac{\text{auditee conc.} - \text{true conc}}{\text{true concentration}} \times 100 \qquad \text{(Equation 1)}$$

$$\text{DRE\%} = \frac{\text{POHC waste} - \text{POHC emissions}}{\text{POHC waste}} \times 100 \qquad \text{(Equation 2)}$$

Second, any positive audit bias means the auditee results are high. Therefore, it must be inferred that the auditee source test results are also high for the POHCs being audited. It is the authors' opinion that bias results of + 50 to + 100 percent are completely acceptable provided the 99.99 percent DRE is still achieved. Results greater than +100 percent need careful scrutiny and must be handled by the agency on a case-by-case basis.

SUMMARY AND RECOMMENDATIONS

Compressed gas cylinders containing 27 gaseous volatile organic compounds at parts-per-billion levels have been used in audits to assess the accuracy of measurement systems during hazardous waste trial burn tests. The 27 gaseous volatile organic compounds were selected on the basis of the anticipated needs of EPA's Office of Solid Waste.

Stability studies indicate that all of the organic compounds tested (with the exception of ethylene oxide and propylene oxide at the 10 ppb level) are stable enough to be used as reliable audit materials. One hundred eighty three performance audits have been initiated (through May 1989) to assess the accuracy

of POHC measurements systems used during hazardous waste trial burn tests. Audit results from VOST and tedlar bag methods have generally been within ± 50 percent of the stated audit concentrations.

It is required that a performance audit using organic gas cylinders be conducted during each hazardous waste trial burn test as a routine quality assurance procedure. Any federal and state agencies and their contractors planning hazardous waste trial burn tests may request a performance audit by contacting Mr. Robert L. Lampe, U.S. EPA, Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, MD-77B, Research Triangle Park, NC 27711.

ACKNOWLEDGEMENTS AND DISCLAIMER

This project was conducted by the Research Triangle Institute, Research Triangle Park, NC under contract number 68-02-4550 of the Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer review and administrative review policies and approved for presentation and publication.

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Table 1. Auditing POHC Measurements*

Group I Compounds	Group II Compounds	Group III Compounds	Group IV Compounds
Carbon tetrachloride	Trichloroethylene	Vinylidene chloride	Acrylonitrile
Chloroform	1,2-dichloroethane	1,1,2-trichloro-1,2,2-trifluoro-ethane (F-113)	1,3-Butadiene
Perchloroethylene	1,2-dibromoethane	1,2-dichloro-1,1,2,2,-tetra-fluoroethane (F-114)	Ethylene oxide**
Vinyl chloride	Acetonitrile	Acetone	Methylene chloride
Benzene	Trichloro-fluoromethane (F-11)	1-4 Dioxane	Propylene oxide**
	Dichloro-difluoromethane (F-12)	Chlorobenzene	O-xylene
	Bromomethane	Toluene	
	Methyl ethyl ketone	Pyridine***	
	1,1,1-trichloro-ethane		
Group I Ranges	**Group II Ranges**	**Group III Ranges**	**Group IV Ranges**
7 to 90 ppb 90 to 430 ppb 430 to 10,000 ppb	7 to 90 ppb 90 to 430 ppb	7 to 90 ppb 90 to 430 ppb	7 to 90 ppb 430 to 10,000 ppb

*All gas standards are in a balance gas of nitrogen.
**The concentration of this compound in the cylinders in the 7 to 90 ppb range is not certified due to stability problems.
***Concentration not certified due to analytical problems.

Table 2. Example of Stability Study (Group 1 Compounds) Cylinder 1-42

ACTIVITY		COMPOUND			
	Carbon tetra-chloride	Chloroform	Perchloro-ethylene	Benzene	Vinyl chloride
MANUFACTURER ANALYSIS					
heoretical ppb	(9.50)	(39.6)	(9.40)	(18.9)	(20.0)
›t Analysis Date	11/17/83	11/17/83	11/17/83	12/06/83	12/06/83
ppb	(7.70)	(42.1)	(9.20)	(15.8)	(18.3)
ıd Analysis Date	12/16/83	12/16/83	12/16/83	12/15/83	12/15/83
ppb	(7.10)	(41.2)	(7.70)	(19.6)	(19.2)
RTI ANALYSIS					
t RTI Analysis Date	1/06/84	1/06/84	1/06/84	1/23/84	1/23/84
ppb	(9.30 ± 0.3)	(40.0 ± 0.8)	(9.40 ± 0.2)	(19.6 ± 0.6)	(20.2 ± 0.6)
d RTI Analysis Day*	59	59	59	49	49
ppb	(9.30 ± 0.3)	(38.7 ± 0.8)	(10.3 ± 0.2)	(20.0 ± 0.6)	(19.0 ± 0.6)
ɜ RTI Analysis Day*	238	238	238	226	226
ppb	(9.50 ± 0.3)	(40.6 ± 0.9)	(9.50 ± 0.2)	(19.4 ± 0.6)	(20.6 ± 0.7)
ı RTI Analysis Day*	404	404	404	375	375
ppb	(9.60 ± 0.3)	(37.1 ± 0.8)	(9.10 ± 0.2)	(19.4 ± 0.6)	(20.4 ± 0.7)
ı RTI Analysis Day*					
ppb	On audit	On audit	On audit	On audit	On audit
ı RTI Analysis Day*	833	833	833	810	810
ppb	(10.5 ± 0.3)	(40.5 ± 0.9)	(11.2 ± 0.3)	(19.7 ± 0.6)	(19.4 ± 0.6)
ı RTI Analysis Day*	1337	1337	1337	1337	1337
ppb	(9.45 ± 0.3)	(40.6 ± 0.9)	(10.1 ± 0.3)	(19.2 ± 0.6)	(20.1 ± 0.6)
ı RTI Analysis Day*	1699	1699	1699	1682	1682
ppb	(9.36 ± 1.9)	(44.2 ± 4.1)	(9.65 ± 1.2)	(18.3 ± 2.1)	(19.3 ± 2.4)

*Number of days after 1st RTI analysis date.

TABLE 3. Trial Burn Performance Audits by EPA Regions

EPA Region	Audits Requested (May 1988)
1	0
2	28
3	5
4	49*
5	33
6	44
7	12
8	1
9	10
10	1
TOTAL	183

*Region 4 includes 9 audits requested by EPA, AREAL at the Research Triangle Park, North Carolina for VOST method validation tests.

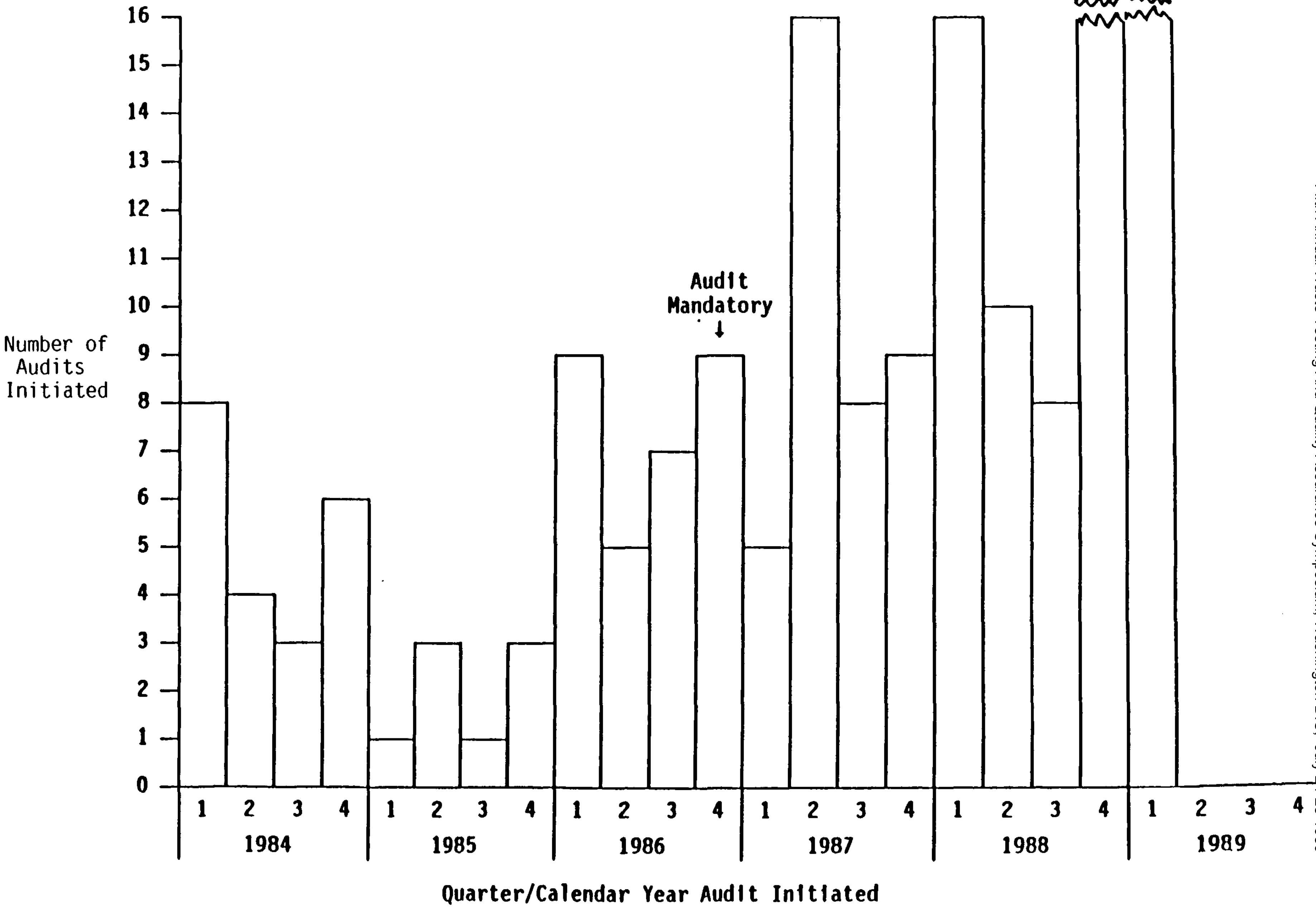


Figure 1. Audits Frequency for RCRA trial burn tests

TABLE 4. Summary of Audits Performed for RCRA Trial Burns (Through May 1989)

Group I-IV Compounds	Based on 151 Completed Audits				Frequency Auditee Results within ± 50 Percent of Audit Concentration	
	Frequency Compounds Selected For Audits	Measurement Sys. Audited				
		VOST[b]	BAG[c]	Other[d]	VOST	BAG
Carbon Tetrachloride	59	49	7	3	41 of 49	6 of 7
Chloroform	31	24	4	3	18 of 24	4 of 4
Perchloroethylene	31	27	4	0	22 of 27	4 of 4
Vinyl chloride	20	18	2	0	12 of 18	2 of 2
Benzene	22	20	2	0	16 of 20	2 of 2
Trichloroethylene	13	12	1	0	10 of 12	1 of 1
1,2-Dichloroethane	11	11	0	0	9 of 11	0 of 0
1,2-Dibromoethane	5	5	0	0	2 of 5	0 of 0
Acetonitrile	4	4	0	0	0 of 4	0 of 0
Trichlorofluoromethane (F-11)	12	11	0	1	6 of 11	0 of 0
Dichlorodifluoromethane (F-12)	6	5	0	1	1 of 5	0 of 0
Bromomethane	4	4	0	0	1 of 4	0 of 0
Methyl ethyl ketone	6	6	0	0	3 of 6	0 of 0
1,1,1-Trichloroethane	8	8	0	0	5 of 8	0 of 0
Vinylidene chloride	3	3	0	0	1 of 3	0 of 0
1,1,2-Trichloro-1,2,2-trifluoroethane (F-113)	4	4	0	0	3 of 4	0 of 0
1,2-Dichloro-1,1,2,2-tetrafluoroethane (F-114)	2	2	0	0	0 of 2	0 of 0
Acetone	2	2	0	0	1 of 2	0 of 0
1,4-Dioxane	2	2	0	0	1 of 2	0 of 0
Toluene	14	12	2	0	8 of 12	2 of 2
Chlorobenzene	13	13	0	0	9 of 13	0 of 0
Acrylonitrile	1	1	0	0	0 of 1	0 of 0
Methylene chloride	2	1	1	0	0 of 1	1 of 1

[a]/183 audits initiated; 151 audits completed; 32 audits currently underway
[b]/GC/MS was used for all VOST analysis
[c]/GC with a specific detector (FID/ECD) was used for bag samples

SMALL SCALE SPILL ABATEMENT PLAN

Ronald J. Osborn, Group Leader Wet Chemistry, Eric J. Cameron, Analytical Chemist, Chemical Waste Management, Inc., Technical Center Analytical Laboratories, 150 West 137th Street, Riverdale, Illinois 60627

ABSTRACT

In any laboratory setting, regardless of how thoroughly trained the personnel or how carefully the tasks are performed, accidental spills are going to happen. Proper management, cleanup, and disposal of the spilled material, and clean-up residue must be properly performed. Before choosing a clean-up strategy, the primary concern should be the safety of the personnel. After a safe course of action is decided upon, the spilled substance must be identified so that the proper method of cleanup can be determined. When the clean-up procedure is completed, all of the contaminated materials involved must be collected and disposed of properly. Finally, the entire situation from spill to disposal must be reviewed and evaluated.

When confronted with a spill in the hazardous waste laboratory, many more variables are involved than in other laboratory settings. For example: Is the spill a toxic material, is it contaminated with PCBs, or is it a complete unknown? In order for the proper cleanup to be implemented, these and many other questions must be answered. Some of the individual questions may seem insignificant, but they become integral parts of the proper clean-up strategy. The Small Scale Spill Abatement Plan asks and provides answers to the many questions which must be answered to properly and completely evaluate and clean up a small scale spill in the hazardous waste laboratory.

INTRODUCTION

A small scale spill is defined here to be a spill that can readily be cleaned up by personnel at the site and does not typically exceed 1 quart in volume. Spills too large to be cleaned up by on-site personnel should be handled by professionals who would employ their own protocol for the cleanup. An appropriate on-site procedure for dealing with spills of a hazardous nature has a logical progression of events which must occur to effectively manage the situation. It is understood that some of the following steps could occur simultaneously if the situation warrants. The major components of the Chemical Waste Management, Inc. Small Scale Spill Abatement Plan include: recognition of the spill; personnel safety; notification of management; identification of the spilled substance; remediation decision; remediation and disposal of

contaminated materials; inspection of spill site; and review of entire procedure. A copy of the Chemical Waste Management, Inc. Small Scale Abatement Plan Flow Chart is included on Page 5. When cleaning up a small scale spill, great care should be taken to avoid creating another hazardous situation.

PLAN

In any scenario regarding a spill, the personal safety of everyone involved should be the first concern. A safety shower and/or eyewash should be employed if a spilled material comes in contact with the eyes or face, rinsing the affected area with copious amounts of water for at least 15 minutes. Similarly, if a spill contaminates skin and/or clothing, a safety shower should be employed in the same manner. Contaminated clothing should be removed and disposed of properly.

Once the safety of all individuals is assured, the spill should be marked clearly for all to see. Personnel exposure to the spill area should be minimized to prevent subsequent personal injury.

After the spill site has been secured, the supervisor should be notified. At this time, it should be determined if further treatment is required for anyone involved with the spill. Professional attention should be sought if it is warranted.

Next, it is important to identify the spilled substance. If it is known, then appropriate clean-up procedures may be initiated immediately. If the substance is unknown, steps must be taken to make a conclusive identification. In lieu of other more obvious identification means, the traits of the substance should be investigated; check the pH, note physical characteristics such as viscosity and turbidity, and any incidental odor associated with the substance. Possible hazard classes should also be identified.

Once the spilled material is identified or at least classified by hazard, it is very important to implement the proper clean-up strategy. The first decision which has to be made is whether the facility has the capability to effectively manage the spill. If it is questionable that the spill is too large, or of a nature in which specially trained personnel must be utilized, the facility's Emergency Coordinator should be contacted. It will be up to that individual to decide whether an outside source should be called in to handle the spill or whether there are on-site personnel capable of effecting the proper cleanup. If in the Coordinator's opinion, the magnitude of the spill exceeds the capacity of on-site personnel, it will then need to be decided whether or not the facility's Contingency Plan

needs to be implemented. The Emergency Coordinator would also be responsible for contacting the proper organization to clean up the spilled material.

If the personnel involved have decided that they can properly manage the spill, they must decide on an appropriate means of cleanup. (It should be noted that if the spilled material is suspected or known to contain PCBs, the Toxic Substances Control Act (TSCA) protocols must be adhered to.) An appropriate means of cleanup could be: an acid, caustic, mercury, or solvent spill kit, if appropriate; or something as simple as paper towels and a mop. The most important factor to consider when a spill has occurred is that the clean-up strategy effectively and completely removes any hazardous condition presented by the spilled material.

Once the spilled material is cleaned up, all materials involved must be properly disposed of. It must be remembered that anything used to clean up a hazardous material becomes a hazardous material itself. With this in mind, an appropriate disposal container must be used. In the event of a PCB contaminated spill, a TSCA approved hazardous waste container must be used.

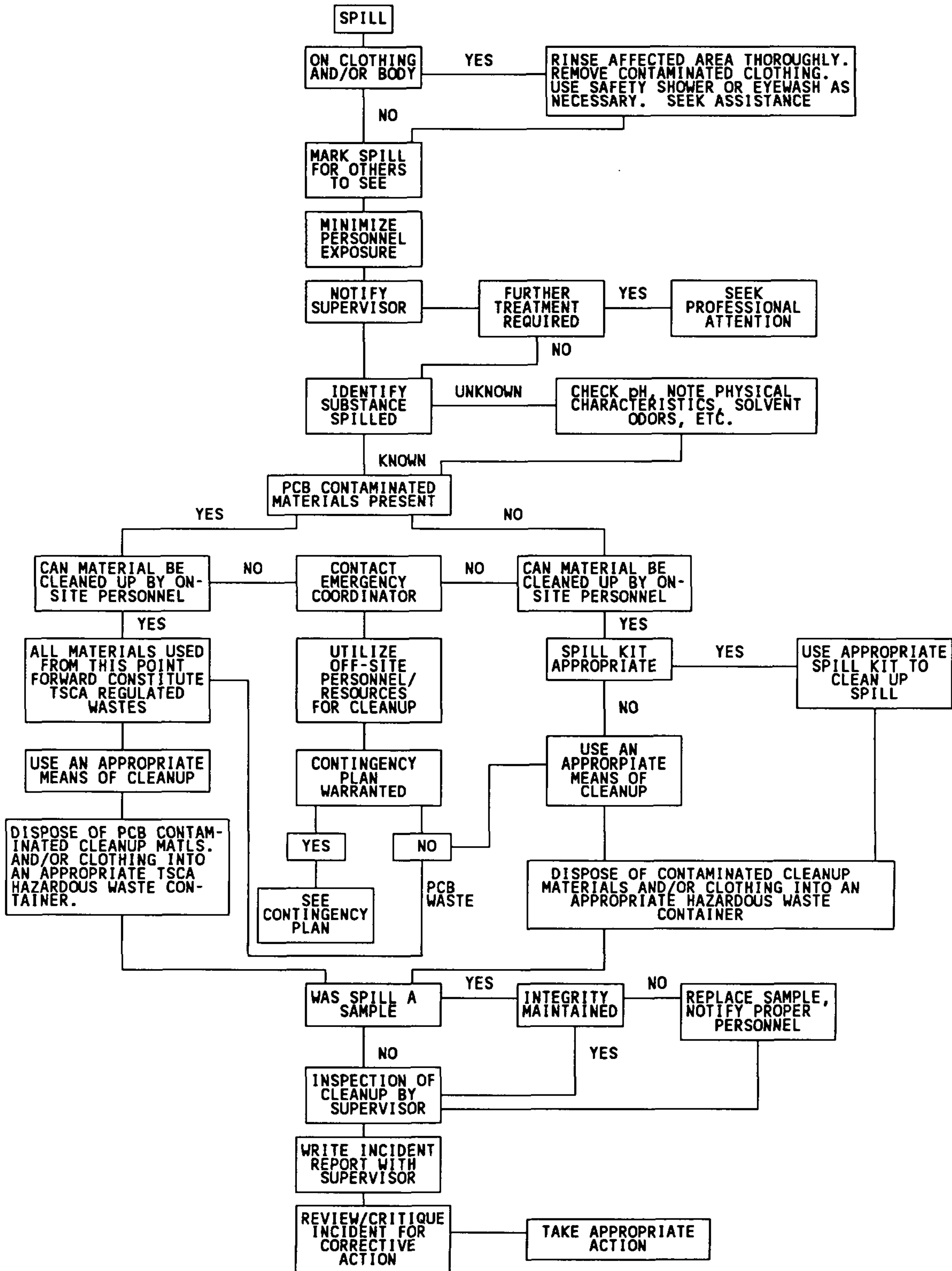
With the proper disposal of the contaminated materials accomplished, the next course of action is for the appropriate supervisor to inspect the area in which the spill occurred. If the spilled material was a sample, the supervisor will have to decide whether or not the sample's integrity was maintained and act accordingly. A thorough inspection of the area affected is essential to the completion of any clean-up procedure. The inspection must include a careful evaluation of the completeness of the cleanup, which may involve one or more but not limited to any of the following: a visual inspection of the area; if the material involved was of extreme pH, wet several small areas with distilled water within the spill site and test with pH paper; if it was an organic material, check for persistent odor, etc. Another component of the inspection is to search for and examine possible causes of the spill as well as measures to prevent recurrence.

Finally, a formal report should be written to include the following information about the spill: date, location, and time of the spill; area affected; personnel affected; the clean-up procedure; how were the materials used and disposed of; address causal factors; description of accident attributing to the spill; and any first aid or further treatment required. This report should then be reviewed and critiqued so that corrective actions can be taken to prevent a spill from recurring.

CONCLUSION

Small scale spills can occur at any time. Developing a plan to manage these situations when they occur can make dealing with a spill safe and straightforward. Every laboratory needs to develop an easy to understand plan to properly manage a spill. A properly organized spill abatement plan should include the following components: recognizing that there is a spill; personnel safety; notification of management; identification of the spilled material; and inspection and review of all aspects of the clean-up procedure, including the corrective action taken.

SMALL SCALE SPILL ABATEMENT PLAN FLOW CHART



THE ROLE OF DATA VALIDATION AND DATA QUALITY OBJECTIVES IN ESTABLISHING DATA USABILITY

WILLIAM J. BERNING, JERALYN GUTHRIE, RICHARD A. CHEATHAM, C.C. JOHNSON & MALHOTRA, P.C., ENVIRONMENTAL ENGINEERS, 2300 15TH STREET, SUITE 330, DENVER, CO 80202

One of the major goals of a project is to produce data of sufficiently known and acceptable quality to use in meeting project objectives. The principal means of determining data quality is through data validation. Data usability is determined through comparison of the data validation results to the stated project objectives of data quality. A frequent and critical error is to consider data validation and data usability to be synonymous.

Data validation is the process by which data quality is determined with respect to data quality criteria that are defined in project and laboratory quality control programs and in the referenced analytical methods. It is important to note the data validation outlined in current EPA guidelines may require project specific adaptations.

Data usability determinations are based on the data validation results and the application of project or site specific factors on these results. Ideally, such factors and the data validation criteria are clearly set forth in the project documentation and include

- the specific level of analytical support required;
- the minimum level of data quality required;
- the means for producing the data desired, e.g., analytical methodology, quality control, corrective actions, subcontract specifications, etc.;
- the requirements for reporting and interpreting the data and the minimum acceptable support documentation (i.e., custody records, QC data).

Data validation, data quality objectives, and data usability are all intimately interwoven and cannot be split out without loss in project data quality and cohesiveness. This presentation will demonstrate and explain their interrelationship and provide guidance in effective project planning. Examples based on actual site histories will be discussed.

THE COST OF LABORATORY ACCREDIATION

GEORGE E. PARRIS, DYNAMIC CORPORATION, 11140 ROCKVILLE PIKE, ROCKVILLE, MD 20852

ABSTRACT. There are a number of state and federal laboratory quality assurance programs some of which result in accreditation/certification of the laboratory by the agency. It has become apparent to the laboratories that (1) many of these programs are very similar in the elements evaluated, the rigor of the evaluation standards, the methods of evaluation (e.g., laboratory audits, performance evaluation samples) and the scope of accreditation/certification, and (2) most agencies act independently often duplicating the activities of other agencies. Although most agencies allow for reciprocity in principle, reciprocity among programs is frequently not available in practice. This state of affairs has encouraged several groups to propose a national universal accreditation program based on the premise that quality assurance will not be jeopardized by such a system and substantial cost for the redundant programs could be saved. These costs may be absorbed by the laboratory, but are often passed to industrial clients or prime remedial action contractors who may subsequently pass the costs to regulatory agencies. This paper will attempt to analyze the magnitude of the cost of quality assurance at three levels: (1) cost of setting up an internal QA/QC system, (2) the differential cost of having that system accredited by a single agency and, (3) the incremental cost of additional accreditations. Both explicit costs (e.g., accreditation fees) and implicit costs (e.g., cost of laboratory labor or foregone work) will be considered. The results will be presented as a unit cost increase on analyses.

QUALITY CONTROL FOR ASBESTOS SURVEY PROJECTS

Nile A. Luedtke, Project Manager, Martin Marietta Energy Systems, Inc., P. O. Box 2003, MS-7400, Oak Ridge, Tennessee 37831-7440

Mitzi S. Miller, Program Manager, Martin Marietta Energy Systems, Inc., P. O. Box 2003, MS-7400, Oak Ridge, Tennessee 37831-7440

ABSTRACT

The Hazardous Waste Remedial Actions Program (HAZWRAP) and the Airborne Hazardous Substances (AIRHAS) Program have been established by the Department of Energy to conduct investigations and analysis related to Asbestos Survey and Abatement projects. This paper outlines the Quality Control (QC) to be implemented for bulk material characterization and airborne fiber analysis during these investigations pursuant to the National Institute for Occupational Safety and Health (NIOSH) and U. S. Environmental Protection Agency (EPA) protocols and certifications.

A comprehensive QC program has been developed to ensure the appropriate planning, sample collection, sample analysis, and QC are maintained. The QC function is responsible to the AIRHAS project managers for ensuring that appropriate project QC requirements for data quality are met.

The QC program consists of three elements: 1) the development of a site specific work/sampling plan, 2) the employment of an approved analytical facility for asbestos determinations, and 3) the analysis of QC samples for data comparison and verification.

The work plan must include all information concerning the site under investigation. It must define sampling requirements for collection, documentation, and shipment of samples including chain-of-custody. The laboratory must be identified and its qualifications outlined. Each work plan shall be approved through a review process prior to initiation of the project.

Analytical laboratories utilized during these investigations must receive and maintain full approval status throughout the duration of the project. Approval is obtained from the AIRHAZ program and involves development of a laboratory QA/QC plan, documentation of personnel certifications and training, the successful completion of outside performance sample analysis, and continuing satisfactory performance during the entire project.

Bulk sample identifications for asbestos require performance of in-house duplicate and referee laboratory split sample analysis. Airborne fiber determinations require field, trip, and laboratory blanks in addition to blind re-analysis of samples. All QC analysis receive independent comparison and evaluation for inclusion in the final report and determination of warranted additional work.

MULTIPLE FORMAT REPORTS FOR THE ANALYTICAL LABORATORY

Norman Low, Scientific Instruments Division, Hewlett-Packard, 1601 California Ave, Palo Alto, California 94304

ABSTRACT

The difficult problem of producing multiple format reports can be reduced by consolidating the data from multiple instruments on a single data system capable of producing an analytical report. The analytical report is reviewed by the chemist before a separate program is run to make final customer reports or standard intermediate files. The final reports can be delivered to the customer in hardcopy or in electronic form. The standard intermediate files are accepted directly into personal computer applications without additional formatting.

INTRODUCTION

Commercial laboratories are increasingly asked to provide analytical data on custom forms. This demand for special reports come from both government and commercial clients. The Environmental Protection Agency's Contract Laboratory Program (CLP) requires a series of report forms along with a diskette as deliverables. Other government agencies have their own forms or modifications of the CLP forms. Commercial customers may require still other reports. There is no prospect that this demand for special reports will decrease in the future.

The diversity of report requirements is due to legitimate end user needs. It is difficult to compare results from different labs if the report formats are drastically different. Even with the standard CLP forms, EPA found that it took significant time and expense to enter the results into their master database. Faced with these same problems, other users have asked for data in a format they could use directly.

Different needs dictate different reports. While special reports makes the process simpler for the end-user, it is made more difficult for the lab. The laboratory is faced with the problem of producing different reports without disrupting the work flow. Organizations are accustomed to standard operating procedures and reports to minimize effort and error. Multiple report formats are time-consuming to produce and to review.

APPROACH

We studied ways of providing multiple format reports with the Hewlett-Packard RTE Mass Spectrometer Data System. This data system can be used to process and report raw data from mass spectrometers, gas chromatographs, and liquid chromatographs. Table 1 shows the options available for raw data input. In the most general case, the data system will accept a signal from an HP 3392 integrator. GC and LC files from the HP Laboratory Automation Systems and other MS data systems may also be used. Once the data files are converted, they may be displayed, quantitated, and reported with the standard MS software. Thus the RTE MS Data System can be used to process most instrument data produced by an organics analysis laboratory.

Instrument	HP Data System
GC	HP 3392, Laboratory Automation System
LC	HP 3392, Laboratory Automation System
GC/MS	Pascal ChemStation, Unix ChemStation, RTE Data System
GC /MS	Pascal ChemStation, Unix ChemStation, RTE Data System

Table 1 - Raw data input options for the RTE MS/DS

1) *Set up sequence*
2) Acquire data on tuning standard
3) Check tune
4) Produce TUNE REPORT
5) Acquire data on calibration standard
6) Quantitate target compounds
7) Check calibration
8) Produce CALIBRATION REPORT
9) Update QA CHART for calibration factors on each compound
10) Acquire data on samples
11) Quantitate target compounds
12) Produce QUANTITATION REPORT FOR TARGETS
13) Update QA CHART for IS areas and surrogate recoveries
14) Identify non-target compounds
15) Library search non-target compounds
16) Quantitate non-target compounds
17) *Review target and non-target compounds*
18) Produce QUANTITATION REPORT FOR NON-TARGETS
19) Produce QA CHART FOR DAILY RUNS
20) Produce CUSTOMER REPORTS
21) Archive files

Table 2 - MS analysis and reporting

Standard file format	Final report produced by
ASCII file	Word processing
RR file	CLP software
Comma delimited file	Spreadsheet, database, charting, forms
Field delimited file	Database
Tagged file	Desktop publishing
HPGL	Desktop publishing, word processing

Table 3 - Standard format files produced by MS/DS

The reports required for any series of analysis may be more than one would expect. In Table 2, we have listed the steps performed during a typical GC/MS analysis. The steps that can be automated *on the RTE MS Data System are shown in normal font. The steps which require manual operations* by the user are shown in italics. The reports (both internal and external) are listed in capital letters.

The process we have developed uses the common RTE MS data format to produce customer reports or standard format files (Table 3). The latter files can be brought directly into PC applications for reports. In the following sections, we will discuss some of the different types of reports that may be generated.

Quality Assurance Reports

Complete quality assurance reports are essential for the standard operating procedures in a laboratory. Unfortunately, operators sometimes forget to maintain the necessary records on a consistent basis. This oversight can be prevented by using the data system to perform this tedious task.

Quality assurance reports include both tabular and graphical formats. Figure 1 shows a tabular report for internal standard areas and surrogate recoveries used to evaluate a GC/MS injection. The RTE MS Data System's Report Writer allows for changes in fonts in a report. This report may be generated

INTERNAL STANDARD AREA CHECK

	>A3245	>A3246	>A3247	>A3248	>A3249
Bromochloromethane	77530	72529	67083	71778	69861
1,4-Difluorobenzene	293546	260338	249252	241706	143050
Chlorobenzene-d5	221389	194369	193700	172003	184525

Figure 1 - QA report

after each run and directed to a specific printer where it is reviewed by the chemist. Also, as part of the acquisition/processing sequence, control charts are automatically updated. At the end of the day or batch or samples, the control chart is printed or plotted. Automatic creation of these reports allow the operator to monitor and document the quality of the analyses performed.

CONTRACT LAB REPORTS

The EPA Contract Laboratory Program deliverables are becoming widely accepted reports even apart from the original program. These forms are popular with other government agencies and commercial clients because they are the closest thing to a standard format for GC/MS and GC data. The output shown in Figure 2 is from a GC file, processed on the MS data system with CLP Plus, a dedicated forms package. The forms may be created either singly or as a group by the RTE MS or LAS data system immediately after data processing.

8E
PESTICIDE EVALUATION STANDARDS SUMMARY
Evaluation of Retention Time Shift for Dibutylchlorendate

Lab Name: HP CLP Plus Lab   Contract: 89-A8-0001

Lab Code: HP1000   Case No.: 1001   SAS No.:   SDG No.: A8001

Instrument ID: GC21   GC Column ID: SP-2100

Dates of Analyses: 06/15/88 to 06/16/88

	EPA SAMPLE NO.	LAB SAMPLE ID	DATE ANALYZED	TIME ANALYZED	% D	*
01	EVALA	D0457	06/15/88	1000	0.0	
02	EVALB	D0458	06/15/88	1033	.2	
03	EVALC	D0459	06/15/88	1105	.1	
04	INDA	D0464	06/15/88	1347	.2	
05	INDB	D0465	06/15/88	1420	.3	
06	TOXAPH	D0466	06/15/88	1452	.3	
07	AR1016	D0467	06/15/88	1525	.2	
08	AR1221	D0468	06/15/88	1558	.2	
09	AR1232	D0469	06/15/88	1630	.2	
10	AR1242	D0470	06/15/88	1703	.3	
11	AR1248	D0471	06/15/88	1736	.3	
12	AR1254	D0472	06/15/88	1808	.2	
13	AR1260	D0473	06/15/88	1841	.2	
14	PBLK01	D0474	06/15/88	1914	.3	

Figure 2 - CLP report

OPTICAL CHARACTER RECOGNITION REPORTS

Optical scanning is an alternative way of entering data into a computer. The error rate is related to the quality of the original document and the fonts used. Special optical character recognition fonts are available for scanning applications. The report shown in Figure 3 was created on the MS data system by utilizing the capabilities of a LaserJet printer.

>GA214

Methylene Chloride	45.11
Acetone	85.87
Butanone	18.97
Benzene	25.54
Toluene	15.42
Chlorobenzene	10.34

Figure 3 - OCR report

BAR CODE REPORTS

Bar codes are becoming increasingly popular in the laboratory for applications such as sample tracking. In situations where analytical results must be entered into another software application, a report can be created where certain fields are printed in bar code format. In the report shown in Figure 4, the analytical results appear in both regular fonts and bar codes. The alternation of fonts is entirely controlled by the report template used by the data system.

FAX REPORTS

Facsimile machines offer fast delivery of reports across the country. Typically, reports are printed and then scanned for transmission to the remote site. The RTE MS Data System can simplify the process even more. Reports from multiple data files may be combined in a single ASCII file, transferred to a personal computer, and sent directly from a fax board. The intermediate steps of printing and scanning a separate report are eliminated.

>GA214

Methylene Chloride	45.11
Acetone	85.87
Butanone	18.97
Benzene	25.54
Toluene	15.42
Chlorobenzene	10.34

Figure 4 - Bar code report

ELECTRONIC MAIL REPORTS

Electronic mail allows for better quality output than facsimile transmission. We have created a file with the Report Writer, downloaded it to a PC, printed it to a file with desktop publishing software, and sent it via electronic mail (HP Deskmanager). The final output was printed on a LaserJet printer attached to a personal computer through the use of the MS-DOS COPY command.

SPREADSHEET REPORTS

Spreadsheets are probably one of the most versatile tools available for reporting. Data may be moved, combined, calculated, etc. Although ASCII text files may be parsed before use, the best procedure is to create a preformatted file which may be used directly. Figure 5 shows analytical data in a Microsoft Excel spreadsheet report.

COMPOUND	PREVIOUS CONCEN	CURRENT CONCEN	CONCEN RATIO
Methylene chloride	45.11	25.56	1.76
Acetone	85.87	56.24	1.53
Butanone	18.97	15.62	1.21
Benzene	25.54	20.86	1.22
Toluene	15.42	15.23	1.01
Chlorobenzene	10.34	13.42	0.77

Figure 5 - Spreadsheet report

CHART REPORTS

The bar graph shown in Figure 6 was created from an RTE report of benzene concentrations in multiple samples. The results were stored in one file which was transferred and imported directly into the HP's Charting Gallery software.

DATABASE REPORTS

The RTE MS Data System allow the retrieval of a wide range of system and sample specific variables. The placement of these variables in the file can be user-defined in a template file. For use in relational databases, separate files may be created for each table. Once these multi-sample files are brought to the PC, each table is loaded with the respective file.

Information stored in a database can be printed in a variety of report formats required by different clients. If all analytical data is checked before it is entered into the database, the database report writer can format the data in any way required without having to worry about transcription errors. Figure 7 shows a report created to find samples exceeding a specified limit.

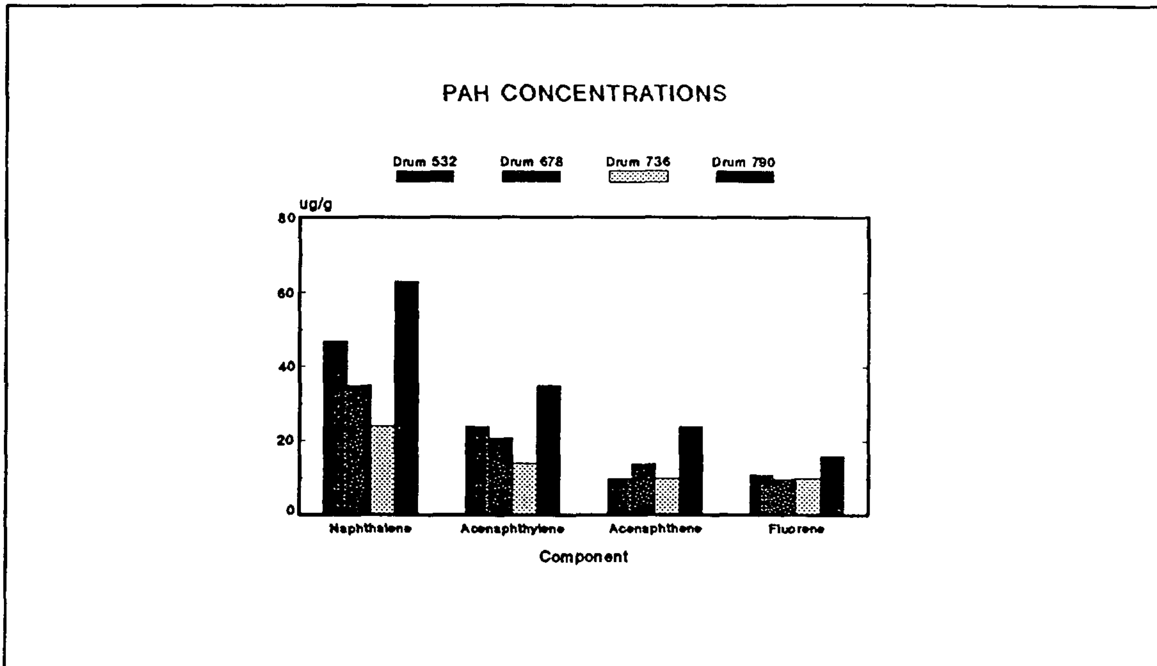


Figure 6 - Charting report

SAMPLES WHERE COMPOUND WAS DETECTED

Data File	Client	Compound	Conc (ug/L)
>FA089	American Solvents Co.	Acetone	32.48
>FA946	American Solvents Co.	Acetone	5.15
>GA024	American Solvents Co.	Acetone	47.97
>GA104	American Solvents Co.	Acetone	69.32
>GA200	American Solvents Co.	Acetone	21.84
>GA214	American Solvents Co.	Acetone	85.87

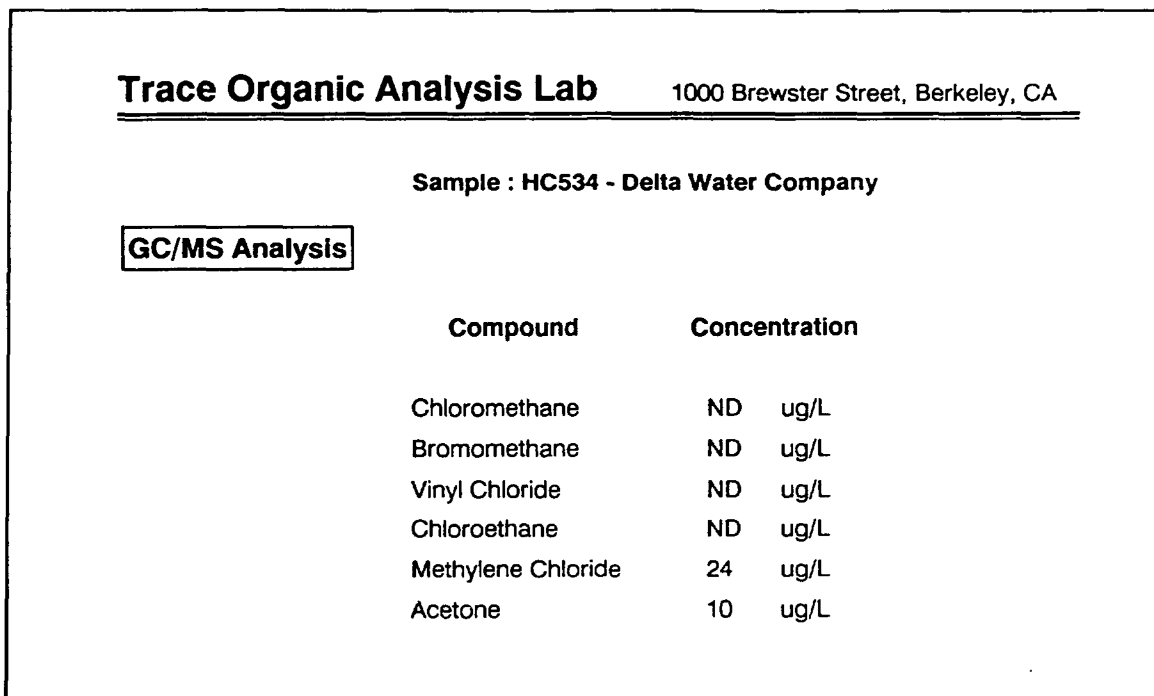
Figure 7 - Database report

FORMS

Files can be formatted for direct input into forms packages. This type of software allow the incorporation of graphics (such as the logo) and complex shading, line styles, etc. to duplicate existing forms used by the laboratory or customer.

DESKTOP PUBLISHING REPORTS

For analytical results that will be incorporated into a larger document, a tagged file can be prepared for desktop publishing software. We prepared a procedure file which rounded the analytical results to two significant digits, replaced the concentrations of those compounds not detected to "ND", and tagged the file with the proper descriptors. The final Xerox Ventura Publisher report is shown in Figure 8.



Trace Organic Analysis Lab 1000 Brewster Street, Berkeley, CA

Sample : HC534 - Delta Water Company

GC/MS Analysis

Compound	**Concentration**	
Chloromethane	ND	ug/L
Bromomethane	ND	ug/L
Vinyl Chloride	ND	ug/L
Chloroethane	ND	ug/L
Methylene Chloride	24	ug/L
Acetone	10	ug/L

Figure 8 - Desktop publishing report

GRAPHICS REPORTS

There are times when graphical output in the form of chromatograms and spectra are part of the final report. Graphics files may be saved in the form of HPGL (Hewlett-Packard Graphics Language) files used to command a plotter. Common PC applications which allow inport of HPGL files include Word-Perfect 5.0, Aldus PageMaker, and Ventura Publisher.

SUMMARY

Data System automation allows the lab to provide a variety of reports with minimal disruption of the work flow. The regular analytical reports from the RTE MS Data System is used for data review. The special QA and customer reports are created automatically by the data system in batch mode without transcription. This process allows the lab to provide custom reports without disrupting the normal operations.

INTERNAL AND THIRD PARTY QUALITY CONTROL AUDITS: MORE IMPORTANT NOW THAN EVER

JEFFREY C. WORTHINGTON, DANIEL LINCICOME, TECHLAW, 12600 W. COLFAX C310, LAKEWOOD, CO 80215

A hazardous waste site investigator develops a Quality Assurance Project Plan (QAPjP) consistent with his/her Quality Assurance Program Plan (QAPP). Implementation of quality control procedures outlined in the QAPjP allow the investigator to ensure that the data quality objectives are met. As emphasis in government programs moves from investigation to litigation, the importance of monitoring quality control procedures related to technical protocols and sample handling procedures has grown.

Monitoring of quality control procedures can be accomplished through the use of internal as well as third party quality control audits. The authors have participated in the audit and review of technical protocols and sample handling procedures in many cases litigated by the EPA and gained a unique understanding of the importance of using internal and third party quality control audits to verify that quality assurance objectives are met.

The frequency and methodology of quality control audits should be specified in the QAPjP. The areas to be audited should be identified and an audit checklist needs to be included in the QAPjP to ensure consistency in the audit process.

Quality control audits of field activities should address the following components at a minimum:

- Review of Statement of Work
- Observation of Sampling Protocols
- Observation of Field Analysis Protocols
- Field Chain-of-Custody
- Field Documentation Methods
- Sample Identification Procedures

Quality control audits of laboratory activities should address the following components:

- Statement of Work
- Observation of Analysis Protocols
- Laboratory Chain-of-Custody
- Laboratory Documentation Methods
- Sample Identification Procedures

At the conclusion of the quality control audit, observations of activities or documents that are inconsistent with the data quality objectives and protocols should be identified in writing and provided to the site manager. A mechanism must exist for ensuring the implementation of corrective action. This can be accomplished by a combination of the following:

- Written plans for corrective action
- Internal surveillance records documenting the implementation of corrective action
- Follow-up quality control audits

The increasing emphasis on litigation demands the implementation of a rigorous quality assurance program.
Periodic internal and third party audits should be conducted to ensure that data quality objectives are met.

INTERLABORATORY QUALITY ASSURANCE THROUGH PROFICIENCY SAMPLE EVALUATIONS

Eugene J. Klesta, Director of Quality Programs, John W. Nixon, Associate Quality Assurance Auditor, Technical Center, Chemical Waste Management, Inc., 150 W. 137th Street, Riverdale, Illinois 60627; Dr. Harold Edelstein, Director, Research & Development, Fisher Scientific, 1 Reagent Lane, P. O. Box 375, Fair Lawn, New Jersey 07410

ABSTRACT

As part of an overall QA program, there must be an assurance that any laboratory performing contract analytical work can meet a set of standards and criteria. A part of the evaluation involves performance on proficiency samples. The application of the program at each laboratory is defined by the sample characteristics, the analytes of interest, and the methodologies applied.

Each data set is monitored by using statistical applications to determine the degree of quality of the analysis, and perhaps, the degree of validity of the procedures applied.

The interlaboratory studies from the Chemical Waste Management, Inc. round robin program are described and reviewed. This program was instituted to identify laboratories which are proficient in analyzing RCRA waste materials. Although the materials are synthetically prepared in the laboratory, the matrices, analytes and concentrations are typical of real waste materials.

The E.P.A. Office of Solid Waste has commented that "real world" samples for SW846 and TCLP analysis should be used rather than artificial spiked samples. We agree and in the near future will set up a program with Fisher Scientific Company to use these samples. We will adjust our round robin analysis program such that this sample analysis data can be generated and then fed back, after statistical evaluation, to the participating laboratories. This will generate a data bank based on "real world" analytical situations and will lead to a high level of confidence in the participating laboratories that their interlab results meet the standardization criteria needed.

INTRODUCTION

As part of an overall QA program, the Chemical Waste Management, Inc. round robin program was instituted to identify laboratories which are proficient in analyzing RCRA waste materials. The program consists of approximately 30 internal company labs and as many as 85 external labs contracted through regional and local Waste Management, Inc./Chemical Waste Management, Inc. divisions.

The program is implemented on a quarterly basis and provides to management beneficial reports on the analytical proficiency for each analyte from each reporting laboratory. Through time, trends are established on totals for each laboratory and for the determination of systematic errors in the reporting or analysis of particular parameters within the lab.

Part II will describe the sample development procedures, the reporting structure, and the statistical applications used for the Chemical Waste Management Round Robin Program. Part III is presented by Fisher Scientific and describes the justification and application of "real world" proficiency samples.

SAMPLE DEVELOPMENT

Evaluation samples must be beyond reproach. They must be both technically sound and defensible. Any lack of confidence in them can not only cast doubt on present results but also provide the basis for doubt on future samples. When evaluation samples are prepared by a quality assurance laboratory, the laboratory should run continuous control of its production process. It should acknowledge any problems and recall doubtful samples. Legitimate questions should be resolved experimentally.[1]

With the unavailability of "real world" reference materials, we have been limited to laboratory standards prepared in matrices that can be easily mixed and blended using common lab techniques.

Some of the considerations taken in the development of the proficiency samples are as follows:

1. realistic materials in a variety of matrices
2. known concentrations (theoretical means)
3. homogeneous
4. established shelf life
5. verification analysis for the analytes of interest.

The concentrations of the samples range in degree but are most commonly at or near the regulatory action levels, i.e., EP TOX metals.

Every effort is made in developing samples of a high degree of confidence and with the assurance that the integrity of the samples is not jeopardized throughout the study. To accommodate these concerns, the QA laboratory staff follows rigorous procedures as the standards are being prepped, bottled, and shipped to the study group. Comprehensive documentation, reagent traceability, established preparation techniques, and proper chain of custody assures a high degree of defensibility. Homogeneity and shelf life of the samples are established as well, prior to use.

REPORTING

Sent along with the samples and chain of custody are the report form and general instructions for sample prep and analysis. Although we do not usually require specific analytical procedures for the analysis, we do recommend standard procedures from EPA, ASTM, and Standard Methods be used. Regardless of the method of choice, the proficiency must meet the established criteria.

The information entered into the data base consists of the laboratory I.D., the analyst, the date of sample prep (when applicable), the analytical procedure, instrumentation used, and the analytical result. The analytical results from each set is then ranked and evaluated for suitability for statistical applications.

DATA EVALUATION

The generated data is accumulated, sorted by parameter, manipulated with statistical applications, and determinations made on the degree of the quality of the data set and the individual analysis.

There are several sets of criteria the laboratories are evaluated on. All members must show proficiency in reporting their results in the prescribed manner and within the allotted time. Their analytical results must fall within the statistical degree of variability of the mean values after statistical outliers are determined and removed.

SUMMARY

We realize the need of using more realistic samples and matrices in our program. A true measure of actual variability in our analytical system can be determined with the use of real world samples. The EPA Office of Solid Waste has commented that real world samples for SW846 and TCLP analysis should be used rather than artificial spiked samples. We agree and in the near future will set up a program with Fisher Scientific Company to use these samples.

We will adjust our round robin analysis program such that this sample analysis data can be generated and then fed back, after statistical evaluation, to the participating laboratories. This will generate a data bank based on real world analytical situations and will lead to a high level of confidence in the participating laboratories that their interlab results meet the standardization criteria needed.

Fisher Scientific is in a position to offer real world samples, to gather the analytical data, to apply the statistics, and to provide the data packages back to the laboratories.

FISHER SCIENTIFIC PROGRAM

There are two ways one can prepare standard samples for analytical testing, one of them is to obtain a clean matrix (earth, sand, oil, "clean ash") and spike the substance with a known assayed analyte. The other way is to obtain real world samples, usually at dumpsites or waste processing facilities such as an incinerator, and process the bulk material for lab use in a controlled methodical way. In both cases, the minimal requirement for reproducibility of the samples is homogeneity of the lot. Spiked analytes can be added to a matrix followed by thorough mixing and similarly so can a real world bulk characterized waste be thoroughly mixed.

The major difference in the use of the samples is the ability of a testing lab to faithfully reproduce a typical client's sample analysis. Spiked samples prepared on a clean matrix will probably give higher recoveries and lead the analyst to an artificially high expectation of data for the same preparation and assay on a client's unknown assay. A spiked sample, prepared fresh with high purity analytes can give a 90+ percent recovery, whereas the client's samples could have much lower recoveries due to the following differences:

1) Exposure of analyte to oxidation, hydrolysis, chlorination (if exposed to city water) and possibly other modifications such as complexation, crystallization and cross chemical reaction between analytes.

2) Aging of the analyte on the matrix which can change the desorption characteristics of the matrix and chemical kinetics of the analyte to the absorbtion/solution rate. The physical surface may change with time, also.

3) Thermal cycles of a real world sample can quicken chemical reactions, and also restructure the solid surfaces of both the analyte and matrix.

Generally speaking, these differences would tend to lower recoveries. For instance, they may generate new chemical species which would interfere with the correctness of the analyte under assay, and as mentioned in 1-3 above, the matrix may hold the analyte with more or less retention affecting the extraction procedure. Only with real world samples can a laboratory properly check all three major needs of an assay test: (1) homogenization and sampling of raw sample, (2) extraction, separation, and concentration of analyte(s), and (3) actual assay measurement of the target analyte(s) and data interpretation.

The spiked matrix sample does have a function in laboratory testing and that is to determine if a particular laboratory instrument is properly working. If a laboratory analyst takes a standard known solution and runs an analysis, one obtains a finite level for instrument sensitivity. One can also obtain a calibration curve for a linear correlation. A spiked matrix will give an indication of the analyte recovery that is available at the theoretical maximum versus the standard analyte solution. In both cases, if the pro-cleanup equipment and instrument is properly working, a good correlation to the known solution

and the matrix extract from the spike shows that the lab techniques and the instruments are functioning properly.

But both can be misguiding for a client's assay when the analyte in question must be extracted from a real world sample. The recoveries will have other impurities due to byproduct chemical degradation and the analyte will have complexing adsorption properties due to aging and thermal reactivity as stated above. Only by extracting and assaying these materials can one hope to get useful data for a client's real sample assay.

HOW THEY ARE OBTAINED AND MANUFACTURED

By arrangement with various waste management/generators of solid waste, our sample manufacturer has procured various stocks of solid waste materials. When reviewing the contents of these available raw material bulks, we attempt to select materials based on variation of heavy metal content, assay level of metal and finally, variation of matrices which are commonly tested by our laboratory customers.

Once the targeted material is accepted, the material is delivered to our manufacturing site and homogenized. We have various pieces of stainless steel equipment to deal both with solids and different types of sludges.

After the proper homogenizing technique, material is sampled from various areas of the bulk mass and bottled. A statistically significant number of the samples are sent to reference labs to correlate the assays. When the round robin labs send their data back to use, a statistical evaluation is performed to get an acceptable tight assay range. For acid digestion and ICP analysis, $\pm$ 10% is acceptable. This range has been arrived at by conversations with the manufacturing chemist, general opinion from our lab customers and informally reviewing the data with members of the Office of Solid Waste at the EPA.

TYPES OF SAMPLES TO BE OFFERED

The solid waste control sample program is based on the need of analytical laboratories to periodically evaluate their testing procedures, equipment and personnel's techniques. In order to achieve this, we must vary the analytes, matrices and SW846 test methods. All this information is documented on an enclosed Certificate of Analysis. As a start-up offering, we have located, bottled and assayed the following heavy metals:

- Chromium
- Copper
- Nickel
- Barium
- Silver
- Lead
- Cadmium

in one or more of the following matrices:

- Fly Ash
- Waste Water Treatment Media
- Circuit Board Coating Sludge
- Electroplating Tank Bottoms
- Raw Sludge
- Incinerated Sludge

We expect to eventually expand the heavy metals range to include all thirteen priority pollutants and to likewise expand the matrices to include various soils, various incinerator components, paint grit, etc.

We also will soon move into providing the organic solid waste analytes such as PCBs in transformer oil, chlorinated pesticides in soils, phenols, nitrosoamines, and PAHs etc.

The methods used for the analysis now include acid digestion (SW846-3050), but will soon include T.C.L.P. and EP Tox. We now assay by I.C.P. but will include A.A. if there is a customer demand for it. The organics will also be by SW846 methods. We will also provide both stable and unstable mixtures using concrete admixtures as determined by landfill requirements. The proper expiration dates will be on the Certificate of Analysis.

Q. C. CHECK SAMPLES AND PROFICIENCY EVALUATION SAMPLES

There will be two types of samples available for lab tests. One is the control check sample to be used by a laboratory which wants to track their periodic trends and evaluate their in-house expertise for an internal quality assurance program. When these samples are used with periodic frequency, a data bank is acquired which will eventually show continuous expertise and high confidence in the laboratory's abilities. This data could undoubtedly be used for legal evidence that the laboratory has a highly credible track record of real world sample analyses.

The other type of product, the Proficiency Evaluation Samples, were meant to serve the needs of governmental agencies and accreditation organizations. For instance, any state D.E.P. which yearly certifies laboratories in their jurisdiction needs to have a series of blind unknown samples for their end user testing lab to assay. We will provide such samples. When a proper State, Federal or other governmental agency places an order for Proficiency Evaluation Samples, we will ship to them a sample with a random sample number on the label and the proper SW846 method to perform. The outer carton of this sample will have a transparent envelope with the Certificate of Analysis enclosed, and any data which will aid the end user such as DOT shipping information will be at the discretion of the agent to send to the end user or not.

These Certificates of Analysis should be removed and kept in a confidential area. When the end user analyzes the samples and returns the data to the agency, the agent can evaluate the data and pass judgement as to certify the end user or not.

CONCLUSION

A statistical QC approach to data from our subscription customers will assure that a periodic trending of data will allow the laboratory to spot poor procedures or drifting trends outside of the collective standard deviation and an awareness of their overall expertise with respect to the other subscription customers.

FOOTNOTE

[1]John K. Taylor, Quality Assurance of Chemical Measurements, (Michigan: Lewis, 1987), p. 157.

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Taylor, John K., Quality Assurance of Chemical Measurements, Lewis Publishers, 1987.

REPORTING ENVIRONMENTAL DATA OF KNOWN QUALITY

P.N. Pink, Scientist, J.S. Jessup, Unit Manager, Environmental Chemistry Unit, Idaho National Engineering Laboratory, EG&G Idaho Inc., P.O. Box 1625, Idaho Falls, Idaho 83415-4123; D.K. Knight, Director, Hazardous Materials Technical Center, Dynamac, 11140 Rockville Pike, Rockville, Maryland, 20852.

ABSTRACT

A comprehensive approach was developed for environmental program documents to integrate sampling, analytical chemical, quality control, and historical data when reporting results to accommodate technical and programmatic data users. The objective of this paper is to present this comprehensive and effective means of reporting the quality and usability of the analytical chemical data generated from the analysis of environmental samples. Most environmental programs require legally admissable data of known quality that will satisfy regulatory requirements and the rigors of potential litigation. Analytical chemical data generated using validated Environmental Protection Agency (EPA) protocols or their equivalent provide the supporting quality control (QC) information necessary to assess the quality of the data; however, no conclusion is drawn as to the programmatic usability of the data. The approach outlined in this paper details a mechanism for assessing, documenting, and reporting what is known about the data quality and consequently the usability of the analytical chemical data generated.

INTRODUCTION

There is an increasing recognition among regulatory agencies, environmental data generators, and data users; that there is a need for an efficient mechanism for reporting environmental data quality and usability (Fairless and Bates, 1989). There is a conceptual notion of the process needed to accomplish this task; however, the details necessary to initiate and execute this task efficiently have not been clearly defined. The concept for the approach to environmental data reporting presented in this paper was developed for generation of Department of Energy (DOE) Sampling and Analysis Data Documents for the Environmental Survey Program administered by the DOE Office of Environmental Audit.

The following points are discussed in this paper:

- who is needed to prepare a document
- what data need to be reported
- how to structure the QC and sample data in a useful fashion
- how to structure summary tables and filter out false positives
- which QC data are used to assess which aspects of data quality
- how to convey the utility of the data to the data user.

WHO IS NEEDED TO PREPARE A DOCUMENT

An interdisciplinary team of people with expertise in sampling, analytical chemistry, quality assurance, statistics, and data management are needed to produce effective environmental data reports. The analytical chemists are responsible for reviewing all analytical data tables to assure their accuracy; writing detailed narratives of the limitations and qualifications (L&Qs) associated with the data; and finally condensing the data into text targeted for the data users. The other team members also contribute to writing the text for portions of the document in their area of expertise. All team members have an opportunity to review the entire completed document. A subcommittee, comprised of the principal team members, resolve questions and incorporate comments generated during the review process. This approach helps to assure that all of the data are accurately reported to the data user.

WHAT INFORMATION SHOULD THE DOCUMENTS CONTAIN

Environmental data reports should present a summary of field and analytical methods, audit findings and responses, performance evaluations, and background data. Detailed field and analytical data evaluations and a concise summary of the limitations and qualifications of the data should be included to integrate all of the quality control information available. This provides the data user with a comprehensive summary of the data and its usability.

Because there is generally 30 to 40% quality control (QC) data generated in support of EPA analytical procedures, it is necessary to succinctly summarize the data obtained. Therefore, detailed QC tables have been developed to accomplish this task. The structure of the QC tables provide calculated values for all sample results and quality control data (e.g. calibration standard response factors, rinsate samples, duplicates, matrix and surrogate spike recoveries, method and field blanks). The sample and quality control data for organic determinations are presented chronologically as the samples were analyzed in the laboratory. Using this approach, it is possible for an independent analytical chemist to technically review the quality of the data and compliance with protocols.

STRUCTURE AND INFORMATION CONTAINED IN THE QC TABLES

Table 1 presents an example of the QC table format for volatile organic data. Due to constraints on the length of this paper, only volatile organic tables have been included as examples. Similar QC tables have been developed for each of the following types of analyses:

- Volatile organics
- Semivolatile organics
- Pesticide/PCBs
- Metals
- Wet chemistry data.

For each of these analysis types, data are presented according to ascending sample delivery group (SDG) number. A SDG for a given type of analysis is an analytical batch with the associated QC data. The data in one SDG QC table may apply to samples from several sampling locations. Environmental problem numbers were also assigned to different sampling locations in order to group the data in a more useful format for the data user.

The column headings for all sample results contain information about the area where the sample was collected, location, sample number and environmental problem, media, and units of measurement. Columns containing quality control sample data are headed with "QC". QC samples (e.g., calibration, blank, spike, and duplicates) are included in these tables with the type of QC sample presented in the heading information. Tentatively identified compounds (TICs) are listed in separate tables by SDG number (See Table 2).

The sequence of data indicated in the organic QC tables is intended to reflect the analysis chronology specified by the EPA Contract Laboratory Program (CLP) protocols. Deviations from the analytical protocols are apparent when reviewing the QC tables. Reported values that are outside of the quality control limits specified in the 10/86 EPA CLP protocol are flagged with an asterisk. Values that fall outside of QC limits require corrective action by the analytical laboratory. The corrective actions and the impact to the data usability are documented in the L&Q narratives. Other qualifying flags that have been utilized in the QC tables are defined as appropriate for the specified analysis type.

Sample holding times, actual and allowed, are reported in days. The field/shipping time is defined as the lapsed time from date of sample collection to receipt by the laboratory, and encompasses field storage of samples and transfer to the laboratory. The analytical (ANAL) holding time is defined as the lapsed time from receipt by the laboratory to sample preparation or to analysis, depending upon the specific analytes. Allowed analytical holding times are specified by the program. Total holding times are the sum of the field/shipping and analytical holding times. Actual holding times that exceed the allowed holding times are flagged with an asterisk.

Several notations or data flags are used to qualify the results from organic analysis. The qualifiers used are as follows:

U - Indicates the compound was analyzed for but not detected. The sample quantitation limit, which precedes the U qualifier, is corrected for sample weight or volume, dilution, and percent moisture as applicable for the indicated sample matrix. A dashed line, "---", is substituted for U-qualified data in the summary tables.

J - Indicates an estimated value. This flag is used either when

estimating a concentration for TICs (an assumed relative response factor (RRF) of one), or when the data indicate the presence of a compound that meets the mass spectral identification criteria but the concentration is less than the sample contract required quantitation limit (CRQL). For example, if the sample CRQL is 10 µg/L, and a concentration of 3 µg/L is calculated, it is reported as 3 J. The sample CRQLs are adjusted for sample weight or volume, dilution, and percent moisture as applicable for the indicated matrix as discussed for the U flag.

B - This flag is used when the analyte is found in the associated analytical blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user that there is a possibility of high bias and/or false positives. This flag is used for a TIC as well as for a positively identified Target Compound List (TCL) compound.

E - This flag identifies compounds whose concentrations exceed the calibration range of the instrument for that specific analysis and warns the data user that low bias is possible.

D - This flag identifies all compounds identified in an analysis at a secondary dilution factor. If a sample or extract is reanalyzed at a higher dilution factor, a "DL" suffix is appended to the sample number for the diluted sample, and all concentration values reported for this analysis are flagged with the "D" flag.

* - This flag indicates that a QC parameter is outside of the control limits specified in the analytical protocol. All asterisks are explained in the limitations and qualifications.

The data for volatile organic compounds are arranged in the QC tables (See Table 1) from left to right in the following order, corresponding to the chronological analytical sequence:

- The initial calibration data include the average RRF and the relative standard deviation (RSD).
- Continuing calibration data include the RRF for the 50 µg/L daily calibration (RRF50) and the % difference (%D), which compares the average RRF from the initial to the RRF50.
- Method blank results.
- Sample results.
- Matrix spike and matrix spike duplicate concentrations are listed, with the percent recovery shown in parenthesis.
- Relative percent difference (RPD) for the matrix spike/ duplicate is listed following the matrix spike duplicate column.

The volatile organic QC tables are formatted vertically as follows:

- The target compounds are listed followed by the surrogate standards. The calibration check compounds (CCC) and system performance check compounds (SPCC) are noted and the protocol control limits are shown at the bottom of each table.

- The surrogate % recoveries are given for each sample, method blank, matrix spike, and matrix spike duplicate.

- "Method blank run (Y/N)", indicates if a method blank was or was not run in association with each sample batch.

- "Tunes out of criteria", refers to the bromofluorobenzene (BFB) tuning criteria specified in the analytical protocol. There will be an entry in this line only if there was a value outside of the protocol specified limits. If there was a value outside of the control limits, the first number provided is the ion which was out of criteria, and the second number is the relative abundance of that ion in percent.

- "Minutes past 12-hour tune" entries flag violations of the protocol that require the continuing calibration, blank, and samples to be run within 12 hours from the time of injection of the tuning compound. If the 12-hour time limit was exceeded, the minutes past 12 hours are noted here.

- The internal standard areas are listed for each internal standard compound for the continuing calibration, method blank, and samples; these values have no associated units of measurement.

- The internal standard retention time shifts are reported in seconds if greater than 30 seconds.

- The dilution factor is reported for all aqueous samples.

- The percent moisture is reported for all nonaqueous samples.

- The field/shipping time, analytical, and total holding times are reported for all samples.

- If the sample has an elevated or decreased CRQL it is noted as "ELEV" or "DECR" respectively.

INCLUSION/EXCLUSION CRITERIA AND STRUCTURE FOR SUMMARY TABLES

Table 3 is an example of a summary table for volatile organic data. The data that are reported in the summary table have been screened to only report results that are attributable to the samples. Field data (e.g. pH, temperature, conductivity, depth, etc.) are also included in the analytical data summary tables. QC data are not reported in the summary tables. Only contaminants detected in the reported sample set

(environmental problem) are listed on the table, rather than all of the target analytes. The inclusion/exclusion criteria are specific to the analysis type being reported; however, the criteria basically follow that which is outlined here for volatile organic data.

Rinsate samples are collected and analyzed to assess possible cross contamination of samples in the field by contaminated sampling equipment. Travel blank samples are sent with each cooler of samples shipped to the laboratory to assess the possibility of cross contamination during shipping and storage prior to analysis. Method blank samples are analyzed with every batch of samples to assess potential contamination introduced during the analytical process. These data are compiled for each project and a statistical assessment of the data are performed. Common laboratory contaminants are defined as contaminants detected in the method blanks at concentrations greater than their CRQLs and/or in greater than 25% of the analyses performed. If the measured concentration for a contaminant detected in a sample exceeds the 95% confidence interval for the mean contaminant concentration determined from blank analyses, it is reported in the results tables and flagged with a "B". Volatile organic contaminants are deleted from the results tables if they are detected in a sample at less than twice the value measured in the specific method blank, rinsate blank, or trip blank associated with the sample. Deletion of these contaminants are documented in the L&Q narratives.

GUIDELINES FOR L&Q ASSESSMENT

The purpose of the L&Q assessment is to document the quantitative and qualitative confidence of analytical data by SDG, sample, and analyte in narrative form. The L&Q narratives are used as the basis for assessing the programmatic usability of the analytical data. The standard quality assurance principles precision, accuracy, representativeness, completeness, and comparability (PARCC criteria) are used as the basis for writing L&Q narratives for each SDG and sample contained in that SDG.

PARCC	DESCRIPTION AND DOCUMENTATION USED
Precision	How close the results are to each other? (Replicate and split samples, and replicate spiked samples.)
Accuracy	How close are the results to the true value? (Initial and continuing calibrations; matrix and surrogate spikes; blanks, and control samples.)
Representativeness	Do the data define the parameters of interest? (Rinsate and trip blanks; analytical and shipping hold times; preservation and storage conditions.)
Completeness	Were the objectives met? (Sampling plan, sample chain-of-custody records, bench sheets, analytical results, data quality objectives.)
Comparability	Are data sets equivalent? (Performance evaluations, adherence to analytical protocols, measurement and reporting units, detection and quantitation limits.)

The L&Q narratives are written by experienced chemists who are familiar with the pitfalls of the analyses they are reviewing and have a solid understanding of the PARCC criteria. These chemists make a systematic assessment of the L&Qs for each SDG and the samples in that SDG by analysis type.

The majority of EPA analytical procedures specify allowable or recommended QC limits based on method performance and statistical limits for accuracy and precision. EPA CLP protocols also impose contractual limits to ensure comparability of data generated and timely turn around of the data. There are occasions when the analytical data will fall outside of these QC limits despite the best efforts of the laboratory. The question then arises, "What impact is there to the usability of the data and how can that be conveyed to the data user?". Often the data fall outside the QC limits due to matrix interferences (as indicated by poor surrogate spike recoveries), large numbers of samples received in a short time span which exceed laboratory capacity, or other factors outside the analysts' control. Of course, there are also instances of poor analytical technique, data reporting, and inadequate review. Recollection and reanalysis of samples due to analytical data falling outside of QC limits is very time consuming and costly. Therefore, it is imperative that the analytical data be assessed to determine the usability applicable to the program objectives.

The assumption is generally made that if the analytical data fall within the established QC criteria for the project, it is acceptable and there is no impact to the data quality. However, by reviewing all of the data from a more holistic perspective, it may become apparent that data which meet the contractual QC criteria in the protocol may be questionable (e.g. false positives or false negatives). It may also be possible to spot trends that indicate a systematic problem. Particularly suspect data may warrant further investigation of the raw analytical data in order to resolve questions and thoroughly assess the data quality. Conversely, data which are outside the QC criteria may meet the data quality objectives for that program, or there may be minimal impact to the data quality.

QC tables condense the analytical data to enable the data reviewer to spot trends or potential analytical problems that may compromise data quality. The sample matrix and field information about the sample are shown in the sample headings on the QC table. This information can provide insight into why some of the QC parameters are out of the analytical control limits specified in the protocol (e.g. a nonstandard matrix such as incinerator ash). QC samples are correlated to field samples to assess potentially introduced contamination (e.g. false positives) and the quantitative accuracy of the data.

Figure 1 and Figure 2 are examples of L&Q narratives for volatile organic data. Figure 1 is an example of narrative comments that are applicable to all of the samples that were reported in that SDG. Figure 2 is an example of narrative comments that are applicable to only a particular sample. These two formats provide a mechanism to document systematic limitations to the data quality verses isolated matrix interferences, carry-over of

high level contaminants from one sample to the next, holding time violations, or other sample-specific limitations to the data quality and usability. The narratives may then be sorted by sample location (environmental problem) or another more convenient arrangement amenable to the data users needs. This format is especially helpful for very large environmental projects comprised of hundreds of samples with multiple analyses.

PRESENTATION OF ANALYTICAL DATA TO THE DATA USER

Once QC and summary tables have been generated, reviewed, and L&Q narratives have been written, all of the tables and L&Q narratives are sorted by sample location (environmental problem), and the textual portions of the report are written. The organization and structure will vary per the needs of the data user and other potential audiences that may receive the reports. Regardless of the style of presentation, all of the data have been concisely condensed into tables, and the L&Qs of the data have been documented in a retrievable format. There are three sections of the DOE documents in which these data are used:

1) Analytical Data Executive Summary. This section is a very brief summary of the range and type of contaminants detected that are attributable to the samples.

2) Analytical Data Evaluation. This section is an evaluation of the types of contaminants detected, spatial or temporal trends at a particular location, and a correlation of all analytical data for all analysis types reported in the associated summary tables.

3) Analytical Data Limitations and Qualifications. This section is where the L&Q narratives are tied together for all analyses (e.g. volatile organics and metals data) performed for a particular location. A textual description of the analytical qualitative and quantitative confidence and subsequent data usability is provided. Documentation of false positive data, and an indication of potential false negatives are also detailed in the L&Q section.

DATA QUALITY LEVELS

Data quality levels are individually determined for sampling design, documentation, field methods, and analytical data to assist the data user in assessing the overall programmatic usability of the data reported.

- Quality Level I data is of known quality, both quantitatively and qualitatively, and meets the objectives of the environmental problem as defined in the sampling and analysis plan.

- Quality Level II data encompasses the widest range of data quality and may be qualified in the limitations sections of the document. Level II data will be useful to the data user in most cases, but additional sampling and analysis may be necessary to confirm reported results.

- Quality Level III data may be useful as an indication of areas requiring further sampling and analysis to fully satisfy environmental problem objectives. Such data has a high probability of providing both false positives and false negatives and should not be used to draw conclusions as to the presence an environmental problem.

SUMMARY

Environmental analytical data can be effectively condensed into QC tables that report all calculated values. The QC tables can be used to assess the limitations and qualifications associated with the reported data. The QC tables also provide the basis for the inclusion/exclusion criteria used for producing summary tables showing contaminants definitively attributable to the samples.

The L&Q narratives provide documentation of analytical problems associated with the data that may impact the usability of the data. They also document the inclusion/exclusion criteria used to produce the summary data tables, and subsequently the programmatic usability of the analytical data. The summary data tables and L&Q narratives are used to write the text for the data evaluation and analytical limitations and qualifications sections of the data documents. This text is targeted to the data user and ties together the historical data, data quality objectives, field data, and analytical data.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Assistant Secretary for Environmental Safety and Health, Office of Environmental Audit, under DOE Contract No. DE-AC07-76ID01570.

Many thanks are extended to the numerous people that have contributed to the DOE Sampling and Analysis Data Documents for the Environmental Survey Program. Special thanks to A. Crockett, V. Fayne, O. Hester, D. Jones, R. Lugar, K. Martin, S. Scown, N. Stanisich, J. Steverson, B. Wiersma.

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U.S. Environmental Protection Agency (EPA) 1986, Statement of Work for Organic Analysis, USEPA Contract Laboratory Program, October 1986.

Table 1. Example: QC Table.

LABORATORY - VOLATILE ORGANIC QC DATA - SDG NUMBER 30901XA FOR INSTRUMENT QC/MS-F

	AREA	QC		QC		QC	TA-08-59	TA-08-59	QC	QC	QC
	LOCATION	INITIAL		CONTINUING		METHOD	INACTIVE	INACTIVE	MATRIX	MATRIX	RELATIVE
	TYPE OF LOCATION	CALIBRATN		CALIBRATN		BLANK	SEPTIC TANK	SEPTIC TANK	SPIKE	SPIKE DUP	% DIFFER
	SAMPLE NUMBER (ENVIR PROB)	VSTD050		VSTD050		VBLKY18FA	82302XX(24)	82301XX(24)	82301XXMS	82301XXMSD	82301XXRPD
	MEDIA	05/17/88		05/18/88		SOIL	SLUDGE	SLUDGE	SLUDGE	SLUDGE	
	UNITS	RRF	%RSD	RRF50	%D	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	
SPCC	Chloromethane	0.59	8.0	0.61	2.1	10 U	16 U	16 U	15 U	14 U	
	Bromomethane	1.13	13.0	1.06	6.5	10 U	16 U	16 U	15 U	14 U	
CCC	Vinyl Chloride	0.62	13.0	0.58	6.1	10 U	26	24	25	23	
	Chloroethane	0.40	12.5	0.38	6.7	10 U	300	450 E	460 E	450 E	
	Methylene Chloride	0.67	14.4	0.62	7.7	5 U	160	190	200	200	
	Acetone	0.46	23.9	0.63	35.0	10 U	260	180	140	200	
	Carbon Disulfide	2.36	10.7	1.95	17.3	5 U	8 U	8 U	7 U	7 U	
CCC	1,1-Dichloroethene	0.92	9.8	0.84	8.5	5 U	210	140	230(120%)	200(86%)	33%
SPCC	1,1-Dichloroethane	2.01	9.5	1.85	7.9	5 U	1100 E	510 E	520 E	530 E	
	1,2-Dichloroethene (total)	1.00	11.6	0.91	9.1	5 U	5600 E	6200 E	7 U	7 U	
CCC	Chloroform	2.78	9.8	2.61	6.1	5 U	320	59	65	57	
	1,2-Dichloroethane	1.88	11.0	1.76	6.3	5 U	130	110	110	110	
	2-Butanone	0.14	22.3	0.14	0.3	10 U	440 E	120	100	130	
	1,1,1-Trichloroethane	0.56	8.9	0.50	10.9	5 U	1200 E	160	170	160	
	Carbon Tetrachloride	0.82	10.5	0.75	8.6	5 U	8 U	8 U	7 U	7 U	
	Vinyl Acetate	0.84	12.7	0.76	9.6	10 U	16 U	16 U	15 U	14 U	
	Bromodichloromethane	1.06	9.1	0.97	8.4	5 U	8 U	8 U	7 U	7 U	
CCC	1,2-Dichloropropane	0.40	9.9	0.36	8.8	5 U	8 U	8 U	7 U	7 U	
	cis-1,3-Dichloropropene	0.58	10.5	0.54	6.5	5 U	8 U	8 U	7 U	7 U	
	Trichloroethene	0.53	9.9	0.49	6.9	5 U	55	33	110(101%)	95(87%)	15%
	Dibromochloromethane	1.16	10.0	1.04	9.8	5 U	8 U	8 U	7 U	7 U	
	1,1,2-Trichlorethane	0.38	12.9	0.34	11.4	5 U	32	9	9	9	
	Benzene	0.70	9.9	0.66	6.3	5 U	8 U	8 U	87(120%)	68(97%)	21%
	Trans-1,3-Dichloropropene	0.53	10.4	0.50	5.7	5 U	8 U	8 U	7 U	7 U	
SPCC	Bromoform	1.18	11.6	1.05	11.0	5 U	8 U	8 U	7 U	7 U	
	4-Methyl-2-Pentanone	0.66	16.1	0.60	9.3	10 U	16 U	16 U	15 U	14 U	
	2-Hexanone	0.51	12.4	0.51	0.0	10 U	16 U	16 U	15 U	14 U	
	Tetrachloroethene	0.60	10.4	0.56	6.0	5 U	8 U	8 U	7 U	7 U	
SPCC	1,1,2,2-Tetrachloroethane	1.16	12.2	1.06	8.6	5 U	8 U	8 U	7 U	7 U	
CCC	Toluene	0.62	10.5	0.60	3.8	5 U	72	47	130(110%)	120(104%)	6%
SPCC	Chlorobenzene	1.02	10.0	0.96	5.9	5 U	8 U	8 U	80(106%)	66(94%)	12%
CCC	Ethylbenzene	0.43	10.4	0.40	6.3	5 U	8 U	3 J	7 U	7 U	
	Styrene	0.90	10.0	0.83	7.0	5 U	8 U	8 U	7 U	7 U	
	Xylene (total)	0.54	10.5	0.50	7.2	5 U	8 U	8 U	7 U	7 U	

LABORATORY - VOLATILE ORGANIC QC DATA - SDG NUMBER 30901XA FOR INSTRUMENT GC/MS-F (Continued)

AREA	QC		QC		QC	TA-08-59	TA-08-59	QC	QC
LOCATION	INITIAL		CONTINUING		METHOD	INACTIVE	INACTIVE	MATRIX	MATRIX
TYPE OF LOCATION	CALIBRATN		CALIBRATN		BLANK	SEPTIC TANK	SEPTIC TANK	SPIKE	SPIKE DUP
SAMPLE NUMBER (ENVIR PROB)	VSTD050		VSTD050		VBLKY1BFA	82302XX(24)	82301XX(24)	82301XXMS	82301XXMSD
MEDIA	05/17/88		05/18/88		SOIL	SLUDGE	SLUDGE	SLUDGE	SLUDGE
UNITS	RRF	%RSD	RRF50	%D	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
Toluene-d8	1.00	2.6	1.00	0.1					
Bromofluorobenzene	1.06	2.0	1.06	0.2					
1,2-Dichloroethane-d4	1.29	6.8	1.19	7.3					
Surr 1(TOL) %Recovery					104	105	108	109	111
Surr 2(BFB) %Recovery					103	94	90	90	86
Surr 3(DCE) %Recovery					96	91	97	101	96
Method Blank Run (Y/N)						YES	YES	YES	YES
Tunes Out of Criteria									
Minutes Past 12-Hr Tune									
Internal Std Area(BCM)			1253474		1102365	1157139	900672	830942	952914
Internal Std Area(DFB)			4125916		3746070	3662568	2838171	2648791	3059230
Internal Std Area(CBZ)			3303637		2996012	2815925	2135578	2014899	2175819
BCM Ret Time Shift									
DFB Ret Time Shift									
CBZ Ret Time Shift									
Dilution Factor					1.000	1.000	1.000	1.000	1.000
Percent Moisture						45	44	44	44
Field/Shipping Time						3	3		
Anal (Allowed) Hold Time						12(10)d*	12(10)d*		
Total (Allowed) Hold Time						15(14)d*	15(14)d*		
ELEVated/DECReased CRQL						ELEV	ELEV	ELEV	ELEV

Min RRF and RRF50 for SPCC = 0.300 (0.250 for Bromoform).
Max %RSD = 30.0% and max %D = 25.0% for CCC.

Table 2. Example: QC Table for TICs.

Tentatively Identified Compounds - Volatile Organics

SORTED BY INSTRUMENT & EPAS

** SDGNO & INSTRID: 30901XA GC/MS-F

Sample Number	CAS Number	Compound	Concentration Units	Qualifier	Retention Time (Minutes)
80301XX	76131	TRICHLOROTRIFLUOROETHANE	12 ug/kg	JB	11.88
82301XX	646060	1,3-DIOXOLANE	65 ug/kg	J	8.64
82301XX	354234	DICHLOROTRIFLUOROETHANE	47 ug/kg	J	9.90
82301XX	76131	TRICHLOROTRIFLUOROETHANE	36 ug/kg	JB	11.92
82301XX		POSS TERPENE	37 ug/kg	J	25.63
82302XX	75376	1,1-DIFLUOROETHANE	13 ug/kg	J	1.70
82302XX	646060	1,3-DIOXOLANE	120 ug/kg	J	8.63
82302XX	354234	DICHLOROTRIFLUOROETHANE	140 ug/kg	J	9.87
82302XX	76131	TRICHLOROTRIFLUOROETHANE	750 ug/kg	JB	11.92
82302XX	78922	2-BUTANOL	42 ug/kg	J	15.72
82302XX		UNKNOWN	11 ug/kg	J	20.68
82302XX		POSS TERPENE	29 ug/kg	J	25.67
VBLKY19FA	76131	TRICHLOROTRIFLUOROETHANE	14 ug/kg	J	11.89

Table 3. Example: Summary Table.

LABORATORY - VOLATILE ORGANIC DATA - ENVIRONMENTAL PROBLEM 24

AREA	TA-16	TA-16	TA-16	TA-16	TA-16	TA-08-59	TA-08-59
LOCATION	BACKFILLED	BACKFILLED	BACKFILLED	BACKFILLED	BACKFILLED	INACTIVE	INACTIVE
TYPE OF LOCATION	LWD POND	LWD POND	LWD POND	LWD POND	LWD POND	SEPTIC TANK	SEPTIC TANK
SAMPLE NUMBER	82108XX	82109XX	82110XX	82111XX	82112XX	82301XX	82302XX
MEDIA	SS SOIL	SS SOIL	SS SOIL	SS SOIL	SS SOIL	SLUDGE	SLUDGE
UNITS	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
SDG NUMBER	82107XX	82107XX	82107XX	82107XX	82107XX	30901XA	30901XA
FIELD MEASUREMENTS							
Depth (ft)	0-5	0-5	0-5	0-5	0-5	3.8-6.8	3.8-6.8
TARGET COMPOUNDS							
Vinyl Chloride	---	---	---	---	---	24	26
Chloroethane	---	---	---	---	---	450 E	300
Methylene Chloride	---	---	---	---	---	190	160
Acetone	---	---	---	---	---	180	260
1,1-Dichloroethene	---	---	---	---	---	140	210
1,1-Dichloroethane	---	---	---	---	---	510 E	1100 E
1,2-Dichloroethene_(total)	---	---	---	---	---	6200 E	5800 E
Chloroform	---	---	---	---	---	59	320
1,2-Dichloroethane	---	---	---	---	---	110	130
2-Butanone	---	---	---	---	---	120	440 E
1,1,1-Trichloroethane	---	---	---	---	---	160	1200 E
Trichloroethene	---	---	---	---	2 J	33	55
1,1,2-Trichlorethane	---	---	---	---	---	9	32
Benzene	---	---	---	---	4 J	---	---
4-Methyl-2-Pentanone	---	---	---	---	---	---	---
2-Hexanone	---	---	---	---	---	---	---
Tetrachloroethene	---	---	---	---	---	---	---
Toluene	---	---	---	---	5 J	47	72
Chlorobenzene	---	---	---	---	4 J	---	---
Ethylbenzene	---	---	---	---	---	3 J	---
TENTATIVELY IDENTIFIED COMPOUNDS							
2-Butanol	---	---	---	---	---	---	42 J
Dibromoethene	---	---	---	---	---	---	---
1,1-Difluoroethane	---	---	---	---	---	---	13 J
Dimethyldisulfide	---	---	---	---	---	---	---
Poss Terpene	---	---	---	---	---	37 J	29 J
Total (Allowed) Hold Time	9(14)d	27(14)d*	27(14)d*	27(14)d*	14(14)d	15(14)d*	15(14)d*
ELEVated/DECReased CRQL	ELEV	ELEV	ELEV	ELEV	ELEV	ELEV	ELEV
Dilution Factor	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Figure 1. L&Q Narrative.

SDG COVER PAGE WITH SAMPLE INDEX
LIMITATIONS AND QUALIFICATIONS NARRATIVES
COMMENTS THAT ARE APPLICABLE TO THE ENTIRE SDG

SAMPLE NUMBER	SOIL	WATER	AIR	PROBLEM NUMBER	REMARKS
** SDG Number: 30901XA					
* Analysis Type: VOLATILES					
30801XX	X			9	VOA TEMP 15-C
30802XX	X			9	VOA TEMP 15-C
30803XX	X			9	VOA TEMP 15-C
30804XX	X			9	VOA TEMP 15-C
30901XA		X		10	
30901XB		X		10	
30902XA		X		10	
30902XB		X		10	
30903XA		X		10	VOA TEMP 15-C EXPLOSIVE
30903XB		X		10	VOA TEMP 15-C EXPLOSIVE
31001XA		X		10	
31001XC		X		10	
31002XA		X		10	
31002XB		X		10	
31003XB		X		10	VOA TEMP 15C EXPLOSIVE
31003XC		X		10	VOA TEMP 15C EXPLOSIVE
50301XX	X			16	HAZ TRANSFORMER OIL
50302XX	X			16	HAZ TRANSFORMER OIL
50303XX	X			16	HAZ TRANSFORMER OIL
80301XX	X			22	VOA TEMP 15C EXPLOSIVE
82301XX	X			24	
82302XX	X			24	
90101XA		X		0	QC
90301XA		X		0	QC
90401XA		X		0	QC VOA TEMP 15-C PRIORITY
90601XA		X		0	QC VOA TEMP 15-C PRIORITY

=> Low Level Soil MS/MSD (82301XX)
All spike recoveries were within the protocol recovery limits. However, the RPD value for 1,1-dichloroethene was 33% (upper QC RPD limit of 22%). Impact to the data is minimal with the problem being in the precision of the data, not the accuracy. The fact that 1,1-dichloroethene was detected at 140 µg/kg in the non-spiked sample could add to the variability of the MS/MSD recoveries for this compound. As the precision for the other four matrix spike compounds were within the QC limits, it is unlikely that the precision of the data for the other samples associated with this MS/MSD were adversely compromised either.

=> All of the method blanks in this SDG met CLP quality control criteria for background contamination except for those run on instrument E on 5/12/88 (VBLK>Y12EA), 5/26/88 (VBLK>Y26EA), and 5/27/88 (VBLK>Y27EA). These 3 blanks had methylene chloride greater than 5 times the CRQL. The data user should consider all comparable concentrations of methylene chloride detected in the associated samples as being attributable to laboratory contamination. (Delete from the results tables.)

Figure 2. L&Q Narrative.

LIMITATIONS AND QUALIFICATIONS NARRATIVES
COMMENTS APPLICABLE TO EACH SAMPLE NUMBER

ANALYSIS TYPE	SDG #	SOIL	WATER	AIR	REMARKS
** Sample Number: 82301XX					
* Environmental Problem Number: 24					
VOLATILES	30901XA	X			

=> MS/MSD run on this sample. See comments on the cover page for this SDG.

=> Analysis of this sample exceeded the allowed holding time by 2 days. Slight possibility of false negatives and/or low bias to sample concentrations. Total holding time 15 days.

=> CRQLs elevated by a factor of 1.6, no impact to data usability.

=> The concentrations detected for chloroethane, 1,1-dichloroethane, and 1,2-dichloroethene (total) exceeded the calibration range as noted by the "E" flag. These values (450, 510, and 6,200 µg/kg respectively) may be underestimated since the quantitative values are outside of the linear range of the instrument (32-320 µg/kg).

=> Value for acetone is biased low by a factor of 1.4 due to a high RRF50 (0.63) for the continuing calibration used for quantitation of this sample. Therefore a more accurate concentration would be approximately 250 µg/kg rather than 180 µg/kg as reported in the tables.

=> Note: Methylene chloride was <u>not</u> detected in the method blank associated with this sample and therefore the results were included in the results tables as were all other concentrations of contaminants detected in this sample.

=> The overall quality of this data is acceptable and demonstrates the survey objective of determining the presence of contaminants.

MULTIVARIATE METHODS FOR THE ANALYSIS OF QA/QC DATA

W. J. Dunn III, University of Illiois at Chicago, m/c 781, Box 6998, Chicago, Illinois 60680; David Bottrell, U. S. Environmental Protection Agency, Box 93478, Las Vegas, Nevada 89193-3478

INTRODUCTION

From the data analytic point of view, the assessment of quality assurance/quality control data is generally considered to be a univariate problem (1). In many instances this is indeed the case. Comparing two methods of analysis for a single analyte is a good example. In some cases, however, it may be more appropriate to use multivariate methods for the analysis of quality assurance/quality control data (2). In comparing the performance of several labs in the analysis of a number of analytes, multivariate methods can be used.

In this report a set of quality assurance/quality control data are analyzed to determine the effect, if any, of an added preservative on the analysis of 24 low molecular weight organic analytes. Standard samples of the 24 analytes were prepared. Each sample was divided in two and a preservative was added to one aliquot. These samples were then submitted to three laboratories, coded here as Lab 1, Lab 2 and Lab 3, for analysis at specified periods. The results are given in Table 1.

There is considerable additional information in these data. In addition to possible variation due to the effect of an added preservative on the results, interlaboratory performance variability may be present in the data. Data analytic techniques can be applied to address both of these questions. In this report, the data are first analyzed to determine if an added preservative has an effect on the 24 analytes. In addition, the performances of the laboratories are compared.

METHOD

The question of whether there is a difference in the analytical results of preserved and unpreserved samples was considered first. The data were grouped by laboratory. There were 6 sets of results from Lab 1 and Lab 2 and 5 sets of results from Lab 3. The laboratory coded PE was the lab which prepared the standard solutions. In each set of results for each laboratory there are 24 analytes analyzed by the same method. For each analyte in each set there are results on the

preserved and unpreserved sample.

The approach taken in the analysis of the data is illustrated for the first analyte, 2-hexanone, from in Table 1. The results of this analyte are reported in the first two columns and these are given in Table 2 for Lab 1.

y_p and y_u are means of the preserved and unpreserved results. There is no reason to assume that the mean value of y_i, y_p, should be different from that of y_k, y_u. Therefore, the differences, $(y_i - y_k)$, are assumed to have known population means, n_i and n_k. Thus for 2-hexanone the variance of differences can be calculated as

$$s^2 = [(10.60 - 0)^2 + (8.20 - 0)^2 + \ldots + (15.60 - 0)^2]/6$$
$$= 115$$

and the standard deviation of differences

$$s = 10.72$$

The population means for the preserved and unpreserved samples are n_i and n_k. If, as assumed, there is no difference in the two types of samples, $n_i - n_k = 0$. The null hypothesis becomes $n_i - n_k = 0$ and the t-statistic can be calculated for the data in Table 2. t is the residual per standard deviation. If there is no difference in the two types of samples, t would be near zero.

$$t_o = [(y_i - y_k) - (n_i - n_k)]/10.72$$
$$t_o = (62.00 - 0)/10.72 = 5.78$$

From tables of t-statistics for 6 degrees of freedom, the probability that 5.78 is greater than zero is 0.999 so the null hypothesis can be rejected. The preserved and unpreserved results are statistically different for this analyte in this lab.

A program was written to apply this test to the data from each analyte and each laboratory. In the case of Lab 1 and Lab 2 there are 6 degrees of freedom in their results and 5 degrees of freedom in the Lab 3 data. The results are summarized in Tables 3 - 6.

AN INTERLABORATORY COMPARISON

It is assumed that the laboratories received identical samples for each analyte. The laboratories, Lab 1 and Lab 2, report 6 sets of results and the laboratory Lab 3 reports 5

sets of results for the 24 analytes. Principal components analysis and a plot of the three principal component scores for the labs shows that there are two groups of labs and one lab which is an outlier to these two groups. The lab coded 10 is the outlier and on exmanination of the data set shows that this represents the set of results for Lab 3 dated October 17, 1988. An examination of the loadings for the second principal component suggests that this is due to the results of this lab for the analyte, carbon disulfide, which has a reported value of 104.00. This is approximately 5 times the values reported in the other labs for this sample and suggests, since these are replicates of 5 samples, that this result represents a sum and not the average of the five results.

Deletion of lab result 10 and derivation of a new 3 component principal components model give the score plot in Figure 1. Here the two groups of labs are again obvious. The analyte, chloromethane is heavily loaded in the first principal component and the reults for this analyte from this lab separates the labs into two groups.

Deletion of variables 3 and 4, the results of analysis of preserved and unpreserved samples of chloromethane lead to Figure 2, a principal components score plot of the 3 component model after deleting the variables 3 and 4. The two groups of laboratories tend to merge into one with some suggestion of two clusters but these are not distinct.

These results are consistent with the results of the data analysis in the first part of this report. The lab coded Lab 3 gave results which were consistently different from the other two labs.

Table 1. Results of the analysis of preserved and unpreserved samples of 24 analytes. Result #1 is the report of laboratory PE on DAY-MONTH-YEAR for the 24 analytes. The data for each analyte are paired under each laboratory. Each analyte concentration is the average of 5 replicate determinations. Columns 1 - 6 in row 1 represent the preserved and unpreserved results for the first three analytes, columns 1 - 6 in row 2 are the next three analytes, etc. The analtyes in the order reported below are 2-hexanone, chloromethane, bromomethane, chloroethane, methylene chloride, acetone, carbon disulfide, 1,1-dichloroethene, 1,1,-dichloroethane, chloroform, 2-butanone, carbon tetrachloride, 1,2-dichlorpropane, trichloroethene, 1,1,2-trichloroethane, benzene, bromoform, 4-methyl-2-pentanone, 1,1,2,2-tetrachlorethane, toluene,chlorobenzene, ethylbenzene, styrene, xylene (total). Missing data are coded with -99 in lab PE.

Result #	Laboratory code	Date
1	PE	010888

.00	51.00	58.00	52.00	55.00	51.00
.00	47.00	2.00	1.00	25.00	50.00
.00	42.00	64.00	63.00	54.00	55.00
.00	51.00	-99.00	-99.00	46.00	45.00
.00	52.00	51.00	52.00	54.00	54.00
00	106.00	54.00	54.00	51.00	50.00
00	55.00	102.00	98.00	50.00	48.00
00	94.00	103.00	98.00	55.00	58.00

Result #	Laboratory code	Date
2	PE	140988

00	39.00	130.00	110.00	67.00	54.00
00	57.00	25.00	18.00	19.00	31.00
00	38.00	59.00	57.00	60.00	55.00
00	47.00	29.00	40.00	46.00	41.00
00	49.00	44.00	47.00	49.00	49.00
00	99.00	43.00	48.00	35.00	48.00
00	56.00	99.00	96.00	47.00	47.00
00	84.00	84.00	78.00	62.00	55.00

3 Lab 1 031088

33.80	23.20	61.20	64.00	65.00	62.60
57.80	55.00	20.80	18.00	23.20	22.00
28.80	31.00	50.00	51.60	60.20	57.20
58.60	57.40	25.40	20.80	49.00	47.40
55.40	51.80	41.40	47.20	54.20	51.80
106.00	100.60	52.60	52.20	44.40	37.80
58.40	45.00	104.00	104.00	47.80	47.40
97.40	94.40	88.20	88.40	54.20	54.40

4 Lab 3 031088

47.00	41.40	34.20	35.40	48.80	49.60
61.00	60.60	19.00	18.40	36.80	40.00
29.80	34.60	53.80	57.60	59.60	62.00
55.60	57.40	31.80	32.60	62.20	62.80
52.60	52.40	47.00	54.60	53.80	52.60
100.40	103.80	52.60	53.00	47.60	45.60
55.60	46.00	95.80	98.60	48.40	49.80
94.40	97.40	89.60	92.60	56.40	59.20

5 Lab 2 031088

46.80	38.00	99.00	96.80	54.60	53.60
65.20	63.60	18.40	17.20	69.00	68.80
28.40	33.20	48.20	51.40	56.00	57.80
53.60	54.00	51.00	47.00	49.00	51.00
49.40	49.80	44.40	50.00	48.80	47.60
98.60	99.40	50.60	51.60	43.20	41.60
52.20	45.20	95.80	96.40	47.40	48.00
93.00	94.20	96.00	97.40	57.20	57.60

6 Lab 1 111088

29.80	21.60	59.20	56.00	49.60	45.60
60.40	57.00	19.00	14.00	20.40	18.60
26.80	31.20	46.00	47.40	55.40	53.60
55.40	53.60	24.40	21.00	48.80	49.40
54.40	53.40	41.40	49.60	53.80	51.80
102.00	101.60	53.80	53.80	42.20	37.40
56.40	45.00	100.00	100.80	47.60	48.20
96.80	96.80	88.40	89.40	55.00	54.80

7	Lab 3	111088			
5.40	41.20	49.00	42.40	48.80	47.00
2.80	60.80	18.40	17.20	39.40	40.80
9.20	55.20	53.40	53.40	60.40	59.60
7.80	57.20	45.80	46.60	65.20	66.20
3.80	54.40	52.00	61.00	58.40	60.00
0.00	112.00	56.40	60.00	49.80	51.20
0.60	51.40	98.80	101.20	52.20	52.00
8.00	96.20	91.60	92.40	58.80	57.80

8	Lab 2	111088			
9.00	28.20	120.00	118.00	56.00	55.40
.60	60.00	19.00	15.80	37.20	34.20
3.60	26.20	44.60	43.60	57.80	57.20
.60	60.40	42.20	34.40	55.20	54.40
3.40	51.80	45.00	50.40	53.80	50.00
3.00	104.00	54.40	51.20	51.20	42.60
.80	51.20	108.00	104.00	50.80	50.20
.00	99.60	79.80	79.20	62.60	63.20

9	Lab 1	171088			
.20	37.20	63.60	55.80	60.80	55.20
.60	60.60	21.20	17.40	28.80	27.60
.40	29.00	51.60	49.60	58.80	56.20
.20	54.80	40.60	35.20	58.40	55.00
.60	58.80	45.60	52.60	60.20	58.60
.00	110.00	60.60	62.40	60.80	55.60
.00	54.60	106.00	100.00	51.40	50.20
.40	93.40	92.00	90.80	58.00	57.00

10	Lab 3	171088			
.00	28.40	50.00	46.40	57.40	54.20
.60	61.20	19.60	17.80	41.60	40.00
.00	110.00	50.80	50.80	58.20	56.40
.40	53.00	26.80	27.20	57.00	56.40
.20	50.20	48.40	52.00	54.00	53.20
.00	102.00	55.00	55.80	40.20	39.60
.80	48.60	99.20	99.00	49.00	48.80
.60	96.60	83.60	83.00	56.40	55.60

11	Lab 2	171088			
44.20	35.20	102.20	108.00	52.40	52.00
56.60	57.40	18.80	15.80	49.80	52.40
21.80	26.80	43.00	44.80	53.20	57.20
50.80	52.60	46.80	40.60	51.80	52.80
50.00	54.20	46.20	54.00	49.40	47.80
97.80	98.40	54.60	51.40	44.80	40.60
57.80	45.20	97.40	98.80	48.20	49.00
92.60	92.60	81.60	84.00	55.80	57.20

12	Lab 1	241088			
33.20	25.00	72.20	60.60	70.00	67.40
71.40	66.00	22.40	18.00	22.20	21.80
53.20	60.60	50.00	49.00	61.40	56.20
55.80	53.20	29.40	25.80	56.20	54.80
61.40	56.80	43.60	51.60	59.00	56.20
108.00	104.80	66.20	63.00	45.40	39.60
61.80	45.80	96.60	96.60	49.20	48.80
95.20	93.40	93.40	91.80	55.80	56.60

13	Lab 3	241088			
53.00	40.20	44.00	43.20	66.00	62.20
60.20	58.20	37.00	34.80	33.20	34.40
27.60	30.80	50.20	49.80	59.40	58.00
57.20	56.20	33.60	32.40	58.80	60.40
53.80	53.60	47.00	54.80	54.80	53.60
106.00	104.00	55.60	55.80	47.80	44.60
59.60	48.60	102.00	102.00	49.80	50.00
96.40	95.60	90.80	93.40	59.60	60.20

14	Lab 2	241088			
41.00	30.40	120.00	116.00	59.40	58.40
60.20	57.80	16.00	14.80	40.60	40.20
21.80	25.00	43.00	44.20	55.00	52.80
50.80	49.40	37.40	33.80	48.60	48.20
48.80	46.80	39.00	44.60	47.40	44.20
96.20	93.40	47.40	44.80	37.40	33.00
47.80	37.80	90.80	89.60	44.60	43.80
91.00	87.60	90.20	89.20	57.20	55.40

15	Lab 1		311088		
32.80	25.40	78.00	72.00	57.40	53.60
18.00	48.80	20.20	16.60	24.00	21.80
34.20	37.80	40.80	43.20	54.60	53.60
51.20	51.60	26.60	23.60	46.20	47.40
56.00	55.40	41.60	48.40	52.80	51.20
)4.00	102.00	62.00	60.60	44.00	41.00
56.20	45.40	94.80	98.40	46.60	46.40
)3.20	93.00	87.00	89.80	55.80	56.20
16	**Lab 2**	**311088**			
7.00	36.00	105.00	108.33	46.50	48.75
4.50	55.25	18.50	15.42	46.50	52.92
1.50	25.42	43.00	47.33	58.00	59.17
3.50	54.00	45.50	39.50	48.50	50.50
4.50	53.42	43.00	50.67	55.50	52.33
5.00	105.00	53.00	52.50	49.00	44.00
3.50	50.75	103.50	99.92	49.00	48.42
8.00	98.67	87.00	87.75	62.00	60.58
17	**Lab 1**		**281188**		
6.80	31.20	51.40	57.80	46.60	45.40
2.40	62.00	17.40	14.60	18.80	19.40
8.80	21.40	39.20	42.20	48.80	50.00
1.20	51.60	36.60	30.20	51.00	52.40
7.20	47.40	38.00	45.40	52.80	51.60
6.40	96.80	57.60	57.20	43.60	42.20
4.40	45.00	90.40	92.40	46.40	45.20
8.00	88.40	80.00	81.80	56.00	56.80
18	**Lab 3**		**281188**		
3.40	29.80	32.00	32.40	49.00	46.40
7.60	56.00	18.40	15.20	25.00	22.80
9.80	22.20	44.80	46.40	60.60	58.60
5.40	53.60	37.80	29.40	57.00	56.40
1.80	49.00	41.80	50.00	53.20	50.80
9.00	96.40	50.20	49.20	44.60	38.20
4.80	42.00	96.00	95.80	47.60	48.40
5.20	93.80	83.80	83.40	57.60	57.20

19 Lab 2 281188

55.80	43.20	110.00	116.00	49.40	47.00
54.40	58.60	20.40	17.40	44.00	45.80
21.00	26.60	43.60	50.40	62.20	62.60
56.60	57.40	54.40	46.80	46.60	55.40
54.80	54.40	40.00	51.80	55.20	53.80
106.00	110.00	56.00	57.00	47.80	44.20
61.60	48.40	95.60	101.20	47.20	48.60
94.40	95.80	78.60	82.40	65.40	64.00

Table 2. Data for 2-hexanone from Lab 1.

Result	Preserved y_i	Unpreserved y_k	Difference $y_i - y_k$
1.	33.80	23.20	10.60
2.	29.80	21.60	8.20
3.	49.20	37.20	12.00
4.	33.20	25.00	8.20
5.	32.80	25.40	7.40
6.	46.80	31.20	15.60
	$\bar{y}_p$ = 37.60	$\bar{y}_u$ = 27.27	Σ 62.00

ble 3. Summary of results. The number under each labortory is the t-statistic for that analyte for comparing the difference in results from a preserved and unpreserved sample. The number in parenthesis is the probability that the null hypothesis, the two treatments are equivalent, can be rejected.

te	Laboratory		
	1	2	3
anone	5.78(>.999)	4.31(>.99)	5.95(>.999)
omethane	2.79(>.97)	2.74(>.97)	-1.65(>.90)
methane	5.51(>.999)	3.98(>.99)	2.11(>.95)
oethane	4.50(>.99)	4.34(>.99)	-0.54(>.40)
lene chloride	5.87(>.999)	4.49(>.99)	5.64(>.99)
ne	4.48(>.99)	-0.97(>.75)	-2.27(>.95)
n disulfide	-5.31(>.99)	-4.75(>.99)	-5.82(>.99)
ichloroethene	-2.68(>.97)	-2.69(>.97)	-4.45(>.97)
ichloroethane	4.36(>.99)	2.04(>.95)	-2.19(>.95)
oform	4.21(>.99)	2.14(>.95)	-1.85(>.90)
anone	5.79(>.999)	1.98(>.90)	5.78(>.999)
n tetrachloride	1.76(>.90)	-2.08(>.95)	-3.30(>.99)
ichloropropane	4.48(>.99)	2.93(>.97)	0.23(<.40)
loroethene	-5.96(>.999)	-4.84(>.99)	-5.74(>.999)
-trichlorethane	5.78(>.999)	2.60(>.97)	5.50(>.999)
ne	4.62(>.99)	1.47(>.90)	0.54(>.40)
form	2.22(>.95)	-2.32(>.95)	3.38(>.99)
hyl-2-pentanone	5.58(>.999)	3.18(>.97)	5.45(>.999)
,2-tetrachloro-			
e	5.89(>.999)	4.84(>.97)	5.87(>.999)
ne	-0.13(<.40)	-2.90(>.97)	0.36(<.40)
obenzene	3.61(>.99)	-2.71(>.97)	-0.97(>.75)
benzene	3.62(>.99)	0.58(>.40)	0.33(>.40)
ne	-1.83(>.90)	-2.93(>.97)	-3.37(>.99)
e (total)	-1.54(>.90)	-0.84(>.75)	1.74(>.90)

Table 3.Analytes for which there is a significant, positive effect of added preservative on the results with a probability of >.90

2-hexanone
bromomethane
methylene chloride
2-butanone
1,1,2-trichlorethane
4-methyl-2-pentanone
1,1,2,2-tetrachloroethane

Table 4. Analytes which there is a significant, negative effect of added preservative on the results with a probability of >.90

carbon disulfide
1,1-dichloroethene
trichloroethene
styrene

Table 5. Analytes for which there is no significant difference in the results of added preservative on the results in two of the three laboratories.

toluene
ethylbenzene

Table 6. Analtyes for which the effect of added preservative is ambiguous. These are analytes which show no effect of preservative in one laboratory or a significant effect in two labs but a significant and opposite effect in the other.

chloromethane
chloroethane
acetone
1,1-dichloroethane
carbon tetrachloride
bromoform
chloroform
1,2-dichloropropane
benzene
chlorobenzene
xylene (total)

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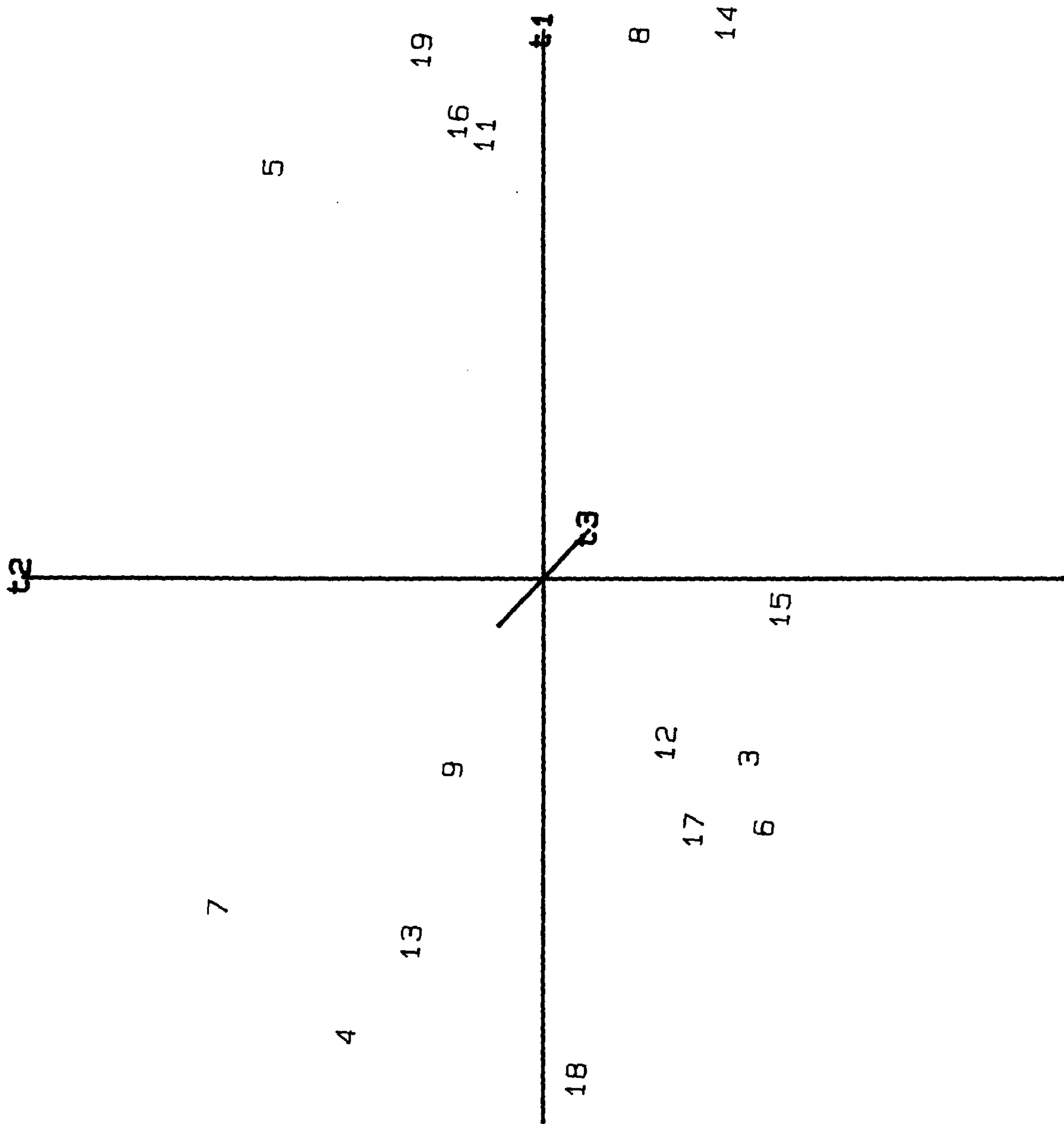
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APPLYING TOTAL QUALITY PRINCIPLES TO SUPERFUND PLANNING

Dean Neptune, Environmental Scientist
Quality Assurance Management Staff
United States Environmental Protection Agency
410 M Street Southwest
Washington, District Of Columbia 20460

ABSTRACT

The Quality Assurance Management Staff (QAMS) has been working with the Superfund staff in the regions and headquarters to help better resolve the uncontrolled hazardous waste site questions relating to environmental data collection:

1) How many samples are enough?
2) Where should samples be collected?
3) What kind of samples should be collected?

These planning questions are all revelant to each important decision that is routinely made during the Superfund site remediation process e.g. Does the site represent an unacceptable risk necessitating remediation. This paper shows how applying total quality principles through the Data Quality Objectives (DQO) process leads to the:

* development of a statistically valid sampling and analysis design which meets decision maker requirements,

* optimization of time and resources in environmental data collection activities,

* quantitative basis of determining data utility to other remedial process decisions,and

* streamlined planning methodology where parallel feasibility activities are started as soon as planning allows.

TOTAL QUALITY PRINCIPLES

The Quality Assurance Mangement Staff (QAMS) began in January 1984 to apply Total Quality Principles to environmental data collection operations in the US Environmental Protection Agency (USEPA). The elements of Total Quality which became the focus of QAMS efforts include:

* improving customer-supplier relationships,
* developing statements of customer needs and performance measures,
* obtaining senior management commitment and involvement,
* providing relevant training, and
* ensuring employee recognition and reward.

To build Total Quality into EPA operations, QAMS has developed a planning tool for assuring that the customer and supplier perform the key planning steps in a thoughtful, methodical manner. This tool, known as the Data Quality Objectives (DQO) Process, begins with an understanding of the environmental problem and results in collecting the information needed to

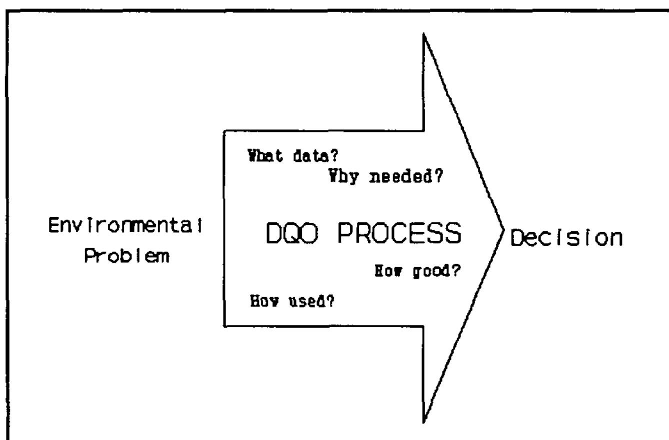

Figure 1. The DQO process establishes the level of uncertainty which the decision maker is willing to accept in results derived from environmental data.

make an informed decision with a known, acceptable, degree of confidence (Figure 1).

The primary products of Superfund efforts, as with other non-manufacturing organizations are decisions. To support these decisions, Superfund has been spending more than $150 million per year and causing responsible parties to spend at least this much to collect the required environmental data. With annual expenditures of this magnitude, the DQO process is clearly warranted. The generic stucture of the DQO process is presented in Figure 2. This structured process assures that the right type and quality of data are produced in a timely, cost-effective manner so that a quality decision is assured.

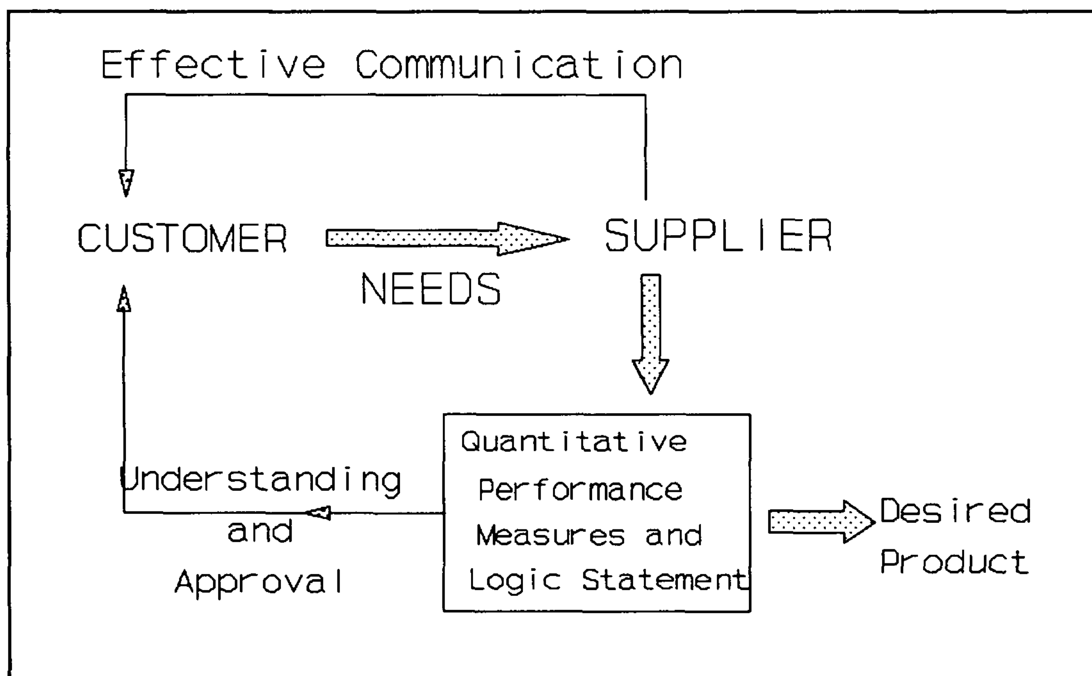

Figure 2. Iterative communication between the customer and supplier is a key feature of the DQO process.

CUSTOMER NEEDS AND PERFORMANCE MEASURES

The DQO Process begins with a consideration of customer needs. The customer's needs must be effectively communicated to the supplier. Multiple iterations may be neccessary before the actual needs are articulated and the customer and supplier reach understanding and agreement on a qualitative description of what is needed. The supplier can develop performance measures from this qualitative statement. Generically speaking, performance measures describe the type and quality of product that will be produced. Once the customer understands and approves these performance measures, the supplier can begin developing the detailed production plan and produce the required product.

THE DQO PROCESS APPLIED TO SUPERFUND DECISIONS

In Superfund, the products are remedial decisions. The customer is the decision maker/data user and the supplier is the data collector.

Although the DQO process was developed for direct application to environmental decision making, the process is generic and can be employed in any decison making process that involves uncertainty.

The DQO process based on this generic model is depicted in Figure 3. This process begins with a careful definition of the environmental problem at hand. The decision is stated in terms of specific action options which will address the problem. The information required to select the appropriate course of action is identified, and the specific role that data will play is very carefully articulated. Next, the type of data needed is specified as is the way it will be used to make a defensible decision (the "logic statement") with the desired degree of

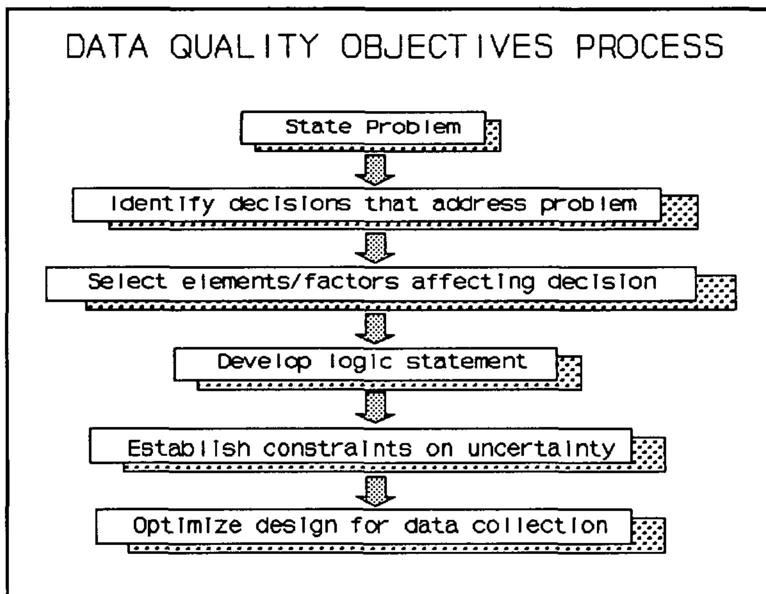

Figure 3. The DQO process includes a comprehensive set of steps in a logical sequence.

certainty (derived from an expression of the aversion the decision maker has to various incorrect decision scenarios). Performance measures are then developed through an iterative process involving both the decision maker and data collector (customer and supplier).

With Data Quality Objectives, the customer has a logical, objective, and quantitative framework for finding an appropriate balance between the time and resources that will be needed to produce the product and the quality of that product (Figure 4).

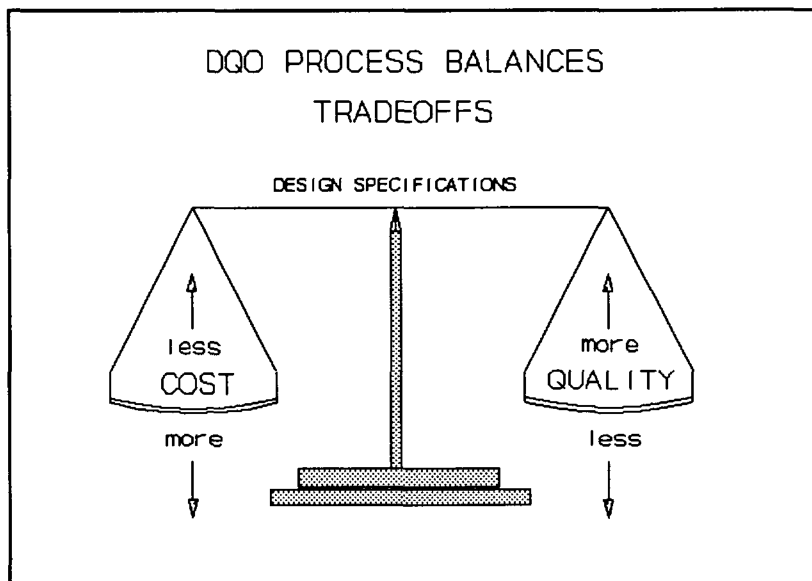

Figure 4. The DQO process provides a logical procedural framework for balancing cost against product quality.

DQOs enable Superfund to develop, optimize, and evaluate statistically valid sampling and analysis designs which achieve the desired

performance. In general, several options within budget constraints that will generate the type and quality of data required to make a quality decision are developed. In the final step of the DQO process, the decision maker selects the design option that best fits his or her needs.

For more information and examples, contact Stan Blacker, Director of EPA's Quality Assurance Management Staff at (202) 382-5763.

SAMPLING AND FIELD METHODS

EVALUATION OF A FIELD-PORTABLE SUPERCRITICAL FLUID EXTRACTION APPARATUS FOR RAPID CHARACTERIZATION OF CONTAMINATED SOILS

Bob W. Wright, Cherylyn W. Wright, Chemical Sciences Department, and Jonathan S. Fruchter, Environmental Sciences Department, Battelle Northwest Laboratories, Richland, Washington 99352

ABSTRACT

Rapid, field-portable methods for measuring the concentrations of semivolatile organic pollutants are desirable for on-site characterization of contaminated sediments and soils. In addition to providing efficient site assessment capability, rapid characterization methods would also be highly useful at sites undergoing remediation treatments. As an alternative to current methods, supercritical fluid extraction (SFE) has been evaluated for in-the-field coal and petroleum gasification waste site characterization. The gas-like mass transfer properties of supercritical fluids allow more rapid extraction rates and more efficient penetration of the matrix than conventional solvent extractions. The method has proved to be rapid, reproducible, and successful in several field trips.

INTRODUCTION

Several modern analytical techniques (e.g., capillary gas chromatography, high performance liquid chromatography, mass spectrometry) are available for the identification and quantification of a range of organic compounds found in contaminated soils and sediments. However, some type of extraction method is generally required to remove the analytes from the environmental matrix. The most commonly employed extraction method (Environmental Protection Agency SW 846 method 3540) requires long extraction times (up to 24 hours for Soxhlet methods), large quantities of ultrapure solvents, and lengthy solvent concentration procedures. Because of these constraints, it is not generally considered to be suitable for field-portable applications. In order to implement remedial measures and to carry out cost-effective site assessments, more rapid and field-adaptable sample extraction methods are desirable. Supercritical fluid extraction (SFE) techniques provide a viable alternative with promising advantages over the current liquid extraction methods (1-4). SFE equipment has the capability of being field-portable; the SFE method is rapid (approximately 30 minutes), and it is highly reproducible for various contaminated or potentially contaminated soils and sediments.

The advantages of SFE accrue from the properties of a solvent at temperatures and pressures above its critical point. The liquid-like solvating power and rapid mass-transfer properties of a supercritical fluid provide the potential for more rapid extraction rates and more efficient extraction due to better penetration of the matrix than is feasible with liquids. The properties of a supercritical fluid are intermediate between those of the gas and those of the liquid phases. The compressibility of a supercritical fluid is large just above the critical temperature, and small changes in pressure result in large changes in the density of the fluid. The density of a supercritical fluid is typically 10^2 to 10^3 times greater than that of the gas. Molecular interactions increase at these higher densities because of shorter intermolecular distances, and solvating characteristics of the supercritical fluid approach those of a liquid. However, the diffusion coefficients and viscosity of the fluid remain intermediate between those of the gas and liquid phases, thus allowing rapid mass transfer of solutes compared to a liquid. The properties of a supercritical fluid are dependent on the fluid composition, pressure, and temperature. Many fluids have comparatively low critical

temperatures that allow extractions to be conducted at relatively mild temperatures. For example, the critical temperature of carbon dioxide is only 31°C. Density or solvating power of a supercritical fluid can be controlled by fluid pressure and/or temperature. In addition, various different fluids or fluid mixtures that exhibit different specific chemical interactions can be used to obtain the desired solvent strength and selectivity.

The present work describes the characterization of two contaminated soil samples by SFE followed by analysis by high resolution gas chromatography. One soil sample was from a coal gasification waste site, while the other was from a petroleum gasification waste site. The coal gasification soil was extracted in the laboratory using replicate SFE and Soxhlet extractions to compare the extraction efficiency and reproducibility of the SFE method versus the conventional Soxhlet method. The petroleum gasification soil was extracted in-the-field as one sample of ten that were extracted during a recent field trip. The SFE method and apparatus that have been used for several in-the-field studies will be discussed.

EXPERIMENTAL

Supercritical Fluid Extraction (SFE). A schematic diagram of the SFE apparatus is shown in Figure 1. A similar apparatus used in "proof-of-concept" and contaminated soil studies has been previously described (1-4). Soil samples of approximately 2 g each (weighed to within ± 0.005 g) were sealed inside the stainless steel extraction cell, which was then placed inside an oven heated to 100°C. The extraction cells were made from approximately 3-in. lengths of 1/4-in. stainless steel tubing capped with Swagelok stainless steel zero-volume 1/4-in. to 1/16-in. column end fittings (SS-400-6-1ZV) containing 1.0 µm pore size sintered stainless steel frits. All samples were extracted with high-purity carbon dioxide (SFC grade, Scott Specialty Gases) at pressures of 325 to 375 bar for approximately 30 minutes. Gas flow rates ranged from 600 to 900 mL/min, with flow restrictors made out of uncoated fused silica of 100 µm I.D. When supercritical carbon dioxide is expanded to a gas, the volume increases by a factor of approximately 10^3. The extraction effluent was bubbled through methylene chloride solvent and the analytes were collected in a glass collection vessel. The glass collection vessel was filled with 1.0 mL internal-standard-containing solution to correct for final volumes and an additional approximately 20 mL methylene chloride. The internal-standard-containing solution was 50 µg/mL of 2-chloroanthracene in benzene. All solvents were distilled-in-glass, high-purity grade (American Burdick and Jackson, Muskegon, MI). A reflux condenser was connected to the collection vessel to minimize solvent losses due to evaporation. The pump head, carbon dioxide inlet line, and condensers were cooled with a refrigerated recirculating water bath cooled to 0°C. Extracts and collection vessel washings (at least three at 1-mL each with methylene chloride) were transferred, combined, and concentrated to approximately 2 mL under a stream of high-purity nitrogen. Samples from a coal gasification contaminated soil were extracted five times in the laboratory to give an idea of the extraction reproducibility, and a petroleum gasification contaminated soil was extracted once in-the-field.

Soxhlet Extraction. Five samples of the coal gasification contaminated soil of approximately 2 g each (weighed to within ± 0.005 g) were placed inside Soxhlet extraction thimbles which had been pre-cleaned for at least 24 hours using 200 mL each of methylene chloride. The samples were then Soxhlet extracted overnight using 250 mL of fresh methylene chloride with an approximate 1 min cycle. The Soxhlet extraction apparatus were wrapped in aluminum foil to prevent possible sample degradation due to

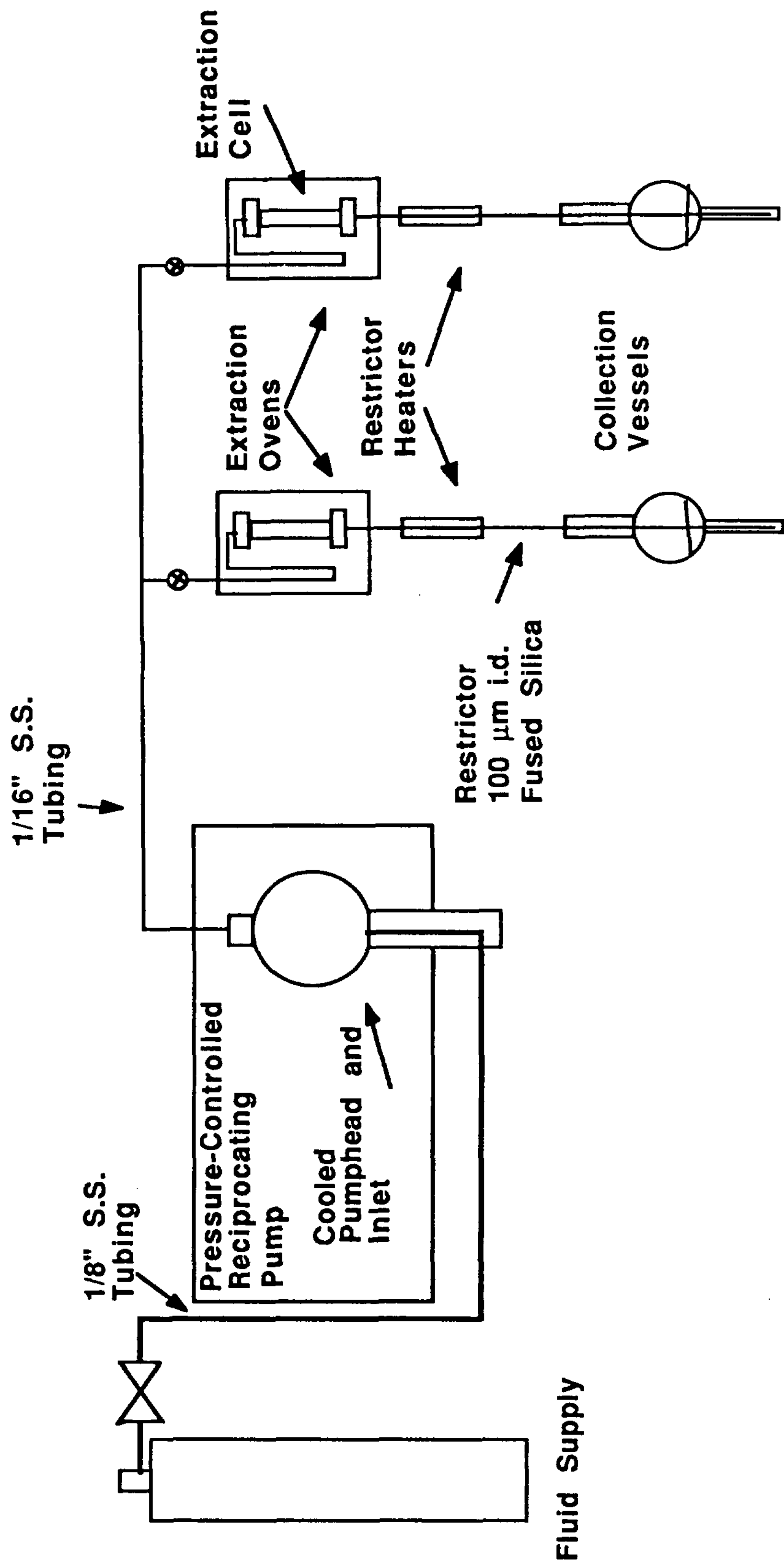

Figure 1. Schematic Diagram of the Field-Portable Supercritical Fluid Extraction Apparatus.

exposure to light. One ml of internal standard containing solution was added to the extracts to correct for final volumes. The extracts were concentrated to approximately 2 ml using a rotary evaporator operated at 40°C followed by a stream of high-purity nitrogen.

High-Resolution Gas Chromatography (HRGC). Soxhlet and SFE extracts were analyzed by HRGC using an Hewlett-Packard (HP) 5890 gas chromatograph equipped with a 30-m x 0.25-mm I.D. fused silica capillary column coated with 0.25-µm film thickness SE-54 (J & W Scientific, Folsom, CA). The capillary column was cross-linked in house using azo-*t*-butane. The oven was temperature-programmed from 50°C to 280°C at 4°C/min with 2 min isothermal at both the upper and lower temperatures. Splitless injection (0.5 min purge) was used with helium as the carrier gas at approximately 50 cm/s linear velocity. The injection port and flame ionization detector were operated at 275° and 300°C, respectively. Selected individual components were quantified using response factors of standard reference polycyclic aromatic hydrocarbons (PAH) relative to the 2-chloroanthracene internal standard. Calibration was performed by linear regression analysis of the PAH chromatographed at three concentration levels. The response factor of a closely eluting or similar compound was used to quantify components for which standard reference compounds were not available. Components in extracts were identified by retention index (5,6), absolute retention times of standard reference compounds, and/or gas chromatography/mass spectrometry using an HP 5985 quadrupole mass spectrometer operated in the electron impact mode at 70 eV. Extracts from the five SFE and five Soxhlet replicates of the coal gasification soil were analyzed in triplicate. The extract from the petroleum gasification soil was analyzed once.

RESULTS AND DISCUSSION

The laboratory-size version of the SFE apparatus has been successfully transported to several field locations and has been used to extract contaminated soil samples. This version of the apparatus utilizes a refrigerated recirculating water bath to cool the pumphead and the extraction cell condensors, and consequently weighs approximately 100 lbs. A more compact version (weighing less than 50 lbs) that utilizes thermoelectric coolers is currently being evaluated in the laboratory. Most of the weight of this smaller device can be attributed to the high-pressure pump. The smaller unit will undoubtedly be easier to transport and operate in-the-field. During field evaluations, the SFE apparatus (laboratory-size version) could be removed from its shipping box and put into service in less than one hour. It requires connection to standard 110 V power and a source of carbon dioxide. Depending on the sample matrix, approximately 5 to 10 samples can be extracted with 1 lb of carbon dioxide. Small aluminum gas cylinders are available that weigh approximately 50 lbs and contain 20 lbs of carbon dioxide. This would service between 100 and 200 extractions and is equivalent to over four cases of liquid solvent assuming 300 mL are needed for each Soxhlet extraction.

The present apparatus is designed to extract a single sample at a time, but it has tandem sample processing capabilities. This allows near continuous extraction of sequential samples since one sample can be connected or removed from the apparatus while the other one is extracted. With 20 to 30 minute extraction times per sample, up to 24 samples could be extracted in a single eight-hour day. Subsequent gas chromatographic analyses of typical complex mixtures easily require up to one hour or more for each sample. Thus, sample preparation can be more rapid than the actual analytical determination. Large quantities of collection vessel glassware and extraction cells are not needed to support the SFE apparatus. Much of the system is self cleaning or can be recycled with minimal

cleaning. Spent extraction cells are free of extractable organics and can be rinsed with water. The collection vessels, however, must be adequately rinsed with an appropriate organic solvent to prevent cross contamination. Other than assuring that a sample will provide representative homogeneity, it is not necessary to pretreat the sample before it is loaded in the extraction cell. Soil samples saturated with water have been successfully extracted by SFE. Since the water is also removed during extraction, the dry sample weight is also available. In some cases it may be necessary to mix small diameter glass beads with highly contaminated soils or very dense clays to allow sufficient porosity for good fluid flow through the matrix.

To date, this SFE approach has been primarily applied to soil samples contaminated with wastes from either coal or petroleum gasification activities. A chromatogram of the SFE extract from a soil sample contaminated with a coal gasification waste is shown in Figure 2. The profile of the chemical components in this sample corresponds to the profile of chemical components typically observed in coal tar (7). The major components of the sample's gas chromatographable portion are identified in Table I, and range from two-ringed polycyclic aromatic compounds (PAC) to six-ringed PAC with their alkylated homologs.

The concentrations of the selected PAC determined from the five replicate SFE extracts of the coal gasification soil are listed in Table I; the concentrations of the major components ranged from approximately 3 to 25 ppm (μg/g). Experiments with other contaminated soil samples have shown that PAC individual component concentration levels ranging from 25 ppb (ng/g) to over 1000 ppm can be successfully extracted using SFE. For comparison of extraction efficiency and reproducibility of SFE versus Soxhlet extraction, the concentrations of the selected PAC determined from the five replicate Soxhlet extracts of the same coal gasification soil are also listed in Table I. With the exception of the two benzopyrenes, there were no significant differences (at 95% confidence limits) between the concentrations of the PAC in the SFE and Soxhlet extracts. The slightly lower concentrations of these two higher molecular weight compounds using the SFE method can be explained by their lower solubility in the supercritical carbon dioxide; as molecular weight increases, solubility generally decreases. Thus, for samples with high concentrations of high molecular weight compounds, longer extraction times may be necessary.

The average coefficient of variation (CV, percent standard deviation) from the replicate extractions and analyses of the compounds listed in Table I (except for naphthalene) was 11.2 for the SFE extracts and 10.6 for the Soxhlet extracts. From a nested analysis of variance, the average CV from the SFE replication was 2.5 with an average CV of 8.7 from the analysis. The average CV from the Soxhlet replication was also 2.5 with an average CV from the analysis of 8.1. CV's of 2.5 for both the Soxhlet and SFE extraction replication are very encouraging as they are related to the homogeneity of the small 2-g sample size. CV's of the magnitudes determined in these reproducibility studies are acceptable for complex mixture analyses.

Interestingly, the colors of the SFE and Soxhlet extracts of the coal gasification soil were markedly different. The SFE extracts were a light yellow color, while the Soxhlet extracts were a dark brown. The darkness of the Soxhlet extracts can likely be attributed to the presence of high molecular weight and/or polar compounds extracted from the soil matrix that were not amenable to the analysis by gas chromatography. Supercritical carbon

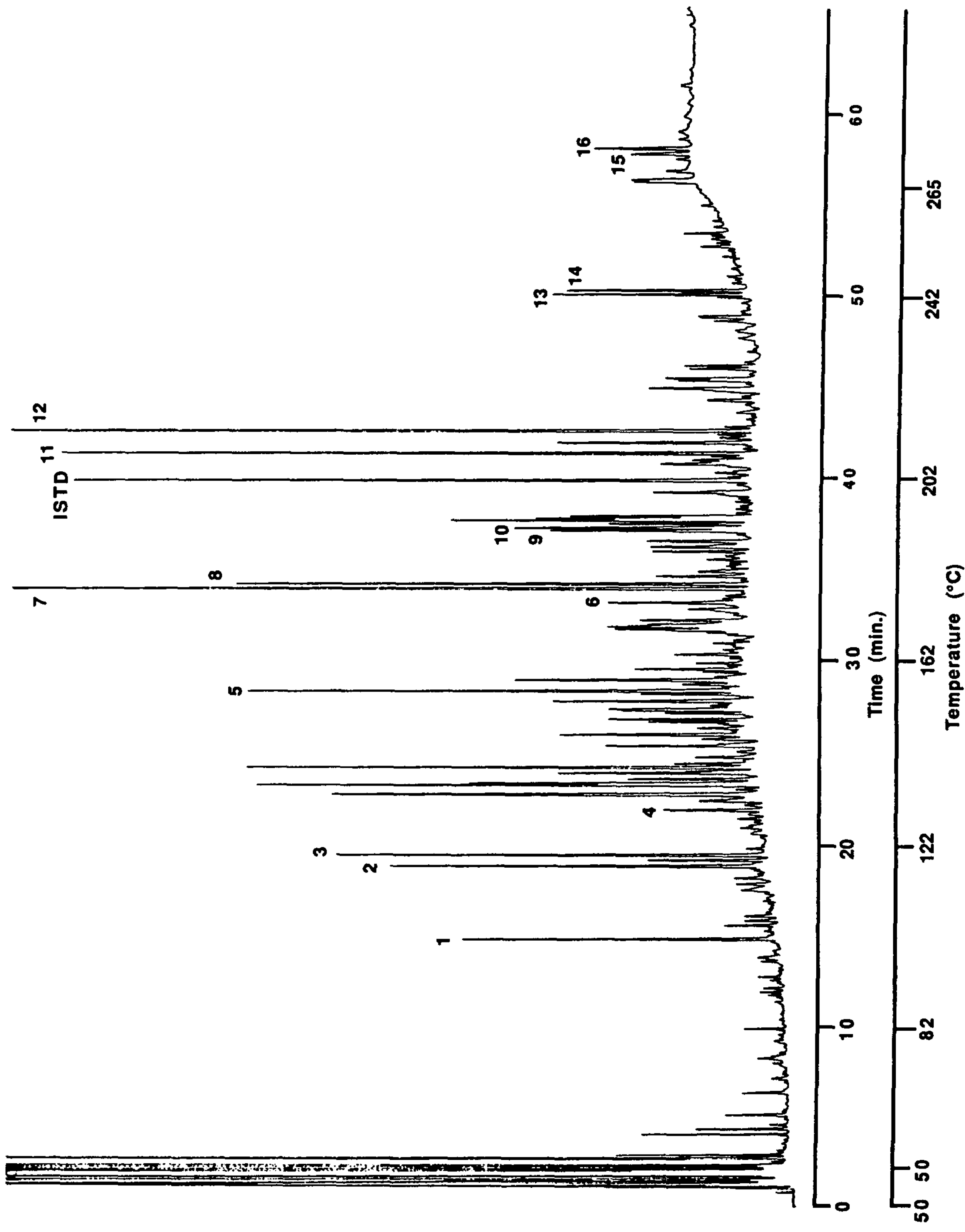

Figure 2. Capillary Gas Chromatogram of the Supercritical Fluid Extract of Soil Contaminated with Coal Gasification Tar Waste. See text for details. Numbers refer to compounds listed in Table I.

Table I. Quantitative Results (µg/g; ppm) of Selected Polycyclic Aromatic Compounds in Contaminated Soils

Peak No.[a]	Compound	Mol. Wt.	Coal Gasification Soil SFE, N=5	Coal Gasification Soil Soxhlet, N=5	Petroleum Gasification Soil SFE
1	Naphthalene	128	4.34 ± 0.31	4.61 ± 2.44	3470
2	2-Methylnaphthalene	142	4.57 ± 0.28	4.74 ± 0.78	1910
3	1-Methylnaphthalene	142	5.91 ± 0.34	6.10 ± 0.64	1210
4	Biphenyl	154			222
5	Fluorene	166	7.86 ± 0.48	8.19 ± 0.45	352
6	Dibenzothiophene	184	3.22 ± 0.17	3.33 ± 0.20	154
7	Phenanthrene	178	17.6 ± 1.5	17.9 ± 1.3	842
8	Anthracene	178	9.06 ± 0.49	9.13 ± 0.38	72.2
9	3-Methylphenanthrene	192	5.01 ± 0.27	5.12 ± 0.20	301
10	2-Methylphenanthrene	192	4.89 ± 0.24	4.94 ± 0.18	295
11	Fluoranthene	202	21.0 ± 0.7	21.4 ± 0.6	206
12	Pyrene	202	24.9 ± 0.7	25.6 ± 0.7	292
13	Benz[a]anthracene	228	9.21 ± 0.72	10.0 ± 0.6	
14	Chrysene	228	9.09 ± 0.61	9.85 ± 0.54	122
15	Benzo[e]pyrene	252	4.18 ± 0.80	5.27 ± 0.58	10.8
16	Benzo[a]pyrene	252	11.3 ± 1.8	13.7 ± 1.1	55.8

[a]Peak numbers refer to Figures 2 and 3

dioxide is a sufficiently good solvent to efficiently extract the PAC of interest, but will not extract those compounds which are not amenable to the gas chromatographic analysis.

A capillary gas chromatogram showing the PAC profile typical of tar wastes from petroleum gasification activities is shown in Figure 3. The concentration levels of selected PAC in the contaminated soil are listed in Table I. Comparing the profile of the petroleum gasification tar to that of the coal gasification tar shown in Figure 2, it is evident that the petroleum tar had a lower average molecular weight. There were many compounds present in the SFE extract of the petroleum gasification soil that were more volatile than naphthalene. This illustrates that the SFE approach is also amenable to the extraction and analysis of these types of highly volatile compounds. During the collection process, tremendous cooling occurs from the carbon dioxide expansion which causes the collection solvent to cool to less than 0°C. This cooling minimizes the loss of highly volatile constituents. Relatively short extraction times (e.g., 10 minutes) could also be used for samples with a known distribution of low molecular weight and highly volatile compounds due to their enhanced solubility in supercritical carbon dioxide relative to higher molecular weight compounds.

In addition to soils and sediments contaminated with varying levels of PAC, the SFE method is amenable to the extraction and analysis of soils contaminated with other organic compounds. As an example, the gas chromatographic profile of an SFE extract from a PCB contaminated soil is shown in Figure 4. Similar extraction conditions were used for the PCB contaminated soil as were used for the coal and petroleum gasification contaminated soils. Organic compounds arising from gasoline or kerosene contamination to soils, or other energy-related waste contaminations would also be amenable to the in-the-field SFE extraction.

SUMMARY

The analytical SFE technique provides a viable alternative with promising advantages over current liquid extraction methods. One of the most significant advantages of SFE is the rapid rate at which analytes can be removed from the environmental matrix. Extraction times of 30 minutes or less have been demonstrated for quantitative complex organic mixture removal from contaminated soils. Such times are comparable to typical analytical determination methods (e.g., gas chromatography), so that the extraction step is not a rate limiting step in the analysis. Comparisons of Soxhlet extraction to SFE indicated that comparable extraction efficiencies and reproducibility can be obtained with SFE. In addition to providing rapid extraction rates, SFE has also been demonstrated to be well suited for in-the-field use since the apparatus is field-portable and large quantities of organic solvents are not necessary.

ACKNOWLEDGEMENTS

This work was supported by the Electric Power Research Institute, Land and Water Quality Studies Program , under contract RP2879-04. The authors thank Andrew J. Kopriva for technical contributions to this work.

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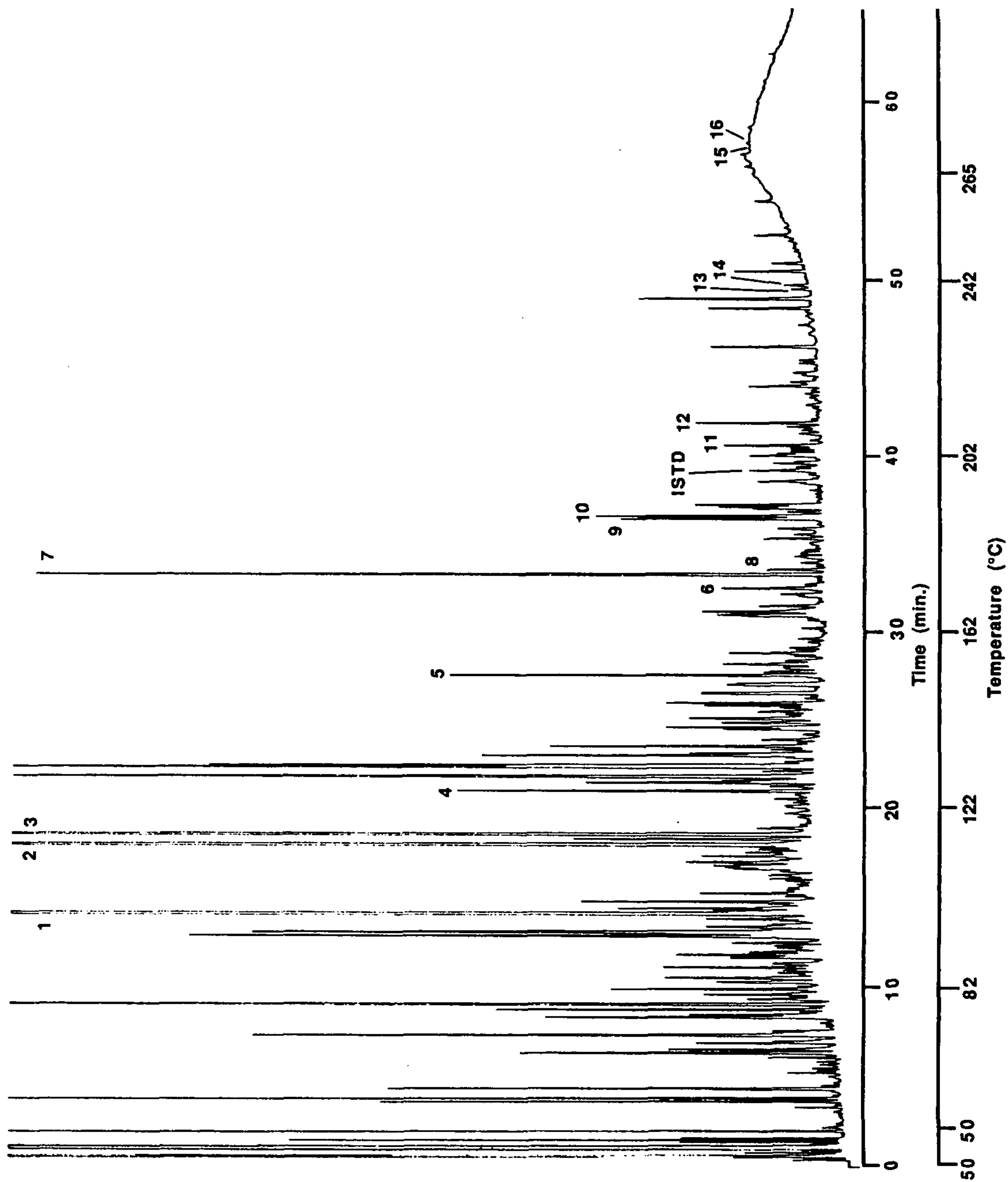

Figure 3. Capillary Gas Chromatogram of the Supercritical Fluid Extract of Soil Contaminated with Petroleum Gasification Tar Waste. See text for details. Numbers refer to compounds listed in Table I.

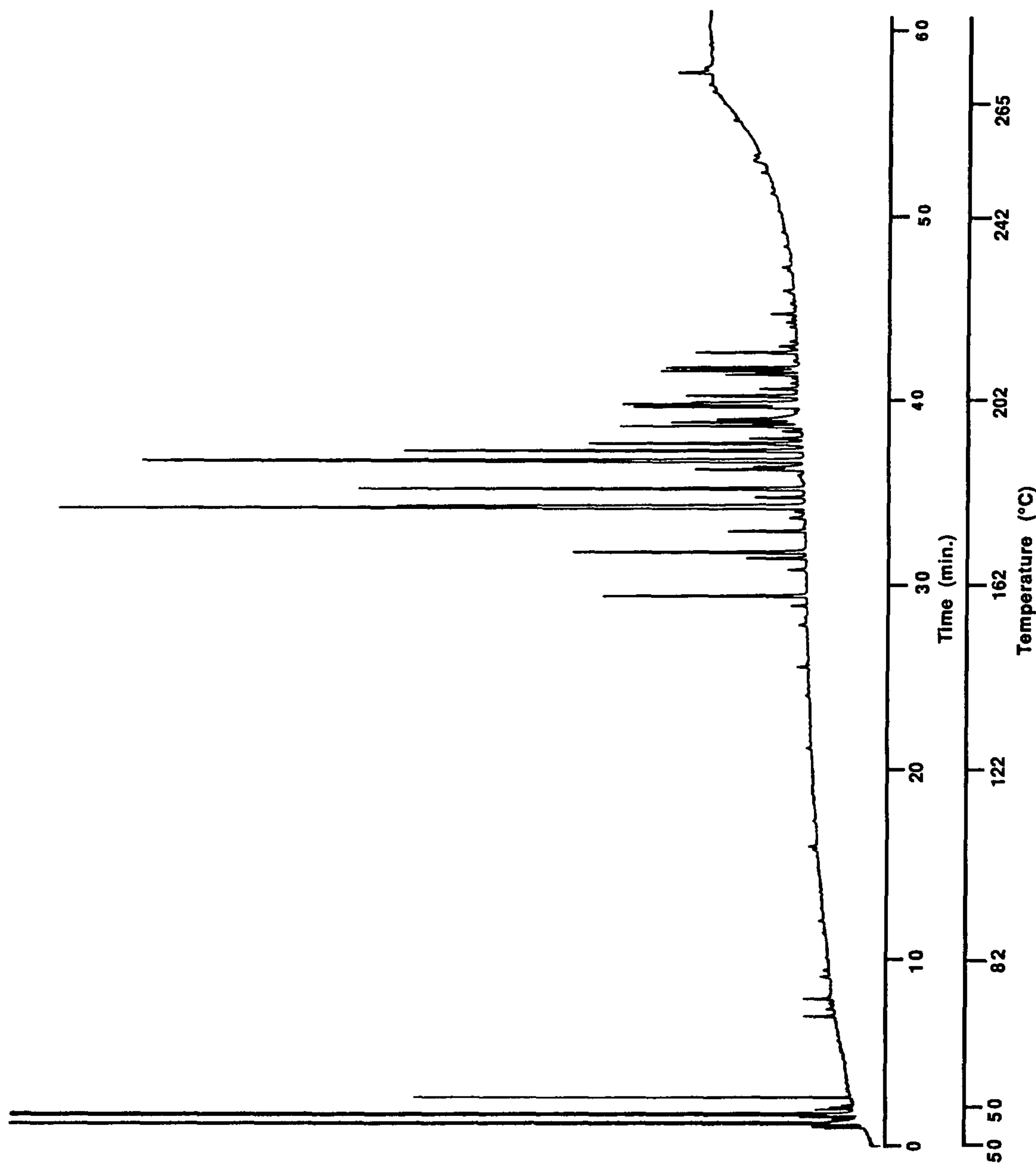

Figure 4. Capillary Gas Chromatogram of the Supercritical Fluid Extract of Soil Contaminated with PCBs. See text for details.

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INVESTIGATIONS OF SAMPLING AND ANALYTICAL TECHNIQUES FOR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (METHOD 8240, SW846)

KAVEH ZARRABI, STEVE WARD, WENDY ELLIS, QUALITY ASSURANCE LABORATORY, 4505 S. MARYLAND PARKWAY, LAS VEGAS, NV 89154, DELBERT BARTH, ENVIRONMENTAL RESEARCH CENTER, 4505 S. MARYLAND PARKWAY, LAS VEGAS, NV 89154, KENNETH BROWN, EXPOSURE ASSESSMENT DIVISION, ENVIRONMENTAL MONITORING SYSTEMS LABORATORY, LAS VEGAS, NV 89193-3478

ABSTRACT. Soil sampling for analyses of VOC's from contaminated sites follows established sampling and analysis procedures. However, examination of the literature on VOC sampling and analysis, questions the accuracy and adequacy of some methods and procedures.

The intent of this research is to identify methods and procedures requiring minimum changes to the current EPA sampling and analysis procedure to insure sample integrity from sampling to analysis. In this work, we examined field and laboratory methods for soil sampling and analysis for VOC's. In particular, Method 8240 of SW-846 was examined and several tests were conducted to examine possible modifications to the method.

Following is a list of tested modifications to Method 8240:

1. A new sampler unit was designed from a commercially available sparger. This sampler can be loaded in the field or in the laboratory and directly connected to the purge-and-trap device without exposing the sample to air. The utility of this unit was evaluated.

2. Soil samples were placed in 40 ml vials and sealed in the field. Tests of the containers as transporting vehicles plus tests to measure VOC losses when the containers were briefly opened in the laboratory to connect them to a modified purge-and-trap sampler unit were assessed.

3. Water saturated with sodium chloride was used instead of pure water for the extraction of the soil samples. This test revealed the efficiency of saline water, compared to pure water, for displacement of the volatile organics.

4. Soil samples were placed in 40 ml vials and cooled to +4°C and -60°C. The vials were opened momentarily to be connected to the purge-and-trap device. This test revealed the effects of matrix temperature on losses of the volatile organics.

5. The soil samples were placed in 40 ml vials and analyzed by Method 8240. The only difference in this test was the use of a sonicator in addition to heating in the extraction step.

   Prior to the above tests, audit samples and a mixing procedure were established to evaluate sample handling losses and soil heterogeneity effects respectively.

IDENTIFICATION OF SURFACES CONTAMINATED WITH EXPLOSIVES USING FALSE COLOR VIDEO IMAGERY

LANG, KENNETH T. AND BROWN, LESLIE C., U. S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY, ABERDEEN PROVING GROUND, MARYLAND 21010-5401; DICK, ROBERT, BARRINGER RESEARCH LIMITED, 304 CARLINGVIEW DRIVE, METROPOLITAN TORONTO, REXDALE, ONTARIO, CANADA M9W 5G2.

ABSTRACT. Defense posture requires that the nation have a stockpile of conventional high explosive munitions for use in defending the nation and repelling hostile actions. To this end there is a significant military munition manufacturing base including production of the high explosives by synthesis and the munitions through load and pack operations. These manufacturing operations can cause the working areas to become contaminated with the explosives through spillage or accidental release of the materials being handled. Significant area contamination is easily identified visually by color, or distinctive differences from the surrounding area. Lesser contamination may not be as easily identified and may not be cleaned up. This lesser contamination is a health and safety hazard that is usually eliminated by an exhaustive mechanical cleanup of the entire facility. In order to reduce the large amount of cleanup work required, a means of identifying those areas of lesser contamination that could be targeted for cleanup was sought. Direct color reagents and fluorescence on the surface were impractical and slow. Still photography using ultraviolet illumination showed promise but was very slow and exposure times were temperature dependent. The film had to be processed at a different site causing a long delay between the examination and the evaluation of the photograph. Recommendations arising from the still photography project indicated that a video camera system may provide more information faster than any still photography system. This paper describes the video camera system, the illuminator, and a confirmatory sampling technique. The system, as field tested, can detect a variety of explosives at less than 100 micrograms per square centimeter on a variety of surface types with a low percentage of false positives. Strengths, shortcomings, and future goals of the system are discussed.

DEVELOPMENT OF A MOBILE LABORATORY SYSTEM FOR ON-SITE ANALYSES OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS USING FT-IR

MARTIN L.SPARTZ, MARK R. WITKOWSKI, JONATHAN H. FATELEY, ROBERT M. HAMMAKER Ph.D., WILLIAM G. FATELEY Ph.D., DEPARTMENT OF CHEMISTRY, WILLARD HALL, KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS 66506; RAY E. CARTER, MARK THOMAS, DENNIS D. LANE Ph.D., DEPARTMENT OF CIVIL ENGINEERING, GLEN A. MAROTZ Ph.D., DEPARTMENT OF PHYSICS AND ASTRONOMY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS 66045; BILLY J. FAIRLESS Ph.D., JOHN HELVIG, JODY L. HUDSON, U.S. ENVIRONMENTAL PROTECTION AGENCY REGION 7, 25 FUNSTON ROAD, KANSAS CITY, KANSAS 66115.

ABSTRACT

A mobile laboratory for on-site analyses of volatile organic compounds (VOCs) in the atmosphere using a Fourier transform infrared (FT-IR) spectrometer is described. Laboratory calibration measurements are presented and discussed. Estimates of detection limits as an average concentration over a path length of 100 meters are made for 26 mid-infrared absorption bands of 21 compounds. These estimated detection limits vary from 5 to 76 parts per billion (ppb). Some results of field measurements carried out at path lengths near 100 meters are presented and discussed.

INTRODUCTION

A mobile system has been developed at Kansas State University to measure volatile organic compounds (VOCs) in the atmosphere using a Fourier transform infrared (FT-IR) spectrometer. The mobile FT-IR spectrometer system was developed to do on-site measurements and analyses so that results can be obtained and reported more quickly.

MOBILE LABORATORY

Mobility is provided by a Journey mobile home designed to house and transport the necessary measurement instruments and the crew. A listing of some of the major features of the Journey mobile laboratory is in Table 1 with a photograph and a schematic diagram of the general layout of the mobile laboratory in Figure 1. The conversion of the mobile home to a mobile laboratory will be a continuing process. At the time of this writing, the unit is configured to house a crew of three and the following instrumentation: the FT-IR spectrometer with its collection telescope, the source of infrared radiation and its collimating telescope, appropriate computers, a weather station, a FAX machine, and a cellular telephone. The additions of a specially designed vacuum system, and a variable path multireflection cell (White cell) to provide path lengths from 6 to 160 meters are in progress. Once the vacuum system and the variable path cell are operational, the capabilites of the mobile laboratory will include canister collection of either atmospheric gases or soil gases for analyses in the variable path cell.

Table 1. Some major features of the Journey mobile laboratory

JOURNEY 40' MOBILE LABORATORY

-FORD 460 cu. in. ENGINE
-JOHN DEERE CHASSIS
-95 GALLON FUEL CAPACITY
-160lb. PROPANE CAPACITY
-80 GALLON WATER CAPACITY
-6.5 KW GENERATOR
-DUAL 13,500 BTU AIR CONDITIONERS
-DUAL 30,000 BTU FURNACES
-HYDRAULIC LEVELING JACKS
-10 CUBIC FOOT REFRIGERATOR
-4 BURNER RANGE W/ CONVENTIONAL OVEN AND MICROWAVE OVEN
-THREE OVERHEAD STORAGE PODS
-MURATA FAX MACHINE
-UNIDEN CP1200 CELLULAR TELEPHONE

The FT-IR spectrometer, shown in Figure 2A, is a Bomem DA02 system equipped with a KBr/Ge beam splitter, a MCT detector (liquid nitrogen cooled), a variable height/depth tripod and a Gibralter 3 degree of motion head; the collection telescope is a 10 inch Cassegrainian.

The source of infrared radiation, shown in Figure 2B, is an air cooled and quartz shielded Nernst glower operating at 2000 degrees Kelvin. This source is located at the focal point of a 20 inch Newtonian telescope (of 80 inch focal length and f/4 optics with gold coated mirrors) in order to generate a collimated beam of infrared radiation.

The mobile laboratory is driven to one side of the site to be surveyed and the FT-IR spectrometer with its collection telescope is set up adjacent to the mobile laboratory. The source of infrared radiation and its collimating telescope are positioned on the opposite side of the site to be surveyed so the collimated beam of infrared radiation may be sent across the site to enter the collection telescope of the FT-IR spectrometer. An alternative arrangement is to place both the source of infrared radiation and its collimating telescope and the FT-IR spectrometer with its collection telescope adjacent to the mobile laboratory. Then a reflector is placed on the opposite side of the site so the collimated beam of infrared radiation is sent across the site to the reflector and reflected back to the collection telescope of the FT-IR spectrometer. In either arrangement, the infrared absorption spectrum of the atmosphere above the site being surveyed is used to identify any VOC's that are present in the path of the collimated beam of infrared radiation.

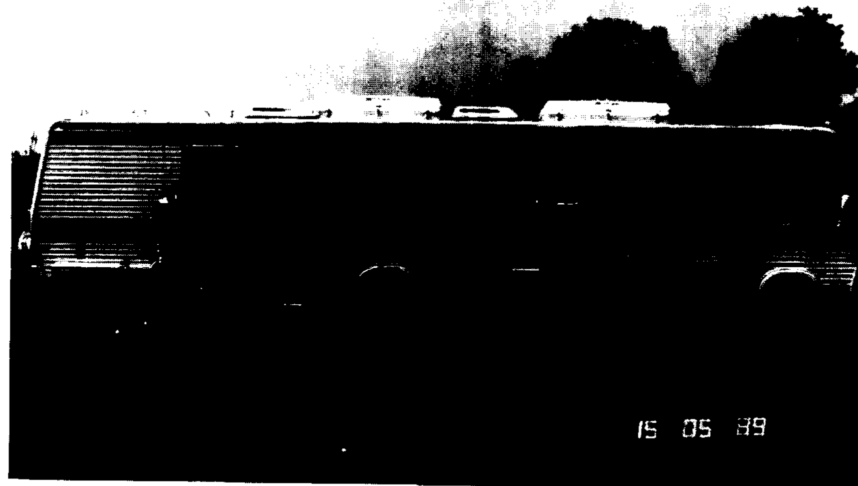
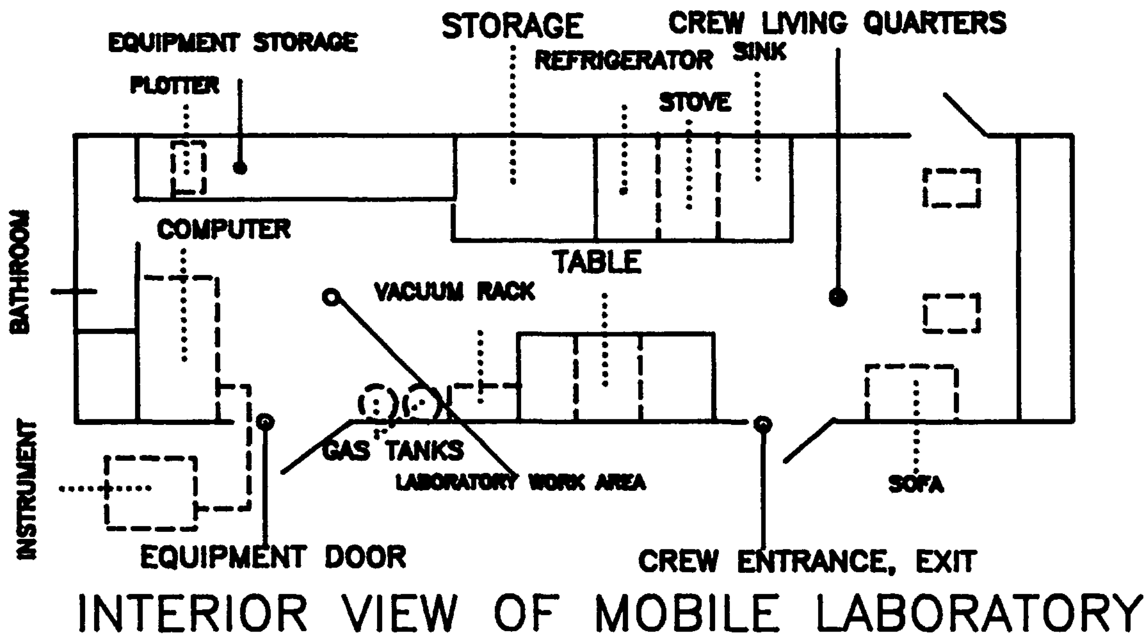


Figure 1. A photograph (A) and a schematic diagram (B) of the mobile laboratory.



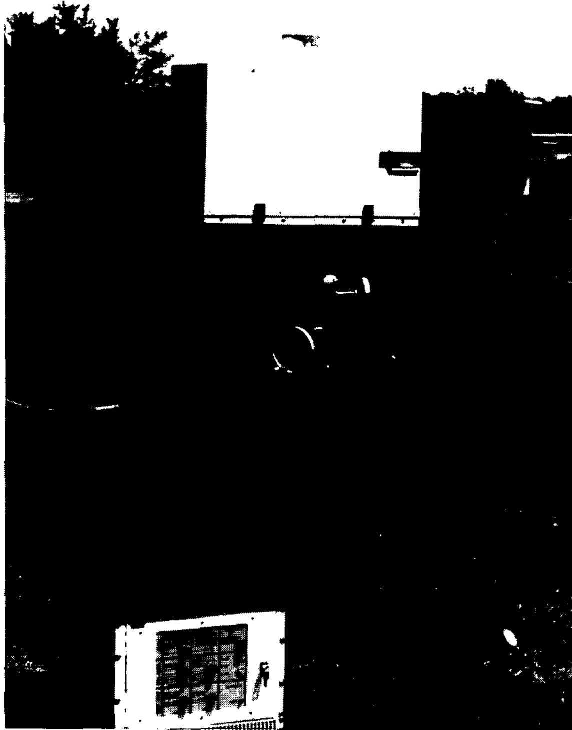
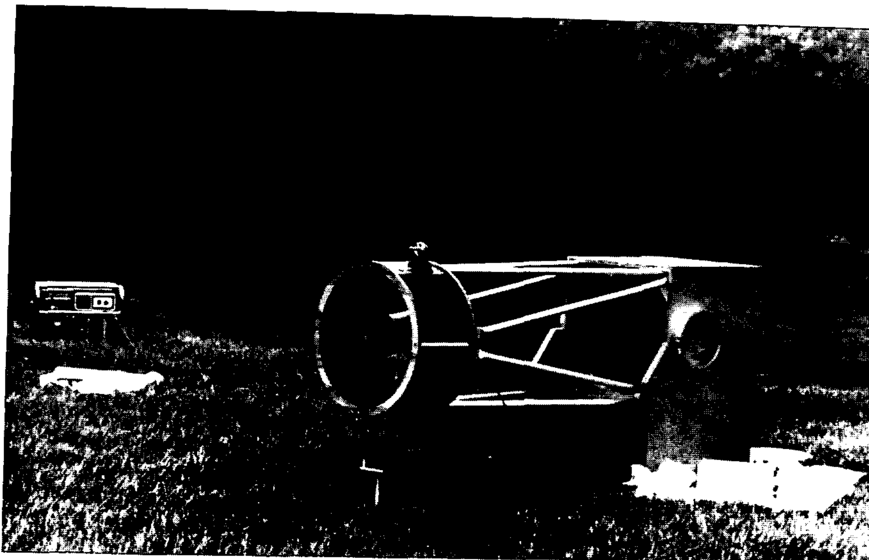


Figure 2. The FT-IR spectrometer and its collection telescope (A) and the source of infrared radiation and its collimating telescope (B).



The arrangement with the FT-IR spectrometer and the source on opposite sides of the site is illustrated in Figure 3 for a grid pattern of 8 spectral scans in one direction and 8 spectral scans in a perpendicular direction. Thus, a total of 16 spectral scans is necessary to spectroscopically interrogate a total of 64 intersection points. If a point source of pollutant emission is located within the grid, appropriate comparisons among the sixteen spectral scans can identify which intersection point is nearest the point source. If the emission is more uniformly distributed, comparisons among the 16 spectral scans will also identify such a condition. A crew of three can set up the instrumentation in about 30 minutes, take data for up to 30 minutes, and take down the instrumentation and move to the next scan position in an additional 30 minutes. The 16 spectral scans would then require 24 working hours and would require 2 to 3 working days. Once the site has been surveyed in this manner, individual samples at intersection points of interest may be taken for delivery to an appropriate EPA laboratory for more detailed analysis. The savings in time and money promise to be substantial compared to taking samples at all 64 intersection points and returning 64 samples to an appropriate EPA laboratory for detailed analysis.

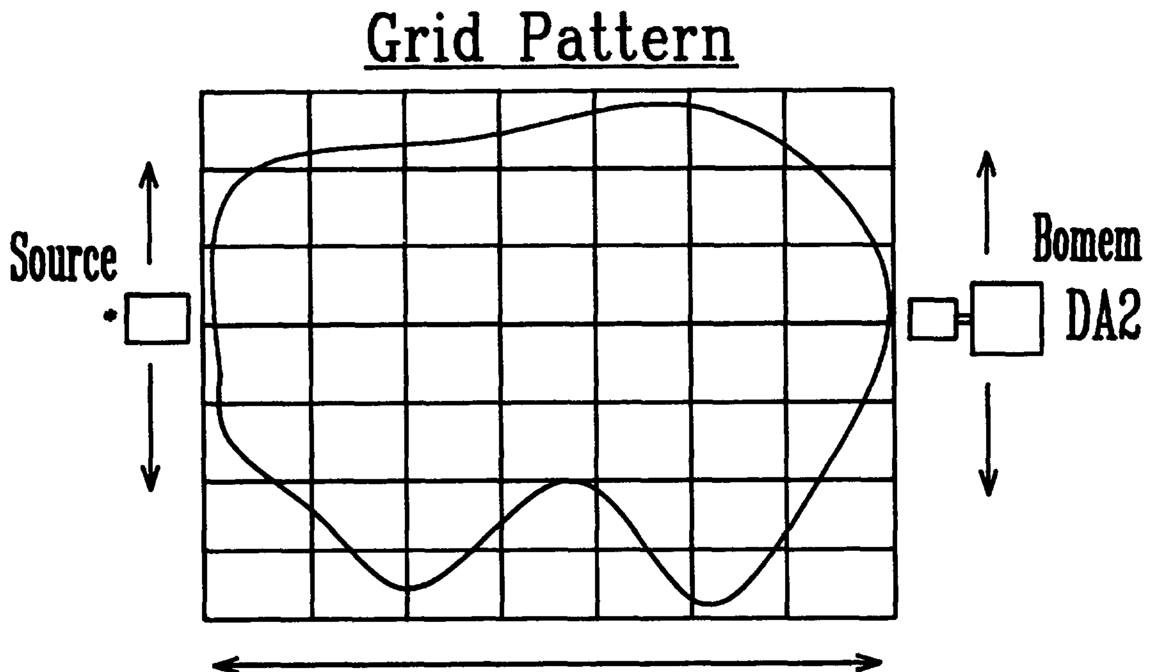


Figure 3. A possible sampling arrangement for obtaining a grid of 64 intersection points by taking 16 spectral scans.

LABORATORY CALIBRATION RESULTS

The task of building a library of calibration spectra has begun. Two uses of the calibration spectra are: (1) to identify the VOCs that are present in the path of the collimated beam of infrared radiation between the source of infrared radiation and the FT-IR spectrometer; (2) to make estimates of the detection limits corresponding to one or more of the absorption bands in the infrared spectrum of each compound in the library. The parameters chosen for recording these calibration spectra appear in Table 2. These calibration spectra were all recorded in a fixed path cell of length 16 cm.

We will soon have our variable path multireflection cell (White cell) operational. This variable path cell may be used in a normal laboratory setting for obtaining calibration spectra at a variety of path lengths if necessary or may be installed in the mobile laboratory and used for on-the-spot analysis. We currently have an air sampling canister containing accurately known concentrations of a multi-component volatile organic compound (VOC) mixture supplied by the EPA Region 7 laboratory for analysis as a test of our methods. A preliminary analysis using the fixed path cell of length 16 cm suggests that the variable path cell will be helpful in the complete analysis of the sample supplied by the EPA Region 7 laboratory.

Table 2. Parameters used in recording calibration spectra

Cell length: 16 cm
Partial Pressure: variable-in range 0.006 - 0.28 torr
Total Pressure (with N_2): ~740 torr (nominal)
Resolution[a]: 0.1 cm^{-1} or 0.5 cm^{-1}
Number of Coadded Scans: 256
Scan Speed: 1.5 cm s^{-1}
Apodization: Boxcar

a. All spectra were recorded at 0.1 cm^{-1} spectral resolution and in many cases the resolution was degraded to 0.5 cm^{-1} by smoothing.

The calibration spectra are used in conjunction with ambient air background spectra obtained in field measurements to make estimates of detection limits as follows. Single beam ambient air spectra taken in the field for a path length of 100 meters are ratioed to obtain the absorbance baseline spectrum of ambient air. The minimum absorbance that would be detectable in a path length of 100 meters is taken as 3 N. N is the peak to peak noise at the wavenumber of the absorption band in the absorbance baseline spectrum of ambient air for a path length of 100 meters. Then use is made of Beer's Law (i.e. A = abc where A is the absorbance of the band, a is absorption coefficient in units of $[(\text{path length})(\text{concentration})]^{-1}$, b is path length, and c is concentration). For a band of the minimum detectable absorbance, A_m, Beer's Law is A_m = 3N = $ab_m c_m$ with b_m = 100 meter and c_m the minimum detectable

concentration in parts per billion (ppb). For the laboratory calibration spectrum, Beer's Law is $A_r = ab_r c_r$ where b_r is 0.160 meter and c_r is the lowest measured concentration in ppb. The value of c_m, the minimum detectable concentration in ppb, is obtained by taking the ratio of the two Beer's Law equations and solving for $c_m = (3N/A_r)(0.160/100)c_r = (4.8x10^{-3} N/A_r)c_r$. In doing these calculations it is critical to note that concentration in molarity does not change in the gas cell for a given amount of material in the fixed volume as total pressure and/or temperature change but concentration in ppb does change. Thus, the value of c_r in molarity must be converted to ppb for the same total pressure and temperature as those for which c_m is being calculated in ppb.

Table 3 contains the minimum detection limits in a path length of 100 meters for all compounds in the library of calibration spectra at the time of this writing estimated by the method described in the previous paragraph. These detection limits correspond to a concentration averaged over a path length of 100 meters at a given total pressure and temperature. Thus, the amount of material between the source of infrared radiation and the FT-IR spectrometer if uniformly distributed along the 100 meter path would be at the concentration given in ppb in Table 3. The applicability of Beer's Law to the absorption bands used to make the calculations in Table 3 was examined by obtaining all calibration spectra at four different concentrations and plotting the results as absorbance versus concentration.

The compromise between resolution and signal-to-noise ratio will be a matter of great significance in the field work. For bands that are broad relative to the spectral resolution chosen in the operation of the FT-IR spectrometer, a higher resolution scan (smaller value of the resolution in cm^{-1}) will have approximately the same absorbance at the band maximum and a higher noise level causing a signal-to-noise ratio decrease and a poorer (i.e. higher) detection limit. Here the lower resolution scan is to be preferred. For the case where the band width is comparable to the spectral resolution chosen in the operation of the FT-IR spectrometer, a higher resolution scan (smaller value of the resolution in cm^{-1}) may yield a dramatic increase in the absorbance at the band maximum along with the higher noise level. In this case, the effect on the signal-to-noise ratio and the detection limit is not easily predictable and each case needs to be evaluated individually. The calibration spectra were recorded at 0.1 cm^{-1} resolution to give the flexibility to degrade the resolution, if desired. This degradation of the resolution is accomplished in the data processing either by smoothing the spectrum or by truncating the interferogram prior to transformation to the spectrum. The calibration spectra in the library contain examples of both cases and some of these examples are presented and discussed later (see Field Work Results). The situation becomes more complicated for spectral regions containing many sharp water vapor absorption bands. Here, the higher resolution data may show the effect of these water vapor bands more clearly and lead to better decisions

Table 3. Estimated detection limits (ppb) for some volatile organic compounds (VOCs) for a path length of 100 meters using an appropriate absorption band from the mid-infrared region.

Compound	Wavenumber (cm^{-1})	Resolution (cm^{-1})	Detection Limit (ppb)[a]
Chlorinated hydrocarbons			
Allyl Chloride	756.9	0.5	67
Carbon Tetrachloride	795.2	0.5	6.3
Chlorobenzene	741.2	0.1	26
Chloroform	772.6	0.5	b
1,2-Dichloroethane	731.3	0.5	34
Methylene Chloride	749.5	0.5	20
Tetrachloroethylene	916.3	0.5	19
1,1,1-Trichloroethane	726.3	0.5	8.1
Trichloroethylene	849.4	0.5	18
Aromatic Hydrocarbons			
Benzene	673.9	0.1	c
Ethylbenzene	2794.0	0.5	31
Pyridine	700.3	0.1	c
Toluene	694.3	0.1	c
Alkane			
Cyclopentane	2966.0	0.5	7.2
Alcohols			
n-Butanol	2967.4	0.5	22.4
	1068.8	0.5	35
Ethanol	1066.1	0.5	31
Isopropanol	2982.7	0.5	19
	956.5	0.5	76
Methanol	1033.4	0.1	18
	1033.4	0.5	8.1
Ketones			
Acetone	1217.7	0.5	36
Methyl Ethyl Ketone	1174.2	0.5	40
Methyl Isobutyl Ketone	2965.4	0.5	18
Ester			
Ethyl Acetate	1241.4	0.5	5.0
Ethers			
Diethyl Ether	1142.9	0.5	9.3
1,4-Dioxane	2863.1	0.5	11
	1138.3	0.5	9.9
Tetrahydrofuran	2981.7	0.5	17
	1084.4	0.5	26

a. These detection limits using concentration in parts per billion (ppb) are for P = 740 torr and T = 298 K.
b. These measurements are being repeated.
c. These bands fall in spectral regions containing sharp water vapor absorption bands and the detection limits are dependent on humidity.

about the best way to proceed. One option would be to use the higher resolution data to subtract out some of the water vapor bands and then degrade the resolution to reduce the noise. This procedure might minimize errors caused by sharp water vapor absorption bands broadened under lower resolution making unsuspected contributions to absorption bands from VOCs.

FIELD WORK RESULTS

Open path scans have been done at five different path lengths as follows: 65, 100, 117, 120, and 250 meters. Extensive initial work was done indoors at a path length of 65 meters along the length of the hallway on the third floor of Willard Hall at Kansas State University in Manhattan, KS. The work at the other four path lengths was done outdoors at Lawrence, KS in collaboration with the group from the Department of Civil Engineering at the University of Kansas headed by Dr. D. D. Lane. The University of Kansas group has developed a plume generator that releases a plume of VOCs of known characteristics as measured by gas chromatography. Work at 120 meters was done in February, 1989. Work completed the week of May 15-19, 1989 was done at 100, 117 and 250 meters. The spectra to be discussed here are from the work completed in May and are for a 100 meter path or a 117 meter path (i.e. 385 feet).

The interferences caused by water vapor and carbon dioxide in the atmosphere are illustrated by the single beam transmission spectra in Figure 4. In Figure 4A (top) the full mid-infrared spectrum containing useful windows is shown while Figure 4B (bottom) contains an expansion of the window that appears to be most attractive for our purposes. Figure 5 illustrates the interference caused by water vapor lines and the poorer signal-to-noise ratio of field spectra for 1,1,1-trichloroethane by comparing the laboratory calibration spectrum in Figure 5A (top) with the field spectrum Figure 5B (bottom) both at 0.5 cm^{-1} resolution. A more favorable comparison occurs for methanol in Figure 6 where the laboratory calibration spectrum in Figure 6A (top) differs little from the field spectrum in Figure 6B (bottom) both at 0.5 cm^{-1} resolution. The average concentration of methanol in spectrum 6B is calculated to be 250 ppb and here an amount approximately 20 times smaller would give the minimum detectable absorbance.

The compromise between resolution and signal-to-noise ratio is illustrated for laboratory calibration spectra for benzene in Figure 7 where the absorption band is of comparable width to the spectral resolution chosen in the operation of the FT-IR spectrometer. Changing from a resolution of 0.1 cm^{-1} in Figure 7A (top) to 0.5 cm^{-1} in Figure 7B (bottom) lowers the peak absorbance by a factor close to 2 and reduces the noise by a comparable but larger factor making it somewhat subjective to choose which presentation is to be preferred for the best detection limit. The decision is complicated by the fact that the 720 to 670 cm^{-1} region contains many sharp water vapor absorption bands and

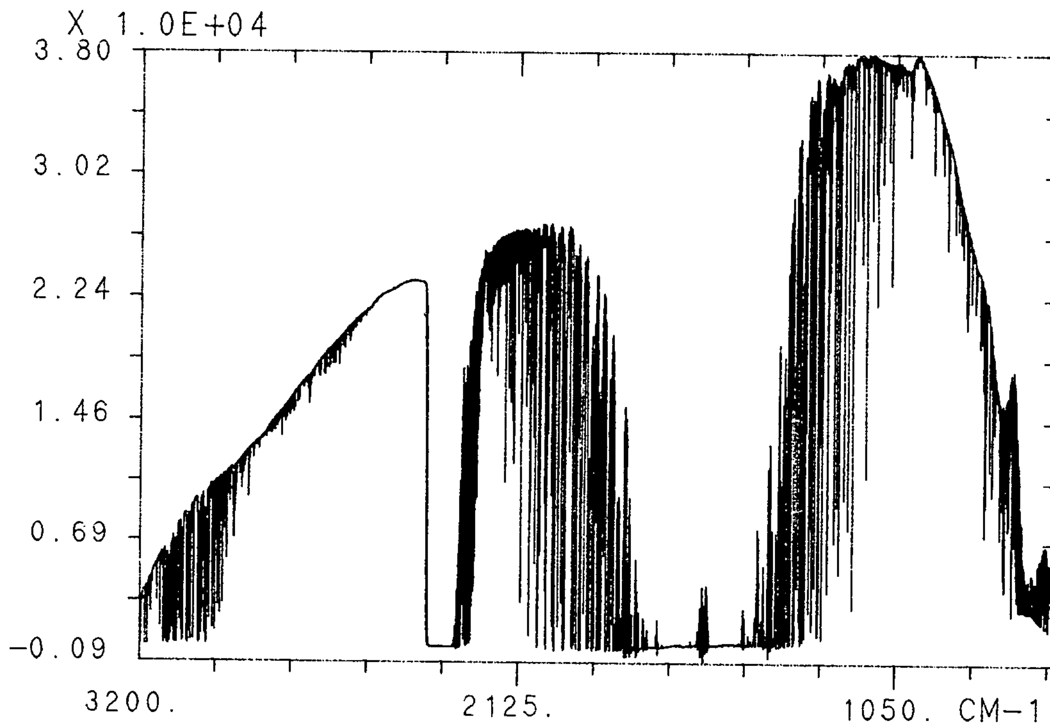
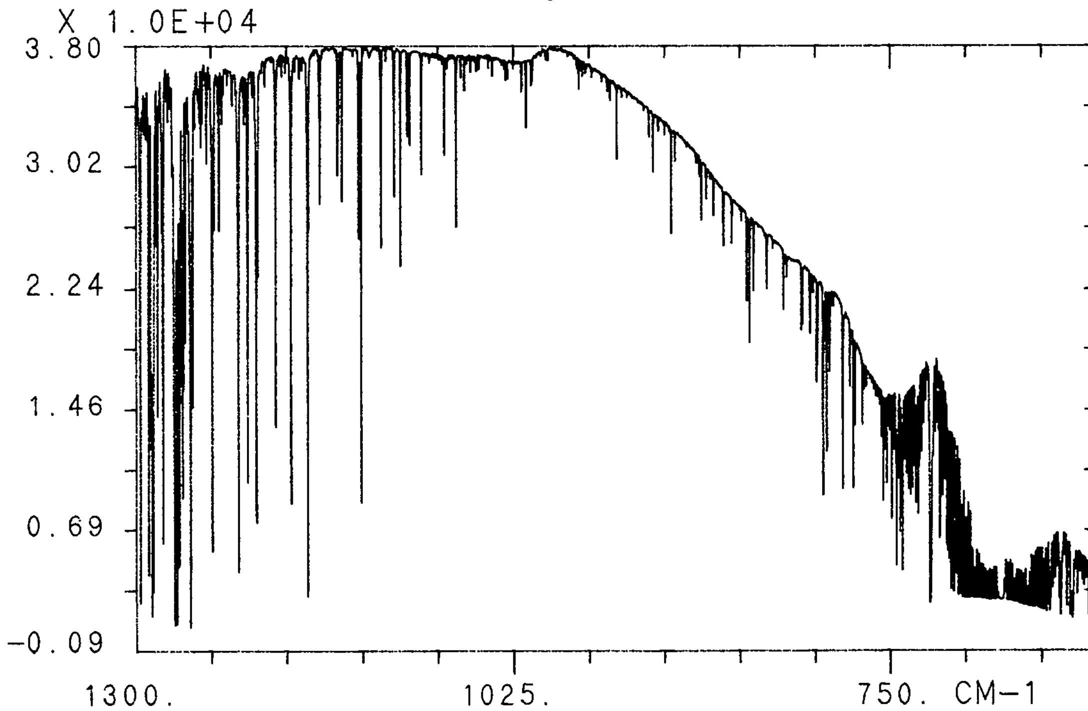


Figure 4. Single beam mid-infrared transmission spectra of 100 meters of ambient air at 0.1 cm^{-1} resolution

A (top) Full spectrum showing both windows
B (bottom) Lower frequency window expanded



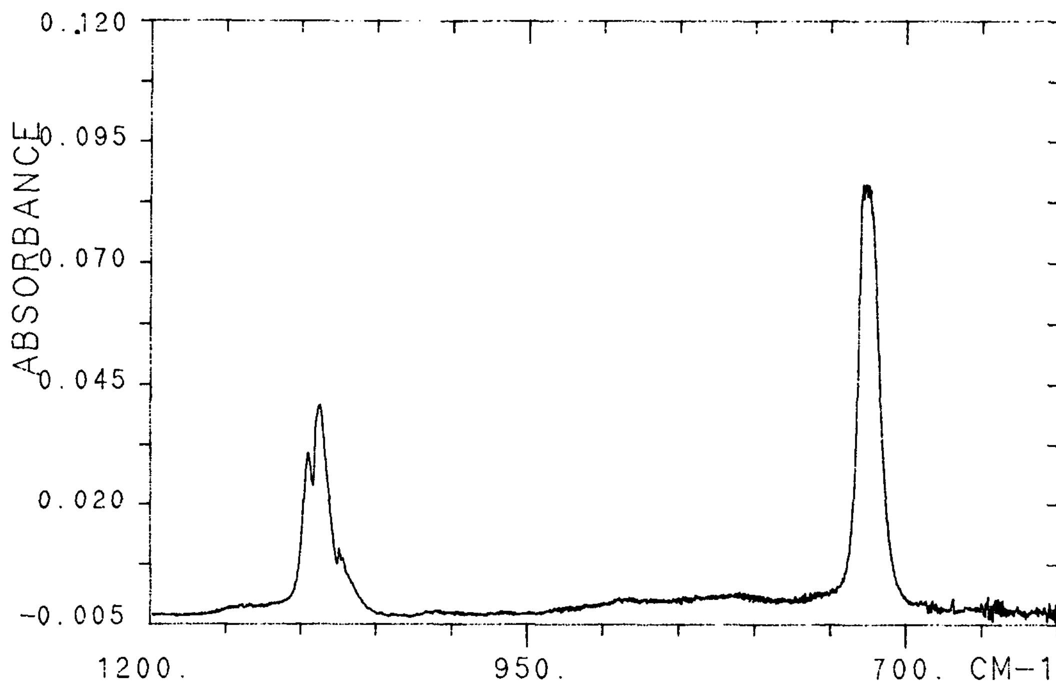
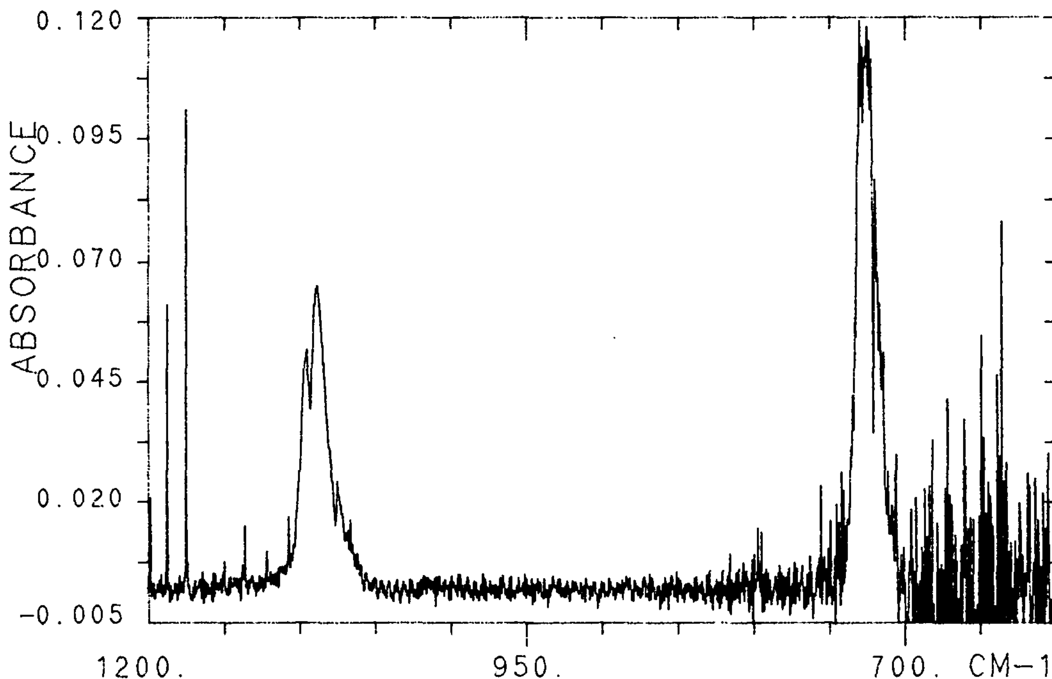


Figure 5. Mid-infrared absorbance spectra of 1,1,1-trichloroethane

A (top) Laboratory calibration spectrum in 16 cm cell at 0.5 cm^{-1} resolution

B (bottom) Field spectrum for 117 meters at 0.5 cm^{-1} resolution



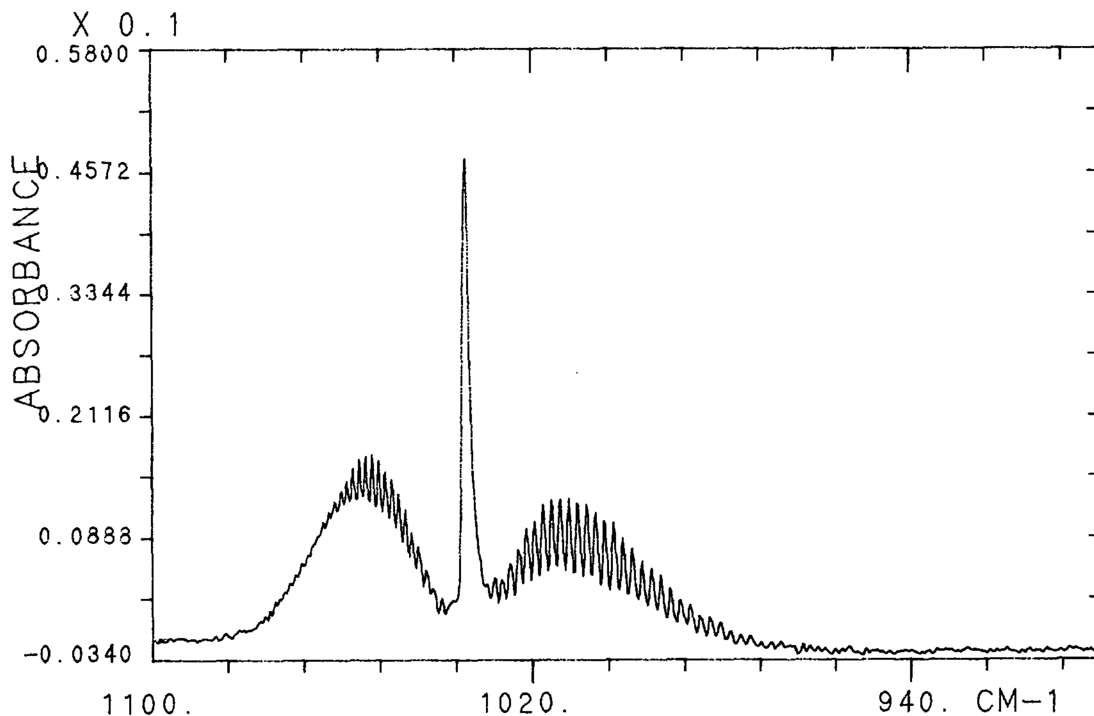
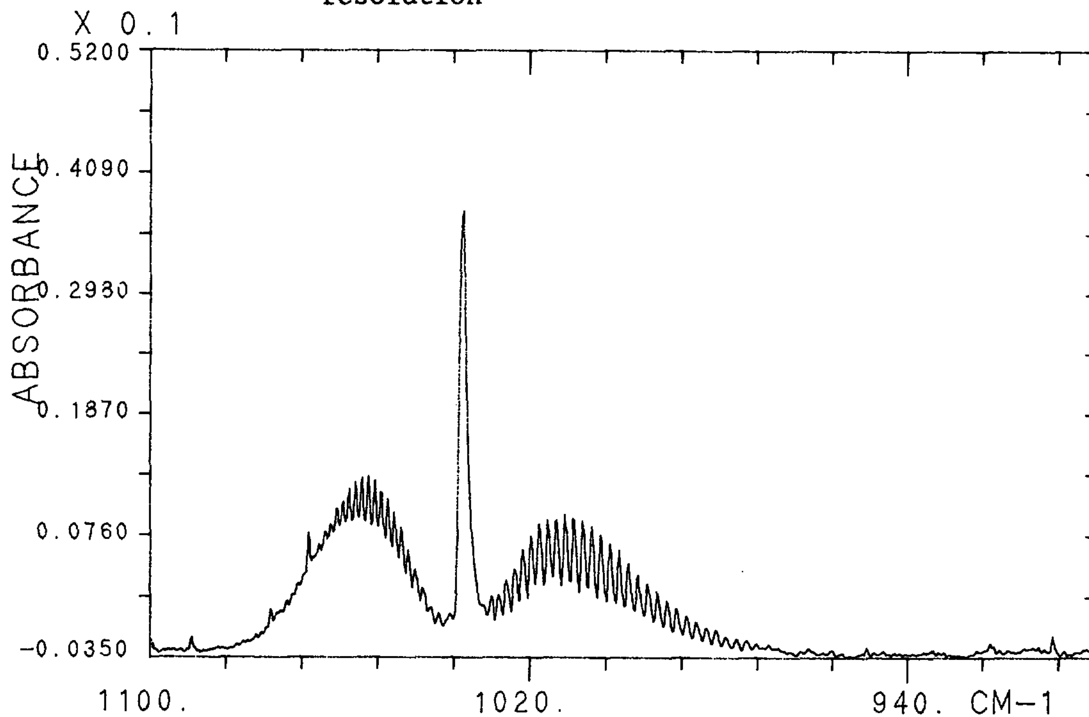


Figure 6 Mid-infrared absorbance spectra of methanol

A (top) Laboratory calibration spectrum in 16 cm cell at $0.5\ cm^{-1}$ resolution

B (bottom) Field spectrum for 100 meters at $0.5\ cm^{-1}$ resolution



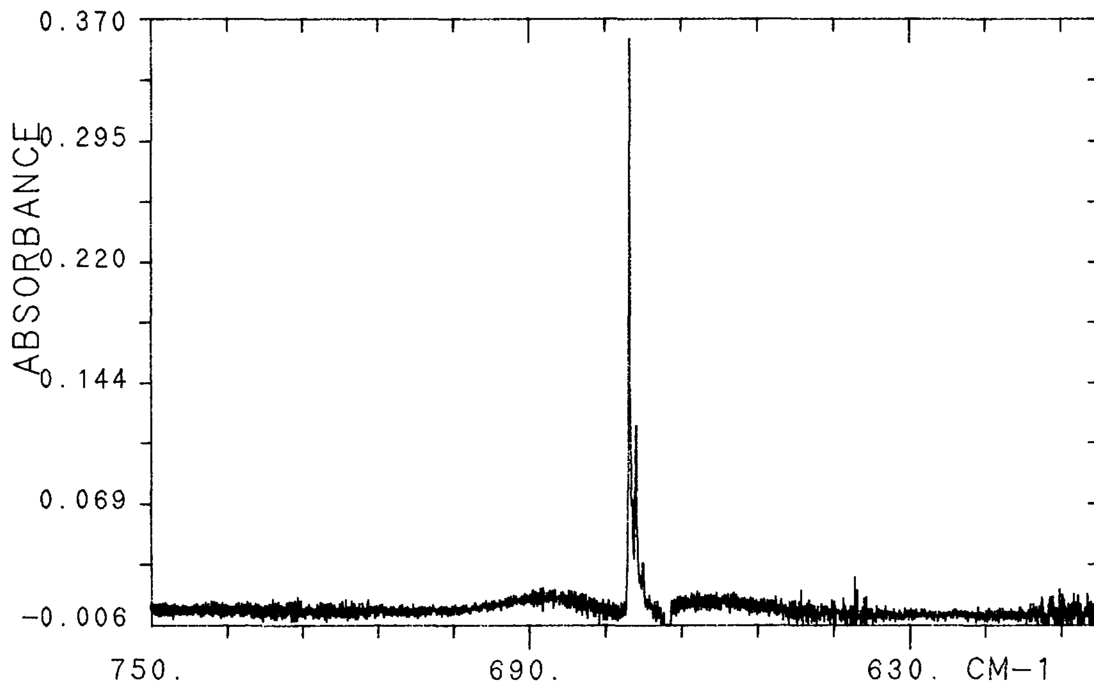
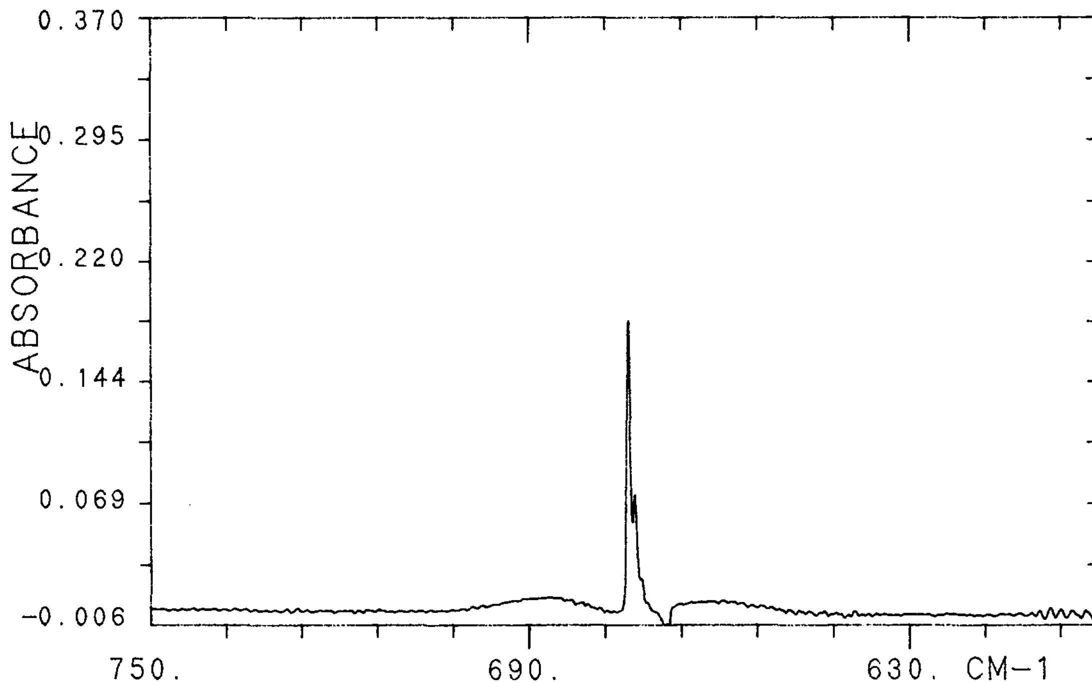


Figure 7 Mid-infrared laboratory calibration absorbance spectra of benzene in 16 cm cell.

A (top) 0.1 cm^{-1} resolution

B (bottom) 0.5 cm^{-1} resolution



high resolution may be necessary to pick out the benzene absorption band among the absorption bands of water vapor. A definite choice is easily made for the case of the field spectra of 1,1,1-trichloroethane shown in Figure 8 where the absorption band is broad relative to the spectral resolution chosen in the operation of the FT-IR spectrometer. Changing from a resolution of 0.1 cm^{-1} in Figures 8A (top) to 0.5 cm^{-1} in Figure 8B (bottom) makes little difference in the peak absorbance and reduces the noise dramatically. Clearly, the spectrum in Figure 8B (bottom) will yield the better detection limit. Experience to date has been that the most favorable resolution to use for a given spectrum may need to be determined experimentally. Our procedure to date has been to record all spectra a 0.1 cm^{-1} resolution and then degrade the resolution by reprocessing the data. Then a comparison of the different presentations as illustrated in Figures 7 and 8 is used to select the best presentation in each case.

When the choice is made to take data at this higher resolution we then have the capability to degrade the resolution by reprocessing the data. There are two alternatives: smoothing the spectrum or truncating the interferogram and then transforming to the spectrum. Experience to date with these two alternatives shows that smoothing gives the better signal-to-noise ratio and correspondingly the better detection limit.

The field work in February, 1989 involved the release of methylene chloride as a known and both the Kansas State University and University of Kansas groups measured an average concentration near 300 ppb. Informal discussions have lead us to believe that to obtain agreement within 20% is excellent. The field work just completed involved the separate release of three materials that were unknown to us. Our spectra identified the unknowns correctly as methylene chloride, acetone and methanol. Additional releases including mixture were carried out but, at this writing, the analysis is not complete and cannot be reported.

SUMMARY

A mobile laboratory for on-site analyses of volatile organic compounds (VOCs) using a FT-IR spectrometer is under development. Detection limits as an average concentration over a path length of 100 meters are estimated to be below 100 ppb. Preliminary field evaluation of the system capabilities is presently underway.

ACKNOWLEDGEMENT

We wish to acknowledge Dr. Donald F. Gurka (EMSL/LV) and Dr. Thomas T. Holloway (Region 7), U.S. Environmental Protection Agency, for their interest in this program and valuable advice on the critical problems to be investigated.

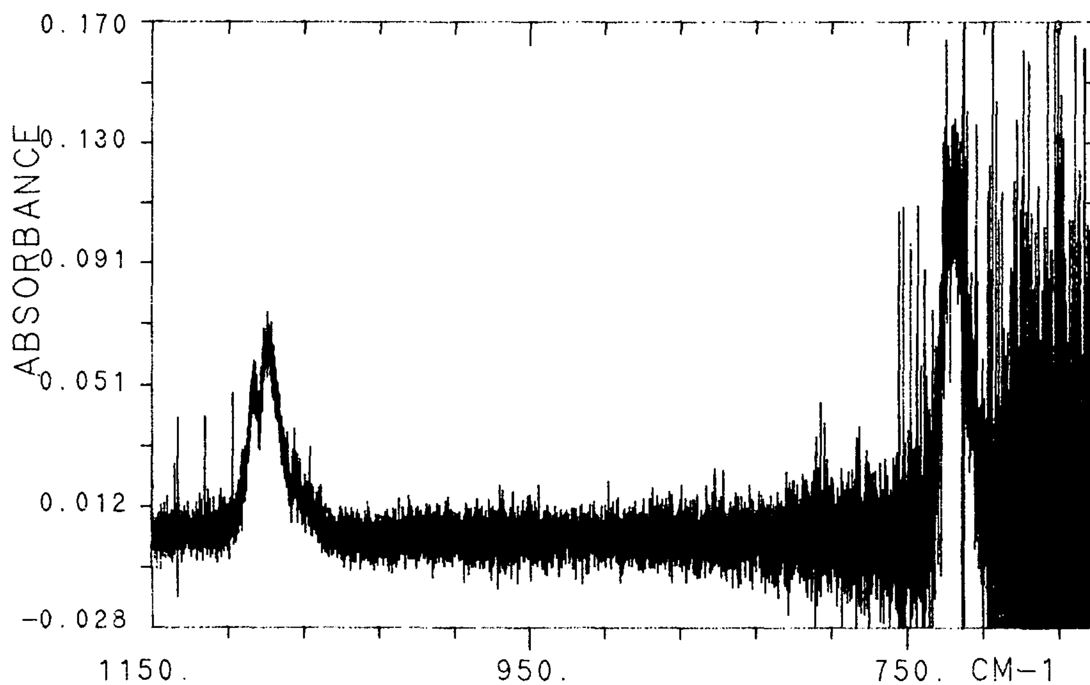
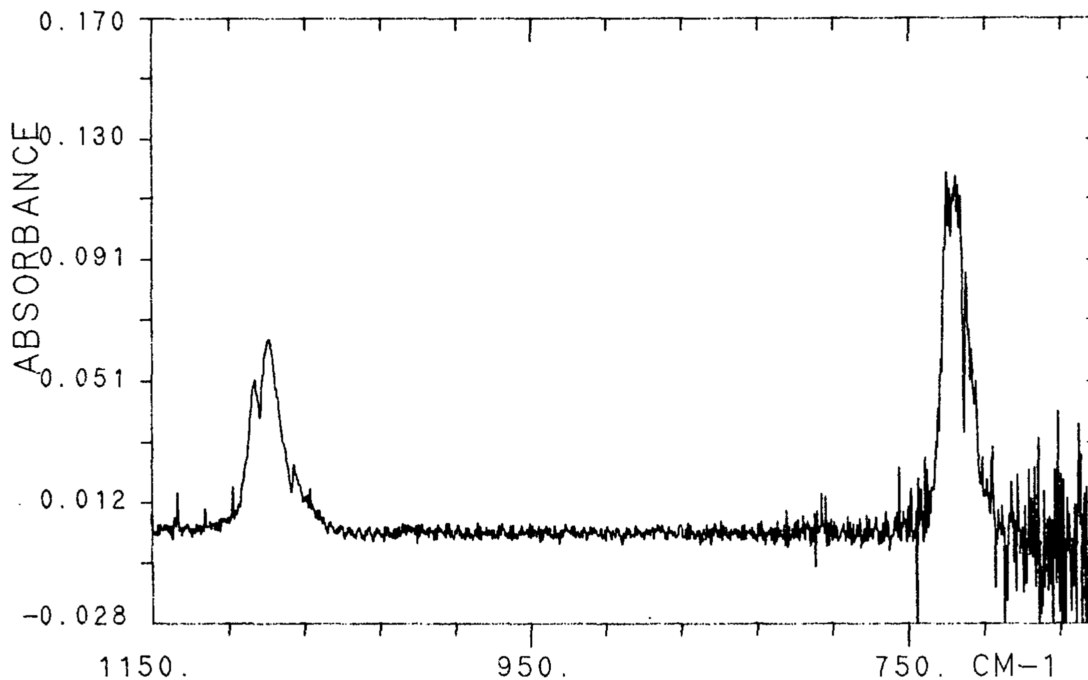


Figure 8 Mid-infrared field absorbance spectra of 1,1,1-trichloroethane (1,1,1-TCA) for 117 meters

A (top) 0.1 cm^{-1} resolution

B (bottom) 0.5 cm^{-1} resolution



A FAST FIELD METHOD FOR THE QUANTITATION OF POLYCHLORINATED BIPHENYLS (PCBs) USING A FIELDABLE GC-MS

Albert Robbat, Jr., and George Xyrafas, Tufts University, Chemistry Department, Medford, Massachustts 02155.

ABSTRACT

A fieldable gas chromatographic-mass spectrometric (GC-MS) method was developed for fast, on-site identification and quantification of polychlorinated biphenyls (PCBs). The screening method consisted injection of an internal standard into the soil followed by direct thermal desorption of sample components using a new MS-sampling probe. The quantitative method included hexane extraction of the soil sample followed by sample probe thermal desorption. PCBs were then detected by selected ion monitoring MS. The combined method is quick with total analysis time of approximately 20 minutes.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are wide spread environmental contaminants requiring extensive sample preparation procedures before analysis. In response to the growing demand for both on-site "screening" and "analytical" quality methods for the detection of these and other environmentally important compounds, we have been developing gas chromatographic-mass spectrometric (GC-MS) methods using a fieldable instrument. Increasingly, EPA has approved field analyses for specific compounds known to be on-site in an effort to improve data turnaround times. This data may be used in support of site characterization efforts concerning Listing Site Investigations and to identify samples known to contain environmental contaminants of interest. Most on-site data have been obtained using total organic analyzers or portable GCs.

Toward this end, we report on two methods which provides either screening and/or analytical quality data for PCBs in soil samples. The field GC-MS dynamic range and minimum detectable quantity are determined. Comparison between direct PCB/soil thermal desorption *and* PCB/soil hexane extraction followed by on-column injection and thermal desorption are presented.

EXPERIMENTAL SECTION

A Bruker Instruments (Billerica, MA) fieldable mass spectrometer and direct air/ surface sampling probe were used in this investigation, see Figure 1. The mass spectrometer consisted of a hyperbolic quadrupole mass analyzer fabricated from a single piece of shock resistant metal-coated glass. The available mass range was between 1 and 400 amu with 1 amu resolution (10% valley definition). The ion detection system was a conventional 17-stage dynode Cu-Be electron multiplier with dynamic range and accuracy of 10^8 and 0.7%, respectively. An ion getter pump (10^{-6} torr) was used to maintain vacuum. The sampling probe assembly included a 10 ft flexible hose and stainless steel tube. A nickel-stainless steel mesh was placed at the head of the tube to prevent dust and particulates from entering the sampling probe assembly. Located within the sampling probe assembly was a 3.5 m, 0.32 mm i.d. SE-54 fused-silica capillary column. The sampling head (tube) and hose can be

linearly programmed up to 260 °C and 240 °C, respectively. The sampling probe assembly was connected to the gas inlet sample transfer manifold of the mass spectrometer. A methylsilicone membrane housed within the sample transfer manifold controlled the flow of gas from the probe assembly to the mass spectrometer. The membrane further served to separate the MS high vacuum region from the probe and preferentially excluded air components relative to organic compounds.

The following materials served as standards in this investigation: pyrene-d_{10}, internal standard (Cambridge Isotope, Woburn MA); a PCB standard solution, see Table 1 for composition and concentration (Ultra Scientific, Hope RI); two PCB/ERA soil media containing 25 and 35 ppm of Aroclors 1254 and 1242, respectively (Environmental Resource Associates, Arvada CO); and two solutions each having 200 ng/μl of Aroclors 1242 and 1254, (Sulpelco, Bellefonte PA).

RESULTS AND DISCUSSION

Figure 2 illustrates a typical screen display, updated every 2 seconds, for PCB components desorbed from the standard solution. Signals A-J correspond to PCB chlorination levels 1 through 8, internal standard, and hydrocarbons. For each letter A-H, four ions were selected corresponding to characteristic ions for that particular PCB chlorination level. Signal I contained three characteristic ions of the internal standard and J four ions commonly found in hydrocarbon mass spectra. The instrument simultaneously monitored all selected ions. When the targeted ions were observed in the correct ion abundances ratios, the screen automatically displayed the name of the compound detected. To simplify field MS operation, instrument parameters were set so that when the four blackened ion signals appearing under each letter were of equal height, the corresponding PCB was said to be detected. The four whitened ion responses indicated background signals. The minimum detectable quantity was determined when the signal/noise was approximately 3/1. The scale on the left represents the ion current on a logarithmic basis. This mode of operation, i.e., viewing of the ion signals, allowed the operator to quickly determine the presence and qualitative concentration of PCBs present in a complex sample media.

The mass spectrometer was found to be linear in the concentration range between 7 and 2100ng of total PCBs (standard solution) injected on-column (after removing the sampling hood). Figure 3 illustrates the corresponding dynamic range plot for total PCB. It should be mentioned that the MS mass range limit precludes detection of isomers whose molecular weight exceeded octachlorobiphenyl. The minimum detectable amount of total PCB in the standard solution was found to be 7ng for those compounds detected.

Table 2 shows the results of two different sets of response factors using the sampling probe attachment. The first set was obtained by taking 10 μl of the standard PCB solution and 10 μl of internal standard *and* injecting them onto a dish covered with aluminum foil. The sample was thermally desorbed using the sampling probe under the following experimental conditions: sampling head (tube) 260 °C and initial hose temperature 150 °C for 30 sec; followed by the hose linear temperature programmed to 200 °C over 30 sec; and then held isothermal at 200 °C for 90 sec. The second set of response factors was obtained using the so-called fast screening approach. Back yard soil (0.4 g) containing 50 ppm of the standard PCB solution and 100 ppm of

internal standard was placed onto the aluminum covered dish and thermally desorbed. As evident by the Table both sampling methods provided response factor data within currently accepted error values for CLP-type measurements. To test the reliability of the second method a different soil sample was evaluated, viz., a standard PCB ERA soil (35 ppm in Aroclor 1242). A 7% deviation from the known PCB concentration was observed. These findings suggest that the fast screening approach can provide acceptable on-site screening data.

To compare the difference in MS response between direct on-column injection and thermal desorption using the sampling probe, the following experiment was performed. ERA soils (0.4 g) containing 25 ppm of Aroclor 1254 *or* 35 ppm of Aroclor 1242 were extracted with 2 ml of hexane. From these solutions, a 10 μl aliquot of extract and 10 μl of internal standard were placed on an aluminum foil coated dish and thermally desorbed (experiment 1). In contrast, a 3 μl aliquot of extract and 3 μl of internal standard were injected on-column and the MS response measured (experiment 2). Comparison of the measured relative PCB concentrations from experiments 1 and 2 revealed 92 % MS response when the samples were introduced by sample probe desorption versus on-column injection. Importantly, the error in the thermal desorption measurement was 3.5% (n=5) and somewhat less (3%) for on-column injection.

Soil extraction experiments were performed to determine optimum hexane amounts, extraction times and corresponding PCB recovery rates. For example, either 0.4 g of back yard soil spiked with 50 ppm of Aroclor 1254 *or* 0.4 g of standard PCB/ERA soil were added to vials containing 2 ml of hexane and shaken for different periods of time. The organic fraction was removed from the vial and analyzed by on-column GC-MS. Volatile sample components were separated by GC under the experimental conditions stated above. Figure 4 illustrated typical results for the PCB/soil extraction experiments as a function of time. Extraction times were varied between 15 seconds and 1 hour. Two minutes was found to be the optimum time required for both the backyard and ERA soils. The average recovery of PCBs from the soils was about 75 ± 3% (n=5) after a single extraction. To obtain greater PCB recovery, multiple 2 ml extractions were performed. It should be noted that PCB/soil recovery efficiencies may vary from one soil/sediment sample to the next due to different matrix adsorption characteristics. Thus, optimum extraction times may also vary depending upon the composition of the soils and sediments studied.

Currently we are investigating this approach with the cooperation of EPA, Region 1 for determining PCB levels in dredged materials from the New Bedford Harbor (MA) Superfund site. It should be noted that the total time required for both fast screening and the more quantitative (e.g., sample extraction) methods require about twenty minutes including sample preparation, injection of internal standard, GC-MS analyses and data processing.

Table 1. Composition of PCB Standard Solution.

#	compound	ng/μl
1	2-chlorobiphenyl	50
5	2,3-dichlorobiphenyl	50
29	2,4,5-trichlorobiphenyl	50
50	2,2'4,6-tetrachlorobiphenyl	100
87	2,2',3,5,5-pentachlorobiphenyl	100
154	2,2',4,4',5,6'-hexachlorobiphenyl	100
188	2,2',3,4',5,6,6'-heptachlorobiphenyl	150
200	2,2',3,3',4,5',6,6'-octachlorobiphenyl	150
209	decachlorobiphenyl	250

Table 2. Response Factors.

	method 1		method 2	
chlorination level	response factor	% error	response factor	% error
1	0.194	20	13.439	19
2	0.202	16	3.747	25
3	0.202	16	3.912	23
4	0.116	12	2.545	16
5	0.100	0	2.021	16
6	0.088	12	1.606	16
7	0.044	12	1.036	23
8	0.028	10	0.356	19

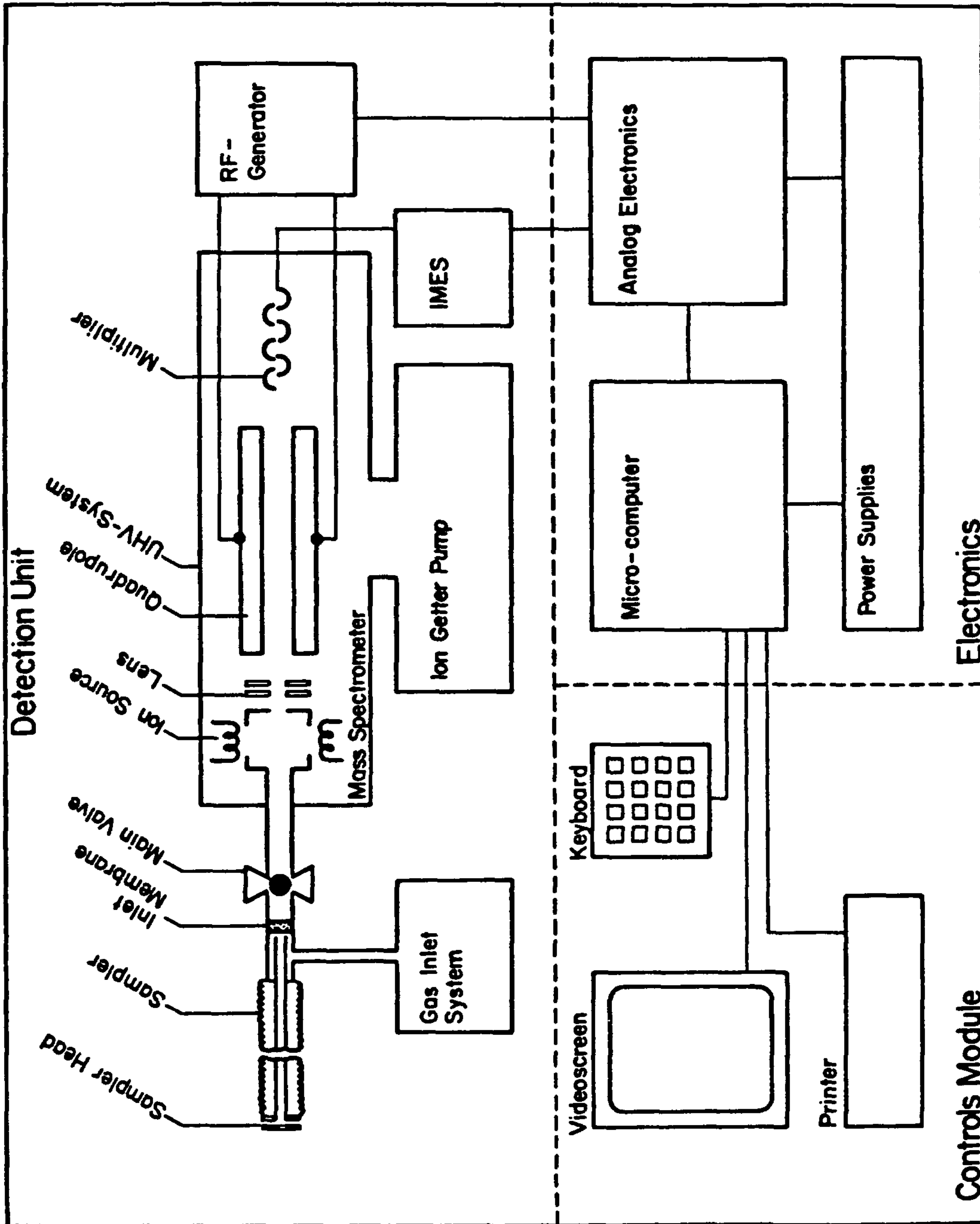


Figure 1: Schematic diagram of mass spectrometer, sampling probe and data aquisition system.

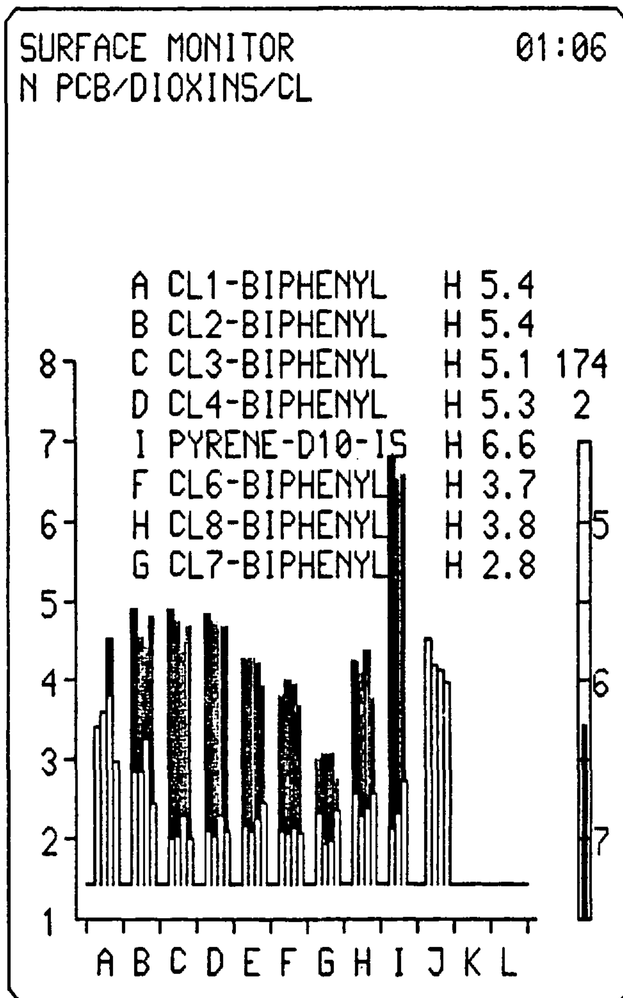


Figure 2: Typical screen display of 200 ng of PCB standard solution using the thermal desorption sampling probe.

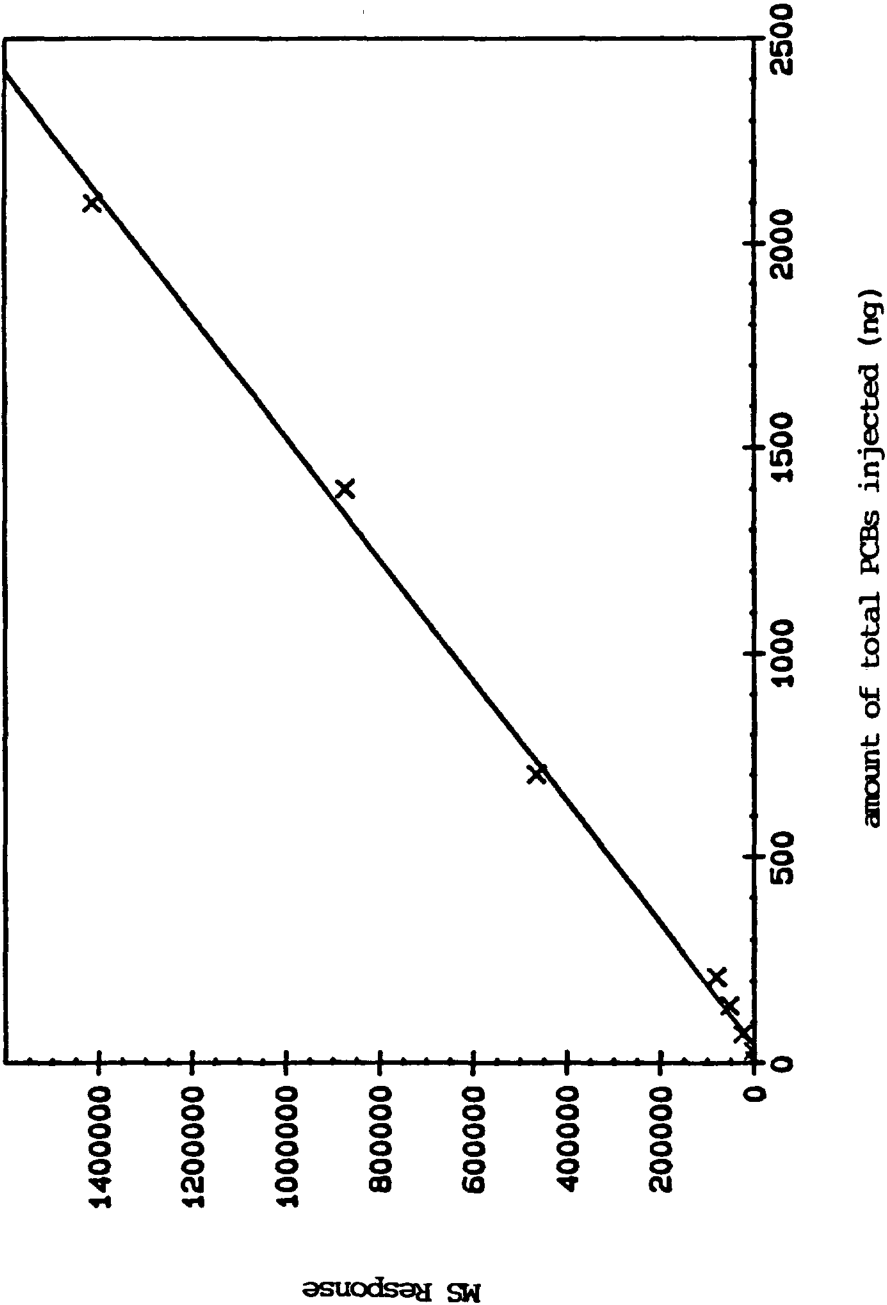


Figure 3: Linear dynamic range plot.

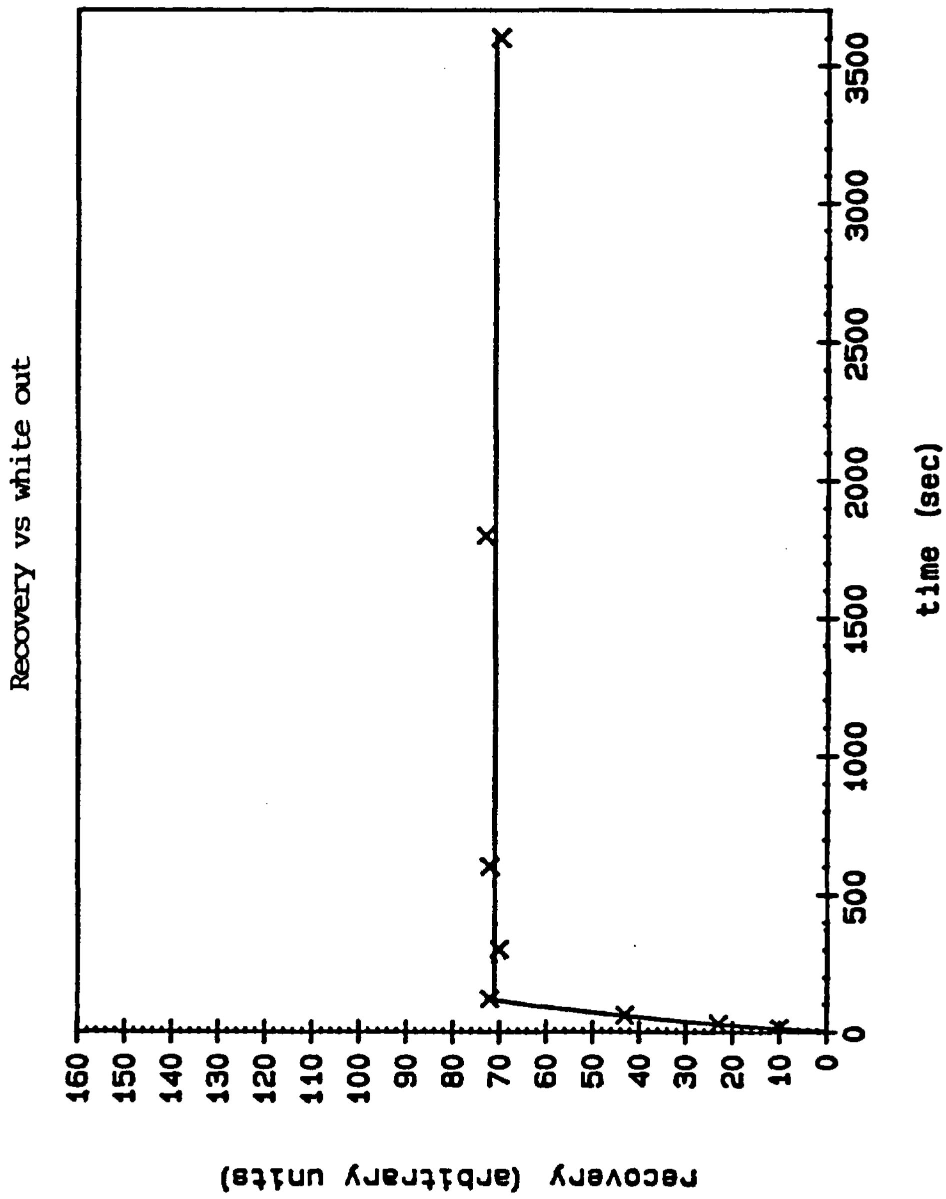


Figure 4: Plot of PCB recovery versus extraction time.

APPLICATION OF THERMAL EXTRACTION GC/MS TECHNOLOGIES FOR RAPID CHEMICAL ANALYSIS OF CONTAMINATED ENVIRONMENTAL SAMPLES.

E.B. OVERTON, C.B. HENRY, B.S. SHANE, T. JUNK, T.R. IRVIN , J.M. NOCERINO, L.C. BUTLER, J.D. PETTY, AND T.R. PRITCHETT, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LA. (EBO, CBH, BSS), TEXAS A&M UNIVERSITY, COLLEGE STATION, TX (TJ,TRI), U.S. ENVIRONMENTAL PROTECTION AGENCY, LAS VEGAS, NV (JMN,LCB,JDP), AND U.S. ENVIRONMENTAL PROTECTION AGENCY, EDISON, N.J. (TRP).

Recent national attention has been focused on the need for rapid assessment and prioritization of hazardous waste sites and site-associated contaminated environments (air, water, soil) resulting from current as well as past industrial activity. A key factor which currently underlies problems with onsite assessment of suspect toxic waste-contaminated areas is the absence of rapid analytical instrumentation (1-2 hours), deployable onsite, for (a) identification of total toxic organic components for evaluation, site characterization, prioritization and remediation, (b) ambient monitoring of toxicants at hazardous waste sites, and (c) characterization of the efficacy of various waste site remediation activities to rapidly clean-up waste sites at minimal cost. We have investigated a promising new analytical technology which has the potential to permit rapid, on-site analysis of semivolatile organic analytes in a variety of sample matrices commonly found at hazardous waste sites. The technology, first developed for the petroleum exploration and development and written for identification of worker compounds in source rock samples, uses thermal extraction of semivolatile organic analytes (SOA) followed by integrated gas chromatographic-mass spectrometric analyses of extracted material. The unique feature of this technology is that a single instrument both extracts and analyzes samples and the data is comparable to results obtained using conventional but labor intensive and time consuming liquid extraction coupled with GCMS instrumental analyses. The extractions cell is made of fused quartz which permits precise and reproducible thermal extraction in an inert environment. Total analysis time, from extraction through GCMS analysis, is on the order of 90 minutes. We have applied this technology for the analysis of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) dioxins (PCDD) and furans (PCDF) and other semivolatile organic analytes in three different types of waste: municipal fly ash, soil contaminated with wood preserving waste, and an estuarine sediment collected near an industrial outfall. The thermal extraction GCMS analyzer (TE-GCMS) provides rapid semivolatile organic analysis with detection limits in the low ppm-mid ppb range depending on analytes. The technique is as specific as conventional GCMS methods but not as sensitive due to the simultaneous thermal extraction of interfering substances.

DIRECT SAMPLING ION TRAP MASS SPECTROMETRY FOR THE RAPID DETERMINATION OF VOLATILE ORGANICS IN ENVIRONMENTAL MATRICES*

Marcus B. Wise, Michael R. Guerin, and Michelle V. Buchanan

Organic Chemistry Section
Analytical Chemistry Division
Oak Ridge, National Laboratory
P.O. Box 2008, MS-6120
Oak Ridge, TN 37831-6120

Analytical methods are currently being developed for the rapid determination of part-per-billion or lower levels of volatile organics in water, soil, air, and oil samples using direct sampling in combination with a Finnigan ion trap mass spectrometer (ITMS). Features of the ITMS which are important to the success of these applications include the ability to perform selective chemical ionization, daughter ion tandem mass spectrometry (MS/MS) with very high efficiency, excellent instrument reliability, and intolerance to relatively high operating pressures. Excellent detection limits, response linearity and reproducibility have been demonstrated for the determination of volatiles in water, soil, and air. Because no chromatography is used, sample turn-around is typically less than 5 minutes. Compound specificity is achieved through the use of selective chemical ionization and tandem mass spectrometry when necessary. Direct sampling is accomplished with a split-open-split capillary restrictor interface which has been designed to accept a wide variety of sampling devices. Volatile organics in water samples can be determined without any sample preparation simply by direct purge with helium into the mass spectrometer sample interface. A helium flow rate of approximately 100 mL/min through a needle sparging apparatus enables reproducible purging of the volatiles from a 20 mL water sample in less than 3 minutes. Soil samples are prepared by adding 15 mL of water to 5 g of soil in order to form a slurry. Purging of the volatile organics is achieved using the same apparatus and conditions as used for the water samples. Chlorinated solvents and gasoline have also been successfully purged from samples of used motor oil without any sample preparation suggesting that direct sampling ITMS or MS may be useful as a rapid method for screening samples at oil recycling centers. Volatile organics in air may be determined either by direct sampling with a sniffer probe or by preconcentration on a resin trap followed by direct thermal desorption into the ITMS. Direct air sampling has an estimated detection limit of approximately 1 ppb while preconcentration is effective for ppt or lower levels of constituents.

SOIL STABILIZATION/FIXATION FIELD METHODS

Gretchen Rupp, Sr. Scientist, UNLV, 4505 S. Maryland Pkwy, Las Vegas, NV 89154; Benjamin J. Mason, Ethura, 13785 N. Applegate Rd., Grants Pass, OR 97527; John J. Barich, Environ. Engineer, USEPA, 1200 Sixth Ave. Seattle, WA 98101; Kenneth W. Brown, Botanist, USEPA, P.O. Box 93478, Las Vegas, NV 89193-3478

ABSTRACT

Initial assessment of soil fixation/stabilization methodology conducted at a number of Superfund sites in Region 10 has shown this approach to be an effective means for remediating contaminated soils of varying physical and chemical composition.

This paper presents the sampling design, the sampling methodology and the sample preparation techniques that were used at selected Superfund sites to determine the efficacy of soil fixation. The soil contaminants at these sites consisted of numerous metals including arsenic, chromium, copper, and lead, a variety of organic matrices that included tar-derived liquids consisting primarily of benzenes, phenols and polycyclic aromatic hydrocarbons, poly chlorinated biphenyls, and various metal, rubber, wood, foam and plastic debris classified as automobile fluff.

The degree and types of contamination within a given volume of soil strongly influences the effectiveness of the soil fixation processes. As such, during the sampling design phase, characterization of the site soils and of the soil contaminants were made. In addition, for better assessment of the fixation processes the sampling designs were deliberately biased towards selecting sampling locations with high concentrations of contaminants. The designs also addressed the behavior of contaminants and their depth or penetration within the soil matrix.

A substantial amount of material was required for the physicochemical analyses and the bench scale fixation tests. Individual samples were collected from pre-selected locations. At each location the collected material was examined for debris. If debris was present, it was characterized as to type and volume. The individual samples were then composited to obtain the necessary volume for all scheduled physical and chemical tests. The composited material was screened and mixed to obtain a homogeneous sample. Aliquots were taken for the following tests: particle size, bulk density, percent moisture, Proctor compacting, permeability, inorganic and organic contaminant analysis, pH, leaching procedures, and bio-assay.

Samples for the fixation tests were taken from the mixing container in a predetermined random order and placed in labeled containers. This material was fixed by especially designed chemical procedures. After

fixing and curing, the fixed monoliths were subjected to some or all of the following tests: bio-assay, durability, permeability, compressive strength, toxicity characteristic leaching procedure, American Nuclear Society Procedure (ANS) 16.1, Material Characterization Center MCC-1 leaching test method, Monofilled Waste Extraction Procedure.

INTRODUCTION

Provisions for permanent remedial measures for the disposal and cleanup of hazardous materials are addressed in the Superfund Amendment and Reauthorization Act of CERCLA and in the Hazardous and Solid Waste Amendments of RCRA. To comply with these provisions and to identify an efficient and cost effective cleanup program at Superfund sites, Region 10 has initiated demonstration projects to test and assess the effectiveness of soil stabilization/fixation on a variety of hazardous materials.

The term "Stabilization/fixation" as used in this paper and defined by USEPA (1986) refers to treatment processes designed to accomplish one or more of the following:

- Improve the handling and physical characteristics of waste.
- Decrease the surface area of the waste mass across which transfer or loss of contaminants can occur.
- Limit the solubility of any hazardous constituents of the waste by pH adjustment or sorption phenomena.

Generally stabilization processes are proprietary, and involve mixing absorbents and solidifying agents with waste materials. Depending upon the waste materials, changes in the processes are commonly required to accommodate specific contaminants.

Four Superfund sites were selected by Region 10 for the assessment of stabilization processes. These were the Western Processing, Frontier Hard Chrome, and the Tacoma Historical Coal Gasification site (THCGS) located in Kent, Vancouver, and Tacoma, Washington, respectively, and the United Chrome site located in Corvallis, Oregon. At each of these sites the soils were characterized, systematically sampled and prepared by EPA and then stabilized by private vendors under contract to EPA. The vendors stabilized the collected material using their products and techniques. The stabilized material was then subjected to a variety of chemical leaching and physical integrity tests by EPA.

In planning these bench tests, the general procedure was as follows:

1. Select the specific tests by which the fixation will be judged. These included analysis of contaminant concentration, one or more

leaching tests, tests of physical integrity, and in some cases bioassays.

2. Develop data quality objectives so the test results can be interpreted at the desired confidence level.

3. Develop a sample matrix for fixed and unfixed materials, so that samples of the correct type, size and number are allocated to the various tests.

4. Devise a site sampling plan and a plan for mixing and stabilizing samples.

5. Formalize these two plans in a detailed field/laboratory protocol.

Because of differing conditions (e.g. contaminants, matrices and soils) the approach selected for site characterization, sample collection, handling and preparation required four site-specific procedural protocols. For illustrative purposes the procedures and methods used for the THCGS and the United Chrome sites only will be discussed. For additional definitive information concerning test results obtained and procedures employed at these and the other two NPL sites see USEPA (1987, 1987a, 1987b, 1988, 1988a, 1988b, 1989, and 1989a.

TREATABILITY STUDY FOR THCGS

The THCGS is a relatively "complicated" site, having multiple contaminants with wastes and debris of all types and sizes. Both organic and inorganic contamination are present. Coal tar is located in a tar pit and a "tar boil" area, and also in shallow soils and ground water immediately adjacent to these areas. Tar-derived liquids are found in lenses at the bottom of two shallow ponds and within shallow fill over much of the site. Their major components are benzenes, phenols, and polycyclic aromatic hydrocarbons (PAHs). PCBs are present in varying concentrations at the top of the shallow soil fill and in the overlying auto fill. PCBs are also present intermittently in fill at depths greater than one foot. Elevated metal levels are found in the auto fluff and in the soil fill, corresponding with the placement of automotive waste. Additional site description information is presented in USEPA (1988).

On the basis of a preliminary evaluation, a stabilization/fixation strategy was identified in the feasibility study (FS) as being potentially promising for remediating this site. It was projected that approximately 15 acres of contaminated soil and automobile fill (fluff) would be excavated to a depth of 1 to 3 feet. The excavated material would then be mixed with sorbents and a cementitious fixative, put back in the excavation and allowed to cure.

Prior to the full scale remediation effort it was decided that a treatability study was needed. The purpose of the bench treatability test was to assess the effectiveness of fixation in immobilizing the metals and organic contaminants found in the site soil, auto fluff and tar. Results from the bench test have subsequently been used to design an on-site pilot treatability study.

SAMPLING DESIGN

The treatability sampling design was based on the FS remedial design, on site characteristics, and on the requirements of the stabilization/fixation technology. For example, the degrees of contamination by tar and other organic compounds within a given volume of soil will influence the effectiveness of soil fixation. The remedial strategy identified in the FS requires that soil and soil containing surficial material be fixed along with materials that have high concentrations of tar-derived liquids. In most part the surficial material was automobile fluff. The interest in tar-derived liquids is that this material will challenge the effectiveness of the fixatives. To satisfy the FS requirements and to assess the stabilization method the sampling design was deliberately biased towards collecting samples with high concentrations of these materials. In addition, samples were collected within the area identified in the FS for excavation and over the approximate depth interval specified in the FS. The volume of sample required was calculated from the treatability design.

SOIL

About 150 pounds of contaminated soil was required for the analytical and associated fixation tests. Soil sub-samples were collected from seven different locations on a grid having 50 foot centers that covered approximately 40,000 square feet. Approximate sampling locations were set forth in the sampling protocol. However, this portion of the site is part of an active metals-recycling facility, and large scrap is stockpiled there. Thus exact sampling locations were chosen by the sampling team, on the basis of accessibility. At each of the sample locations a hole about 16 inches deep was dug. From a vertical face on one side of the hole a 3-inch thick, 12-inch deep and 8-inch wide sample was collected. An attempt was made to collect samples for volatile determination from the vertical face by pressing a 40 ml VOA vial into the side. However, the soil was too compact, so VOA samples were generated later in the laboratory.

Soil sub-samples were passed through a 3/8-inch screen into a large, shallow wooden box. This screen size was chosen to insure physical homogeneity in the small monoliths to be used in treatability testing. Once all the soil had been screened it was mixed top to bottom and side to side for several minutes using a shovel. Then 14 pre-cleaned

one-gallon glass jars were lined up around the box, and one scoop of soil was placed in each, in succession, until all were full.

FLUFF

About 100 pounds of contaminated automobile fluff was required for the analytical and associated fixation tests. The site remedial investigation (RI) report indicated that tar-derived liquids are migrating from the ponds and into the automobile fluff. As such, the collection of fluff samples containing tar-derived liquids in the vicinity of the ponds satisfied the FS requirements for fixing surficial and tar-derived liquid containing materials.

Fluff was collected and composited from four locations equally spaced along a 600 foot long transect bordering the two ponds. Each sub-sample was collected by excavating approximately 50 lbs of material from the surface to a depth of 2 feet. The collected material was spread on a plastic sheet and photographed. Objects larger than 3 inches were separated by hand, identified and excluded from the sample. The remaining material was screened through a 3/8-inch screen and then mixed. Foam material that was less than 3 inches in size but would not pass through the screen was collected and added to the sample. After mixing, the material was placed in one-gallon precleaned glass containers in the same way the soil jars were filled.

In-place bulk density of the auto fluff was determined by a modification of the sand-cone method. Because fluff "particles" are of varying size, ranging up to several inches, a relatively large volume must be used in the determination. A hole of about a cubic foot was dug in the fluff. The excavated material was bagged and brought to the laboratory for standard weighing, drying and re-weighing. The volume of the excavation was determined by filling it with styrofoam "peanuts;" These were poured into the hole from a calibrated one-gallon pail.

The automobile fluff contains sizable chunks of plastic, rubber, non-ferrous metals and building rubble. For any projects larger than bench-scale it will present materials-handling difficulties. The sampling protocol (USEPA 1988) included a field procedure for systematically sampling the debris and classifying it with respect to size, composition and volume proportion. This information will be needed in planning full-scale fixation. It was not needed for the bench trials; because the procedure is very time-consuming it was not carried out.

TAR

About 2.5 gallons of tar was required for the analytical and fixation tests. These samples were collected by scooping tar from below the surface of the tar pit and placing it into one gallon glass containers.

QUALITY ASSURANCE/QUALITY CONTROL

Sampling procedures followed the guidelines set forth in USEPA, 1983, 1984 and 1989b. They included steps to prevent cross-contamination, to create uniform, homogeneous composites of materials for the various tests, to collect sufficient material to allow for breakage losses, replication, and archiving of materials, and to document field activities according to standard CERCLA requirements.

Sample shipping and sample documentation followed standard CERCLA methods. Complete chain of custody was established. Raw-material samples were shipped and stored on ice. Sample handling was expedited to meet holding-time requirements. Insofar as possible, laboratories were notified by telephone of forthcoming sample shipments, and any special sample handling requirements.

Chemical analyses were performed according to CLP protocols. The physical and engineering tests were conducted according to standard procedures developed by EPA's Center Hill Laboratory in Cincinnati, Ohio, which are based on the ASTM standard methods for determining strength and durability of concrete and permeability of soil. The leaching tests were conducted by the EPA's Manchester Laboratory, which is certified to perform TCLP extractions (ANS 16.1 is not widely used, and there is no certification procedure for this test). Sand blanks were tested alongside site materials in both types of extractions. Chemical analyses were performed by CLP laboratories.

It was originally planned to fix and test mixtures of site soil and auto fluff. Shortly before the trials it was decided to also sample coal tar, and to test the tar and the tar-soil mixes. These tests yielded valuable information about the behavior of volatile compounds in the fixed mixtures. In TCLP extracts of raw samples VOAs were quantified using a zero-headspace extractor. However, facilities were not available to control or monitor volatile emissions during material mixing, fixation and curing. Hence data on volatiles are considered qualitative.

Data quality objectives for this project are described in the (USEPA 1988). All chemical composition data generated during the project were validated by U.S. EPA Region 10, according to CLP standards.

FIXATION AND SAMPLE TESTING

The raw (unmixed) sampled materials were processed at EPA's Manchester Laboratory six days after sampling. Processing was performed by personnel from EPA Region 10, and Silicate Technology Corporation (STC), the vendor of the proprietary fixation reagents.

Prior to fixation, separate containers were filled with raw materials for TCLP extraction and for analysis of phenols, volatile organics, semi-volatiles and PCBs, and metals. These samples were labeled, stored on ice and sent to the analytical laboratories.

The coal tar was extremely viscous and difficult to handle. Prior to mixing and fixation, it was warmed overnight in a hot-water bath under a fume hood to improve its handling properties.

The materials that were fixed and their ratios included:

- Pure soil
- 1:1 soil:auto fluff
- 3:1 soil:auto fluff (3 sets of samples)
- pure coal tar
- 1:1 soil:tar
- sand (clean commercial sand)

Two mixtures of soil with auto fluff were tested because, in full-scale fixation, most of the surficial material treated would be a mixture of the two. Fluff was expected to detract considerably from the physical integrity of the monolith, and it was desired to ascertain the ratio that would yield an acceptable product. In every procedure triplicate samples of the 3:1 soil:auto fluff mix were tested. This allowed for estimation of the precision of the tests.

The materials were processed in two-kilogram batches. All mixtures were on a weight:weight basis. Fixed mixtures were poured into small molds and cured for specified periods under controlled temperature and humidity.

Fixed monoliths were subjected to the following tests:

- chemical analysis for metals, phenols, PAHs and PCBs
- TCLP extraction
- ANS 16.1 extraction
- apparent moisture content, bulk density
- compressive strength
- permeability
- wet/dry durability
- ANS leaching, strength and permeability following wet/dry stressing.

The results indicated that fixation reduced the mobility of the different classes of contaminants to varying degrees. A full report on the project is given in USEPA 1989.

TREATABILITY STUDY FOR UNITED CHROME

Sampling by the State of Oregon's Department of Environmental Quality (DEQ) and the USEPA indicated that the soils at this site were contaminated with chromium, a major portion of which was in the chromium VI valence state. The highest soil concentrations occurred in a dry well of about 750 square feet located on the west side of the building housing United Chrome. According to the operators of United Chrome Products, Inc. the dry well was used from 1956 to 1975 to dispose of floor drippings, washings, and product rinsate. These wastes were collected in a sump within the building, neutralized with sodium hydroxide and/or soda ash, and then, disposed in the dry well.

Similar to the THCGS approach it was decided that a treatability study was needed to obtain initial baseline data. Data from this initial effort were used to assess the effectiveness of the tested stabilization processes, and to design an on-site pilot treatability study.

SAMPLING DESIGN

To assess the toxicity of the fixation reagents and uncontaminated soils, bioassays of fixed background soil were planned. Background soil was collected from a site approximately 200 feet south of the United Chrome property. Contaminated soil was collected from the center of the dry well, in an area where orange-yellow staining indicated very heavy chromium contamination.

The soil from both sites was collected by excavating a 3 foot by 3 foot by 6 inches deep hole. The excavated soil was screened through a 3/8 inch screen, mixed with a shovel to obtain homogeneity, quartered and then placed into 25 lb. capacity containers. Aliquots of the raw soils were collected for fixation, for biological assay tests and for the chemical analysis of chromium, lead, strontium and manganese. Simple field permeability tests and sampling for soil bunk density were also planned. However, the soils contained so much coarse gravel that neither of these was possible. The results of the chemical analyses are presented in Table 1.

Table 1. Average Metal Concentration in Background and Dry Well Soils mg/Kg-dry wt

Metal	Background	Dry well
Chromium (Total)	64	72000
Chromium (Hexavalent)	<3	6700
Lead	11	29000
Strontium	60	20000
Manganese	350	350

The hexavalent chromium determinations were made by the CH2MHill laboratory in Corvallis. The remaining analyses were made by the EPA Region 10 laboratory.

The nine replicate dry well samples had coefficients of variation ranging from 3 percent (chromium) to 13 percent (strontium), indicating that the field soil mixing and random filling of sample containers effectively homogenized the soil. Coefficients of variation for the background soil ranged from 3 to 47 percent; despite extensive field mixing, the very low levels of metals in these subsamples were thought to be responsible for poor replication.

LABORATORY TESTING AND RESULTS

Raw soils (both background and dry well) were subjected to particle size analyses and Proctor compaction testing. These data were used in designing the on-site pilot treatment tests.

Soils were fixed by U.S. Waste Management, the Vendor of the proprietary fixation reagents, using an optimum "Mix-of-Record" (MOR). Soils were cast into small cylinders, which were cured at 100% humidity from 28 to 47 days.

Similar to THCGS both physical and chemical tests were performed on the fixed material. Physical tests included unconfined compressive strength, permeability, and wet/dry weathering. Chemical leaching tests performed included TCLP Monofilled Waste Extraction Procedure (MWEP), and the ANS 16.1 test.

The leaching test results indicated that fixation was very effective in immobilizing chromium in the dry well soils (see USEPA 1989a for complete results). Physical tests indicated the fixed material had a very low permeability and moderate compressive strength, and was not degraded by cyclic welling and drying. The results were sufficiently promising to proceed with large-scale pilot testing.

CONCLUSIONS AND DISCUSSION

Treatability testing for soil fixation/stabilization poses special requirements at the sampling design, field sampling and sample handling stages of the project. Experience gained during the THCGS and United Chrome studies shows what these requirements are and how they can best be incorporated into project planning.

When the efficacy of soil fixation is being tested (i.e. the question is "will it work at all?") it is desirable to evaluate a worst-case scenario. Project managers accustomed to planning representative sampling should deliberately bias site sampling towards the collection of highly-contaminated materials. It is assumed that the RI has generated site information that makes this possible.

For treatability testing, it is recommended that sampling encompass both the surface area and the vertical interval of material that may potentially be excavated and stabilized. Sampling at United Chrome was from the surface of the dry well. Deeper sampling, performed later for the pilot tests, encountered nodules of heavy-metal (including chromium) precipitate that required special handling before fixation. These nodules had not been found in either the RI or sampling for the bench fixation study.

Sample collection methods for treatability testing are the same as those used for any other field sampling. As always, keeping the equipment requirements simple minimizes decontamination requirements. This is especially important when sampling is deliberately targeted towards the most-contaminated material on the site.

The importance of homogenizing samples thoroughly cannot be overemphasized. Soil contamination at CERCLA sites routinely varies by orders of magnitude over scales of a few feet. If composite samples are not completely mixed, the composition of the unfixed soil is uncertain, and the success of fixation is difficult or impossible to evaluate.

The amount of soil and waste materials to collect from the site is principally determined by the mass requirements of the various tests. Allowance is made for replication, loss, and breakage. In all four Region 10 studies, enough material was collected to create a number of extra monoliths, to be archived and tested in later years. Since data on the long-term behavior of fixed wastes are rare and very valuable, most investigators who have the facilities now archive extra monoliths.

At many sites, soil fixation/stabilization will require special handling of portions of the surficial materials. The debris within the auto fluff at Tacoma is one example of this; the metal nodules in the United Chrome dry well are another. Before pilot or full-scale soil fixation, investigators will need to define these special materials and

devise treatment/handling methods. This need not be done for the bench treatability tests, but the field sampling for the bench tests may be an appropriate time to perform the additional sampling necessary to define these special materials.

At present, treatability testing is frequently done by personnel who have not been involved in the site RI/FS process. If those planning the treatability study are unfamiliar with the site, their planned activities, particularly field sampling, may be impossible to carry out, or may require major on-the-spot modifications. Study planners should be very familiar with the RI report and should walk the site at least once, preferably with the Remedial project manager. The more that is known about the site, the better the treatability study plan will be.

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APPLICATION OF GY's SAMPLING THEORY TO THE SAMPLING OF SOLID WASTE MATERIALS

Charles A. Ramsey, Michael E. Ketterer, and Joe H. Lowry
United States Environmental Protection Agency
National Enforcement Investigations Center
Box 25227, Building 53, Denver Federal Center
Denver, Colorado 80225

ABSTRACT

Sampling the environment is not a trivial task. Several sampling-related error sources exist; these usually are transparent to the sampling team, and could invalidate the results of the investigation. It is only through the proper understanding of these errors and their mitigation that proper environmental sampling can be conducted. Fortunately, a sampling theory developed by Pierre Gy can be used to measure and mitigate all sampling errors. This paper presents a brief explanation of Gy's sampling theory and demonstrates its application to environmental sampling. This will be used to show inadequacies of current sampling guidelines.

INTRODUCTION

The goal of an environmental investigation is usually to determine the level of contamination in a material of interest. This "material" is referred to as the target population. In order to determine the contamination level, some type of chemical analysis will be necessary. In almost all cases, it is impractical to analyze the entire target population. This necessitates the collection of a smaller "sample" from the target population for instrumental analysis. This sample must have the same characteristics as the target population or the analysis will give misleading conclusions about the target population.

Representativeness is a measure of how close the measured properties of the collected sample are to the actual target population. There is no way to collect a perfectly representative sample, except by luck, but methods exist to assure that the collected sample reflects the characteristics of the population to within the desired degree of representativeness. The collected sample cannot be perfectly representative due to errors in sample collection and analysis that cannot be avoided.

The methods to measure a sample's representativeness/error, though theoretically quite complex, can be reduced into a relatively simple protocol which can be implemented in the field during the sampling episode.

Sample representativeness is determined from statistical analysis of the sampling error. When dealing with statistics nothing can be 100 percent certain as there is always at least some error. The degree of certainty is referred to as the "confidence level". The higher the confidence level the more "certain" the statistical conclusion, thus the more certain that the result obtained is correct. A commonly used confidence level for scientific "certainty" is the 95 percent confidence level. When statistics are employed with sampling to determine the errors associated with quantification of the level of contamination, certain assumptions are made. If these assumptions are not accurate, the statistical conclusion will not be accurate. Most statistical tests used in sampling the environment require that the sampled population be normally distributed and that the samples collected are from random locations within the sampled population.

Random sampling is referred to as probabilistic (as opposed to non-probabilistic) sampling. Simply stated, each portion of the target population is just as likely to be selected for sampling as any other portion of the target population. An example of a non-random sampling process is authoritative sampling, which is non-probabilistic. This sampling occurs when the sampler exercises some judgement in selecting samples from the target population. An example of authoritative sampling is where the sampling effort is restricted to a yellow patch of concrete because the sampler believes it to be contaminated with hexavalent chromium.

Probabilistic (random) sampling techniques are used when the goal of the investigation is to collect a representative sample to quantify the average property of the target population. Non-probabilistic (authoritative) sampling is used when the goal of the investigation is to determine the presence or absence of a contaminant, not to accurately characterize the average level of contamination of the entire population.

With authoritative sampling, the accuracy and precision of the sampling effort cannot usually be determined and conclusions drawn from the analyses apply only to the samples taken, not to the entire target population. It is important not to use authoritative sampling techniques

when the goal of the investigation is to measure the average characteristic of the target population. An example where authoritative sample is appropriate would be in determining if a drum has leaked onto the ground.

In some cases, the collection of a representative sample is no more work than collection of an authoritative sample; in other cases it is more difficult. The only difference between representative and judgment samples is the employment of a sampling plan based on sound sampling theory in the former case. If there is no extra effort required to collect a representative sample, it should always be done as there is more information available for the same effort.

There is another reason that random sampling is preferred over authoritative sampling: without some type of random sampling, the possibility exists that the sample locations become dependent on the judgement of the sampler. Thus, the results of an investigation could be contingent on the sampler's perspective. Biases of this type might invalidate the results of the study. In addition, random sampling would remove any liability from the sampler as to why certain sampling locations were chosen.

Before sample plan design can begin, there are several factors that must be considered that will impact the sampling. The first and most important is the purpose of the investigation. A sampling effort aimed at proving the presence of 1000 kilograms of hazardous waste is a much different proposition than simply demonstrating that a hazardous substance is present onsite. Second, the confidence level of the results must be considered. Preliminary site investigation would require a lower confidence level than a criminal investigation. Third, the target population(s) must be delineated. If the waste has diverse characteristics, it needs to be stratified into populations that have similar characteristics. If the waste material is not properly stratified, large variations in the analytical results will occur. Fourth, the sample locations must be determined (probabilistic or non-probabilistic). It is quite possible that practical considerations limit access to the entire population. In these cases a smaller "available" population will have to be defined before the random locations are selected. Finally, these sampled locations will be referred to as the "sampled" population. It is important that all these different populations be identified for possible future statistical analysis. These ideas are also applicable in the

laboratory where the chemist must subsample from the field sample in order to perform the analysis. For example, the arbitrary removal of a one gram subsample from a one kilogram field sample without properly addressing sampling errors may well lead to analytical results which are inapplicable to the one kilogram lot.

There are many errors associated with any environmental investigation that fall into three main groups: sampling, preparation, and analytical errors. Of the three, sampling errors are the least understood and are often a major source of error. It is only these errors that are discussed in this paper. Error manifests itself in two ways: accuracy and precision. Accuracy is achieved when the analytical results from the sample provide an unbiased estimation of the actual contamination of the sampled population. If a sample is not taken correctly, it cannot be accurate. Precision is achieved when multiple samples of the same material yield the same analytical conclusions. A lack of precision (high coefficient of variation) prevents quantification of the contaminant levels with a high degree of confidence. Both are important; the results must be both accurate and reproducible or the sample is not representative.

Some sort of sampling error measurement at the onset of the sampling process is, therefore, very important. It is the sampling error which controls representativeness which in turn, controls the statistical inferences available from the analytical results. The usual scenario, however, is that one samples authoritatively, hopes that the objectives are met, and is then faced with resampling when they are not.

In situ sampling error determination is also important during field investigation for judicious allocation of limited resources. Particularly where time and manpower are limited, an understanding of the sample mass required to achieve the goals of the investigation is vital. For example, suppose several piles of hazardous waste, each in excess of 1000 kilograms, are present at a site. All are determined, through field measurements, to contain similarly high levels of lead. The objective of the survey is to prove the presence of 1000 kilograms of a hazardous waste. One pile in particular consists entirely of fine particles (< 1 mm), while the others contain a range of fragment sizes up to 10 cm. Sampling theory considerations (vide infra) would identify the pile of fine material as being the most plausible population to sample. In this scenario, it is most

appropriate to properly sample the fine pile and ignore the rest.

The errors associated with sampling are caused directly or indirectly from two sources; 1) compositional and 2) distributional heterogeneity. Compositional heterogeneity results when different particles within the target population have different levels of contamination (e.g. some of the small particles are contaminated but the larger particles are not). Distributional heterogeneity is due to a non-random distribution of the particles throughout the population (the contaminated fine particles are on the bottom of a pile and the uncontaminated large particles are on the top). It is through sampling theory that the consequences of a material's compositional and distributional heterogeneity can be identified and minimized.

Sampling errors result when too small of a sample mass is collected. This is easily visualized if previous concepts are recalled. If the total population is collected, there is no sampling error. If only a single particle from the population is collected, the sampling error is at a maximum (this particle might be contaminant free or a "nugget" of contamination; either way, it cannot be representative). The sample mass usually required is somewhere between the two extremes. Too small of a sample mass usually results in a Poisson distribution of the analytical results. The data from a Poisson distribution will have mostly low values, with only a few high values. If the chemical constituent is congruent with a Poisson distribution, the applications of classical statistics based on normal distributions are invalid. Some analysts will reject the high values as outliers in order to make the remaining values appear to be normally distributed. This is the **wrong** approach; it is these rejected values that contain the information the investigation is after. Rejection of these values will bias the investigation. The reason the "outliers" are rejected is to improve the precision of the results. This improved precision is only artificial and ignores the fact that the high values belong to the population of results expected for that particular sample size. This lack of precision is caused by improper sampling and can only be improved by proper resampling (Ingamells and Pitard, 1986)

GY SAMPLING THEORY

Pierre Gy, a French engineer, adapted portions of several empirically derived sampling theories developed by his

peers during this century and formulated a mathematically based, comprehensive theory applicable to sampling situations of any nature. His theory is explained in detail elsewhere (Gy, 1982). Application of Gy's sampling theory allows collection of a representative sample by addressing the compositional and distributional heterogeneity of the material to be sampled. These heterogeneities lead to four distinct sampling errors that affect the accuracy and precision of any sampling effort.

The first error is called the Fundamental Error. Fundamental Error results when fragments (particles) of the material to be sampled have different chemical compositions. When a sample is collected it must be representative of all the particles or it cannot be representative of the target population. The sample must contain an adequate mass of the same relative proportion of the different sized particles as the target population or Fundamental Error will occur. The Fundamental Error can be estimated without having any concentration-related information available, although a better estimate can be acquired if such information is available.

The second error is the Grouping and Segregation Error. Grouping and Segregation Error is caused by the non-random distribution of the particles throughout the target population (distribution heterogeneity) and the impossibility of collecting samples one particle at a time. This non-random distribution can be caused by many factors, including fragment density heterogeneity, fragment size heterogeneity, fragment shape heterogeneity, air turbulence, gravity, vibrations, or anything that might tend to separate the fragments. Gy's theory demonstrates that this error is bounded by zero and the Fundamental Error level.

The third error, Long Range Heterogeneity Error, occurs when there is a different concentration of the contaminant of interest in different locations within the sampled material. Long Range Heterogeneity Error can be considered as a natural variation, because it is not always considered to be error; the objective of the investigation might also be to determine it. Long Range Heterogeneity Error is caused by spatial trends in the level of the contaminant contained in the waste material or cyclic changes in the level of contamination. While the Long Range Error can be determined through field analytical methods or preliminary sampling episodes, it cannot be determined in the absence of some concentration-related information.

The fourth sampling error is the Materialization Error. While this error is simple in concept, it is the cause of many biases that occur in sampling. The Materialization Error can be broken into two parts, the Delimitation Error and the Extraction Error. Delimitation Error is a bias that results when a sample of the wrong shape is collected. The proper shape for a one dimensional population (e.g. a flowing stream or elongated pile) is a slice, for a two dimensional population (e.g. a flat pile) it is a cylinder and for a three dimensional population (e.g. a large pile of complex shape) a sphere is proper. While the first two sample shapes are possible to collect, collection of a sphere is impossible. For this reason the dimensionality of a population should be reduced where possible. For example, a three dimensional pile can be converted to a two dimensional system using a bulldozer, or its entire contents can be fed onto a conveyor belt, thus converting it to a one dimensional population.

The Extraction Error results when the ideal sample shape is not collected. A theoretical boundary exists for all sampling instruments. This boundary can easily be seen if a coring device is imagined. The inside diameter of the circular metal coring device is the outer boundary of the sample. All particles whose center of mass lies within this boundary when the coring device punctures the target population should become part of the sample, and those whose center of mass is outside this boundary should not become a part of the sample. A rule of thumb that can be used when selecting the proper coring device is to be sure the inside diameter of the coring device is at least three times the diameter of the largest particle in the target population.

Materialization Error is caused by either improper selection of sampling device or improper use of the correct sampling device. Some devices (often including devices sold for that purpose and always including devices such as coffee cans and pop bottles) are fundamentally inappropriate and should never be used for sample collection. Similar examples exist in the analytical laboratory, such as most commercially available spatulas. Even if proper Increment Delimitation is achieved, proper Increment Extraction may never be. The converse is also true.

Fundamental Error is also the only error that can be estimated before sampling commences. This is the error which should be addressed first in any sampling episode, since if this error by itself is out of control, there is

no sense in continuing with the planned investigation. Fortunately, two methods exist for reducing the Fundamental Error. The first is to reduce the particle size of the entire target population to be sampled. While this is not practical for most field investigations, it is applicable for laboratory sub-sampling. The second way to reduce the Fundamental Error is to increase the sample mass. This method is the easiest way to reduce the Fundamental Error in the field, but there are some practical sample size limitations.

The remaining sampling errors are difficult, if not impossible, to quantify prior to sampling. Fortunately, these errors are easy to reduce to a minimal level; therefore, reduction of these errors should **always** occur in any investigation. Grouping and Segregation Error can be sometimes be reduced by homogenization of the entire target population; however, this approach is frequently impractical and often aggravates the situation. This error is more properly reduced by collection of many increments to make up the sample. Materialization Error is reduced by correct use of the proper sampling device. Long Range Error is reduced by separation of the target population into multiple, smaller populations.

A simplified, generally applicable equation which relates Fundamental Error to sample mass and the size of the largest particles present in the sampled population is as follows:

$$S^2 = 18*f*e*d^3/M_S \qquad (1)$$

where S^2 is the relative variance of the contaminant concentration due to sampling, f is a dimensionless factor related to particle shape, e is the population's average density (gm/cm^3), d is the diameter of the largest particles (cm), and M_S is the mass of the sample (gm). This Equation represents an upper-bound estimate of the imprecision that could be expected **due to particle size representativeness alone** and does not account for all the Fundamental Error that might occur (measurement of the total Fundamental Error applicable to all sampling situations is beyond the scope of this paper). In addition, other sampling errors such as that related to the distributional heterogeneity, as well as those associated with preparation and laboratory analysis must be considered. An example of the calculation of the Fundamental Error using Equation 1 is as follows: suppose $f = 0.5$ (typical; see Gy, 1982 for details), $e = 2.5\ g/cm^3$, $d = 1.0$ cm, and $M_S = 100$ grams; $S^2 = 18*0.5*2.5*1^3/100 = 0.225$, which corresponds to a

coefficient of variation of 0.47. Equation 1 shows that two ways to reduce this error would be to reduce the particle size of the sampled material prior to sampling or to increase the mass of the sample to be collected. In the example given above, if the sample mass is increased to 1,000 grams, the variance will decrease to 0.0225 (S = 15 percent). If the particle size of the entire population is reduced to about 4.6 mm, with the same 100 gram mass, the variance will also decrease to 0.0225 (S = 15 percent). It is through application of this simple equation that the sampling protocol can be developed to suit the needs of a particular study.

When using Gy's sampling theory, if nothing other than particle size is known, an upper bound for the Fundamental Error (considering only particle size representativeness) can be obtained. If, however, other information can be obtained regarding the characteristics of the sampled material, the Fundamental Error can be estimated. If the estimated Fundamental Error is less that this "worst case", less sample will need to be collected. The only method to obtain this information in a timely manner is through the use of field analytical techniques. The Fundamental Error can be estimated by empirically measuring what is referred to as the Sampling Constant, C. The Sampling Constant is the case-specific value of the product 18*f*e in Equation 1 and can be estimated by measuring the variability of the analyte's concentration within the target population. In addition, field analysis can used to determine if the contaminant of interest exists in the population and at what levels or if other contaminants exist. Field analysis can also identify different populations within the site for stratified random sampling and reduction/identification of Long Range Error. Examples of methods practical for field use include portable X-ray fluorescence, near-infrared spectroscopy, potentiometry, conductimetry, and colorimetry.

PROBLEMS WITH LARGE FUNDAMENTAL ERROR

Fundamental Error should always be kept below 17 percent to prevent any significant biases from occurring if too few samples are at your disposal, which is often the case (Pitard, 1989). As the Fundamental Error exceeds 17 percent, the analytical results tend to follow a Poisson distribution. The total imprecision from all sources (sampling, preparation, analysis) can be larger than 17 percent without causing significant biases if much of the variance is from sources other than Fundamental Error.

However, poor precision by itself is problematic, as it decreases the reliability of the statistical inference.

EXPERIMENT

In order to demonstrate the power of sampling theory and field analytical techniques a case investigation will be presented using actual data.

Twenty five samples of a dry, soil-like waste material were collected from an area approximately 10 by 100 feet. Samples were collected with a split spoon from randomly selected one foot square grids. The survey's objective was to determine if 1,000 kilograms or more of the waste material sampled exhibited the RCRA EP toxicity characteristic with respect to lead. The maximum particle size of the waste material was 1 cm. Care was taken to minimize the Grouping/Segregation and Materialization Errors through collection of multiple increments per sample, and by proper tool selection.

Application of Equation 1 suggests that the Fundamental Error for 100 grams of this material should be no larger than 47 percent. The actual total error (including sampling, preparation, and analytical error) observed for the analytical results of 25 samples was 45 percent. The sources of the 45 percent error from this experiment were investigated (only Fundamental and Long Range were considered) to determine the predictive capability of sampling theory. The Sampling Constant for total lead was determined by analyzing the variability of the total lead content with X-ray Fluorescence. The overwhelming majority of the variance in the EP lead results could not be explained by the total lead Fundamental Error (2.3 relative percent). Exploratory data analysis showed that the EP lead sample variability was better correlated to the waste alkalinity than to the total lead content. The means that there were two Fundamental Errors and two Long Range Errors that must be considered for this investigation: one due to the total lead and one due to the factors that affected the amount of extractable lead. The measurement errors are presented in Table 1. These errors, which are measurable in the field, accurately predicted the observed variation in the analytical results. The average level of EP lead was 10.8 mg/liter with a standard deviation of 4.9 mg/liter (coefficient of variation = 45 percent).

As can be seen the Fundamental Error is less than 17 percent, thus the average value is most likely accurate. Nonparametric statistical tests indicated that there is

Table 1

Type of Error	Error (%)
Fundamental Error of Alkalinity	8.6
Fundamental Error of Lead	2.3
Long Range Error of Alkalinity	44.
Long Range Error of Lead	17.

99.99 percent confidence that the mean value of 10.8 mg/liter is indeed greater than the regulatory threshold of 5.0 mg/liter. This inference was obtained from all 25 samples collectively; however individual samples did not adequately represent the target population (indeed, three of the 25 samples were not EP toxic for lead).

The precalculation of Fundamental Error and Long Range Error is very important in this case, because the EP value is near the regulatory threshold. Most investigations would probably have taken only take three to five samples to quantify the EP lead level of this waste. If only five samples were collected there would not have been enough evidence to show that the waste was toxic at the 99 percent confidence level; however, with 25 samples, it was shown that the waste is toxic at the 99.99 percent confidence level.

PROBLEMS WITH CURRENT SAMPLING GUIDANCE

"Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods", EPA Publication SW-846 [Second Edition, 1982 as amended by Update I (April, 1984), and Update II (April, 1985)] states that increasing sample mass does increase precision. However, no suggestions are given to calculate appropriate sample masses. SW-846 also does not address the issue of bias from non-normal distribution of analytical results--simple transforms of the data may not be adequate!

A lack of appreciation for the Fundamental Error and its implications is evident in current procedures such as Method 1310 (Extraction Procedure). For example, this test may be applied to large materials, such as a pile of waste containing fragments up to 30 mm in diameter. The Method fails to specify the appropriate field sample sizes (in this case about 7 kilograms) to ensure representativeness. Furthermore, in order to obtain a representative (Fundamental Error = 17 percent) 100 g subsample for extraction, one would need to reduce the entire 7 kilograms to 4 mm maximum diameter prior to

splitting. Comminution of this material to 9.5 mm (mentioned in Method 1310) would yield a Fundamental Error of 44 percent for a 100 g sample. Equation 1 clearly points out these deficiencies and suggests pertinent remedies.

Fundamental Error is of concern when the particles to be sampled are large. If the material to be sampled is composed of submicron particles, Fundamental Error is of little concern. This is the case for liquids and gases; the molecules are nothing more than small particles. Application of Equation 1 demonstrates that even very small samples of liquids and gases have little Fundamental Error associated with them. This does not mean, however, that sampling of liquids and gases is always done correctly; other sampling errors still apply. Materialization Error is perhaps the major source of error in the sampling of liquids and gases.

CONCLUSION

The purpose of an environmental investigation is to usually to determine if the target population possesses characteristics that are hazardous to the environment or in violation of some regulatory statute. It is impractical and impossible to collect the entire target population for analysis, and therefore some type of statistical sampling strategy must be employed. From the results of this statistical sampling, certain inferences can be made regarding the target population. Since not all the target population is analyzed, it is impossible to guarantee with 100 percent confidence that the statistical inference is correct.

However, any desired confidence level up to but not including 100 percent can be achieved through the application of sampling theory. The greater the accuracy that is desired, the more resources one must expend in the sampling effort. It is important to measure and control sampling error before the investigation begins so that vital resources are not wasted. In order to take full advantage of the power of sampling theory, certain characteristics about the waste material are best determined prior to sampling. These characteristics are most easily measured with field (portable) instruments. Further applications of sampling theory and field analysis are under study at NEIC.

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HAZARDOUS SITE SAMPLING AND ANALYSIS PLAN PREPARATION: ROLE OF CLP SPECIAL ANALYTICAL SERVICES

WILLIAM J. BERNING, JERALYN GUTHRIE, RICHARD A. CHEATHAM, C.C. JOHNSON & MALHOTRA, P.C., ENVIRONMENTAL ENGINEERS, 2300 15TH STREET, SUITE 330, DENVER, CO 80202

Site specific characteristics, such as the variety of sample matrices, the potential or known contaminants, and the analytical and legal requirements in a RCRA or CERCLA sampling effort will dictate the analytical approach taken to a study. The data and analyses offered under the U.S. EPA Contract Laboratory Program (CLP) Routine Analytical Services (RAS) program often may not sufficiently address the analytical or quality control requirements of a given project (e.g., when analysis of RCRA parameters is needed). When program or budget considerations necessitate the use of CLP resources under the above circumstances, the project (on site) manager may need to access the Special Analytical Services (SAS) program of the CLP to meet project data quality objective (DQO) requirements. The SAS program can provide either RCRA or CERCLA program site studies with a powerful tool with which to tailor the resources of the CLP to their specific project needs. Following are some of the key request form content requirements to be met in order to maximize the effectiveness and utilization of data obtainable through the SAS program. The SAS request(s) should be prepared during the initial phases of project planning and should be incorporated in such documents as the Quality Assurance Project Plan (QAPP) and/or Sampling and Analysis Plan (SAP), as well as the Laboratory Analytical Protocol (LAP) and should pertain directly to the DQOs. Incorporation of the SAS request into project deliverable documents allows for the defacto approval (sign-off) of the SAS request by the U.S. EPA in terms of its consistency with the project DQOs. Upon determination of the analytes of interest and the appropriate analytical methodology, the QA/QC requirements specified in the project documents must be reconciled with the QA/QC procedures required by the referenced analytical methodology. Correct use of the SAS program at this point allows for the production of analytical data of maximal technical quality by anticipating and correcting, in advance, possible analytical difficulties (e.g. matrix interference) presented by the samples and the analytical methods themselves. Costly re-sampling and/or re-analysis may therefore be prevented. Successful preparation and award of an SAS request must be followed by proper integration of the SAS based analytical needs into the actual sampling activity and the analytical data validation. Adherence to the principles outlined above will help ensure a maximally effective and minimally interrupted sampling effort, as well as establishing access to the best data available under given project and budgetary constraints.

This paper will present specific generic SAS requests that were prepared by the authors for use in both RCRA and CERCLA investigations. These requests were incorporated into the project documents, approved for site use by the U.S. EPA, and successfully implemented. We will also discuss specific problem areas and pitfalls in relation to both SAS request preparation and CLP laboratory implementation of the SAS "Subcontract."

SAMPLING PROTOCOL DEVELOPMENT FOR HAZARDOUS WASTE

Becky Eatmon, Disposal Superintendent, Chemical Waste Management, Inc., Emelle, Alabama, 35459 - Dr. Mark Marcus, Director Analytical Programs, Chemical Waste Management, Inc., Technical Center, Riverdale, Illinois 60627

ABSTRACT

Many of the sampling devices, procedures and protocols used for hazardous waste sampling have been developed and adapted from water or soil sampling procedures. In every case significant modification and flexibility in these procedures are necessary to successfully sample hazardous waste material. A great deal of experience at site operational level has been gained over the period of years that the RCRA program has been in effect.

A set of sampling protocols have been prepared by our operating sites to utilize our collective experience in sampling and to standardize our sampling protocols across our company.

General protocols were needed that address: Sample Training; Safety - Personal Protective Equipment; Chain-of-Custody/Labeling; Sample Management - Container, Preservations, Holding Times, and Sample Facilities and Decontamination.

Specific protocols utilizing the aspects from general protocol were then defined for specific sampling circumstances routinely encountered during the management of hazardous waste. The protocols include: solids in drums; liquids in drums; bulk solids; bulk liquids; stationary tanks; surface impoundments; in-line liquids; waste piles; laboratory subsampling liquids; laboratory subsampling solids.

Procedures have been developed by Chemical Waste Management (CWM) operating sites, and the collective information has been developed into general protocols that apply to all sampling events. They form a core of guidelines that ensure adequate sampler training, address safety issues and personal protective equipment, track the sample movement through a chain-of-custody and labeling, and manage the sample to assure valid analytical data can be obtained. Without these basic protocols, the subsequent specific protocols lose their reliability.

The first of the general protocols is Sampler Training. This protocol was developed to ensure the competency of all the personnel who perform sampling.

CWM requires the supervisor to administer proper training to each subordinate in the sampling and safety procedures. This training is documented and made available for review. The sampler is responsible for following the sampling protocol exactly as written and demonstrated during his training program.

Both trainers and samplers must meet minimum qualifications. The trainer must be familiar with the Quality Assurance Standard Operating Procedures in sampling, all the Sampling Protocols and Site Specific Practices. Trainers must also be able to perform the sampling tasks themselves (for demonstration purposes) and have one year's experience with hazardous waste management. When this is not practical, attendance at an approved seminar as a substitute is acceptable. Finally, the trainer must possess adequate communications skills. The sampler must be physically able to perform the sampling tasks, be a high school graduate or equivalent, and complete the appropriate sample training.

Training of the sampler will be given when assigned to a sampling activity, repeated within two months, and then once a year thereafter or as requirements change. All records of training and the sampler's qualifications are documented and maintained in the employee's training file.

The training procedures involve several required steps that must be reviewed and documented. They are: 1) a review of the written Sampling Protocol by the trainee; 2) supervisor's discussion of the procedure; 3) trainee's observations of the procedure as performed by the trainer, including a question/answer session; 4) performance of the procedure by the trainee under direct supervision of the trainer; and 5) trainee proficiency test. This test requires the trainee to sample a waste previously sampled by the trainer. Duplicate laboratory analytical results are determined, and results must be within the acceptance criteria of <20% relative error. If results are within this criteria, the trainee is certified as proficient in this procedure. If not, the problem(s) are identified and corrected, and the training steps repeated again.

Each of the above steps must be documented and include any written data, initialed and dated by the trainee and trainer, and requires the Laboratory Manager's signature for the analytical portion approval. CWM uses a standard form to document training. A certification form is used to document final approval which requires the supervisor's signature. These documents are placed in the employee's training file.

This training procedure is required for all the general protocols, to include: Safety; Personal Protective Equipment; Chain-of-Custody/ Labeling; Sample Management-Container Preservation/Holding Times; Sample Facilities and Decontamination; and other specific protocols as required.

As the final step in training, periodic internal audits of the sampling procedures are carried out to evaluate performance and compliance. In addition, when results from the laboratory disagree with other reference data, sampling differences are a consideration and re-sampling may be required.

As regulations mandate changes, protocols must be revised and personnel re-trained.

Personal Protective Equipment is the second general protocol. It establishes protection for sampling and non-sampling personnel in the sampling area during a sample event. It defines guidelines for the selection of protective equipment during sampling.

Responsibilities are delegated to three people: 1) the Site Safety Officer; 2) the Laboratory Manager (or his designee; and 3) the Sampling Personnel. The Site Safety Officer generates a Task Requirement Sheet for each type of sampling event which specifies the location, job, materials handled, and all safety equipment required. It is reviewed, approved, and dated by the Safety Officer, Regional Industrial Hygienist, District and Regional Health and Safety Managers. In addition to the Task Sheet, the Safety Officer trains the Sampling Personnel in the use and care of the personal protective equipment (PPE). This training is documented and placed in the employee's training file.

The Laboratory Manager/Technical Manager (or designee) ensures the mechanism is in place to inform the sampler of the necessary information to determine the appropriate PPE. A Site Specific Practice (SSP) will be written to describe the method used to provide hazard class information to the sampler so he can make an informed decision regarding PPE. If this issue is addressed in another site document, this particular SSP is not necessary.

The Sampling Personnel are responsible for the safety equipment they use during the sampling event.

The third general protocol addresses Chain-of-Custody and Labeling of Samples. It ensures both the sample's trackability and integrity from the point of sampling, analysis, and through proper disposal. Scope of the protocol includes all incoming, in-process, and outgoing sampling events.

Responsibilities are split between the General Manager, who determines the personnel responsible for the laboratory sample logs, and the Sampling Personnel, who must maintain the security of the sample until delivered to the laboratory, complete all documentation, and perform the sampling. The third person responsible for the sample is the Laboratory Sample Custodian who maintains the integrity and security of the sample while in the laboratory.

Chemical Waste Management sample labeling requires the sampling personnel to complete the label in black, indelible ink at the time of sampling and affix it to the sample container. The following minimum information is required: 1) sample I.D.#; 2) name of sampler; 3) sampler's initials or signature; 4) date and time of sampling; 5) sample location; and 6) laboratory number. Additional site specific information may be included.

Documentation is required in this protocol also. Discrepancies identified during the sampling event are recorded along with the Manifest number. Log books and tracking sample custody also require the minimum label

information be recorded.

Any deviation from the sampling protocols must be recorded as should preservation and holding times (where applicable). Unusual conditions should also be recorded (i.e. - extreme weather conditions).

The protocol requires the sampler maintain custody of the samples until they are delivered and logged into the laboratory logbook. At this time, the Laboratory Sample Custodian is responsible for the samples.

CWM utilizes a Chain-of-Custody record as needed whenever shipment of a sample is necessary. The original Chain-of-Custody record accompanies the sample and a copy is retained by the originator. Should a sample be split, a new Chain-of-Custody is generated. Some facility permits require recordkeeping involving the Chain-of-Custody and these should be addressed.

The fourth general protocol is Sample Container, Preservation and Holding Time Requirements. This protocol ensures suitable sample containers, sample preservation, and holding times are utilized. CWM applies this to all Special Waste and NPDES Sampling.

Responsibilities are delegated to the Sampling Supervisor, Laboratory Manager, and the Sampling Personnel. As such, the Sampling Supervisor ensures the required sample container is provided. The Sampler must use this container, preserve the samples as required by this protocol, and follow required disposal practices.

The Laboratory Manager generates an SSP which identifies container construction, size(s), container recycling, and sample preservation. He will also identify the sample sizes required by the laboratory for analysis.

Container construction should be of material immune to chemical attack. Polyethylene or glass are common except when the waste contains hydrofluoric acid. The closure for the container should also be chemically resistant and form a leak-tight seal.

Container size should: 1) identify the appropriate volume for the sampling device; 2) contain minimum amount required for analysis; 3) contain one complete sampling event or multiples thereof and should be addressed in the SSP for the specific sampling event.

Container, preservation, and holding times for waste samples obtained for RCRA purposes may be found in a table such as SW-846, Third Edition, Table 2-16. For samples obtained under the Clean Water Act, including NPDES and industrial pretreatment regulations, 40CFR Part 136, Table II should be utilized (unless state or local requirements take precedence).

For sample container recycling we strongly encourage disposable containers. If not feasible, decontamination is critical and requires an

SSP to include: 1) cleaning of all surfaces in contact with waste; and 2) triple rinsing with a final rinse - organic wastes generally require rinsing with a solvent such as mineral spirits. Aqueous waste requires sufficient volume of rinse water and the final rinse with reagent water. Other waste should be rinsed with a solvent specified by the Laboratory Manager.

Sampling Facilities and Decontamination of Sampling Equipment is the fifth general protocol. Its purpose is to ensure that suitable sampling facilities are available and that satisfactory decontamination of the equipment is performed. Responsibilities are assigned to the General Manager, who must provide sampling facilities and appropriate sampling decontamination equipment. The Sampling Personnel are required to follow the Sampling Protocols, Site Specific Practices, and maintain the sampling equipment. Finally, the Laboratory Manager/Technical Manager is required to develop a Site Specific Practice if the existing protocol is insufficient for any sampling event.

Sampling facilities require practical equipment to include a design which accommodates easy, complete, and safe access to the waste to be sampled. Sampling platforms and catwalks have proved to be very functional for this purpose. Shelters should be available for the sampling area and personnel. If sampling equipment is to be decontaminated or disposed, the facilities should be readily available. Safety equipment is mandatory and includes at a minimum an eye wash, emergency shower and fire extinguisher.

Storage should be provided for an inventory of sampling equipment, to include clean, unused supplies and a separate storage area for contaminated equipment. Both areas should remain locked with sampling personnel having the only keys. Daily supplies of equipment should be stored on location in lockers. A sample carrier should be available for carrying a sample or multiples thereof.

If equipment is disposable, suitable facilities should be immediately available, and if segregation by disposal method is required, then separate facilities should be maintained. Equipment will be placed in separate waste containers to be disposed of according to regulatory/PAP requirements.

If disposable equipment is not used, then appropriate decontamination procedures must be followed. Attention should be focused on waste-contacting surfaces by cleaning until visually clean and then triple rinsed with an appropriate solvent.

Organic waste sampling equipment should be cleaned with a suitable solvent, typically mineral spirits, but the solvent must specifically be approved by the Technical Manager. If the equipment to be cleaned is used for sampling aqueous waste, then large amounts of water followed by a final reagent water rinse should be used. Equipment should then be air-dried and stored in the designated area for clean equipment.

Water or other spent cleaning solvents must be held until the Laboratory Manager sees that the intended disposal method is appropriate. Final equipment rinse will be collected for analysis on a schedule set out by the Laboratory Manager.

If re-usable sample containers are used, the outside surfaces must be decontaminated to allow labels to adhere to the surface and prevent contamination.

Specific protocols, using aspects derived from the above general protocols, have been defined for specific sampling events that are routinely encountered during the management of hazardous waste. These protocols are: 1) solids in drums; 2) liquids in drums; 3) bulk solids; 4) bulk liquids; 5) stationary tanks; 6) surface impoundments; 7) in-line liquids; 8) waste piles; 9) lab subsampling liquids; and 10) lab subsampling solids.

All of these specific protocols and conceivably others, as developed, establish common guidelines except where noted. Responsibilities for the Sampling Personnel, the Sampling Supervisor, Laboratory Manager, and General Manager are similar from protocol to protocol. In each case, the Sampling Personnel are responsible for all equipment and tools used during sampling and must notify their supervisor if replacement is needed. If discrepancies are determined during sampling, the sampler should notify management.

The Sampling Supervisor is responsible for purchasing sampling equipment, and the Laboratory Manager must develop SSP's when these specific protocols are insufficient to cover all aspects of the sampling event. The General Manager is required to provide shelter and suitable facilities for the sampling event. Unique procedures apply to each specific protocol, which will be discussed below.

The first specific protocol is Sampling of Solids and Semi-Solids in Drums and Pails, and the procedure ensures that a representative sample of waste in drums is obtained. The sample should be small enough in portion to be transported and handled conveniently in the laboratory but accurately represent the waste.

Various types of sampling equipment are used and most common are the scoop, concentric tube thief, soil sample auger, and corer. The scoop is a device that is of suitable size for the quantity and size of the particles to be sampled. It is used for taking small, equal portions at random spots near the surface of the waste material.

The tube thief is also a grain thief. It has an inner movable tube. Both the inner and outer tubes have several openings to allow free flowing solids to pass into the inner tube. The thief is removed from the material and the inner tube emptied into a sample container.

The soil sample auger is similar to a large drill bit with a handle. It is screwed into the material and pulled straight out, and the sample increment is taken from this portion.

Finally, there is a corer which is a metal or plastic tube which has had about 1/3 to 1/2 of the side cut out to form a slot its entire length. Usually, it is about 4 feet long and has a sharp angled point. The sample is removed with a spatula.

In addition, the sampler is usually equipped with scissors, tongs, hammer, and a chisel. Using the physical state of the waste, be it powdery, homogeneous, heterogeneous, compacted, large chunks or sticky, the Sampler selects the correct sampling equipment. For example, a scoop or thief is used for powdery waste and scooped. Compacted waste may require a hammer and chisel to break it up or possibly a soil auger, which is inserted by screwing it into the material and pulling it straight out.

Sampling equipment should be constructed of materials inert to the waste sampled. Commonly these are steel,aluminum or plastic. Tools utilized for drum opening consist of a bung wrench, screwdriver, crescent wrench, ratchet, breaker bar, paper rags, and others as deemed necessary. Sample containers should be defined in an SSP developed by the Laboratory Manager.

The sampling procedure for drummed solids include review of the paperwork (manifest, profile sheet, MSDS, and other facility documentation), collecting and transporting the sampling equipment to the sampling area. Drums should be inspected for integrity, labeling, and piece count. If discrepancies are identified, they should be reported to the Supervisor.

If not done so already, the drum(s) should be numbered uniquely. The Sampler should then proceed to open, inspect, and sample the drums. If liquids or other discrepancies are present, this should be documented.

The sample container should be capped, and the outer surface cleaned and the label affixed. The drums should be closed and the sampling equipment disposed or decontaminated (as in Protocol #5). Note: sampling equipment may be used repeatedly only within the same waste stream to prevent contamination.

The collected samples should be taken to the laboratory and recorded in the log book. Up to ten drums of identical waste may be composited into one sample. Should analysis indicate discrepancies, resampling may be necessary.

The second specific protocol addresses Sampling of Liquids and Sludges in Drums and Pails, and it outlines how a representative sample should be obtained. Responsibilities are as outlined above for the Sampling Personnel, Sampling Supervisor, Laboratory Manager and General Manager.

Sampling equipment consists of a measuring stick, plastic tube, coliwasa,

long-handled sludge sampler, and various tools such as those described in the specific protocol for solids in drums.

The plastic tube used to obtain a sample has a small diameter, 1/2" or less, which yields a vertical representation of the drum. A coliwasa also obtains a vertical sample. It usually is a glass, plastic, or metal tube with an end closure that can be opened and closed while submerged in the waste. The sludge sampler is a curved, hoe-like tool and is used to scoop sludge material from the drum.

The sampling procedure begins with a review of the paperwork (manifest, profile sheet, MSDS, etc.). The sampler inspects his sampling equipment, ensures it is clean and transports it to the sampling location. Drums should be inspected for integrity, labeling, and piece count. If irregularities are identified, they should be reported to the Supervisor. The drums should then be numbered uniquely, if not done so already, opened, and measured to determine volume, presence, and amount of solids. These findings should be documented.

If using the plastic tube to sample, it should be rinsed first by inserting until it reaches the bottom, the top covered with the thumb to form a vacuum and then slowly withdrawn allowing the contents to flow back into the drum. This should be repeated two times to rinse adequately. The sample should then be obtained, the entire tube's contents drained into the sample container, the cap placed on the container, and its outer surface cleaned and labeled.

Should the Sampler use the coliwasa, he should first open the end valve and rinse it three times by slowly immersing it to the bottom of the drum and fully withdrawing each time without vigorously hitting the bottom. Once this is completed, he should sample by opening the end valve and immersing once more to the bottom, close the end valve, and withdraw the coliwasa. The entire contents should be drained into the sample container.

If sludges are detected, the sludge sampler should be extended into the drum and a scoop of the solid-like material removed and transferred to a sample container. The proportion of liquid to solid should be recorded. The container should be capped, cleaned, and labeled.

Repeated usage of the tube or coliwasa is accepted only for the same waste stream. Otherwise, the disposable equipment must be discarded in the appropriate waste container (not in the waste drum), and reusable equipment must be decontaminated according to Protocol #5. Samples should then be transported to the lab and recorded in the books.
Compositing into one container cannot exceed more than tne drums. However, drums with solids may not be composited. Individual samples of both the liquid and solid must be obtained, and not mixed with any sample from another drum. If analytical irregularities are identified, resampling may be necessary.

The third specific protocol is the Sampling of Bulk Solids and Semi-Solids. The purpose is to collect a portion of waste small enough in size to be transported and handled conveniently in the laboratory while still accurately representing the waste material.

Responsibilities of the Sampler, Sampling Supervisor, Laboratory Manager and General Manager are as previously discussed. If compositing is an option, it must be addressed in a SSP developed by the Laboratory Manager.

Sampling equipment is commonly the same as that used in sampling drummed solids, to include, but not limited to, a scoop, a split tube thief (corer) a soil sample auger, a grain thief, and other equipment as outlined in the SSP. Choice of the equipment is determined by comparing the waste characteristics to the equipment design. For example, if the waste is a heterogeneous solid, a thief or tongs may be required. If it is powdery, a shovel, scoop, or thief may be acceptable. The equipment should be inert to any waste it comes in contact with and is commonly made of steel, aluminum, or plastic.

The sampling procedure begins with review of the paperwork (manifest, MSDS, site documents, etc.) and an inspection of the truck to ensure the wheels are chocked and the tarp removed from the entire load. The next step is to collect the sampling equipment and transport it to the sampling area. The waste load is inspected for discrepancies (i.e., free liquids, small containers, etc.) and if present, they are documented. The sampling equipment is then selected and a sample obtained from each load unless specifically instructed otherwise. A minimum of three samples are needed (front, middle and back), which may be composited into one container. The outside of the container should then be cleaned, labeled, transported to the laboratory, and logged in. Equipment should be decontaminated according to Protocol #5 or, if disposable, discarded into the appropriate waste container.

Compositing is only to the extent of the individual samples collected from one waste load. If further compositing is allowed in the laboratory, it is addressed in an SSP developed by the Laboratory Manager after determining the action level and limit of quantifications of the analyte of interest. If corrective action is needed, resampling may be needed.

The fourth SSP is the Sampling of Bulk Liquids and Sludges. This protocol ensures that representative samples are obtained from bulk shipments and outlines the procedure for pulling this sample from a tanker truck.

Responsibilities for the Sampler, his Supervisor, the Laboratory Manager and General Manager are as discussed previously.

Equipment consists of a coliwasa, two empty containers (i.e., 5 gallon bucket), an "S" hook, paper towels, sample containers and labels, and marking pens.

The Sampler should first inspect his sampling equipment to ensure it is

clean and then take it to the sampling area. Quite often, a sampling catwalk is not available, and in this case, the empty buckets and "S" hook are used for sample and equipment transport up and down the tanker ladder. Tankers are sometimes under pressure, and the relief valve should be slowly opened to release the pressure before opening the hatch slowly.

The sample container should be opened and placed in a bucket. Before drawing the sample, the coliwasa should be rinsed first as described under the specific protocol for drummed liquid. The sample should then be obtained and the entire contents of the coliwasa emptied into the sample container. Residual should be drained back into the tanker and the coliwasa wiped with a rag and then placed in a bucket on the ground with the coliwasa leaning against the tanker for support.

The sample container should be capped and wiped clean, labeled, and all rags and clean-up debris placed in the second bucket and lowered to the ground. The tanker hatch should then be closed and secured. The sampler then cleans his sampling equipment with the appropriate solvent and properly discards the debris. The sample is taken to the lab and logged in and the sampling equipment returned to the designated storage area.

Special note should be given to certain situations. Some tankers have multiple compartments, and these should be sampled and labeled as individual units. Tankers sometimes have a sludge layer and should be sampled as explained in the specific protocol for liquids and sludges in drums.

Should the laboratory determine discrepancies in the analaysis, re-sampling may be necessary.

The fifth specific protocol addresses Sampling of Liquids and Suspended Materials in Stationary Tanks, and its purpose is to ensure that a representative sample is obtained from these tanks.

Responsibilities involve the Sampler, his Supervisor, the Laboratory Manager and General Manager as described previously. Equipment is similar to other sampling events such as sample containers, labels, rags, etc., with the exception of the weighted bottle or Bacon-bomb sampler. Both of these units allow personnel to lower the unit into the liquid, open the sampling device at predetermined levels, obtain a sample, close the unit, and raise the sampler out of the tank.

The method used to sample a tank is determined by the configuration of the tank, and one of the following four methods should be used.

Tanks that are mechanically mixed require that the tank be mixed for a minimum of 30 minutes. A bucket should then be placed under the sample port and at least three times the sample port volume drained into the bucket for rinsing purposes. The sample container should then be placed under the port, filled, and the sample port closed. The sample container should be closed, cleaned, and labeled. The material collected in the

bucket should be recycled back into the tank.

Some tanks have multipoint sampling which requires samples be drawn from several ports which are arranged vertically on the tank. A sample should be taken from the top, middle, and bottom of the liquid and labeled as such. The sample ports should be drained as described in the mechanically mixed tank before pulling the sample and the discarded liquid recycled to the tank. The sample container should be cleaned, labeled, and taken to the laboratory and logged in.

The weighted bottle or Bacon bomb is used to obtain liquid samples from the top of a larger stationary tank. A sample must be obtained from at least four (4) points - a top sample no more than six (6) inches from the surface, an upper, middle, and lower sample. The bottle or Bacon-bomb must be inspected to ensure it is clean and functional and lowered to the predetermined depth, opened, filled, and raised. The sample is poured into the container, labeled, delivered to the Laboratory, and logged in. The equipment is cleaned with the appropriate solvent and stored.

Other tanks allow sampling through a sample port during a recirculation loop, but only if the tank contains liquid and pumpable slurries. The tank must first mix adequately by allowing at least half the tank to be circulated prior to sampling. Rinsing and sampling from the port should proceed as described in a mechanically mixed tank. If analytical discrepancies arise, re-sampling may be necessary.

The sixth specific protocol describes Sampling of Ponds, Lagoons, and Surface Impoundments and ensures that representative samples are obtained from the liquid and/or bottom sediments. This procedure serves as a guideline for development of a Site Specific Practice (SSP) that will both ensure a representative sample and meet physical, chemical and regulatory objectives.

The General Manager designates an individual(s) responsible for developing the Site Specific Practice and for sampling. The Laboratory Manager assists in developing the SSP (if not the designee) and determines the sample volume sufficient for analysis, duplicates, etc. He also determines container preparation and sample handling as discussed in Protocol #4. The Safety Officer establishes the safety requirements. The Sampling Personnel are required to perform sampling as described in the SSP and CWM Protocols.

Sampling equipment consists of a broad range of materials, and selection often is dependent on the sampling event objective and whether the lagoon/pond is hazardous or not. It can range from a rowboat (used for non-hazardous, multiple point sampling) to a sampling valve on a re-circulation pump to a conduit or other extender equipped with a clam shell. It may even require use of a crane with a clam shell bucket for hazardous waste sampling.

Safety equipment and PPE requirements vary widely, and so the Site Health

and Safety Officer specifies the equipment and also prescribes unique equipment, such as life jackets, safety harnesses, etc.

To prepare for sampling, larger equipment, such as a boat or crane, should be scheduled. The sample containers, equipment, and safety supplies are gathered and loaded into the sample vehicle (boat, etc.). The Sampler(s) should notify management of the sampling activity.

Sampling should proceed as directed in the SSP noting unusual observations. He may utilize a weighted bottle, Bacon-bomb, dipper, Van Dorn sampler, clam shell, or some other type sampling device as outlined in the SSP.

If compositing is allowed, the Laboratory Manager will specify under what conditions in the SSP. Should analytical discrepancies arise, re-sampling may be necessary.

The Site Specific Sampling Plan developed for each sampling event must define the purpose, physical state, volume, hazard properties, and composition of the material. It should address how to access the sampling point and should be consistent with pertinent site permits, regulatory requirements, etc., as required.

It will specify the sampling point(s), the number of samples, and type required (vertical or horizontal stratification). If needed, a three-dimensional grid system will be drawn for each pond/lagoon to be sampled, identifying the sample points.

The seventh specific protocol is a procedure for Sampling of In-Line Liquids and Sludges, and it ensures that a representative sample of in-line liquids is taken from the flow of a process stream. This may include open or closed channels, and the procedure describes how to sample either one.

Responsibilities include those of the Sampling Personnel, Supervisor, the Laboratory Mamager and General Manager as were discussed earlier.

Equipment, such as containers, labels, markers, and rags, is similar to other Specific Protocols. The sampling devices may be a beaker, bucket, timecycle, flow response, or demand sampler. The sampling personnel should inspect the equipment to ensure it is clean and dry and then purge it with three volumes of the sample prior to collecting the final sample. Grab samples are common and they describe the characteristics of a stream's flow at a given moment in time. However, if the stream is variable, inconsistent results may be obtained.

Automatic samplers should be operated according to the manufacturer's directions and the Site Specific Practices. Surface water sampling should be according to procedures in the Manual for Groundwater Monitoring and refer to the Specific Protocol for Stationary Tanks for grab samples of closed pipes utilizing the recirculation loop.

The sampling container should be cleaned, labeled and field log(s) or chains-of-custody completed. Equipment should be decontaminated and then the samples carried to the laboratory. If analysis indicates discrepancies, re-sampling may be required.

The eighth Specific Protocol addresses Sampling of Waste Piles and Miscellaneous Waste. This procedure ensures that representative samples will be obtained from these sources and establishes the guidelines to be followed to generate a Site Specific Practice.

The General Manager must designate someone to write the SSP, and the Laboratory Manager must assist and determine the volume of sample to be collected, allowing for duplicates, fortifications, etc. The Site Safety Officer will specify the safety requirements, and the Sampling Personnel will follow the SSP. As a point of reference, review should be made of the Specific Protocols.

Waste Piles may utilize sampling equipment already addressed in previous protocols for moist or dry solids or even sludges (specific protocol for drummed or bulk solids). Underground tanks may require larger diameter corers or perhaps confined space entry procedures and sampling with sparkless tools.

The Site Specific Practice must include, at a minimum, the goal of the sampling event, the physical state, volume, hazardous properties, and composition of the material to be sampled. It should also address how to access the sample point and the equipment to be used. Consideration should be given to any site permits, regulartory requirements, etc.

Sample locations, the number of samples required, and compositing must be pre-determined and, specified,if any. The type of sample is described, such as vertical or horizontal stratification. If discrepancies in analysis occur, re-sampling may be necessary.

The ninth Specific Protocol involves Subsampling and Taking Test Portions of Liquids and Sludges and ensures that a representative subsample or test portion is obtained for physical and chemical analysis.

The Laboratory Manager is responsible for developing the Site Specific Practice and all employees who obtain these samples must follow this protocol and the Site Specific Practices exactly.

For discussion, a subsample is a portion that is representative of the original sample. A test portion is a representative portion of the original sample used for analysis, unless the method specifies otherwise. A split sample is one portion of those derived from the division of the original sample into two or more representative and approximately equal parts.

Equipment consists of the subsample container and a pipet. The sample is

first agitated thoroughly and, if it is a monophase liquid, it is immediately poured into a suitable container. If the liquid contains settled solids and they do not settle within 30 seconds, the solids are considered part of the liquid and must be poured into a suitable container or a large diameter pipet used. Should the solids settle within 30 seconds or bubbles form after agitating, the solid is treated as a separate constituent. Quantities of each constituent should be transferred with a pipet in proportion to the original sample into the subsample container.

If the liquid is multilayered, but layers do not form within 30 seconds of agitation, it should immediately be poured into the subsample container. If layers and solids do settle within 30 seconds, quantities of each layer should be transferred with a pipet, in proportion to the original sample, into the subsample container.

The same procedure for obtaining subsamples should be used to obtain test portion(s). If the sample has layers to be analyzed separately, a subsample should be obtained and labeled accordingly. Then a test portion of this subsample obtained. Test portion containers should be labeled accordingly.

The tenth Specific Protocol addresses Subsampling and Taking Test Portions of Solids and Semi-Solids. The purpose is to ensure a representative subsample or test portion be obtained and provides guidelines to do so. In addition, a Site Specific Practice will address areas requiring more detail.

The Laboratory Manager is responsible for developing a Site Specific Practice as needed and all employees who obtain subsamples or test portions must follow this protocol and the SSP exactly.

A subsample and test portion are the same as defined in the ninth SSP.

Equipment usually consists of a spatula, tongs or scissors, scoop or spoon, tube, mortar and pestle, and labeling equipment. Using the appropriate equipment, a sample should be obtained. If it is an homogeneous solid, a portion of the material should be transfereed to another container and labeled accordingly. If the sample is an heterogeneous solid, transfer an approximate proportional quantity of each component should be transferred from the original container to the subsample container and labeled accordingly.

A test portion should be obtained by using the appropriate subsample equipment. A representative portion of the solid is then pulled for the test method utilized. If analytical discrepancies occur, re-sampling may be necessary.

Utilizing the experience gained in the many samples and years Chemical Waste Management has logged, the above protocols were developed and have become a valuable tool in our operation. Major importance is placed on

SAMPLING PLAN GUIDANCE: HOW TO GENERATE QUALITY ENVIRONMENTAL DATA

Christine M. Andreas, Project Manager; John Mateo, Quality Assurance Officer, Response Engineering & Analytical Contract, Roy F. Weston, Inc.; William Coakley, Quality Assurance Officer, US EPA Environmental Response Team; GSA Raritan Depot, Woodbridge Avenue, Edison, New Jersey, 08837.

ABSTRACT

Recently, we have witnessed the sophistication of analytical instrumentation to detect contaminant levels to the parts per trillion. Unfortunately, the techniques and methodologies employed for sample collection and handling have not advanced at the same rate. Regardless of the sophistication of analytical instruments, the results obtained are only as good as the samples collected. In an attempt to ensure the best quality sample is obtained and delivered to the laboratory, specific criteria should be addressed in the development and implementation of a field sampling plan.

The sampling plan document should be developed based on two underlying principles. First, the data use objectives should be clearly identified and articulated in the plan. These objectives should be considered and incorporated into all aspects of the plan. Second, a plan must be developed and written in an implementable, practical fashion. Another consideration which is of primary importance is communication. While this is fundamental to the development of sampling plans, it is currently not widely practiced by many project planners. Communication between the Project Manager, field crew, laboratory, and all others involved in or with the sampling event is critical to proper design and smooth implementation of the plan. Communication must be initiated early in the planning stages and continue throughout all project activities.

The importance of a thorough and carefully prepared field sampling plan cannot be over emphasized. As sample collection methods are far from precise, a comprehensive sampling plan can eliminate many of the variables which will exist if no plan is prepared. Sampling plans must be stand alone documents in the field and must provide all the necessary information to execute the sampling episode. It is highly recommended that sampling plans be event specific. This will facilitate clearer association between the intended use of the data and the methodologies necessary to generate the quality of data desired.

It is imperative that the sampling plan begin with a clear articulation of the intended use of the data. If the data use objectives are not

readily identifiable, a historical characterization of the site background may be useful in establishing these objectives. If the objectives are clearly defined, background characterization may permit planners to focus and refine the investigation strategy. Next, the quality assurance aspects of the sampling plan should be described.

Typically, the Quality Assurance (QA) components of a sampling plan consist of a number of basic sections. These sections will address: (1) background; (2) data use objectives; (3) Quality Assurance/Quality Control (QA/QC) Objectives; (4) sampling methodologies; (5) project organization and deliverables, and 6) quality assurance requirements.

At a minimum, the QA components of a sampling plan should address historical information about the site, purpose of sampling and rationale for number of samples collected, locations and analytical parameters. Field quality assurance should be addressed by discussing decontamination procedures, types of blanks, duplicates, type of sampling equipment, sampling procedures, sample bottles, methods used for preservation, and proper sample handling procedures. Actual analytical methods, holding times and laboratory selection should also be addressed in the plan.

Once a carefully developed field sampling plan has been prepared, actual execution is critical. Communication between the project manager, the field sampling team and the laboratory performing the analysis is essential. Many times the absence of this communication has resulted in problems that were not realized until the data came back from the laboratory and it was too late.

Essentially, a well developed sampling plan, in conjunction with a knowledgeable field crew, improves the chances for generating quality environmental samples and reliable analytical data for the end user.

INTRODUCTION

This paper is intended to provide the reader with a basic understanding and appreciation for the fundamental Quality Assurance (QA) components of a sampling plan. This paper will address why one would want to include QA components in their plan or event (beyond addressing regulatory requirements) and what this QA means for the intended use of the data. It is the authors' goal to clarify the meaning and implication of the various QA components so that those with responsibility for preparing and implementing sampling plans will have a better appreciation for how, when, and where to apply the components which will achieve their intended data use. Understanding these fundamental questions allows a planner to develop a sampling plan which will generate quality data that meets the overall objectives of the event.

Preparation of a successful sampling plan begins with the articulation of data use objectives based upon what is known about a site and what needs to be known about the site. Once the intended use of the data is made clear, the next major task is to build a sampling plan which integrates the QA components in a manner which will generate data of sufficient quality to support the intended use. This activity requires communication between the developers and the executors of the plan. This team is typically comprised of project managers, technical discipline representatives (e.g. statisticians, analytical chemists), and the field technicians (Figure 1).

The sampling plan provides the field team with a blueprint for how to conduct activities at the site. Careful preparation of the plan improves the chances that the objectives of the event will be met. However, even the best of plans cannot be implemented adequately unless all members of the team are prepared to play their respective roles and communication is maintained. More times than expected, no communication or miscommunication of information was the primary cause for an event to fall short of meeting its objectives. A merger of quality planning and communication will ensure collection of quality environmental samples.

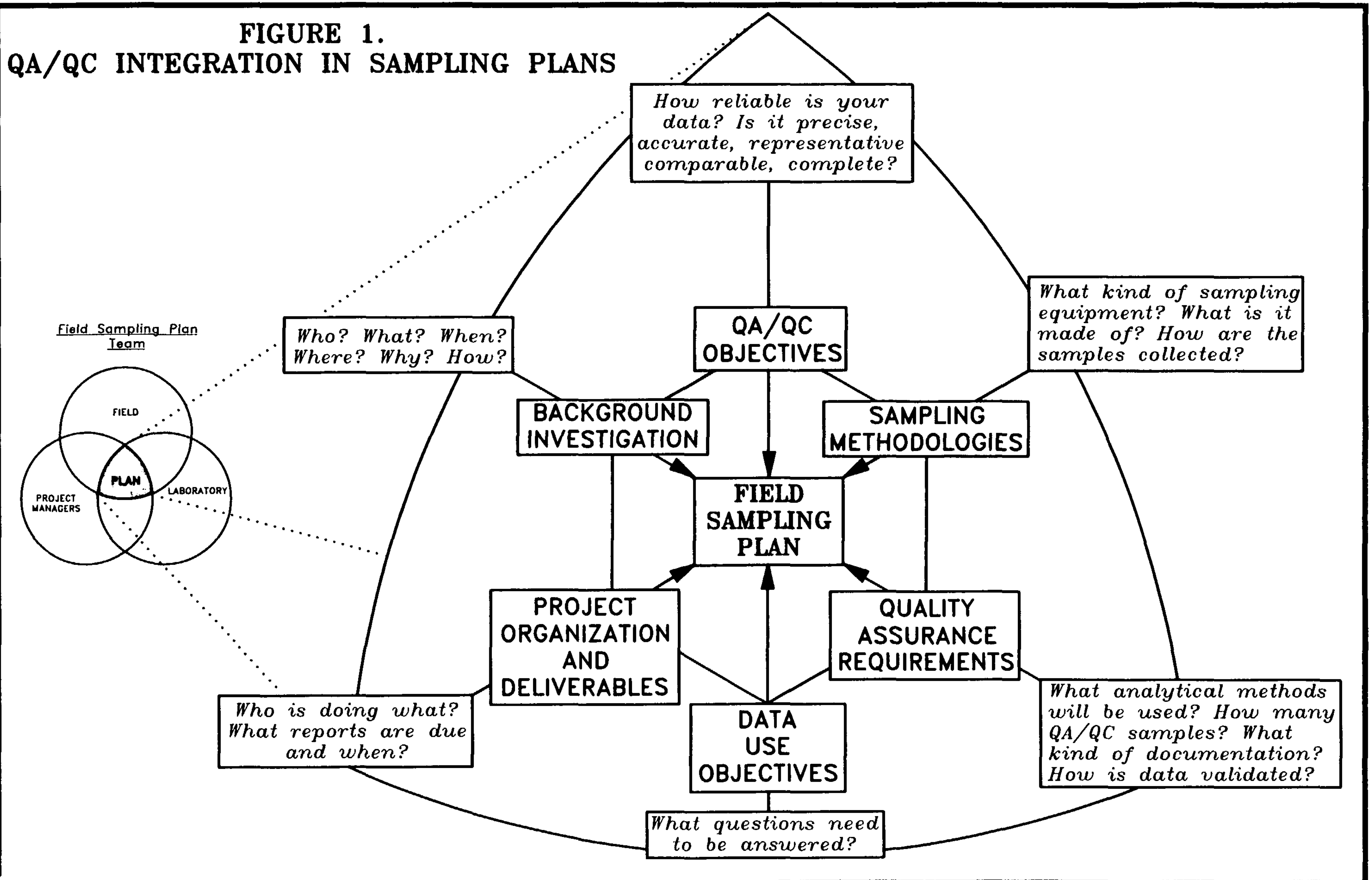
This paper is divided into a number of sections which mirror the QA components previously mentioned: (1) background; (2) data use objectives; (3) Quality Assurance/Quality Control (QA/QC) objectives; (4) sampling methodologies; (5) project organization and deliverables; and (6) quality assurance requirements. In essence, the aforementioned items must be included in the sampling plan event to reliably ensure overall data quality.

BACKGROUND

Ideally, although sometimes not available, background information can address the questions of what, when, where, and how much waste, contamination, remediation, and risk is present or requires assessment. If you know the data use objectives, background information may be used to scope the project.

Knowledge of past events or recent occurrences at the site is useful information in the selection of sampling locations, target compounds and analytical methods. The description of historical activities at the site should include any chemicals which have been treated, stored or disposed of on or at the site, as well as any violations or citizen complaints. Data may come from sources such as local, state or federal files or agency representatives, as well as waste manifests, inventories, geological surveys and/or previous response actions. Aerial photographs should also be inspected and included in the background section.

FIGURE 1.
QA/QC INTEGRATION IN SAMPLING PLANS



A region and site map are very useful and any previous maps which exist indicating areas of contamination or process units should be included. The size of the investigation area and overall site should be referenced as well as the proximity of the site to homes or sensitive environments.

A complete background section will provide the sampling team with important up-front information about the site. This is particularly useful where the sampling team is unfamiliar with the site and their first encounter may be the sampling episode. Although such an arrangement is least desirable, it is nevertheless often the case. Within practical means, a visit to the site prior to the development of a sampling plan is highly recommended. The value of a personal, see-for-yourself survey of the site cannot be over emphasized. When you are reading a description of the site, or even reviewing photographs, your perception will be limited by factors such as the author's or photographer's perspective or abilities. In person, one is able to perceive the site and surrounding environs on levels that may not be realized until issues arise later regarding sampling design. Many times an entire sampling strategy needs revision once in the field because the issue of accessibility was never evident in the file materials. It is likely that the cost of delays or in-the-field modifications will far exceed the cost of any preliminary site visit.

Background information should always be as complete as possible so that subsequent decisions regarding health and safety and sampling methodologies are grounded in maximum fact and minimum assumption. The site background should be updated and/or at a minimum reviewed, prior to each sampling event.

If there is reason to suspect a certain compound or class of compounds for this particular event, the QA aspect of the sampling plan should reflect that information. In addition, volume and concentration ranges of the contaminants should be specified. This will assist the planners in identifying appropriate sampling equipment and analytical methodologies and detection limits.

DATA USE OBJECTIVES

The use of the data is the most critical information needed prior to design and implementation of the sampling plan and event. Developing a plan based on clear data use objectives will maximize the probability of generating useable data for the decisions required. While this may seem a basic tenet, it is the most often overglossed, overgeneralized or even overlooked element of the plan. The data use objective is a statement of what you want the data for, what questions you have to answer, and/or what decisions you have to make or use the data to support.

Data use objectives of a sampling plan may include, but are not limited to the following: (1) determining the presence or absence of contamination; (2) determining the magnitude or concentration level of contamination; (3) determining the impact of the contamination; and (4) determining the performance of a remedial measure. The event specific or project specific objectives should be clearly defined in this section of the plan. Vague or all encompassing objectives (e.g. this data may be used for screening purposes as well as for health risk assessments) may lead to unnecessary, conservative quality control measures which are costly and probably wasteful. There should be an explicit purpose for every sample collected and measurement taken, although data may serve multiple purposes.

The real essence of the objective statement will be dependent upon how the data is to be evaluated. For example, data may be evaluated against existing State or Federal guidelines, or some existing data base, permit level or any other applicable evaluation criteria. These criteria will establish a framework for the data use objectives by indicating items such as detection limits, analytical methods and performance ranges.

Hence, if one is determining the performance of treatment technology, and there is an established discharge permit level, it is fairly straight forward to design a sampling strategy to serve this purpose. Determining the extent or magnitude of contamination without a benchmark (i.e. background or state action level for a given matrix) would yield a costly, comprehensive sampling grid design.

QUALITY ASSURANCE/QUALITY CONTROL OBJECTIVES

How reliable must your data be? How confident do you have to be that the result is in fact the analyte, and the concentration claimed by the laboratory, that it is representative of the sample location, matrix, and site and it is a comparable and complete piece of data?

QA/QC objectives are statements about the desired reliability of the data to be generated. QA/QC objectives are really defined by determining how precise, accurate, representative, complete, and comparable the data must be to satisfy the data use objective.

Accuracy is a determination of the agreement between what is measured and a true value. It is the measure of bias inherent in the system. Accuracy is usually evaluated by surrogate and matrix spiked samples and performance samples.

Precision is the degree of reproductibility of a particular measurement methodology. This parameter is usually evaluated by replicate samples or measurements.

Simply stated (though not quite simple to implement), representativeness is the degree to which samples or measurements represent the condition or population of interest from which they were taken. Representativeness is difficult to achieve because of high variability in the environment. Nevertheless, there are statistical approaches to sampling design and collection which can be applied dependent upon intended data use.

Completeness is a measure of the quantity of data that must be acquired to meet the data use objective. Comparability is the degree to which data from one set can be compared to another. It is an assessment of similarity for how the samples or measurements were collected, prepared, and analyzed.

Completeness and comparability are often overlooked parameters for controlling data. However, one should determine the level of data points below which a decision cannot be supported. With regard to comparability, it is always important to have sufficient information about the data to ensure that correlations are not attempted on dissimilar data sets unknowingly. This is quite clear when comparing non-detectable results at various detection limits or analytes which are different species by virtue of the analytical methods employed.

With respect to analytical procedures, characteristics of the QA/QC objectives may be minimal and allow for non-qualitative to semi-qualitative results. They may require confirmed analyte identification or allow for non-definitive results (without confirmation). Definitive identification is analyte identification confirmed by a second analytical method. Definitive quantitation may be balanced against gross quantitation, with (or without) confidence limits. For example, gross quantitation of results may be acceptable or definitive quantitation with analyte quantitation verified by an alternate method or repeat of a preliminary verification method may be desired. Verification need not be limited to these extremes; for example, the percentage of definitive identification and/or quantitation, and the determination of confidence limits (precision and accuracy) could vary. A significant portion of the data collected for a large extent of contamination survey might be generated by an unconfirmed, gross quantitative screening method that is further substantiated by a subset (e.g., 10 percent) of samples where the analyte identification and quantitation is verified by alternate methods.

SAMPLING METHODOLOGIES

This portion of the plan addresses the questions of what types of sampling devices are appropriate, what are the sample matrices, and how will the samples be documented and handled. Based on the answers to these questions, a sampling network will be developed which addresses sample collection, analysis, and corrective action procedures.

In addition, it is recommended that a field sampling summary table be prepared (Table 1). This table should specify the number of samples required per parameter per matrix, the number of QA samples, the required preservatives, appropriate sample containers and sample volume. This summary presentation makes a useful tool for preparing sample containers for the field, executing complete sample collection and ensuring proper handling of the samples. Table 1 was prepared based on collection of groundwater sample. It should be modified for each sampling event.

Sampling equipment proposed for sample collection must be identified. Furthermore, material of construction (fabrication) of the sampling devices should be specified and it should indicate whether the equipment will be dedicated to a particular sampling location. If the equipment is dedicated, listing a standard decontamination procedure is optional and can be used in the event a problem arises in the field and decontamination is required. However, if dedicated sampling equipment is not to be used, a detailed decontamination procedure (including the sequence of steps and solvents to be used) must be specified in the plan.

The sampling design must be clearly described and provide justification for the locations selected. A site map is invaluable to this portion of the plan.

Sample collection methodologies should be fully described. Reference can be made to standard operating procedures as long as deviations from these procedures are identified and documented.

Sample documentation is critical to maintaining the integrity of the samples collected as well as aiding in the eventual interpretation of results. The plan should describe the minimum documentation requirements for the sampling event. This may include field log books, field data sheets, site drawings, photographs, a record of field activities, weather conditions, identification and description of sample locations.

Of equal importance to proper sample documentation is proper labeling of sample bottles and completion of chain of custody forms. Chain of custody forms are critically important if the site is or will come under litigation. Chain of custody records are maintained from the time the sample is taken to its final deposition. Because of this, the custodies also serve as inventory or tracking records for samples collected and analysis requested.

Provisions for corrective action procedures should be outlined in the plan. In the event that corrective actions are required, the field manager will be able to take the necessary and/or required steps. In the event that external constraints or field conditions necessitate

TABLE 1. FIELD SAMPLING SUMMARY

							QA/QC OBJECTIVES							
ANALYTICAL PARAMETERS	ACTION LEVEL	MATRIX	CONTAINER TYPE AND VOLUME (#CONTAINER RQ'D)	PRESERV-ATIVE	HOLDING TIME	NUMBER OF SAMPLES	REPLICATES	RINSATE BLANKS	TRIP BLANKS	P.E. SAMPLES	MATRIX SPIKE	METHOD REFERENCE	DETECTION LIMIT	TOTAL FIELD SAMPLES
VOA		W	40ml vial (2)	4°C	7 day							624/CLP		
BNA		W	32oz amber glass (2)	4°C	7/40 day							625/CLP		
PESTICIDES		W	32oz amber glass (2)	4°C	7/40 day							608		
PCBs		W	32oz amber glass (2)	4°C	7/40 day							608		
P.P. METALS		W	1 liter polyethylene (1)	NO_3 pH<2 4°C	6 mon							EPA-600/ CFR 40		
CYANIDE		W	1 liter polyethylene (1)	NaOH pH>12 4°C	14 day							SW846		
PHENOLS		W	1 liter amber glass (1)	H_2SO_4 pH<2 4°C	28 day							604/ CFR 40		

changing the plan, notation should be made in the field log book followed by documentation upon return to the office.

Sample handling procedures should also be outlined. The field team should know what to do in the event of damage and should always be prepared with extra bottles. Procedures for sample shipment should be reviewed with the field crew.

Depending on the complexity of the field event, a detailed schedule of work should be prepared for all activities at the site. This schedule should detail the planning stages of the event, as well as the field and analytical portions of the job. The proposed schedule should allow for contingencies, such as weather, equipment failures, etc. This will allow for smoother implementation of all related activities.

PROJECT ORGANIZATION AND DELIVERABLES

This section should list the project manager(s), field sampling leader, health and safety and quality assurance personnel, along with their respective responsibilities. This section should also include the name and address of the laboratory performing the analysis and the laboratory contact and telephone number. The actual field sampling crew should also be identified if possible. This is important information for the field crew to have in the plan when, as usually happens, the implementation changes due to site conditions or unforeseen problems. A plan which contains response peoples' names is a directory for assistance to the field crew.

The deliverable section of the Plan should detail the type of report(s) which will be generated from this activity. This may include trip reports, status reports, analytical reports or final reports.

QUALITY ASSURANCE REQUIREMENTS

This section should detail the appropriate data quality indicators and QA/QC protocols, based on the quality assurance objectives specified earlier in the plan. The QA/QC objectives will determine the type of evaluation followed by the laboratory. References to analytical methods should be specified in this section.

It is paramount that analytical (laboratory) personnel be consulted in the development of this portion of the plan. The tools or methods of assessment to meet the data objectives will be determined here.

Some of the methods that can be used to satisfy the data quality objectives include, but are not limited to: spot tests, paper strip tests, indicator tubes, chemical reactions producing color, gases, or precipitates. Electronic meters such as Geiger counters, pH meters and conductivity meters may be used. Gas chromatographs equipped with

flame ionization or flame photometric detectors, GC/MS and X-ray fluorescence or atomic absorption spectrometers may also be used.

Holding times between sample collection and analysis are important for assessing potential degradation or loss of analytes of interest. In some instances, the exceedance of holding times may result in undervalued sample results. Trip blanks are used to assess the potential for cross contamination of volatile organics during sample handling and shipment. They should be prepared at the laboratory performing the analysis and incorporated at a rate of one per shipment container. Field rinsate blanks are used to evaluate the effectiveness of the field decontamination procedure at eliminating cross contamination between samples stations when one device is used repetitively. The field rinsate blank is prepared by running analyte free water over and/or through the decontaminated sample implement. Field blanks are run for the same analysis as the environmental samples. Replicate samples (collocated samples) are obtained in the same manner as the environmental samples. They are interpreted to assess the variability in the sampling technique or environmental matrix.

In order to assess precision and accuracy, the incorporation of spike samples (usually in the form of matrix spikes/matrix spike duplicates and surrogate spikes) is required. Spike samples involve the introduction of known concentrations of select analytes (usually those that are suspected of being present in the environmental sample) and determining recovery efficiencies. The utilization of matrix spike duplicates allows one to determine degree of variance around the value reported as well as any bias effect due to the matrix or lab. This will be critical if the analyte in question has a specific action level and as part of the data use objective, it is deemed a critical sample for decision-making.

The inclusion of performance evaluation (or proficiency) samples will aid in assessing the accuracy of the overall laboratory output and hence the reliability of the data. Other QA items to be included in the plan design and implementation are instrument calibration, tuning, and performance checks.

Collectively, this QA information provides a documented basis for proving that requirements were implemented so that the data generated could meet its intended purpose. This documentation also provides a potential road map to problem areas should the resultant data fail to meet its intended purpose.

A final QA requirement to be specified in the plan, carried on in the field and most importantly applied to the summation of the sampling event is that all project deliverables should receive a peer review prior to release.

Data validation, which may be prepared separate from the QA requirements section, describes the criteria used to ensure that the analytical results received from the laboratory are valid and accurate for the quality assurance objective chosen. This section will utilize the QA requirement indicators to determine the quality and hence the validity or useability of the data for its intended purpose. The focus of this portion of the plan is to identify the parameters and their respective windows of acceptibility. Data which falls outside the limits of its intended use (e.g. detection limits are above action levels) are essentially not usable, with some exceptions.

CONCLUSIONS

In summary, the way to collect quality environmental samples and data is through the development and implementation of a comprehensive, yet practical, sampling plan. Development of the plan starts with the articulation of clear data use objectives. These objectives, with background information on the site, are correlated by a team of experts representing project management, analytical, and field personnel. Through the development of the quality assurance components to the field sampling plan, this team will create a realistic sampling and analytical strategy. Effective communication, initiated at the planning stage and carried through the implementation stage will ensure that quality samples/data achieve their intended purpose.

SPECIALIZED MOBILE LABORATORIES FOR FIELD SCREENING

TERENCE ASA WHITT, THERESA M. SAVOIE, APPLIED SCIENTIFIC ASSOCIATES, A DVISION OF HARMON ENGINEERING ASSOCIATES, INC., 1351 OAKBROOK DRIVE, SUITE 110, NORCROSS, GA 30093

The number of hazardous waste site investigations and cleanup projects involving contaminated soils, wastewater, sludges, and drums has increased dramatically in recent years and will continue to increase, based on regulatory projections. Due to the vast analytical requirements during the assessment of hazardous waste sites, the capacities of standard contract laboratories have been saturated. This has necessitated the development of innovative alternative methods of achieving timely, cost effective, analytical results.

One alternative is the utilization of mobile laboratories. Unlike major "stationary" analytical laboratories, mobile on-site laboratories can be custom designed to concentrate their resources toward the specific requirements of the individual waste site. In this manner, the mobile laboratory can streamline the analysis to produce fast accurate results that can be used to direct field crews, set drilling plans, predict disposal criteria, establish levels of personnel safety and many other aspects of the project. In addition to enhancing the efficiency of various project activities, low operating costs of mobile laboratories can be achieved when the laboratory is properly utilized.

Over the past four years many field techniques have been utilized and developed to reduce time and cost but retain the required quality control for the varying field projects.

These methods include HPLC methods for phenols and PAH's, GC/Purge & Trap methods for volatiles, and extractions techniques for PCB, PCP, and metals.

A NEW METHOD FOR THE DETECTION AND MEASUREMENT OF AROMATIC COMPOUNDS IN WATER

JOHN D. HANBY, HANBY ANALYTICAL LABORATORIES, INC., 4400 S. WAYSIDE, SUITE 107, HOUSTON, TX 77087 (713) 649-4500

ABSTRACT

A Field Test Kit procedure for the rapid analysis of petroleum aromatic hydrocarbons over a wide range of concentrations in water and soil has proven of extreme utility in accurate assessments at spill sites, hazardous waste areas and underground storage tank removal locations. The extraction/colorimetric procedure used provides quantitative results for aromatic compounds down to 10 ppb. The kit was used to evaluate diesel oil concentrations at the Ashland Oil spill on the Monongahela and in conjunction with EPA studies of the oil concentrations in the Ohio river at Wheeling, West Virginia. A study of gasoline-in-soil at concentrations ranging from 5 mg/Kg to 10,000 mg/Kg was conducted. The colorimetric results from the procedure in both water and soil are determined by comparison to a color chart.

UV/VIS spectrophotometric studies were performed to determine the relationship of concentration to color intensity (reflectance). Studies were performed on the use of the reaction to detect alkyl halide presence in water samples. Purge and Trap GC analysis precision was compared to Field Test Kit results. A series of gasoline-in-soil samples were evaluated using an organic vapor analyzer in a "headspace" mode and comparisons were made to Field Test Kit results.

The analytical superiority of this method of water/organic solvent extraction was shown in a series of laboratory studies conducted with the Field Test method versus the use of organic vapor monitor "headspace" techniques in a variety of soils over a range of aromatic concentration in both water and soil matrices.

EVALUATION OF TEST KIT METHODS FOR DETERMINING TOTAL CHLORINE IN USED OILS AND OIL FUELS

ALVIA GASKILL, JR., EVA D. ESTES, DAVID L. HARDISON AND LAWRENCE E. MYERS, RESEARCH TRIANGLE INSTITUTE, RESEARCH TRIANGLE PARK, NORTH CAROLINA; 27709; STEVE FINCH, RICHARD HAGSTROM AND TED LINDE, DEXSIL CORPORATION, HAMDEN, CONNECTICUT, 06517

ABSTRACT

A 1985 EPA regulation prohibits the sale for burning in non-industrial boilers of used oils and oil fuels contaminated above specified levels with certain metals and total chlorine. This regulation establishes a rebuttable presumption that used oil containing more than 1,000 ppm total chlorine has been mixed with halogenated solvents and is a hazardous waste. If the rebuttal is successful, the oil can be sold as fuel up to a level of 4,000 ppm total chlorine.

One means of establishing the chlorine content of the oil is to test it for total chlorine. Several methods exist involving bomb oxidation of the oil followed by wet chemical analysis of the combusted sample for chloride. The bomb combustion step is time consuming and ofter produces unsatisfactory results. Various alternative test methods have been developed. RTI conducted a study for Dexsil Corporation of three Dexsil developed test kit based methods. Two of the kits are designed to replace the bomb oxidation preparation step with a chemical dehalogenation step which is followed by either a colorimetric or potentiometric titration to a quantitative endpoint over the range 600-6000 $\mu g/g$ chlorine. A third kit designed for field use also provides for a quantitative determination over the range 200-4000 $\mu g/g$ chlorine.

RTI prepared the test samples for the laboratories participating in the collaborative study and analyzed the test results to determine the precision and bias of the methods. This paper describes the evaluation methods used and the results of the study.

Fifth Annual Waste Testing and Quality Assurance Symposium
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