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# Table of Contents

# ORGANICS

51

# THERMOSPRAY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/ MASS SPECTROMETRY METHODS DEVELOPMENT*

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## ABSTRACT

Thermospray high performance liquid chromatography/mass spectrometry (LC/MS) has proved to be a sensitive technique for many nonvolatile, thermally labile compounds. In thermospray LC/MS the entire effluent is delivered to the ion source. This ensures a representative sampling of the analytes and also maintains good sensitivities. The options of ionization by buffer-assisted ion evaporation, filament, or discharge are available using the thermospray technique. Furthermore, these methods of ionization are affected very little by surface effects within the interface so thermal degradation is minimized. Therefore, it is a viable technique for analyzing for fragile biochemically important compounds (DNA adducts, glutathiones, etc.) The main problem with thermospray LC/MS is the small amount of structural information provided in a thermospray spectrum. Various approaches that serve as potential solutions to this problem are forwarded in this paper.

## INTRODUCTION

There has been a recent effort in the analytical community in general and in the Environmental Protection Agency in particular to adapt mass spectrometry to the online characterization of environmental samples for their nonvolatile or thermally labile components. Historically, this task has been complicated by the use of high performance liquid chromatography (HPLC) to separate these intractable compounds and the difficulty of interfacing HPLC with a mass spectrometer because of the highly different pressure regimes under which these two techniques operate. The moving belt

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***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.

interface and the direct liquid introduction were two early attempts to interface HPLC to mass spectrometry. These two techniques showed some successes, but were limited in their applications. The moving belt interface was of limited utility for reverse phase solvents, and direct liquid introduction required splitting the effluent from the HPLC so only about 10 percent of the sample was sampled into the mass spectrometer.

The thermospray liquid chromatography/mass spectrometry (LC/MS) interface provides both a liquid phase to vacuum interface and an ionization technique for the mass spectrometer. The use of a volatile buffer such as ammonium acetate enables ionization in the interface by buffer-assisted ion evaporation. Since the pressure in the thermospray ion source is high, ion-molecule reactions follow. This provides a mechanism for generating pseudo-molecular ions of high intensity for many compounds. With ammonium acetate as the buffer, the predominant charged species present in the ion source are ammonium adducts, $NH_4^+(X)_n$, where X represents the solvent(s) used in HPLC and n is a small number (usually 0-3). The ion-molecule reaction

$$NH_4^+ + B \rightarrow BH^+ + NH_3 \quad (1)$$

is dependent upon the proton affinity or gas phase basicity of the compound B. If this quantity is greater than the proton affinity of ammonia, then reaction (1) proceeds as written and the protonated species $BH^+$ is observed. If the proton affinity of B is less than that of ammonia (i.e., ammonia is the stronger base), one can still observe adduct ions such as $BNH_4^+$, but usually at lower intensities than the protonated molecules. Since many compounds that are not amenable to gas chromatographic methods and must be analyzed by HPLC have a relatively high proton affinity, the sensitivity of thermospray for these compounds is usually good. As with any emerging technology, the thermospray interface has advantages over what has been currently available and some limitations. This paper will summarize these advantages in instrument performance. In addition, several possible techniques will be presented to generate more structural information using the thermospray interface.

## EXPERIMENTAL

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 that has been described previously in detail elsewhere[5,8]. This repeller was operated at a

voltage range of 200-250 V in the enhancement mode and at 400 V in the repeller-collision activated dissociation (CAD) mode. Tandem mass spectrometric CAD spectra were generated in daughter ion scans with an argon pressure of 1 mT and a collision energy of 20 eV. The discharge in the ion source was activated for negative ion experiments.

The HPLC instrumentation consisted of a Rheodyne Model 7125 injector valve fitted with a 10-$\mu$L 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, 0.1 M ammonium acetate, postcolumn via the thermospray interface into the ion source.

## RESULTS AND DISCUSSION

The entire effluent from the HPLC is directed into the ion source by the thermospray interface. This prevents loss of sample due to splitting and offers the potential for optimum sensitivity. Other criteria needed to ensure the maximum signal per analyte are ion sampling considerations and kinetic and thermodynamic factors involving the molecular and ionic species in the ion source. The detection limits for many compounds by thermospray introduction have been in the low nanogram range (1-30 ng) in the full scan mode[1-3]. However, higher detection limits have been reported for compounds not amenable to buffer-assisted ion evaporation. For example, the chlorinated phenoxyacid class of herbicides were reported to have detection limits of 10 $\mu$g positive-ion detection in this mode[4]. To make the interface more universal in its scope of compound classes, a modification was made to the ion source with the addition of a wire-repeller[5]. Table I lists the limits of detection (LOD) for some chlorinated phenoxyacid herbicides and dyes that were detected under conditions of optimal sensitivity with the new wire-repeller. The LOD's for these compounds show enhancements from 10-1000 times over what has been previously reported.

There are certain compounds that still show poor LOD's even under these conditions. The phenoxyacid herbicide 2,4,5-T has an LOD of 170 ng. However, if the discharge in the ion source is activated and the negative-ion mode is used, the LOD for 2,4,5-T is 6.5 ng. Since this compound is chlorinated, electron capture is an efficient mechanism for ionization. In addition, the use of the negative ion electron capture mechanism initiated by discharge (or by filament) promotes

Table I. Limits of Detection under Buffer-Assisted Ion Evaporation with a Wire-Repeller (Positive-Ion Mode).

| COMPOUND | LOD (ng) |
|---|---|
| Dicamba | 13 |
| 2,4-D | 2.9 |
| 2,4,5-T | 170 |
| Disperse Blue 3 | 0.050 |
| Solvent Red 23 | 5.0 |
| Basic Green 4 | 0.67 |

additional fragmentation or dissociation. With buffer-assisted ion evaporation the major species is (are) the protonated molecule or the ammonium adduct or both. Very little other fragmentation, if any, is usually observed in the positive ion mode. In certain cases depending upon analyte, additional fragmentation may take place because of labile bonds or the destabilization of the protonated molecule. However, under negative ion electron capture processes, more dissociation is observed. In fact, dissociation electron capture becomes a major process with some electronegative compounds. Using the example of 2,4,5-T again, major ions produced in the discharge negative ion spectrum of this compound include the $M^-$, $(M-H)^-$, $(M-HCl)^-$, $(M-HCOOH)^-$, $(M-CH_2COOH)^-$, $(M-Cl-COOH)^-$ and $(M-Cl-CHCOOH)^-$ ions.

The ionization used with the thermospray LC/MS interface is affected very little by surface phenomena and wall effects so thermal degradation is minimized. Other LC/MS interfaces (e.g., particle beam) could be subject to surface effects and, thus, some compounds have potential for thermal degradation in such systems. The thermospray system has been used to characterize some fragile biochemically important compounds that have some application in exposure assessment monitoring (e.g., DNA adducts of the carcinogen, 2-acetylaminofluorene[6]). The electron ionization spectra of phenoxyacid herbicides have been shown to include thermal degradation ions under particle beam introduction if care of the ion source surfaces is not taken[7].

A major disadvantage of the thermospray LC/MS interface that has been mentioned above is that the interface usually generates only one or two ions per compound. This results in a lack of selectivity because little or no structural information is generated. This is a serious consideration when performing non-target analysis because a spectrum with one or two ions per compound is not suitable for being matched

against a library of spectra. There are some approaches that are potential solutions to this problem. Among these are use of MS/MS techniques to deconvolute the information in the thermospray spectra. A successful application of triple quadrupole mass spectrometry to the thermospray introduction for environmental samples was demonstrated for organophosphorus pesticides[2]. Disulfoton was identified by virtue of its daughter ion CAD spectrum in which the protonated molecule at m/z 275 was subjected to collision with argon atoms and the product ions detected. Two chromatographic peaks containing the m/z 275 ion eluted within 1.5 minutes of each other under thermospray introduction. Since these two peaks showed only a m/z 275 ion in both of their mass spectra, it was only upon application of CAD techniques that these peaks were resolved. The major product ion from the CAD of m/z 275 from disulfoton is m/z 89; only one of these two peaks showed an m/z 89 upon CAD.

Another possible solution to the problem of little structural information is the use of repeller-induced fragmentation. Application of a potential of approximately 400 V to a wire-repeller in the ion source of a thermospray system results in spectra with increased fragmentation compared with regular buffer-assisted ion evaporation spectra. In fact, the spectra produced under such an arrangement show similarities to both the electron ionization spectra and the CAD spectra for the same compounds[8]. Both mechanisms may, indeed, be taking place in the ion source. However, in this mode the sensitivity was lower by two orders of magnitude than in normal buffer-assisted ion evaporation.

For electronegative compounds the discharge negative ion mode, as has been mentioned above, can greatly facilitate structural interpretation. Usually, this mode generates much fragmentation with good sensitivity.

## SUMMARY

The thermospray LC/MS interface has proved to be an effective instrument for analyzing for nonvolatile compounds. The advantages of thermospray over other LC/MS techniques have been the relatively high instrument sensitivity for many compounds, the generation of ions without an external ionization source, and the production of simple spectra which almost always provide molecular weight information. The disadvantages have been its selective sensitivity (compounds with low proton affinities will often show low sensitivities) and the absence of significant molecular fragmentation. Efforts in developing methods using thermospray LC/MS have concentrated on improving the instrument performance for increased sensitivity and selectivity. Four steps were taken

in this direction: (1) the use of a wire-repeller to enhance sensitivity; (2) the operation of the triple quadrupole mass spectrometer in the daughter ion mode; (3) the use of a wire-repeller to effect CAD in the ion source; and (4) the use of the discharge enhanced negative ion mode. The last three steps were used to increase the selectivity of the system.

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# 52 INVESTIGATION OF IMPROVED PERFORMANCE IN HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/ PARTICLE BEAM/ MASS SPECTROMETRY SYSTEMS

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## ABSTRACT

Several types of particle beam interfaces for high performance liquid chromatography/mass spectrometry (HPLC/MS) systems are now commercially available. During the investigation of their performance characteristics, enhanced positive ion abundances were observed for coeluting compounds and with the addition of ammonium acetate to the mobile phase. The ammonium acetate enhancements are attributed to improved chromatographic efficiency for basic compounds, such as benzidine, and to a particle beam carrier process for two of three particle beam interfaces. A third particle beam interface with a universal membrane separator has no significant carrier phenomena. This carrier process can enhance sensitivity in particle beam HPLC/MS by improving analyte transport through the interface, particularly at low concentrations. However, with all three interface designs, coeluting substances may cause strong positive bias and non-linear response which may adversely impact quantitative analysis. In addition, ammonium acetate has been found to cause serious column bleeding on some C18 columns. This column bleed can contaminate the particle beam interface, and ion source, causing sensitivity degradation over time and therefore, poor precision in integrated ion intensities.

The different particle beam interfaces have been used to study a variety of non-gas chromatographable compounds in order to maximize sensitivity and to determine their capabilities in quantitative analysis. Efforts were also made to improve system ruggedness and reproducibility, over at least an eight hour period, by proper column conditioning, column choice (i.e. carbon loading of C18 packing), and mobile phase composition modification through post column addition of non-aqueous solvents. These have all been found to improve overall system performance with mean relative standard deviations of signal intensities in the range of 5-15% for most compounds.

53

# LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY METHODS FOR THE ANALYSIS OF AROMATIC SULFONIC ACIDS IN HAZARDOUS WASTE LEACHATES AND GROUNDWATER MONITORING WELL SAMPLES

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## ABSTRACT

A method is described for the analysis of highly polar aromatic sulfonic acid pollutants in aqueous matrices. It is based on anion exchange liquid chromatography with detection *via* both particle beam mass spectrometry (electron impact and negative chemical ionization) and UV absorption spectrophotometry. Anion exchange chromatography uses either Dionex OmniPac columns with a membrane suppressor for removal of sodium salts in the eluant, or Scientific Glass Engineering SAX columns with ammonium acetate eluant. The method is developed and validated for six aromatic sulfonic acid standards, and then used to characterize target and nontarget compounds in lyophilizates from three Stringfellow hazardous waste leachates. Leachate samples include upstream, downstream, and a charcoal treated mixture. Lyophilization retains essentially all the organic carbon, which is 513, 46.8 and 453 ppm respectively (by total organic carbon [TOC] analysis). Charcoal treatment removes priority pollutants but not most of the TOC, which is primarily highly polar, nonextractable and nonpurgable material. In addition to 4-chlorobenzenesulfonic acid (from 53 to 69% of the TOC), seven additional major aromatic sulfonic acids are tentatively identified. All are sulfonated and chlorinated aromatic byproducts probably from DDT manufacture.

## INTRODUCTION

A common problem in the characterization of the organic pollutants in aqueous leachates from hazardous waste sites and ground water monitoring wells is that most these pollutants are too polar, nonvolatile or thermally labile to be analyzed *via* conventional gas chromatography based methods. Organic components in aqueous leachate samples from the Casmalia and Stringfellow California hazardous waste sites, and in drinking water from Santa Clara, California, have been successfully resolved *via* anion exchange liquid chromatography particle beam mass spectrometry (Brown *et al.,* 1990 a and b). These samples had been historically difficult or impossible to analyze using conventional analytical methods.

The Stringfellow U.S. EPA Superfund site in California poses specific analytical problems common to many waste sites that may be addressed best *via* LC-MS methods. Most organic compounds contained in aqueous leachates from this site are not characterized by GC-MS based methods. Analysis of Stringfellow bedrock groundwater shows that less than 1% of the total dissolved organic materials are identifiable *via* purge and trap analysis, and are compounds such as acetone, trichloroethylene *etc.*, whose physical properties are ideally suited for GC-MS separation and confirmation (SAIC Report, 1987). Most of the organic materials contained in these leachate samples are highly polar, nonpurgable and non-extractable compounds that have not been previous characterized. The major waste stream originating from Stringfellow sampled at upstream and downstream locations is shown to have 45% and 40% respectively of the total organic carbon as PCBSA (measured by ion chromatography and UV detection). This compound, a waste product from the manufacture of DDT, was known to be present because of a history of disposal of "sulfuric acid" waste (Ellis *et al.*, 1988). Conventional reversed phase chromatography fails to resolve or give any retention using any combination of elution solvents of the organic materials in Stringfellow leachates (Brown *et al.*, 1990b). PCBSA and its two isomers 2- and 3-chlorobenzenesulfonic acids have been detected by anion exchange chromatography particle beam mass spectrometry (Brown *et al.*, 1990a). The utilization of inductively coupled plasma mass spectrometry as a detector with anion exchange chromatography of Stringfellow leachates shows that all the major organic components contain both chlorine and sulfur, and are consistent with being other chlorinated aromatic sulfonic acids (Brown *et al.*, 1990a).

In response to this problem a method has been developed to resolve and confirm aromatic sulfonic acids with six commercially available standards based on anion exchange chromatography, electron impact (EI) and negative chemical ionization (NCI) particle beam mass spectra and UV absorption spectroscopy. The method is then applied to the characterization of the major organic components of the total organic carbon contained in Stringfellow hazardous waste leachates.

## MATERIALS AND METHODS

Liquid Chromatography Particle Beam Mass Spectrometry. Instrumentation consists of a Hewlett-Packard 5988A mass spectrometer equipped with a Hewlett-Packard particle beam LC interface and 1090 HPLC (Hewlett-Packard Co., Palo Alto, CA, USA). Ionization modes are electron impact, and negative chemical ionization with isobutane as a reagent gas. LC methods are initially developed on a Hewlett-Packard 1050 LC equipped with a 1040 diode array detector and 79994A "Chem Station" for data acquisition. The diode array detector is used to produce UV spectra of individual peaks of materials resolved *via* anion exchange chromatography.

Anion exchange chromatography columns are made by Dionex (Sunnyvale, California USA) (OmniPac -100 and -500) and Scientific Glass Engineering (SGE) (Ringwood, Australia) (Model 250GL-SAX, 25 cm X 2 mm). Gradient elutions use sodium carbonate or sodium hydroxide solutions and acetonitrile in the case of the Dionex OmniPac columns, and ammonium acetate buffer and acetonitrile with the SGE columns. The Dionex micromembrane suppressor is used to convert nonvolatile sodium salts to the corresponding hydrogen form before introduction into the particle beam mass spectrometry interface, *e.g.*, NaOH -> $H_2O$.

Six commercially available aromatic sulfonic acids are used as model compounds for analysis by HPLC-UV and HPLC-MS because similar compounds have been tentatively identified in groundwater monitoring well samples and hazardous waste leachates, and because as a class they are not analyzable *via* traditional chromatographic methods, *e.g.*, gas chromatography. The spiked sample volumes are chosen based on the concentration of the final sulfonic acid solution required for analysis (Table 1). The spiked water samples are lyophilized and the following procedure is applied regardless of the sample volume. Seven mL of methanol and 42 mL of acetone are added to the lyophilized residue, and the mixture is sonicated for 20 min. at room temperature. The mixture is set aside for 1 hour and filtered through filter paper (Whatman No.1). acetone (30 mL) is used for washing the container and the filter paper. The solvents are removed by rotary evaporator from the combined solution of the filtrate and the washing solution. The residue is dissolved in 0.8 mL of methanol and the solution is transferred to a vial. This procedure is repeated three times and the combined solution is dried under a nitrogen stream at 30 degrees C. Methanol (250 $\mu$L) of is added to the residue and the solution is used for HPLC-UV and HPLC-PB-MS analysis.

Lyophilization (freeze drying) is used for recovery and concentration of Stringfellow aqueous leachate samples, although the volatile fraction is sacrificed. Thus, an aqueous sample (5 to 2,000 mL) is freeze dried (Freezemobile 12 SL, the VirTis Co., Gardiner, N.Y. USA) over 1 to 72 hours, the residue is extracted with methanol (2 to 200 mL), the inorganic salts are precipitated by addition of equal amounts of acetone, and finally the filtered soluble phase is evaporated under reduced pressure. This precipitation step may be repeated for samples containing very high levels of inorganic salts. The final residue is redissolved in methanol (0.25 to 20 mL) for injection.

TOC of Stringfellow leachates is determined *via* a Dohrman DC 180 total organic carbon analyzer (Rosemount Analytical Division, Santa Clara, CA, USA). It is measured initially for the whole aqueous leachate sample and then for a lyophilized sample reconstituted to its original volume in distilled water.

Table 1. Spike and recovery results for six sulfonic acid standards spiked into tap water (TW) and distilled water (DW). PHBSA = 4-hydroxybenzenesulfonic acid; BSA = benzenesulfonic acid; PCBSA = 4-chlorobenzenesulfonic acid; PTSA = 4-toluenesulfonic acid; XSA = xylenesulfonic acid; 1-NSA = 1-naphthalenesulfonic acid.

| QUANT SPIKE (ppm) | MATRIX | VOL. (mL) | N | METHOD | % RECOVERY (± SD) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | PHBSA | BSA | PCBSA | PTSA | XSA | 1-NSA |
| 0.01 | DW | 300 | 12 | I | | | 77.5 ± 5.3 | 94.1 ± 7.1 | 84.9 ± 10 | 82.9 ± 5.0 |
| 0.01 | TW | 300 | 12 | I | | | 77.9 ± 8.0 | 73.4 ± 9.4 | 75.3 ± 10 | 77.5 ± 9.4 |
| 1.00 | DW | 10 | 6 | II | | | 85.4 ±4.4 | 80.7 ± 5.2 | 91.6 ±7.6 | 87.4 ± 4.6 |
| 1.00 | TW | 10 | 6 | II | | | 74.3 ± 7.0 | 74.9 ± 9.8 | 87.8 ± 12 | 78.8 ± 11 |
| 100.0 | DW | 5 | 9 | II | 71.1 ± 5.3 | 76.5 ± 6.5 | 90.9 ± 6.6 | 90.4 ± 3.9 | 82.5 ± 5.3 | 90.1 ± 6.3 |
| 100.0 | TW | 5 | 9 | II | 64.7 ± 6.9 | 78.5 ± 3.3 | 89.2 ± 4.6 | 81.7 ± 6.1 | 83.4 ± 10 | 86.7 ± 4.9 |

## RESULTS AND DISCUSSION

Recovery of aromatic sulfonic acid standards spiked into tap water and distilled deionized water are shown in Table 1. Method detection limits ranged from 2-20 ng injected on column. UV chromatograms of these standards using the Dionex OmniPac 500 and the SGE SAX anion exchange columns are shown in Figure 1. The corresponding particle beam mass spectrometry total ion chromatograms and electron impact mass spectra for the first four eluting aromatic sulfonic acids are shown in Figures 2 and 3 respectively.

The anion exchange chromatograms of the upstream Stringfellow lyophilizate with UV absorption spectrophotometry (230 and 265 nm, SAX columns) along with tentatively assigned structures of individual eight peaks are shown in Figure 4. There are at least 14 different major peaks present in this chromatogram. UV spectra of peaks 2-14, showing two distinct $\lambda$ maxima in the regions of 210-230 and 255-270 nm are consistent with the presence of aromatic benzenoid chromaphores. Relatively stronger long wavelength absorption at the 265 nm detection window for peaks 7, 8 and 9 (Figure 4, bottom trace) suggests that they have $\alpha$-unsaturated substitution. For example, model aromatic compounds without $\alpha$-unsaturation have nearly two orders of magnitude smaller extinction coefficients in the region of 244 to 268 nm (Sadtler, 1979).

Figure 5 shows both electron impact (EI) and negative chemical ionization (NCI) particle beam LC-MS full scan chromatograms corresponding to the UV detection chromatograms seen shown in Figure 4. Chromatography conditions are identical as those used with UV absorption detection. The better peak resolution with UV detection allows the intelligent use of software deconvolution algorithms to resolve the mass spectra of individual peaks.

Total organic carbon (TOC) and PCBSA concentrations of the Stringfellow upstream, downstream and charcoal treated mixture leachates samples are shown in Table 2. The lyophilization process of these aqueous leachates does not result in a significant loss of TOC, suggesting that these analytical methods are being applied to the most of the organic pollutants present in these samples. Since the proportion of the upstream and downstream leachates that are mixed for charcoal treatment is unknown, the amount of TOC removed by the treatment cannot be precisely determined. However, the treated leachate has 88.3% of the TOC compared to the upstream leachate suggesting that charcoal treatment does not remove most the aromatic chlorinated sulfonic acids present.

The EI spectrum of a standard of PCBSA with anion exchange chromatography shows a $M^+$ ion at 192 with an isotope pattern consistent with the presence of a

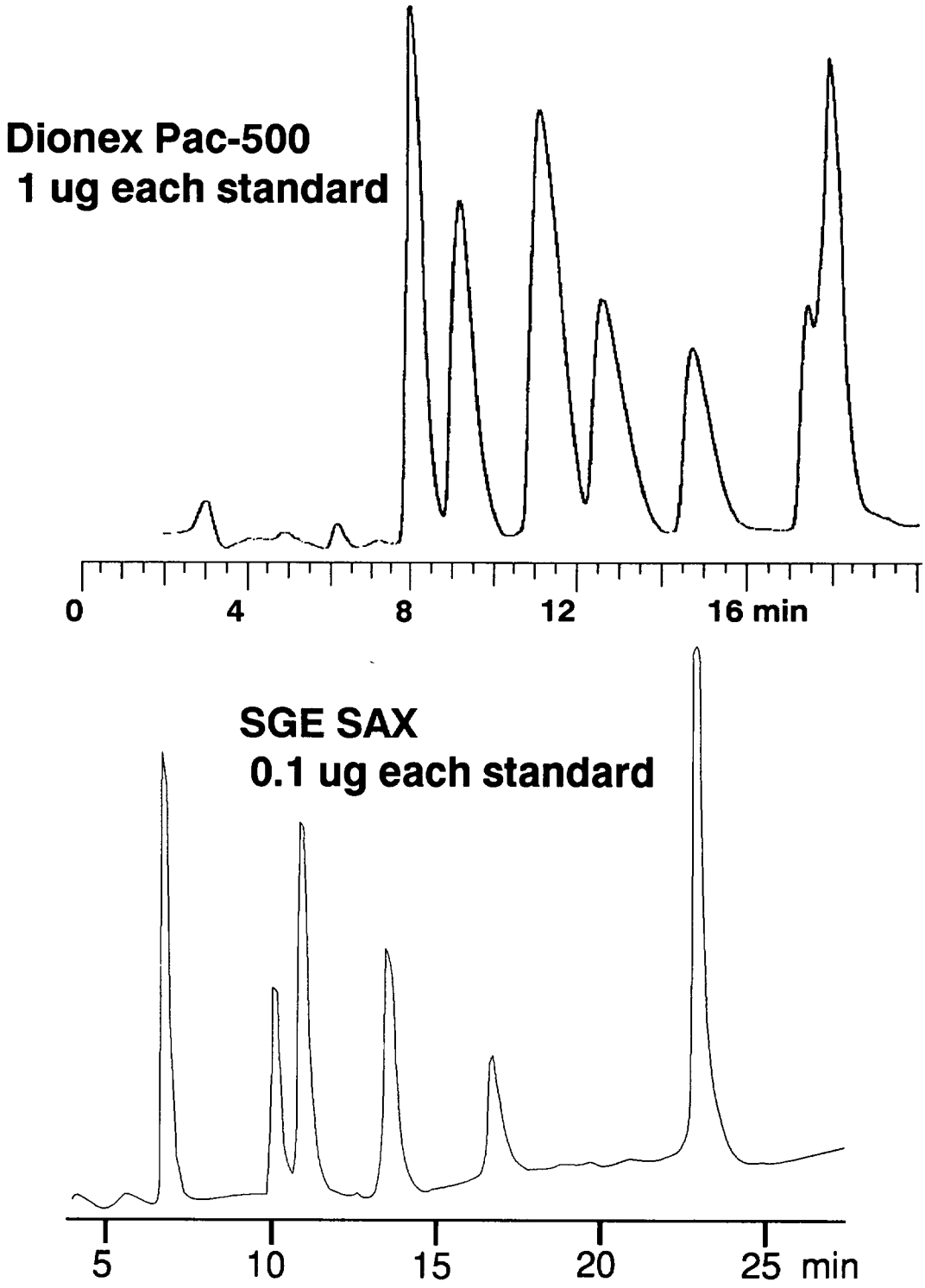
Table 2. Concentrations (ppm) of total organic carbon (TOC) and 4-chlorobenzenesulfonic acid (PCBSA) in upstream, downstream and charcoal treated[a] Stringfellow aqueous leachates.

| SAMPLE | TOC ppm ± SD [b] (percent of upstream) | PCBSA ppm ± SD[b] (percent of TOC) |
|---|---|---|
| **Upstream** | **513 ± 22.7 (100)** | **334 ± 17.2 (69)** |
| **Downstream** | **46.8 ± 7.6 (9.1)** | **27.6 ± 2.6 (60)** |
| **Charcoal Treated** | **453 ± 3.0 (88.3)** | **241 ± 7.3 (53.2)** |

[a]Charcoal treatment is used at the Stringfellow site for removal of priority pollutants from the leachate stream.

[b]SD = Standard deviation based upon three samples.

Figure 1. UV absorption anion exchange chromatography of six aromatic sulfonic acid standards. Top trace uses the Dionex OmniPac 500 column with sodium carbonate elution; bottom trace uses a SGE SAX column with ammonium acetate elution. Detection is at 254 nm.



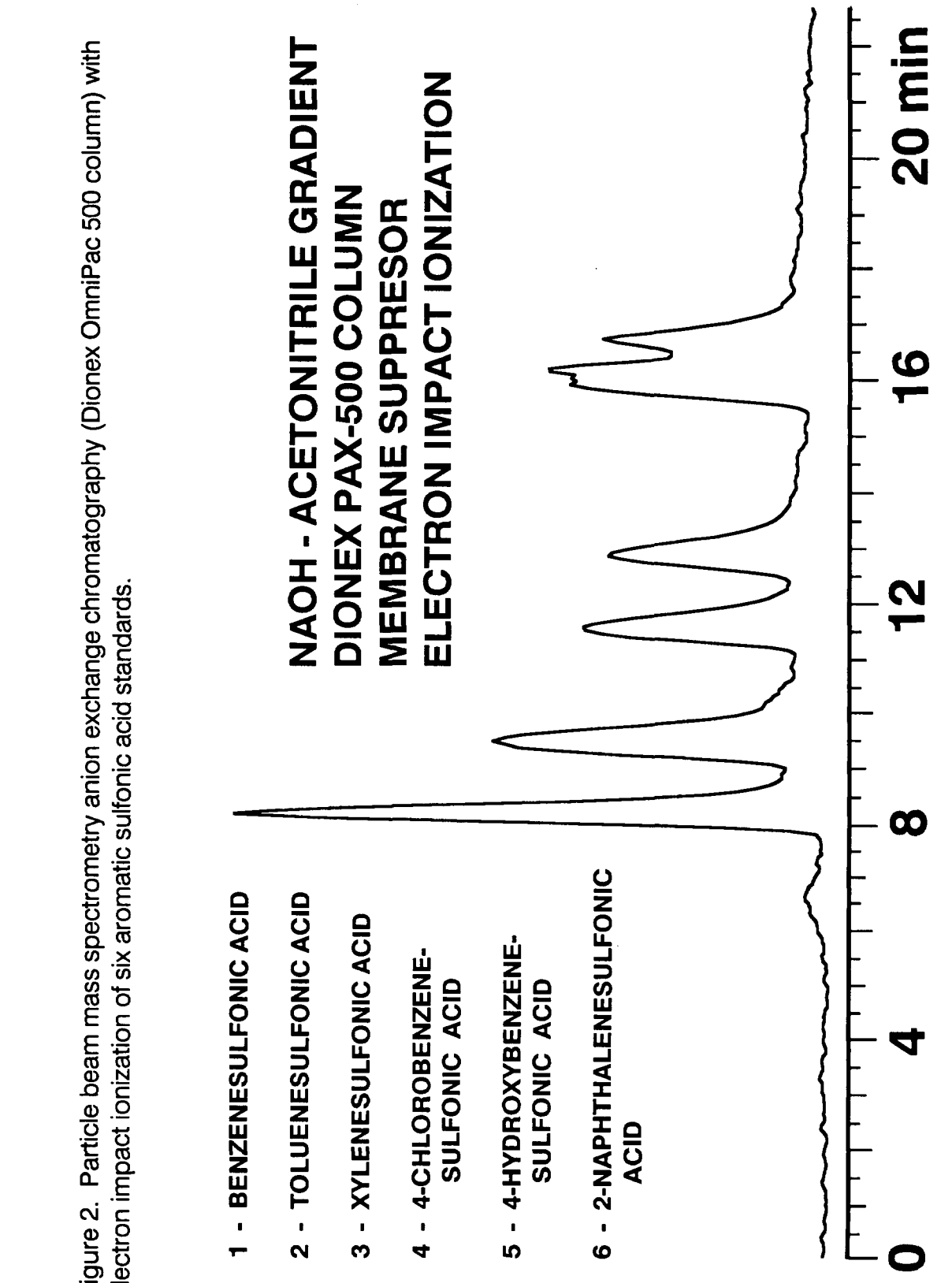



Figure 2. Particle beam mass spectrometry anion exchange chromatography (Dionex OmniPac 500 column) with electron impact ionization of six aromatic sulfonic acid standards.

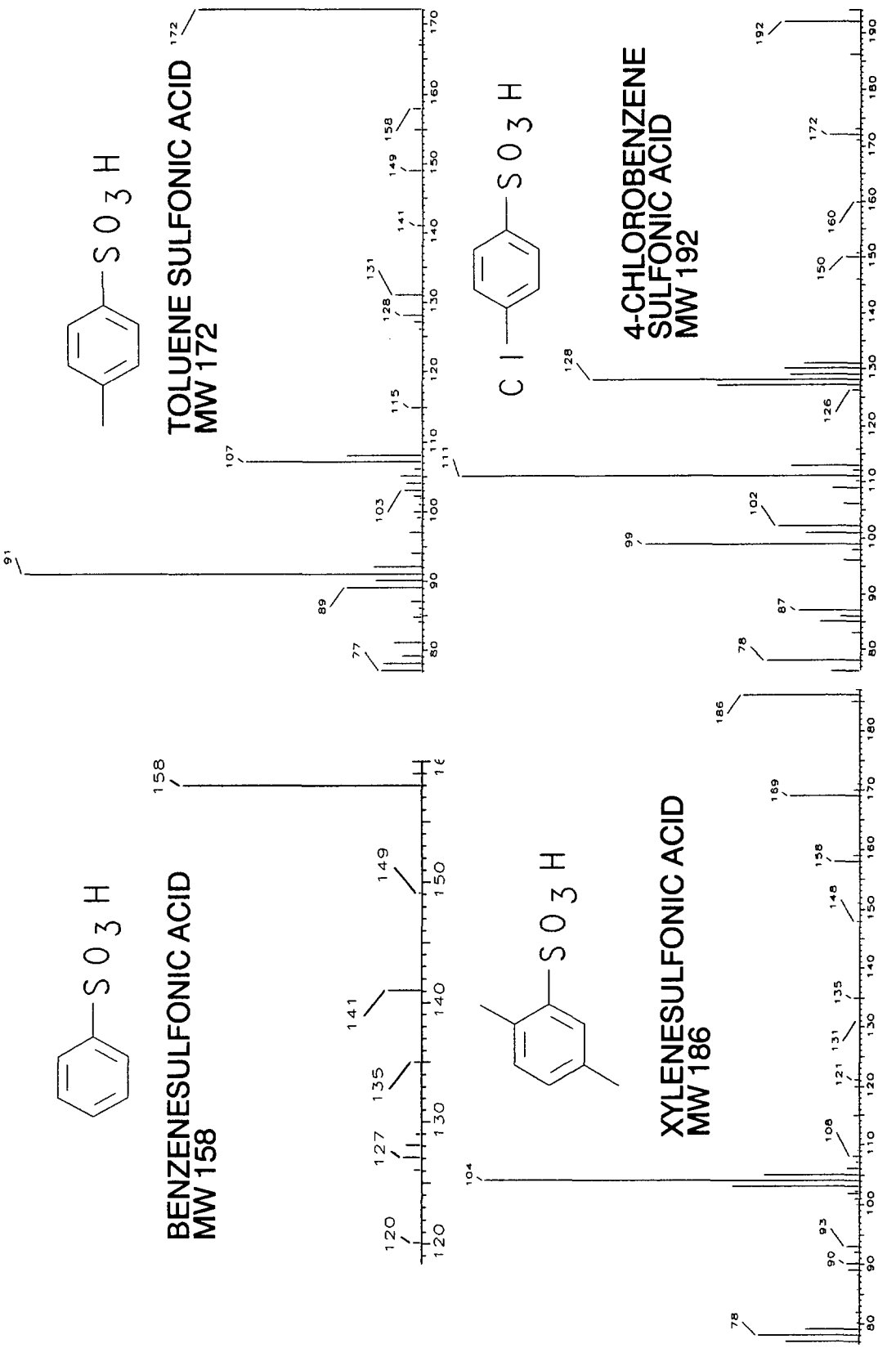



Figure 3. Electron impact ionization particle beam mass spectra of 4 aromatic sulfonic acid standards, resolved by anion exchange chromatography with the Dionex OmniPac 500 column.

Figure 4. UV absorption anion exchange chromatography (SGE SAX column) of Stringfellow leachate samples with tentatively assigned structures of compounds in peaks 3 - 10.

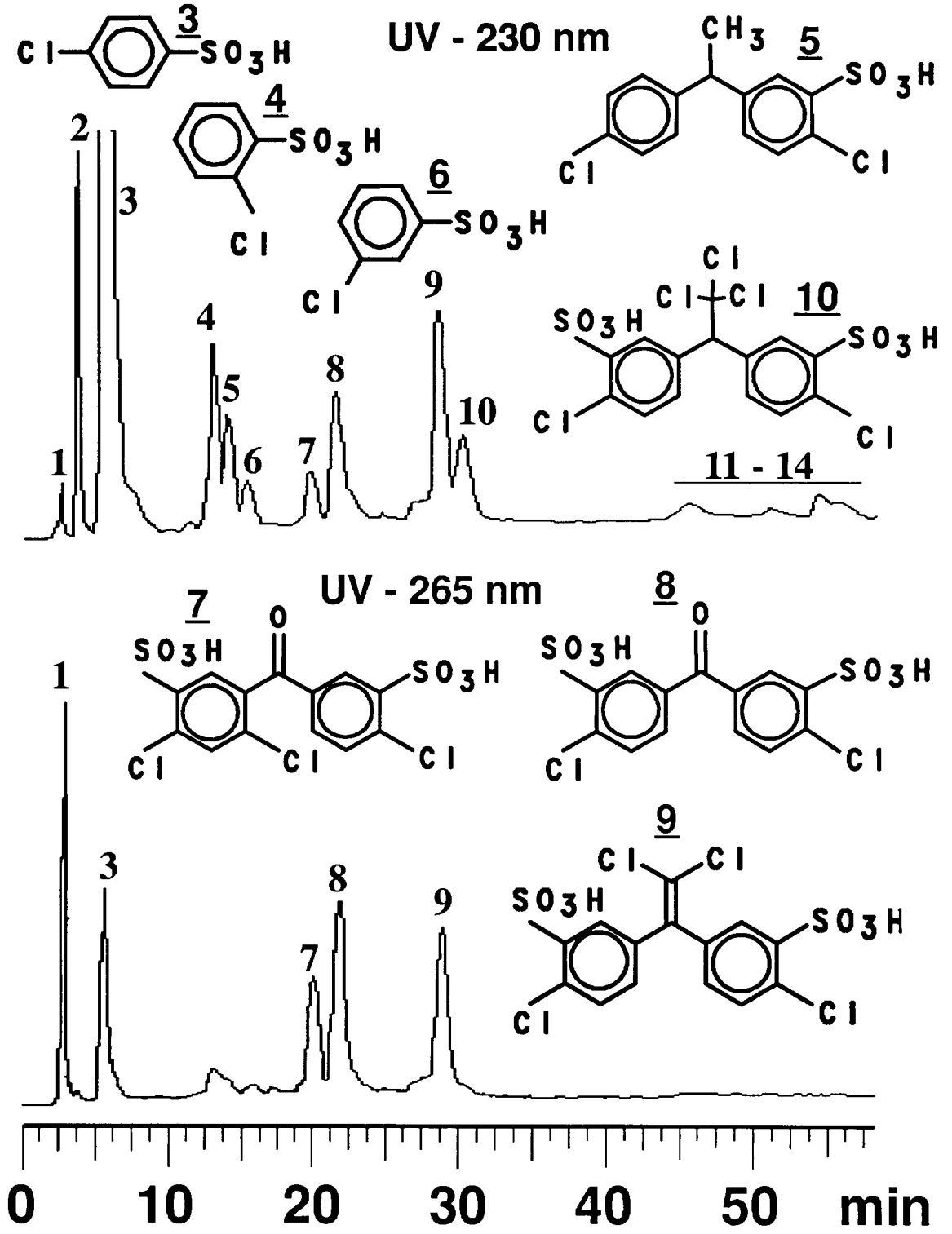
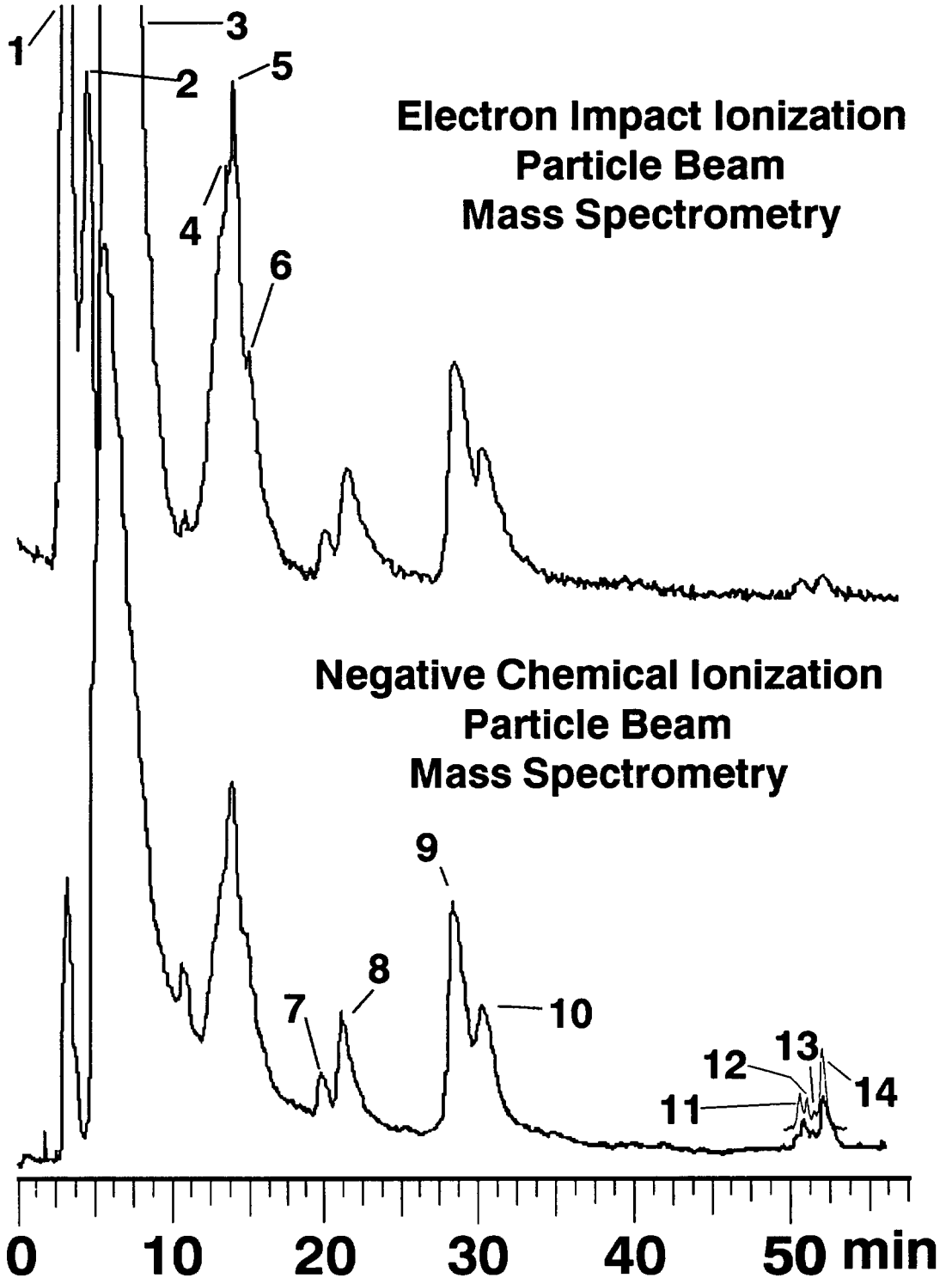


Figure 5. Particle beam mass spectrometry anion exchange chromatography (SGE SAX column) with electron impact (top trace) and negative chemical (bottom trace) ionization of Stringfellow leachate samples.



single chlorine; a small M - 17 ion at 175 (loss of OH?); a M - 64 base ion at 128 (loss of $SO_2$); a large M - 81 ion at 111 (loss of $SO_3H$); and large ions at 99 (m - 93) and 75 (m - 117). Under NCI conditions the spectrum of PCBSA shows a $M^-$ ion at 192 with an isotope pattern consistent with one chlorine; a small M - 1 at 191; and a M - 36 base ion at 156 (loss of HCl). Essentially identical spectra in both EI and NCI modes are recorded for peaks 4 and 6, which have been tentatively identified as the 2- and 3-chlorobenzenesulfonic acid isomers of PCBSA. The suggested relative isomer retention time is based upon comparison to the relative retention time of the carboxylic acid analogs 4-, 2-, and 3-chlorobenzoic acids. The relative elution order of these three standards using similar anion exchange chromatography conditions is 4-, 2-, and 3-chlorobenzoic acid.

Tentative identification of five other chlorinated aromatic sulfonic acids in Stringfellow leachates. Table 3 summarizes the data in EI and NCI mass spectrometry for the 14 major peaks present in the anion exchange chromatography particle beam mass spectrometry of lyophilized Stringfellow leachates. Negative chemical ionization data was particularly useful for assigning molecular weights, and electron impact data for providing structural information based upon fragmentation patterns. Previous data (Brown *et al.,* 1990a) from inductively coupled plasma mass spectrometry had indicated that probably compounds in all 14-major peaks contain chlorine and all except peak 2 contain sulfur atoms. The fragment ion series that occurs in several of the spectrum of unknowns, with ions at 191, 175, 111, 99 and 75 m/e in EI; and 156 m/e in NCI is consistent with the presence of a chlorobenzenesulfonic acid moiety (Table 3). Analysis of isotope clusters is complicated by the presence of multiple chlorine atoms, sulfur atoms and M-1 and M-2 ions resulting from deprotonation of the aromatic sulfonic acids. These tentatively assigned compounds (Figure 4) as with PCBSA also may be expected to occur in the sulfuric acid waste products from DDT synthesis.

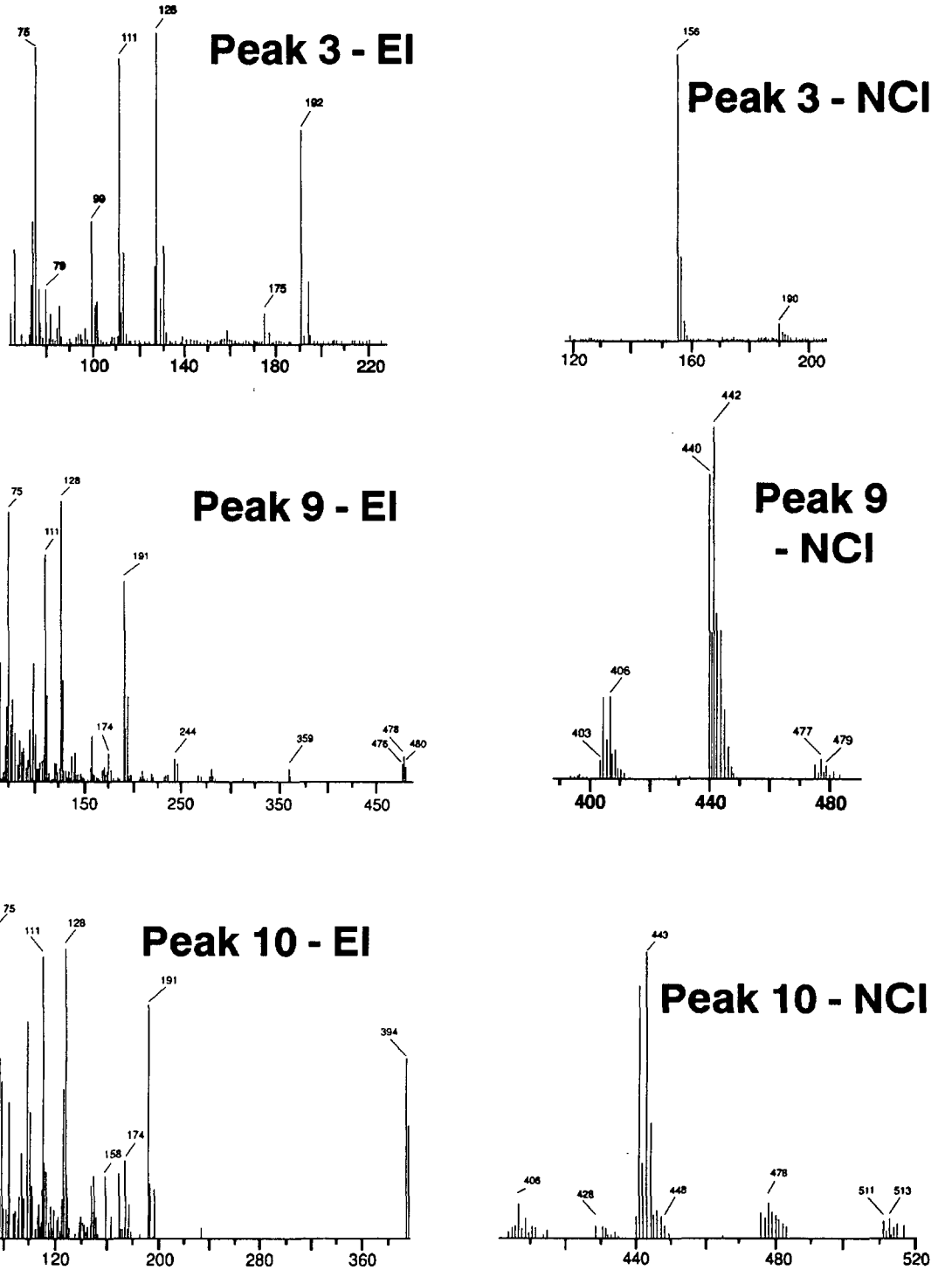
Although the EI spectra of the tentatively identified structures shown in Figure 4 are not available, the spectra of many of the corresponding non sulfonated analogs are available for comparison. The EI spectra of 4,4'-dichlorobenzophenone (for comparison to structures for peaks 7 and 8) shows a small parent ion at 250, a base acylium ion at 139 and a large corresponding chlorophenyl ion fragment at 111 m/e. Benzophenone itself shows the base acylium ion, and the unsymmetrical 3,4-dichlorobenzophenone shows both possible acylium ions. The corresponding benzophenone fragmentation pattern with the assigned structures are seen for EI spectra of peaks 7 and 8 (Table 3).

The EI spectra for DDT (for comparison to the structure for peak 10) shows a base ion corresponding to loss of $CCl_3$ and smaller clusters corresponding to loss of 1, 2

Table 3. Summary of anion exchange particle beam mass spectra of leachates from Stringfellow ground water with electron impact and negative chemical ionization mass spectrometry.

| PEAK NO. | NEGATIVE CHEMICAL IONIZATION | ELECTRON IMPACT IONIZATION |
|---|---|---|
| 1 | 627-631 (19, $M^-$); 592-601 (40, M-Cl); 522-530 (100, M-3Cl); 508-516 (82); 497-505 (22); 485-490 (42, M-4Cl). | 497-502 (3); 437-443 (4); 405-412 (62); 264-269 (42); 221-227 (15); 174-176 (100). |
| 2 | Not Observed | 96 (25); 79 (100). |
| 3 | 191-194 (5, $M^-$, M-H for 1 Cl); 157 (30, M-Cl); 156 (100, M-HCl). | 192-194 (70, $M^+$ 1Cl); 175-177 (10, M-OH); 128-130 (100, M-SO2); 111 (95, M-HSO3); 99-101 (40); 75 (98). |
| 4 | 191-192 (<1, $M^-$, M-H for 1 Cl); 157 (30, M-Cl); 156 (100, M-HCl). | Same as Peak 4. |
| 5 | 329-334 (11, M-1, $M^-$ for 2 Cl); 294-296 (100, M-HCl). | Not Observed |
| 6 | 191-192 (<1, $M^-$, M-H for 1 Cl); 157 (30, M-Cl); 156 (100, M-HCl). | Same as Peak 4. |
| 7 | 444 (1, $M^-$); 408-412 (9, M-HCl to M-Cl); 373-378 (100, M-2HCl to M-2Cl); 337-342 (16, M-2HCl-Cl to M-3Cl), 156 (2, C6H4SO3 fragment). | 219 (4, $^+$COC6H3ClSO3H fragment); 191-193 (40, ClC6H3SO3H fragment); remaining ions at 128-130; 111; 99-101 and 75 appear in approximately the same ratio as with PCBSA (Peak 3). |
| 8 | 408-414 (10, M-2H to $M^-$); 373-378 (100, M-HCl-H to M-Cl); 338-340 (7, M-2HCl to M-2Cl); 156 (2, C6H4SO3 fragment). | 219 (86, $^+$COC6H3ClSO3H fragment); 191-193 (60, ClC6H3SO3H fragment); remaining ions at 128-130; 111; 99-101 and 75 appear in approximately the same ratio as with PCBSA (Peak 3). |
| 9 | 475-483 (6, M-H to $M^-$ for 4 Cl); 440-447 (100, M-HCl to M-Cl); 404-410 (40, M-2HCl to M-2Cl); 156 (80, C6H4SO3 fragment). | 476-480 (9, $M^+$); 191-193 (70, ClC6H3SO3H fragment); remaining ions at 128-130; 111; 99-101 and 75 appear in approximately the same ratio as with PCBSA (Peak 3). |
| 10 | 511-519 (3, M-1 to $M^-$ for 5 Cl); 476-484 (12, M-HCl to M-Cl); 440-448 (100, M-2HCl to M-2Cl); 156 (32, C6H4SO3 fragment). | 394-396 (58, M-1H-CCl3); 191-193 (74, ClC6H3SO3H fragment); remaining ions at 128-130; 111; 99-101 and 75 appear in approximately the same ratio as with PCBSA (Peak 3). |
| 11 | Three distinct ion series. First Series: 584-588 (20, $M^-$); 549-555 (100, M-Cl to M-HCl); 513-518 (12, M-2Cl-H to M-2Cl); 504-510 (100, M-SO3); 468-476 (75, M-SO3-HCl); 424-429 (15, M-2SO3); 389-395 (26, M-2SO3-Cl). Second Series: 486-490 (80, $M^-$); 450-457 (38, M-HCl to M-Cl); 414-416 (10, M-2HCl). Third Series: 462-464 (2, $M^-$); 426-429 (15, M-HCl). | Not Observed |
| 12 | 392 (2, $M^-$); 357-363 (100, M-Cl); 322-325 (33, M-2Cl); 312-318 (25, M-SO3); 277-282 (M SO3-Cl); 156 (6, C6H4SO3 fragment). | Not Observed |
| 13 | Not observed | Not Observed |
| 14 | 438-444 (10, $M^-$); 403-408 (100, M-Cl); 358-363 (90, M-SO3); 323-327 (M-SO3-Cl) | Not Observed |

Figure 6. Electron impact (EI) and negative chemical (NCI) ionization particle beam mass spectra of peaks 3,9 and 10 from the total ion chromatogram shown in Figure 5.



and 3 chlorine atoms from the parent. The parent ion is minute. The loss of the $CCl_3$ fragment is also seen in the EI spectra of peak 10 (Figure 6).

The EI spectra for DDE (for comparison to the structure for peak 9, Figure 6) is distinguished from that for DDT in that for DDE the parent ion is also the base ion. Fragmentation for DDE involves only sequential loss of 1, 2 and 3 chlorine atoms. A parent ion is also seen for the structure assigned to peak 9 (but not for peak 10), along with the chlorobenezenesulfonic acid moiety fragment (Table 3).

## ACKNOWLEDGMENTS

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54

# LC/MS DATA COMPARED TO TRADITIONAL METHODS DATA

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## ABSTRACT

LC/MS using thermospray interface is a relatively new analytical tool. There is little information available in the literature regarding LC/MS for use with pesticides.

While incorporating the LC/MS for use in the laboratory it was necessary to validate the results by comparison with traditional methods data. The LC/MS was run in tandem with the UV/VIS and the post column HPLC.

A review of the LC/MS method development spanning the past two years is presented along with the comparison data generated on the traditional instruments.

## INTRODUCTION

In the State of California, assembly bill AB1803 was passed requiring water purveyors to perform a series of pesticide analyses including EPA method 632. The initial samples were basically clean and the matrices posed no real problems for identification. As the client base broadened, the types of matrices increased to include soils, waste waters and produce. The difficulty of the matrices increased also. A great number of the samples originated from agricultural chemical manufacturing facilities. Frequently these samples contained a mixture of chlorinated pesticides, organophosphorous pesticides, carbamate pesticides, urea pesticides and chlorophenoxy acid herbicides all at varying concentrations. The sample preparation and clean up became very involved, and positive identification became a critical issue.

Examining technological alternatives, the LC/MS held the most promise for solving some of the problems being encountered. As a result, an LC/MS was installed in March of 1988. Initially, the majority of analytes incorporated in the screening were those listed in EPA method 632.

## EXPERIMENTAL

Thermospray was designed for a 1 ml/min flow rate. Previous chromatography as prescribed by 632 used flow rates of 2ml/min. To compensate, the 632 flow rate was cut by one half and the gradient rate was increased by a factor of two.

A methanol/water gradient was used mainly due to the cost difference between methanol and acetonitrile.

Thermospray sensitivity seems to drop as the organic composition of the gradient increases. To maintain the greatest sensitivity for the late eluters, the gradient is held at a 10% water solution for a period of time instead of ramping to 100% methanol. Spectra of the analytes were generated from single injections of high concentration standards. The resultant peaks were large enough to be seen in a total ion chromatogram. As a matter of protocol it was necessary to obtain quantitation values from historical techniques in order to check the capabilities of the LC/MS with the thermospray unit.

Apparatus and Materials

(a) Liquid Chormatograph (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) equipped with new thermospray source.

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

(d) 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.

(e) Filter Photometric UV/VIS detector (Hewlett Packard)

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

(g) Programmable Flouresence Detector (Hewlett Packard 1046 A)

(h) Rotary evaporator (Buchi RE111)

(i) 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)

Samples used were delivered from outside sources as blind samples. Spike samples were made in the laboratory from laboratory pure water.

HPLC Conditions for LC/MS·

The mobile phase, consisiting of methanol and water containing 0.1 molar ammonium acetate with 1% acetic acid, was solvent programmed with linear gradients as follows: internal 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 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 conditions were survey dependent.

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.

HPLC Conditions for UV/VIS

The mobile phase, consisting of acetonitrile fixed with 0.1% phosphoric acid and water was solvent programmed with linear gradients as follows: initial mixture of 10 percent acetonitrile/ 90 percent water to 100 percent acetonitrile with a 45 minute ramp; held for 5 minutes; to 10 percent acetonitrile/ 90 percent water; held for 5 minutes. The flow rate was 1 ml/min. The wavelength was 254 nm.

HPLC Conditions for Fluorecence Detector

The mobile phase consisting of water and methanol was solvent programmed with linear gradients as follows: initial mixture of 20 percent methanol/ 80 percent water with a 15 minute gradient; held for 3 minutes; to 100 percent methanol with a 1 minute ramp; held for 5 minutes; to 20 percent methanol/ 80 percent water with a 5 minute gradient; held for 5 minutes. The flow rate was 1 ml/min, the excitation wavelength was 230 nm, the emission wavelength was 465 nm.

Sample Preparation

One liter aliquots of aqueous samples were extracted in accordance with EPA Method 5310 and concentrated to a 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 reconstitued to a final volume of 1 ml. Internal standards were added at a concentration of 1μg/ml. Injection size per sample was 100 μL.

## RESULTS AND DISCUSSION

Originally the method was developed as a screening tool for low level confirmation. The chromatography was not an issue since the data system was being used to extract ion profiles for a specified number of possible chemicals. A series of method spikes were prepared containing eight urea pesticides at three, ten and twenty times the detection levels. The detection level of interest was 0.1 μg/L. The results were generated on both the LC/MS and the UV/VIS detector. The comparison between the two methods was acceptable and a field validation using this method was attempted.

Fifty-five water samples were submitted for analysis. These samples contained on the average of two to three urea pesticides. The samples also contained two to three triazine herbicides. Upon analysis of these samples several problems arose. Fluometuron, diuron, and siduron all have similar primary ions. In addition, the elution pattern for these compounds using the original chromatography was very close. Diuron eluted between fluometuron and siduron. Some of the samples were spiked with fluometuron and/or siduron at concentrations five times that of diuron. As a result, the Diuron was not seen in the extracted ion profiles. The presence of the triazine herbicides also caused interfences.

Two steps needed to be taken to optimize the method and make it applicable under real world conditions. The chromatography had to be improved and the sensitivity at the low ends needed to be increased. The chromatography was improved by extending the analytical run time and modifying the gradient. A new thermospray source was introduced by Hewlett Packard making the desired detection levels achievable.

Utilizing the new and improved method, ten real world samples were submitted for analysis. Two sets of quality control spikes were analyzed along with the samples. The spiking levels were at the detection levels for the first set and at five times the detection levels for the second set. The quality control results are tabulated in Tables 1 and 2.

The sample results are given in Table 3. Good quantitation was achieved as well as excellent spectra.

The samples contained some interesting information that was discovered using the spectral information. Appendix 1 is a UV scan of one of these samples. From the mass spectrometer data, the extracted ion profiles and the spectra confirmed the presence of diuron. Note the peak at retention time 13.2 looks as if there is a shoulder present. The mass spectral information identified the shoulder as monuron. The main peak is simazine. The monuron present is actually below reporting levels. The LC/MS was able to identify this barely discernable peak.

A significant amount of data was generated for comparison of LC/MS and UV/VIS data. The data is excellent in comparison and in most instances meets the percent reproducibility criteria for replication in a single analysis.

Post column data using fluoresence detection was also compared to LC/MS generated data. The results are presented in Table 4.

SUMMARY

HPLC/MS using the thermospray interface provides a versatile technique capable of identifying multiple classes of compounds in a wide variety of matrices, eliminating some of the need for sample cleanup.

Thermospray liquid chromatography mass spectrometry has proven to be a powerful tool for the identification and quantitation of compounds when the target analyte list is known and the standards are available.

TABLE 1
COMPARISON SPIKE RECOVERIES

| Analyte | Actual µg/L | UV-VIS µg/L | Per Cent Recovery | LC/MS µg/L | Per Cent Recovery |
|---|---|---|---|---|---|
| Fluometuron | 0.513 | 0.4404 | 85.9% | 0.4633 | 90.3% |
| Diuron | 0.515 | 0.4856 | 94.3% | 0.6316 | 122.6% |
| Siduron | 0.500 | 0.4726 | 94.5% | 0.6241 | 124.8% |
| Neburon | 0.504 | 0.4914 | 97.5% | 0.5445 | 108.0% |
| Monuron | 1.485 | 1.157 | 77.9% | 1.2394 | 83.4% |
| Linuron | 1.022 | 0.8587 | 84.0% | 1.2818 | 128.2% |
| Chloroxuron | 0.500 | 0.368 | 73.6% | 0.3989 | 79.8% |
| Tebuthiuron | 0.252 | 0.2133 | 84.6% | 0.3043 | 120.8% |

TABLE 2
COMPARISON SPIKE RECOVERIES

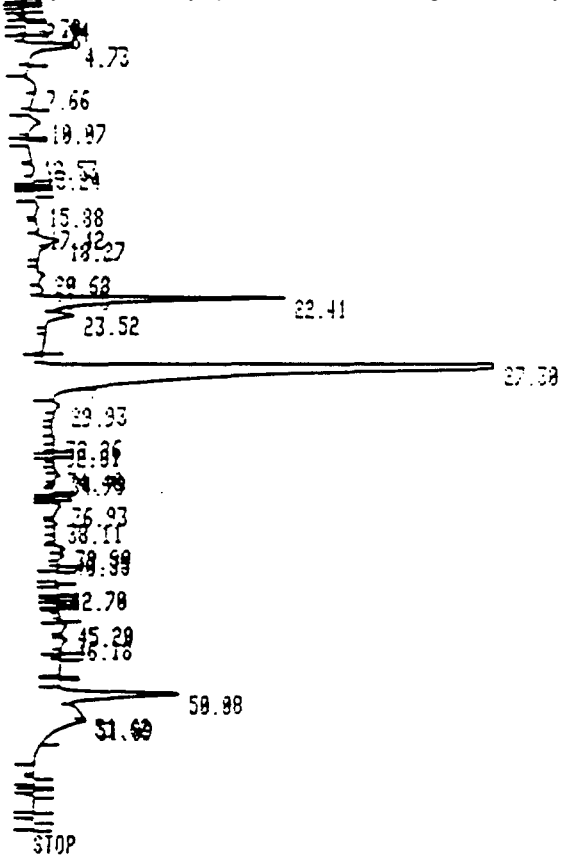
| Analyte | Actual µg/L | UV-VIS µg/L | Per Cent Recovery | LC/MS µg/L | Per Cent Recovery |
|---|---|---|---|---|---|
| Fluometuron | 0.513 | 0.4756 | 92.7% | 0.4669 | 91.0% |
| Diuron | 0.515 | 0.5058 | 98.2% | 0.5842 | 113.4% |
| Siduron | 0.500 | 0.5360 | 107.2% | 0.4739 | 94.8% |
| Neburon | 0.504 | 0.5084 | 100.9% | 0.6324 | 125.5% |
| Monuron | 1.485 | 1.2165 | 81.9% | 1.4698 | 99.0% |
| Linuron | 1.022 | 0.9302 | 91.0% | 1.1015 | 107.2% |
| Chloroxuron | 0.500 | 0.4585 | 91.7% | 0.505 | 101.0% |
| Tebuthiuron | 0.252 | 0.2177 | 86.4% | 0.2237 | 88.8% |

TABLE 3
COMPARISON OF REAL WORLD SAMPLES RESULTS

| Compound | LC/MS Results | UV/VIS Results |
|---|---|---|
| Diuron | 0.1840 µg/L | 0.1466 µg/L |
| Diuron | 0.7681 µg/L | 0.8199 µg/L |
| Diuron | 1.2803 µg/L | 1.222 µg/L |
| Diuron | 1.2474 µg/L | 1.4684 µg/L |
| Diuron | 0.1285 µg/L | 0.1206 µg/L |
| Diuron | 1.002 µg/L | 1.2857 µg/L |
| Diuron | 0.3967 µg/L | 0.1746 µg/L |
| Diuron | 1.2903 µg/L | 1.2903 µg/L |
| Diuron | 0.6629 µg/L | 0.6180 µg/L |
| Diuron | 0.9719 µg/L | 1.130 µg/L |
| Diuron | 0.3717 µg/L | 0.3988 µg/L |
| Linuron | 0.59 µg/L | 0.43 µg/L |
| Monuron | 0.63 µg/L | 0.46 µg/L |
| Linuron | 0.75 µg/L | 0.45 µg/L |
| Monuron | 0.56 µg/L | 0.56 µg/L |

TABLE 4
COMPARISON OF REAL WORLD SAMPLE RESULTS

| Compound | LC/MS Results | Post Column Results |
|---|---|---|
| Carbaryl | 0.0075 µg/g | 0.008 µg/g |
| Carbaryl | 0.0183 µg/g | 0.015 µg/g |
| Carbaryl | 0.458 µg/g | 0.58 µg/g |
| Carbaryl | 0.0119 µg/g | 0.0075 µg/g |
| Carbaryl | 1.84 µg/g | 1.35 µg/g |
| Aldicarb | 13.6 µg/L | 12.4 µg/L |
| Carbofuran | 3.5 µg/L | 3.3 µg/L |
| Aldicarb | 12.74 µg/L | 9.6 µg/L |
| Carbofuran | 3.39 µg/L | 2.64 µg/L |
| Aldicarb | 34 µg/L | 16.4 µg/L |
| Carbaryl | 0.101 µg/L | 0.06 µg/L |
| Carbaryl | 0.12 µg/L | 0.09 µg/L |
| Carbaryl | 0.064 µg/L | 0.049 µg/L |
| Methiocarb | 1.86 µg/L | 1.6 µg/L |
| Carbaryl | 0.359 µg/L | 0.15 µg/L |
| Carbaryl | 0.09 µg/L | 0.03 µg/L |
| Carbofuran | 7.6 µg/L | 3.21 µg/L |
| Carbaryl | 2.79 µg/L | 2.81 µg/L |
| Methomyl | 1.5 µg/L | 0.63 µg/L |
| Aldicarb | 28 µg/L | 15 µg/L |
| Carbofuran | 3.76 µg/L | 3.0 µg/L |
| Aldicarb | 27.4 µg/L | 17 µg/L |
| Carbofuran | 3.97 µg/L | 4.0 µg/L |

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WORKFILE ID: C
WORKFILE NAME: 100µL 39857W
SAMPLE # 21 .1df
12/19/89

AREA%

| RT | AREA | TYPE | AR/HT | AREA% |
|---|---|---|---|---|
| 2.70 | 1932 | PV | 0.059 | 0.012 |
| 2.94 | 3026 | PB | 0.026 | 0.018 |
| 3.46 | 10589 | BV | 0.249 | 0.065 |
| 4.73 | 355599 | PV | 0.406 | 2.167 |
| 7.66 | 98408 | PV | 0.787 | 0.600 |
| 10.07 | 86300 | BP | 0.511 | 0.526 |
| 12.53 | 14810 | PV | 0.476 | 0.090 |
| 13.14 | 25448 | VP | 0.476 | 0.155 |
| 15.8 | 17540 | BP | 0.515 | 0.107 |
| 17.42 | 18015 | VV | 0.453 | 0.110 |
| 18.27 | 135270 | VV | 0.413 | 0.825 |
| 20.68 | 33375 | VV | 0.367 | 0.203 |
| 21.75 | 24359 | VV | 0.406 | 0.149 |
| 22.41 | 1214500 | VV | 0.348 | 7.403 |
| 23.52 | 251410 | VV | 0.537 | 1.532 |
| 27.38 | 1.2260E+07 | PB | 0.431 | 74.727 |
| 29.93 | 42388 | BV | 0.410 | 0.258 |
| 32.26 | 11299 | PP | 0.265 | 0.069 |
| 32.81 | 4556 | PP | 0.173 | 0.028 |
| 34.48 | 11884 | PV | 0.239 | 0.072 |
| 34.79 | 24195 | VV | 0.292 | 0.148 |
| 36.93 | 52938 | PV | 0.478 | 0.323 |
| 38.11 | 10381 | VV | 0.253 | 0.063 |
| 39.39 | 43282 | PV | 0.389 | 0.264 |
| 40.35 | 33464 | VV | 0.296 | 0.204 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

55 ANALYSIS OF ENVIRONMENTAL SAMPLES FOR POLYNUCLEAR AROMATIC HYDROCARBONS BY PARTICLE BEAM HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY

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Polynuclear aromatic hydrocarbons (PAH) comprise a class of potentially hazardous compounds of environmental concern. Method 8310 is used to determine the concentration of PAH's in ground water and wastes and is the only high performance liquid chromatography (HPLC) method currently available in the SW-846 Test Methods Manual. To extend the detection of these compounds to mass spectrometric-based methods, the PAH's were selected for a study to evaluate applications of particle beam HPLC/MS. Initial studies with PAH standards indicated that lower molecular weight PAH's (M. W. < 210 daltons) cannot be accurately measured, but that heavier PAH's can be characterized, including those with molecular weights greater than 300 daltons. Thus, particle beam HPLC/MS exhibits the potential to analyze for heavy PAH's not included in current EPA methods. Comparison of chromatograms from the HPLC/UV system with the total ion current traces from the particle beam HPLC/MS shows that the chromatographic integrity was maintained through the mass spectrometer. Statistical optimization techniques were incorporated into the design of the experiments used to test the method. Method detection limits, precision, accuracy, ruggedness, and spectral quality will be discussed. The method was evaluated with standard reference materials.

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contract 68-03-3249 to Lockheed-ESC, 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.

# 56 Current Status of Infrared and Combined Infrared/Mass Spectrometry Techniques for Environmental Analysis

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Background. Currently, the Environmental Protection Agency monitors a few hundred extractable, GC-volatile organic compounds by gas chromatography/mass spectrometry (GC/MS). This approach characterizes only a small subset of volatile organics, uses quadrupole GC/MS alone, and is dependent on the availability of authentic standards for GC retention time confirmation, quantitation, and user created reference spectra. Gas chromatography/Fourier transform infrared spectrometry (GC/FT-IR) is a viable alternative, or a supplementary technique, to GC/MS for environmental analysis. The isomer discrimination and functional group capability of this technique provide useful information which is often unobtainable from GC/MS.

GC/FT-IR Until 1986, the GC/FT-IR technique did not have the sensitivity to monitor weak infrared absorbers at the low nanogram range, but newer FT-IR systems can identify very weakly absorbing polynuclear aromatics (PAH's) at the 25-50 ng level, thereby ensuring the capability to routinely monitor most environmental contaminants at low ppb.

Recent standards-based GC/FT-IR work indicates quantitative precision comparable to that of total and single ion chromatogram GC/MS. Preliminary results on the infrared absorption coefficient approach indicates quantitation capability to within ±25% of the true concentration when a reference spectrum of the unknown compound is unavailable. Such a "semiquantitation" approach, used in conjunction with the FT-IR group frequencies in method 8410, could be the basis of an environmental screening approach.

Directly-Linked gas chromatography/Fourier transform infrared (GC/FT-IR/MS). Although GC/FT-IR is a powerful tool when used alone, it is more powerful when linked to a mass spectrometer creating the technique of GC/FT-IR/MS. Such a technique provided confirmed qualitative information (identification or compound class) on 41 percent of the jointly detected analytes found in six real environmental samples.

Computer Software for Hyphenated FT-IR Techniques. No integrated commercial software is currently available to acquire and process the data generated by linked GC/FT-IR/MS systems. Preliminary versions of such software have been reported but much remains to be accomplished. Needed work includes the optimization of

reference spectral databases (separate volatile and nonvolatile compound spectra, elimination of research chemical spectra (over 80 percent of CIS-NIH-NBS mass spectra), and the addition of new reference spectra from FT-IR and MS users.

Current Status. The current status of the EMSL-LV in-house and extramural GC/FT-IR and GC/FT-IR/MS programs will be discussed, with emphasis on qualitative and quantitative aspects and their implication for the Agency's tentatively identified compounds (TIC) effort.

Notice: This article has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency.

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57 METHOD PERFORMANCE DATA FROM EMSL-LV

Paul Marsden and the Methods Research Branch, U.S. Environmental Protection Agency, Environmental Monitoring and Systems Laboratory, 944 E. Harmon, Las Vegas, Nevada 89119

The Environmental Monitoring and Systems Laboratory at Las Vegas (EMSL-LV) is evaluating a variety of methods, primarily for OSWER monitoring programs, with the support of our on-site contractor, Lockheed Engineering Services Corporation. Our laboratory activities range from short-term method performance studies to long term research projects. Several long-term projects, off-line supercritical extraction (SFE), infrared spectrometry (GC/FT-IR), preconcentration for trace level metals analysis, inductively coupled plasma/mass spectrometry (ICP/MS), and liquid chromatography/mass spectrometry (LC/MS), are being presented as separate papers at this symposium. This presentation will provide a sampling of results from EMSL-LV performance studies of useful monitoring techniques; description of experimental design will be minimal.

(1) Table-top mass spectrometers are now available that offer lower detection limits than standard "floor model" quadrupole instruments. Data will be presented on the calibration linearity and the performance of ion trap and mini-quad systems for the analysis of complex waste extracts. (2) On-line SFE has been applied to analysis of fly ash for PAH's, dioxins, and dibenzofurans. Although on-line SFE is a more difficult technique to apply routinely than the off-line method, it can give useful information rapidly with little sample preparation and requires no solvents. (3) The Turbovap is a commercial

device that allows evaporation of organic extracts without the attention of a technician. Data will be presented on the recovery of CLP target compounds using the Turbovap. (4) GC retention gaps may be used routinely in the laboratory to make large volume injections of solvent or to allow determination of polar analytes. Performance data, analyte lists, and matrix suitability will be provided for these modified GC injectors. (5) The electron capture detector (ECD) is used to provide the requisite sensitivity for halogenated toxicants. Unfortunately, the ECD also responds to non-halogenated chemicals causing method interferences and elevated chromatographic baselines. Performance data for the more selective electrolytic conductivity detector (Hall) will be provided. Suitability of the Hall detector for routine analysis of organochlorine pesticides in water and solid samples will also be discussed.

NOTICE: Although the research described in this article has been supported by the United States Environmental Protection Agency, it has not been subjected to policy review and does not necessarily reflect the views of the Agency. Therefore, no official endorsement of specific techniques should be inferred. Mention of trade names or commercial products does not constitute endorsement nor recommendation for use.

58

# SUPERCRITICAL FLUID EXTRACTION

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The driving force behind the use of supercritical fluids is 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. Supercritical fluids have low viscosities and thus the solute diffusivities are much higher in supercritical fluids than in the common solvents currently used in conventional extraction techniques. Consequently, extraction efficiencies are much higher, the extraction conditions can be adjusted to separate analytes selectively, and the solvent and the extract can be completely separated in the release step by reducing the pressure to ambient pressure. We are in the process of developing an efficient extraction technique for soil and sediment matrices using supercritical fluids. Initial efforts were directed at supercritical fluid extraction using carbon dioxide with and without modifiers. The effects of pressure, temperature, sample moisture content, sample size, analytes concentration, and matrix were investigated for various classes of compounds including polynuclear aromatic hydrocarbons, polychlorinated biphenyls, organochlorine pesticides, chlorinated benzenes, phthalate esters, organophosphorus pesticides, etc. All experiments were performed using a Suprex Model SE-50 supercritical fluid extractor. Extracts were analyzed off-line by gas chromatography with either an electron capture, a flame ionization, or a flame photometric detector. A generic protocol on the use of supercritical fluid

extraction in the analysis of environmental and hazardous waste samples has been drafted.

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.

59

# THE UTILIZATION OF QUANTITATIVE SUPERCRITICAL FLUID EXTRACTION FOR ENVIRONMENTAL APPLICATIONS

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## ABSTRACT

The usefulness and ease of utilizing supercritical fluid extraction (SFE) directly coupled to capillary gas chromatography (GC) as quantitative or qualitative analytical problem-solving tools will be demonstrated. As an alternative to conventional liquid solvent extractions, SFE presents itself as a means to achieve high extraction efficiencies of different compounds in complex solid matrices in very rapid time frames. Moreover, SFE has an additional advantage of being able to achieve distinct extraction selectivities as a function of the solubilizing power of the supercritical fluid extracting phase. For on-line SFE/GC, the extraction effluent is directly transferred to the analytical chromatograph. On-line SFE/GC involves the decompression of pressurized extraction effluent directly into the heated, unmodified split capillary split injection port of the GC. In this respect, SFE introduction into GC can be used as an alternative means of GC injection, comparable to such modes of injection as pyrolysis and thermal desorption.

## INTRODUCTION

Supercritical fluids have been used successfully for years for different industrial applications (1). A large scale application of supercritical fluid extraction (SFE), for example, is to increase crude oil recoveries from porous rocks in oil fields by pumping in gases such as carbon dioxide and nitrogen. In this environment, the pressures and temperatures are high enough that supercritical conditions exist and contribute to enhanced recoveries. Extractions using supercritical fluids are attractive when compared to conventional liquid extractions for a number of reasons. While supercritical fluids have solvent strengths that approach those of liquid solvents, they have lower viscosities ($10^{-4}$ N-sec/$m^2$ versus $10^{-3}$ N-sec/$m^2$) and higher solute diffusivities ($10^{-4}$ c/$m^2$/sec versus $10^{-2}$ $cm^2$/sec). These properties improve mass transfers from solid or liquid matrices and thus significantly decrease the overall time needed for supercritical fluid extractions. By increasing the density, the solvent strength of a supercritical fluid increases. Therefore, conditions can be optimized for the extraction of a specific solute or class of solutes from a complex matrix by changing the extraction pressure or temperature. Close to the critical point of the supercritical fluid, temperature or pressure changes can change solute solubilities by a factor of 100 or even 1000. By using different supercritical fluids for extractions, such as carbon dioxide, nitrous oxide, and sulfur hexafluoride, preferential extraction can be achieved for different solutes. Moreover, the use of fluids that have low critical temperatures (i.e. $CO_2$ and $N_2O$) allow extractions under thermally mild conditions, thereby protecting thermally labile components. Since supercritical fluids, such as $CO_2$, $N_2O$ and $SF_6$ are gases at room temperature, off-line component collection or concentration is greatly simplified. Because supercritical fluids undergo expansive (Joule-Thompson) cooling upon decompression, even volatile components can be quantitatively and efficiently collected into solvents off-line after extractions. It is also possible to directly interface supercritical fluid extraction with analytical chromatography, such as capillary gas chromatography (GC) and, supercritical fluid chromatography (SFC). Recent reports have demonstrated the potential of using SFE as an alternative to time consuming, less efficient and less quantitative conventional liquid solvent extraction techniques. Specific solutes ranging from environmental priority pollutants to spices and fragrance components have been qualitatively and quantitatively

extracted using supercritical fluids from a variety of liquid and solid sample matrices (2-10). Direct interfaces of SFE to capillary GC and SFC (7-20) have been also demonstrated.

The benefits of directly coupling SFE to GC are that no sample handling is required between the extraction step and the GC separation step and that extraction effluents can be quantitatively and reproducibly transferred for on-the-fly analyses. When employing flame ionization detectors, no detector responses (i.e. solvent peaks) appear for reasonably pure supercritical fluid grade $CO_2$ or $N_2O$. This permits the determination of volatile solutes which are often masked by liquid solvents when using conventional extraction techniques. Moreover, when modifiers such as methanol or propylene carbonate, are used to augment the solubilizing power of primary supercritical fluids, they elute as distinct peaks in respective GC or SFC separations. The limitations of coupling SFE to GC are defined by the volatility constraints of higher molecular weight solutes in complex matrices that may not necessarily completely elute from GC columns.

This paper will demonstrate the applicability of SFE/GC techniques towards the quantitative and qualitative characterization of some environmental matrices.

## EXPERIMENTAL

On-line SFE/GC was performed on a Suprex Model SFE/50 stand-alone extractor equipped with an electronic Valco four-port high pressure selector valve and a Hewlett-Packard Model 5890 gas chromatograph equipped with a split/splitless capillary injection port and flame ionization detector. Figure 1 shows a schematic diagram of the SFE/GC interface. The Suprex SFE/50 extractor consists of a 250ml syringe pump with pressure limits up to 500 atm. The oven of the extractor was large enough to accommodate multiple extraction vessels or extraction vessels up to 50 ml in volume. The electronically actuated Valco four-port selector valve was used to perform the static and dynamic extractions and to divert the extractor effluent flow into the injection port of the GC. The controlling software of the Suprex SFE/50 permitted the automatic operation of the four-port selector valve and automatically initiated the run on the GC after dynamic transfer of the extractor effluent. Both 1/32 inch O.D. X 0.007 inch I.D. stainless steel and 15 or 25 micron I.D. fused silica tubing have been used as transfer lines between the SFE/50 and the 5890 gas chromatograph. When stainless steel tubing was used, it was necessary to restrict the flow by crimping to allow a flow of 40-80 ml/minute of expanded decompressed gas at the specified extraction pressure. The transfer line tubing was inserted 35-40 mm directly into the split/splitless capillary injection port which was kept at 225°C to minimize the Joule-Thompson cooling which occurred when the supercritical fluid phase decompressed. For purposes of solute focusing, it was also necessary to cryogenically cool the gas chromatographic oven. The oven was kept cool long enough to allow the dynamic transfer of the respective vaporized solutes onto the head of the capillary gas chromatographic column. The level of cooling depended on the volatility of the solutes of interest. Generally, the GC oven was never cooled below -50°C which would cause freezing of the decompressed carbon dioxide.

## RESULTS AND DISCUSSION

The use of SFE on a quantitative analytical scale presents a number of distinct advantages when compared to conventional solvent extractions. Depending on the sample matrix, the nature of supercritical fluids allows for rapid extractions in usually less than one hour with high extraction efficiencies. Moreover, the ability to transfer the SFE effluent to a GC or SFC in an automated fashion permits sensitive quantitative or qualitative determinations of solutes in different solid or liquid matrices.

The quantitative reproducibility of on-line SFE/GC was investigated by performing comparative triplicate analyses using SFE with split GC and flame ionization detection and conventional syringe split GC injections of methylene chloride extracts of the spiked clay shown in Figure 2. The operating conditions for SFE included 400 atm pressure of supercritical $CO_2$ at 60°C for 20 minutes using 650mg quantities of clay in a 500 microliter SFE vessel. A 50 meter X 0.2 mm I.D. methyl silicone (PONA) capillary GC column was used to provide the separation. The SFE effluent was transferred directly to the capillary GC injection port using a fused silica 15 micron I.D. transfer line. All peak identities were confirmed using a mass spectrometer. Table I lists the peak area reproducibility results for selected priority pollutants in the clay.

Table 1. Comparison of Peak Area Reproducibility for Priority Pollutants in Spiked Clay with On-Line SFE/GC and Conventional GC Split Injections.

| Priority Pollutant | % RSD* SFE/GC | % RSD* Split GC | Concentration (ng/ul) |
|---|---|---|---|
| 2-chlorophenol | 1.8 | 2.0 | 50 |
| Naphthalene | 2.1 | 4.6 | 200 |
| 1-chloronaphthalene | 5.6 | 8.1 | 60 |
| Hexachlorobenzene | 5.8 | 7.8 | 50 |
| Phenanthrene | 4.0 | 3.8 | 300 |
| Pyrene | 4.2 | 5.6 | 200 |
| Benzo(a)pyrene | 5.5 | 6.4 | 20 |

*Based upon raw peak areas resulting from an average of three replicates.

As can be seen, the SFE/GC results compared favorably with those obtained by conventional syringe GC injections. Moreover, the percent relative standard deviations for the SFE/GC-FID results include contributions from sample inhomogeneity, weighing, and technique errors as opposed to only injection and integration errors for the methylene chloride extract injections. It was also very important to thoroughly grind the clay sample before loading the SFE vessel to obtain consistent results. Certain matrices, such as some clays, have sufficient density to trap certain solutes for longer periods of time thereby disrupting the efficiency of the extraction process. Figure 3 shows a SFE/GC-FID chromatogram of another environmentally important sample matrix namely, marine sediment. Approximately 1 gram of this sediment was extracted in a 5 milliter vessel at 300 atm using supercritical $CO_2$ at 60°C for 40 minutes. The same 50 meter PONA column was used to provide the GC separation. As can be seen, the sediment was contaminated with a mixture of aroclors at 5 to 10 ppm levels (as determined by external standard calibration standards and retention times). If an electron capture detector would have been used, significantly more sensitivity and selectivity could have been provided for the aroclors. Since this particular sample contained significant amounts of water (~30%), approximately 1 gram of sodium sulfate was added to the sediment in the extraction vessel as an adsorbent. In general, on-line SFE with a split GC injector is more capable of handling wet samples without restrictor plugging as opposed to on-line SFE with an on-column GC injector (18). The conventional sample preparation procedure for this marine sediment generally involves 6-8 hours of multi-solvent extractions and 2 hours of concentration before injection into a GC-MS as opposed to a total sample preparation and analysis time of 80 minutes for the SFE/GC technique. Another example of using on-line SFE/GC for quantitative analyses is shown in Figure 4 with the determination of aromatics and chlorinated aromatics in contaminated soil which was taken from a spill site. Approximately 170 mg of the soil was extracted in a 0.5 ml

vessel at 375 atm using supercritical CO2 at 50oC for 30 minutes. A 30 meter x 0.25 mm I.D. DB-Wax capillary column was used to provide the GC separation. Hexachlorobenzene was used as an internal standard which was spiked directly into the soil before extraction. Table II lists the quantitative results for replicate analyses of the soil.

TABLE II. Replicate SFE/GC-FID Determinations of Aromatics and Chlorinated Aromatics in Contaminated Soil

| | CONCENTRATION (PPM)* | | | |
|---|---|---|---|---|
| COMPOUND | 1 | 2 | 3 | 4 |
| ethylbenzene | 44 | 40 | 42 | 43 |
| cumene | 30 | 30 | 32 | 34 |
| 2-chloronaphthalene | 51 | 50 | 51 | 48 |
| 1,2,4 trimethylbenzene | 25 | 26 | 29 | 24 |

*Based upon internal standard calculations

## CONCLUSIONS

The use of directly coupled SFE/GC as an analytical techniques has shown excellent potential for the quantitative and qualitative characterization of different solutes in different matrices of environmental significance Using on-line SFE/GC, an entire analysis which includes the extraction, concentration, clean-up, and analytical separation steps, can be accomplished in usually less than one hour. Selective extractions can also be performed by varying parameters such as pressure, temperature, and type of supercritical fluid extracting fluid. Moreover, the analytical versatility and flexibility of the technique can be further enhanced by the utilization of such chromatographic detectors as mass spectrometry, electron capture, nitrogen-phosphorus, and sulfur-specific.

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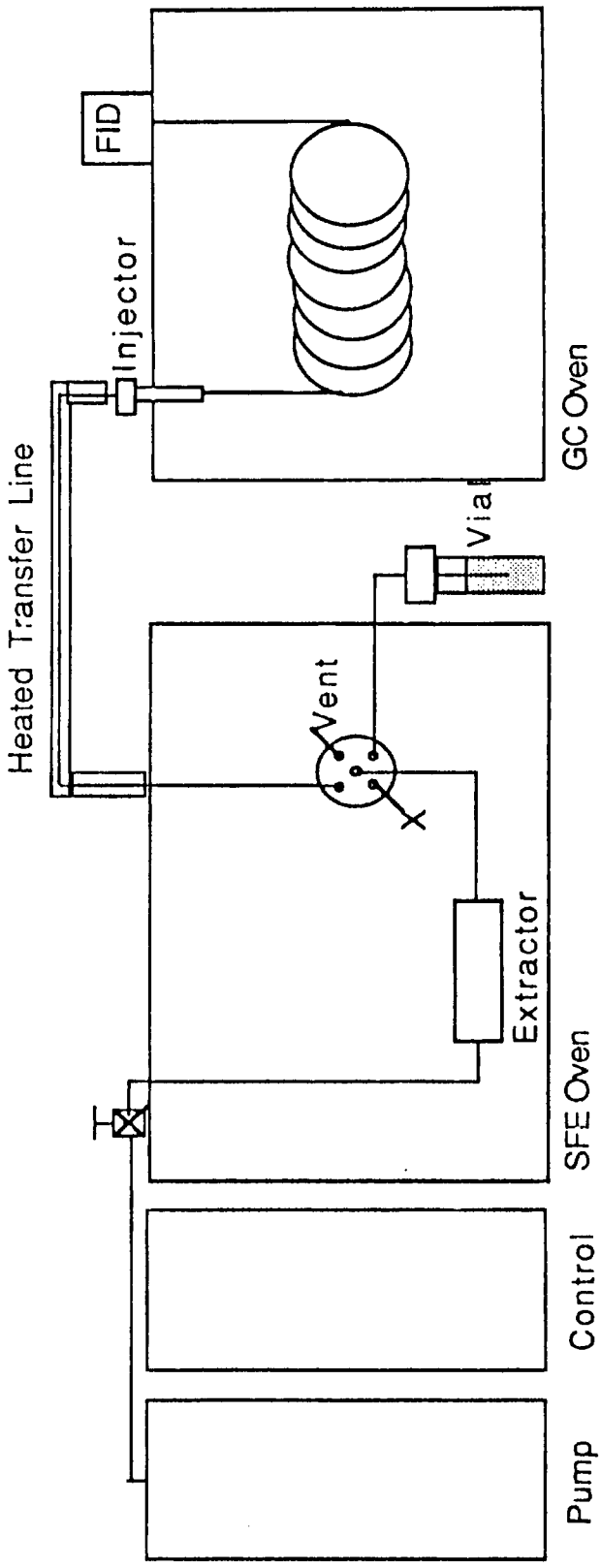


**Figure 1. On-Line SFE/GC Schematic Diagram**

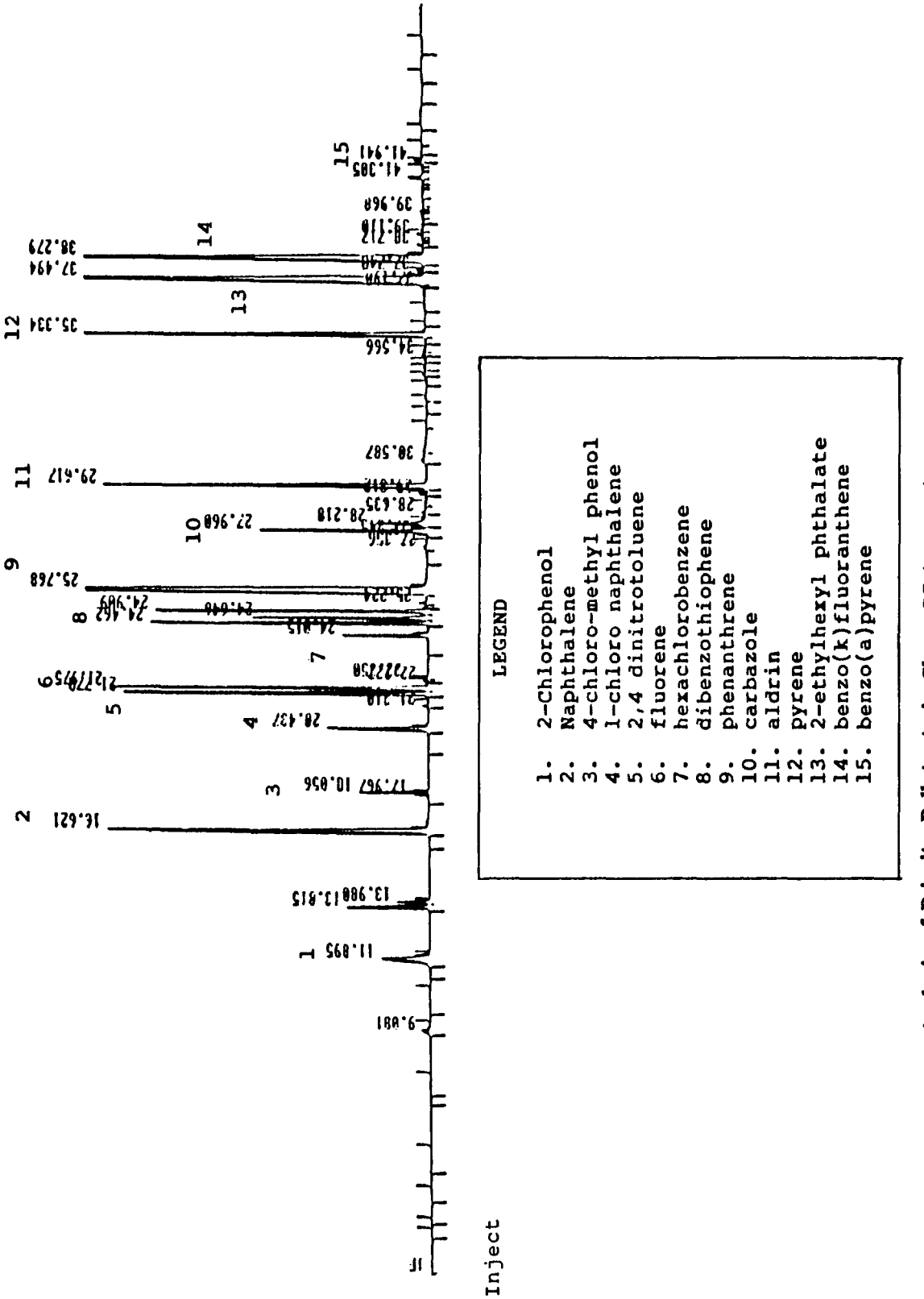


**Figure 2. SFE/GC-FID Analysis of Priority Pollutants in Clay. GC temperature program: 0°C (20 minutes) programmed to 300°C at 7°C/minutes.**

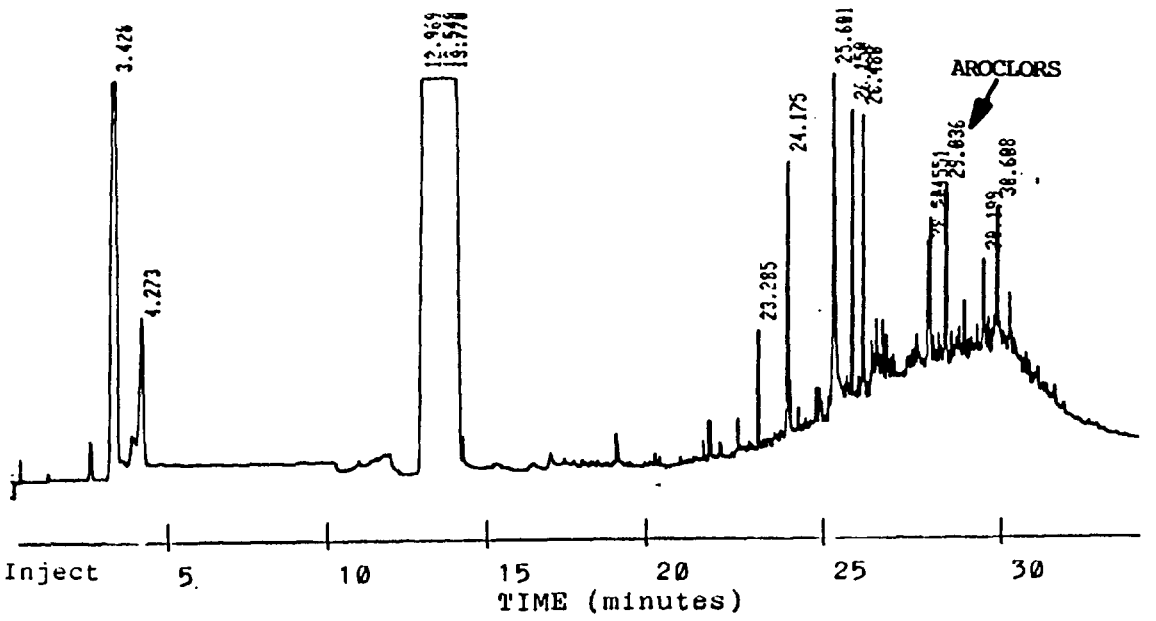


**Figure 3.** **SFE/GC-FID Analysis of aroclors in marine sediment at low ppm levels. GC temperature program: -15°C (5 minutes) programmed to 300°C at 15°C/minute.**

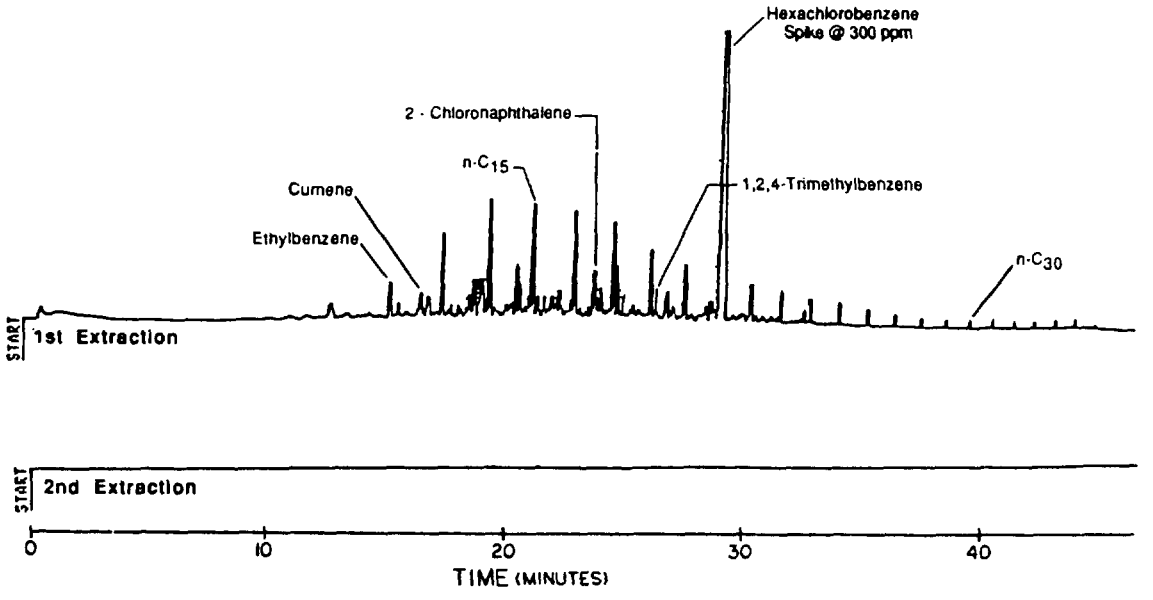


**Figure 4.** **SFE/GC-FID Analysis of pollutants in soil. GC temperature program: 30°C (7 minutes) programmed to 310°C at 7°C/minute.**

60

# QUANTITATIVE SUPERCRITICAL FLUID EXTRACTION (SFE) AND COUPLED SFE-GC ANALYSIS OF ENVIRONMENTAL SOLIDS AND SORBENT RESINS

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## ABSTRACT

The extraction and concentration of organic pollutants from environmental solids and sorbent resins is often the slowest and most error-prone step of an entire analytical scheme. Liquid solvent extractions take several hours to perform, and result in a diluted sample that often must be concentrated prior to analysis. In contrast, supercritical fluid extraction (SFE) can yield quantitative recovery of organic pollutants from soils, sediments, air particulates and sorbent resins in a few minutes. SFE is simple and inexpensive to perform, and generates no liquid solvent waste. Since many supercritical fluids are gases at room temperature, analyte concentration steps are simplified, and the SFE step can be directly coupled with capillary gas chromatography (SFE-GC) using conventional split or on-column injectors. On-column SFE-GC yields maximum sensitivity since all of the extracted analytes are quantitatively transferred into the capillary GC column for cryogenic trapping prior to conventional GC analysis. With SFE-GC, quantitative analysis of environmental solids including extraction, concentration, and GC separation can be completed in less than one hour. Excellent quantitative agreement with National Institute of Standards and Technology (NIST) certified standards has been achieved. The use of SFE and coupled SFE-GC for the rapid and quantitative extraction and analysis of PCBs, PAHs, heteroatom-containing PAHs, and pesticides from a variety of matrices including soils and sediments (including the new standard marine sediment from NIST), and Tenax and polyurethane foam (PUF) sorbent resins will be described. Multiple extractions, spike recoveries, and the extraction and analysis of certified standard reference materials will be described to support quantitative claims for SFE and SFE-GC.

## INTRODUCTION

The development of methods for extracting organic pollutants from environmental samples has received relatively little attention from analytical chemists, particularly when compared to the level of research effort that has been focused on separating and identifying organic pollutants after they have been extracted from the solid sample. While analytical methods such as GC/MS have been developed that can separate and identify hundreds of compounds per hour, the preparation of environmental samples still commonly uses extraction techniques (e.g., liquid solvent extraction in a Soxhlet apparatus) that were in routine use when Tswett first reported chromatographic separations in 1906. Interest in developing sample extraction methods that do not require large volumes of liquid solvents has been fueled by desires to increase sample throughput at a lower cost, to reduce the personnel exposure and waste disposal problems associated with liquid solvents, to selectively extract target analytes, to develop extraction methods that are field-portable, as well as to develop extraction methods that can be directly coupled with conventional chromatographic instrumentation (1-17).

Supercritical fluids have several characteristics which make them attractive for extracting organic pollutants from environmental solids and sorbent resins. Since mass transfer in a supercritical fluid is ca. two orders of magnitude faster than in liquid solvents, quantitative SFE extractions can often be performed in 10 to 30 minutes. The solvent strength of a single supercritical fluid can be controlled by simply changing the extraction pressure (and to a lesser extent, the temperature), which allows the solvent strength to be optimized for particular compounds of interest. Frequently-used supercritical fluids such as $CO_2$ and $N_2O$ are gases at ambient conditions, which simplifies concentration steps and allows the SFE step to be directly coupled with capillary gas chromatography (SFE-GC). The use of supercritical $CO_2$ is particularly attractive since it is non-toxic, relatively inert, and inexpensive (on a per extraction basis). The venting of $CO_2$ into the atmosphere during sample concentration steps is also much less objectionable than present methods which result in the emission of huge quantities of liquid solvents. (For example, a chemist that uses a gallon of gasoline to drive to work causes ca. 10 kg of $CO_2$ to be emitted. The same 10 kg of $CO_2$ would allow several hundred SFE extractions to be performed.)

As for any newly emerging analytical technique, the generation of qualitative results using SFE has been much simpler than the generation of quantitative results. This paper focuses on the use of SFE and SFE-GC to perform quantitative extractions and analyses of environmental samples ranging from soils and marine sediments to air particulates to pollutants collected on sorbent resins. The quantitative abilities of SFE and SFE-GC will be demonstrated by multiple extractions, spike recoveries, and the analysis of certified reference materials.

## EXPERIMENTAL

Supercritical fluid extractions were performed using syringe-type supercritical fluid pumps (Suprex and ISCO) and either $CO_2$, $N_2O$, or $CO_2$ with added methanol modifier. Supercritical pressures were maintained inside the extraction cells (0.1 to 10 mL depending on sample size) with 20, 25, or 30 $\mu$m i.d. X 150 $\mu$m o.d. fused silica capillary tubing for outlet restrictors. Temperature was maintained during extraction by inserting the cell into a thermostatted tube heater. For non-coupled SFE, the extracted species were collected by inserting the outlet restrictor into a vial containing ca. 2 mL methylene chloride (3,8). GC/FID and GC/MS analyses of these extracts were performed in a normal manner. The direct coupling of the supercritical fluid extraction step with gas chromatography (SFE-GC) was achieved by inserting the SFE outlet restrictor directly into the capillary gas chromatographic column through the on-column injection port (on-column SFE-GC, refs 4,13) or by inserting the restrictor into a split/splitless injection port through an SGE septumless injector (split SFE-GC, refs 9,15). Extracted species were cryogenically trapped in the capillary GC column which was held at -30 to 5 °C. After the extraction was completed, the restrictor capillary was withdrawn from the injector and gas chromatographic analysis was performed in a normal manner. For further experimental details on the methods used for the samples described in this study, see references 3, 8, and 14 (for off-line SFE) and references 4 and 13-15 (for on-line SFE-GC).

## RESULTS AND DISCUSSION

Proving quantitative recovery of analytes is difficult since spiked samples do not necessarily represent the native matrix, and the exact concentration of a pollutant cannot be known in a real-world sample. Three general approaches have been used in our laboratory to investigate the ability of SFE to yield quantitative recovery of organic pollutants from environmental solids and sorbent resins. These approaches, and representative results are discussed below.

### Multiple Extractions of Native Analytes

A simple method to estimate the ability of SFE to obtain quantitative extraction is to extract the same sample multiple times. This approach assumes that quantitative recovery has been achieved when no more analyte can be extracted. While this assumption is probably valid when an analyte is associated with only one type of site on the sample matrix, it is possible that the target analyte is bound to several different sites in an environmental matrix, and that a particular extraction condition only recovers analytes associated with "weak" sites. Nonetheless, multiple extractions do provide a

simple way to estimate when an extraction is completed. This is demonstrated in Figure 1 by multiple SFE-GC extractions and analyses of pesticides from an agricultural soil sample. As can be seen by the atomic emission detector (AED) chromatograms for chlorine at 479 nm, the second 10-minute extraction had no significant peaks, indicating that the first 10-minute extraction was sufficient to quantitatively recover the aldrin and dieldrin pesticides.

Multiple extractions (using SFE-GC/MS) of a polyurethane foam (PUF) sorbent that had been soaked in a coal gasification wastewater are shown in Figure 2. Note that the first 10-minute extraction (top) had high concentrations of the phenols and N-heterocycles, while the second 10-minute extraction yielded no significant species indicating that the first 10-minute SFE step was sufficient to quantitatively recover the pollutants from the PUF sorbent.

For many environmental matrices, the largest quantity of pollutants are extracted very rapidly, but smaller quantities of the same pollutants continue to be found in extracts collected after "quantitative" recovery was thought to have been achieved. This is demonstrated in Figure 3 by extraction rate plots for PAHs from soil collected from a railroad bed. This 1-gram sample was extracted off-line using ca. 1 mL/minute of supercritical $CO_2$ (400 atm). Several fractions were collected throughout the extraction and analyzed by capillary GC to allow the extraction rate curves to be constructed (percent recovery data is based on the total quantity of each analyte extracted in 100 minutes). As shown in Figure 3, fluorene, phenanthrene, and pyrene were recovered better than 90% during the first 15 minute extraction indicating that not much additional time would be needed to achieve quantitative extraction. However, traces of all these species were still found in the extract collected from 70 to 100 minutes. Also note that the extraction rates are slower as the molecular weight of the PAH increases. While the oxygen-containing PAHs (e.g., dibenzofuran) showed extraction rates like those of the PAHs having similar molecular weights, the N-containing PAH (carbazole) was among the slowest species to extract.

## Spike Recoveries

Spike recoveries are also utilized to determine the ability of SFE and SFE-GC techniques to yield quantitative results. Spikes have the advantage that the analyst knows what quantity of the test analytes has been added to a test matrix, and thus can know when quantitative recovery has been achieved. However, the use of spike recoveries is always hampered by the question of how representative the spike compounds are of the "real" organic pollutants found in a particular matrix. Spike recoveries may be most valid for determining extraction efficiencies from sorbent resins, since samples collected on sorbents are normally extracted relatively soon, and do not have the chance to "age" like solids such as soil and air particulate matter. The use of spike recoveries is demonstrated

in Figures 4 and 5 by the off-line SFE of PAHs from Tenax-GC resin; and alkanes, PAHs, heteroatom-containing PAHs, and PCBs from a PUF sorbent plug. Note that PAHs ranging from naphthalene (M=128) to coronene (M=300) were quantitatively recovered from the two sorbent resins in 15 to 20 minutes. Interestingly, carbazole was not quantitatively recovered from the PUF sorbent with a 20-minute extraction and was also the slowest extracting species from the railroad bed soil (Figure 3). However, PCBs extract readily from the PUF and were quantitatively recovered in 10 minutes.

## Extraction of Certified Standards

Perhaps the most convincing demonstration of the abilities of SFE to yield quantitative recoveries results from the extraction and analysis of certified standard reference materials. The National Institute of Standards and Technology (NIST) has three native environmental matrices for which they have certified the concentrations of several PAHs based on 16 to 48 hour Soxhlet extractions. We have determined the concentrations of the individual PAHs on each of these standards using off-line SFE (for the diesel exhaust particulate, SRM 1650), on-column SFE-GC (for the urban dust, SRM 1649), and split SFE-GC (for marine sediment, SRM 1941). A comparison of the results obtained based on conventional liquid solvent extractions (NIST certified concentrations) and our SFE techniques are shown in Figures 6, 7, and 8. SFE gave excellent agreement with the certified concentrations for all of the matrices and PAHs, yet SFE required only 10 to 30 minutes per extraction (compared to 16-to 48-hours for the liquid solvent extractions used by NIST). Also note that both the on-column and split SFE-GC analyses (urban dust and marine sediment) required less than one hour per sample including sample extraction, concentration, and GC separation. In addition, SFE required either no liquid solvent (for SFE-GC) or reduced the amount of liquid solvent used from ca. 500 mL/sample to ca. 2 mL/sample (for off-line SFE).

## SUMMARY

Quantitative extraction and analysis of a variety of organic pollutants from a range of environmental solids has been demonstrated by spike recoveries, multiple sequential extractions, and the analysis of certified standard reference materials. Although SFE and SFE-GC techniques are undergoing rapid development, we have found some general comments that are useful to consider before attempting to develop and utilize quantitative analytical-scale SFE methods:

1) The most widely used supercritical fluids such as $CO_2$ lack sufficient polarity to extract polar and high molecular weight analytes from most matrices. Unless very non-polar analytes (e.g., n-alkanes) are being extracted, extraction efficiencies are

better at high pressures (e.g., 400 atm) than relatively low pressures (e.g., 200 atm). As a very general rule-of-thumb, organic pollutants that can be analyzed using conventional capillary GC techniques are likely to be quantitatively extracted with pure $CO_2$ or $N_2O$ at pressures around 400 atm, although the addition of a solvent polarity modifier may be necessary, particularly for highly sorptive matrices such as fly ash (2,6).

2) The flow rate (and total volume) of the supercritical fluid used for an extraction is very important to monitor. Higher flow rates make it more difficult to collect the extracted analytes since the volume of the supercritical fluid expands greatly when depressurized to ambient pressure (e.g., 1 mL/min supercritical $CO_2$ expands to ca. 500 mL/min of gaseous $CO_2$). In our experience, analytes can be efficiently collected using off-line SFE with supercritical fluid flows of up to ca. 1.5 mL/min, while on-line SFE is limited to flows of ca. 0.2 to 0.5 mL/min.

3) Because of the flow and analyte collection considerations described above, SFE works best with smaller samples ($<10$ gram for off-line SFE, and $<1$ gram for coupled SFE-GC), simply because the total volume of the cell (and associated dead volumes between the individual particles of sample) can be smaller. Larger samples can be quantitatively extracted, if necessary, but will normally require longer extraction times, and more elaborate extraction cells. In addition to using smaller samples, extraction times can also often be shortened by completely filling the extraction cell (to reduce void volume), particularly when cells larger than 1 mL are used.

## ACKNOWLEDGEMENTS

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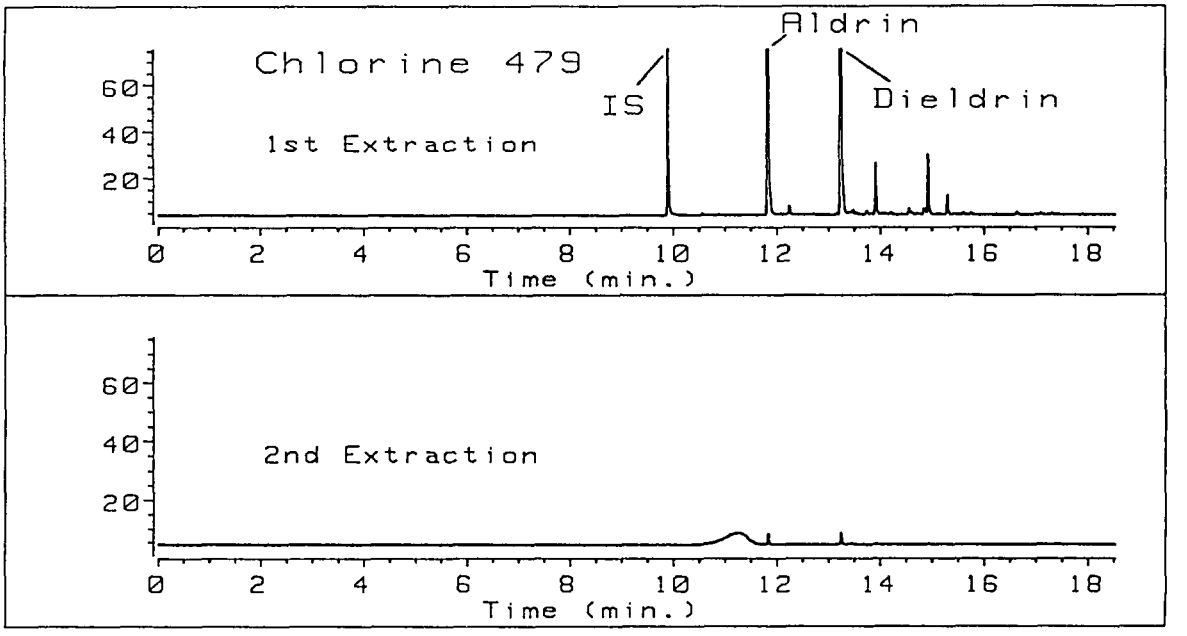


Figure 1: Sequential SFE-GC/AED (atomic emission detector) analyses of a 100 mg soil contaminated with ca. 40 ppm of pesticides. The chromatograms show the emission line for chlorine. Each extraction was for 10 minutes using 400 atm $CO_2$ (45 °C). The oven was held at 5 °C during the extraction step, then rapidly heated to 70 °C, followed by a temperature program at 15 °C/min to 320 °C. Separations were performed with a 20 m DB-5 x 250 $\mu$m i.d. (0.25 $\mu$m film thickness) column.

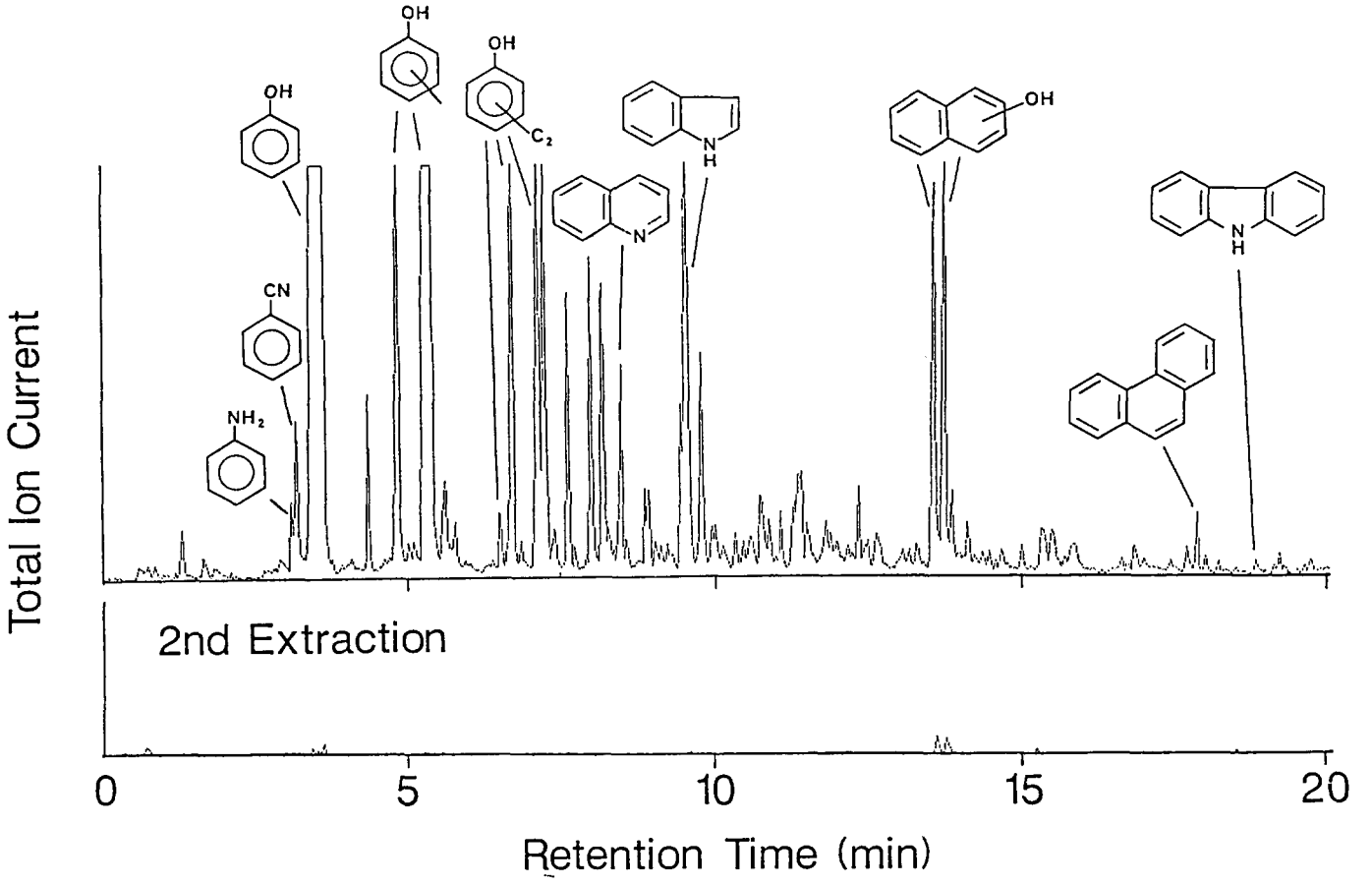


Figure 2: Sequential split SFE-GC/MS analyses of a wet PUF sorbent plug that had been soaked in a coal gasification wastewater. Each extraction was performed with 400 atm $CO_2$ (50 °C) for 10 minutes. The oven was held at 5 °C during the extraction step, then rapidly heated to 70 °C, followed by a temperature program at 8 °C/min to 320 °C. Separations were performed with a 20 m DB-5 x 250 $\mu$m i.d. (0.25 $\mu$m film thickness) column.

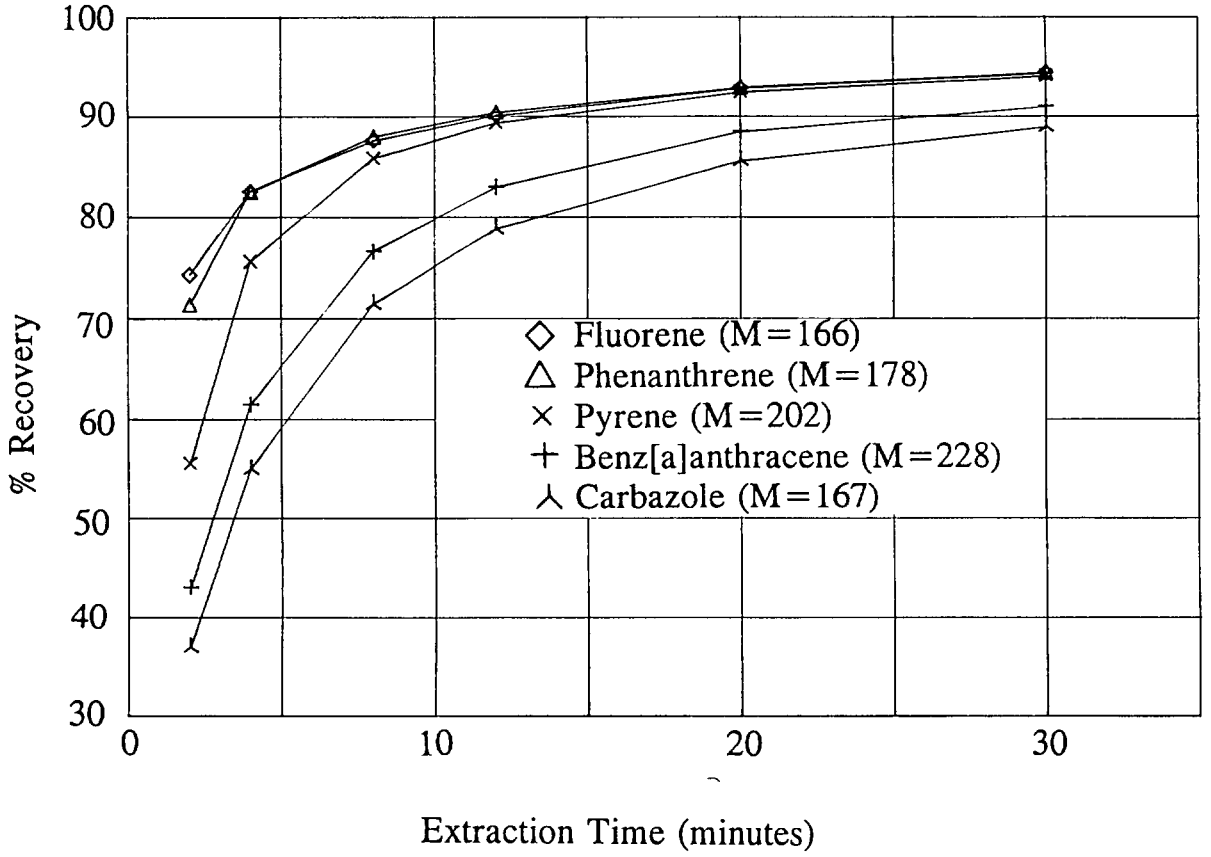


Figure 3: Extraction rates of PAHs from railroad bed soil. A 1-gram sample was extracted off-line at ca. 0.5 mL/min $CO_2$ (400 atm, 50 °C). The recoveries for each PAH was based on the assumption that quantitative recovery was achieved in 100 minutes.

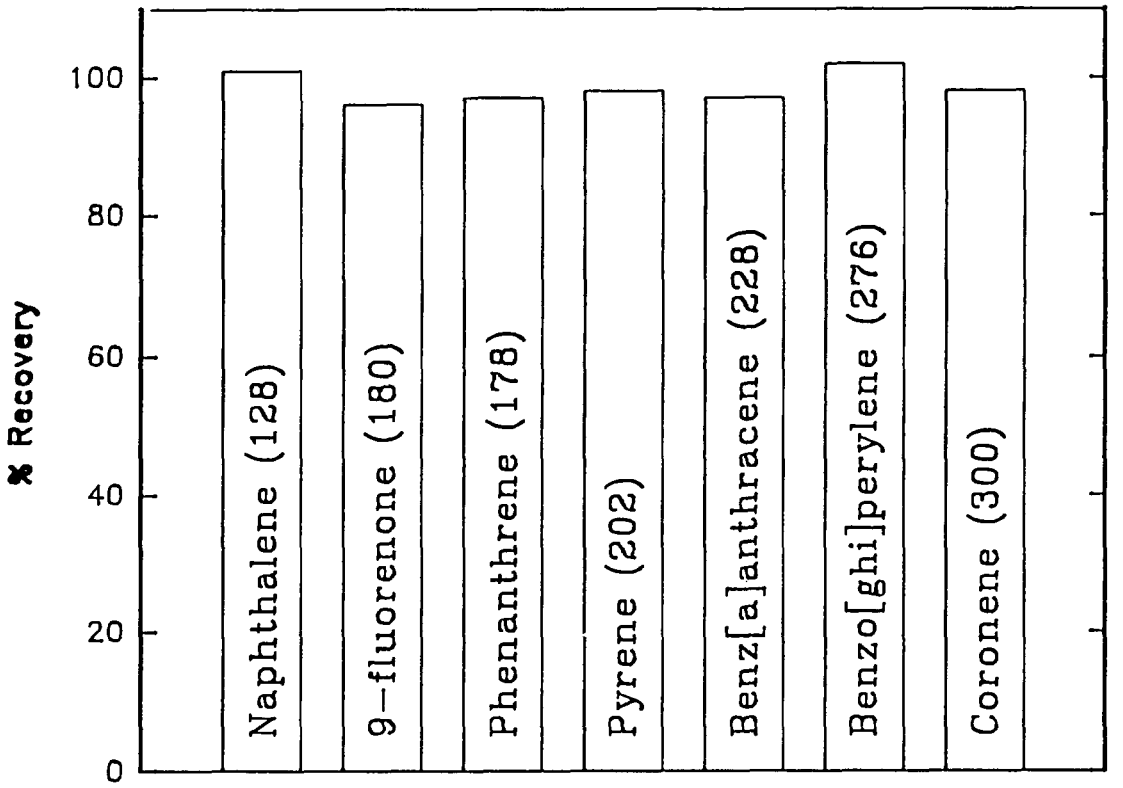


Figure 4: Recovery of PAHs from Tenax-GC using a 15-minute off-line extraction with $CO_2$ at 200 atm (45 °C). Adapted from reference 3.

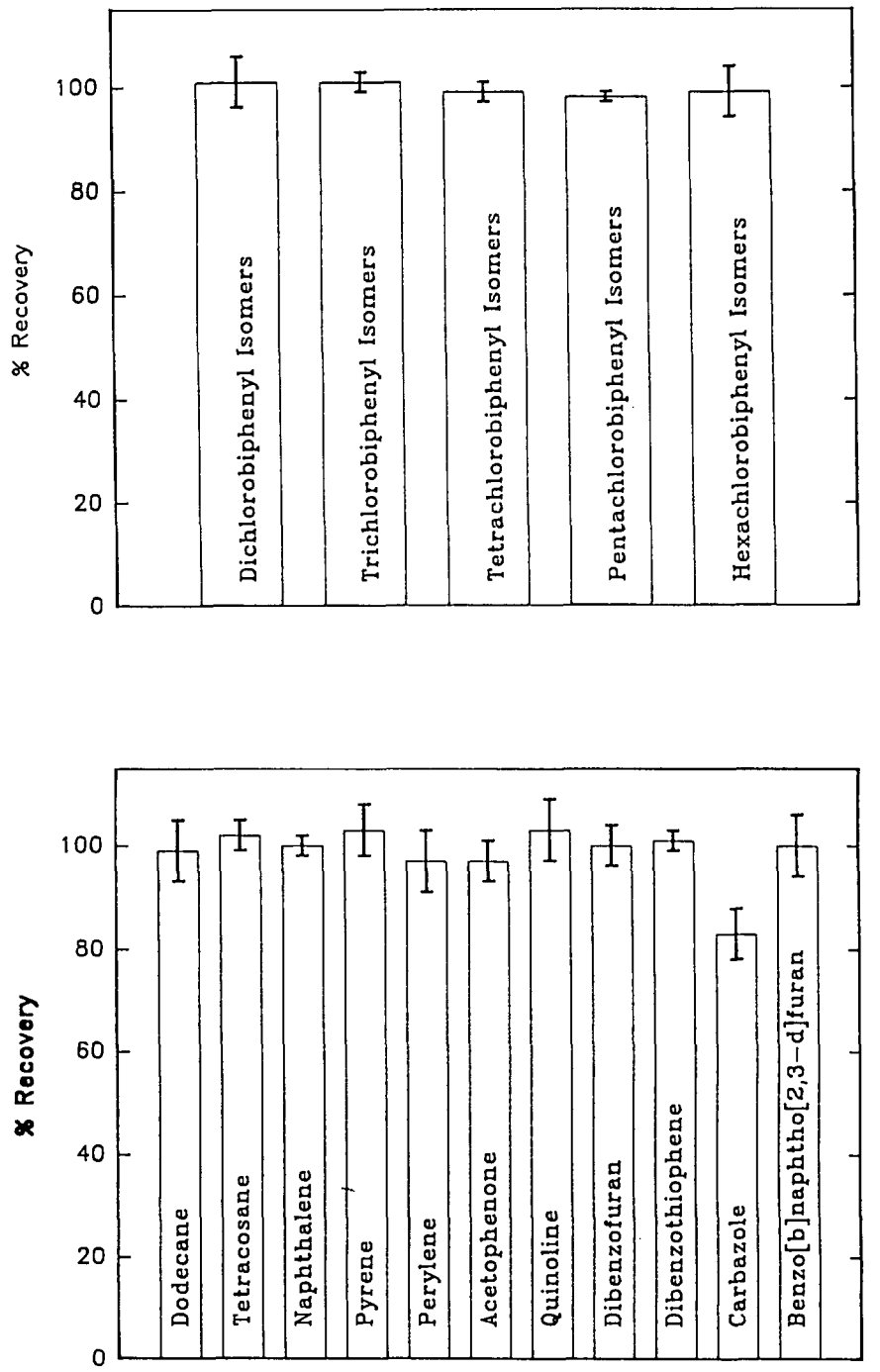


Figure 5: Recovery of organic pollutant spikes from polyurethane foam (PUF) using off-line SFE with 380 atm $CO_2$. Extraction times were 10 minutes for the PCBs (top) and 20 minutes for the alkanes, PAHs, and heteroatom-containing PAHs (adapted from reference 14). The error bars represent three replicate extractions for the PCBs, and four replicate extractions for the remaining spikes.

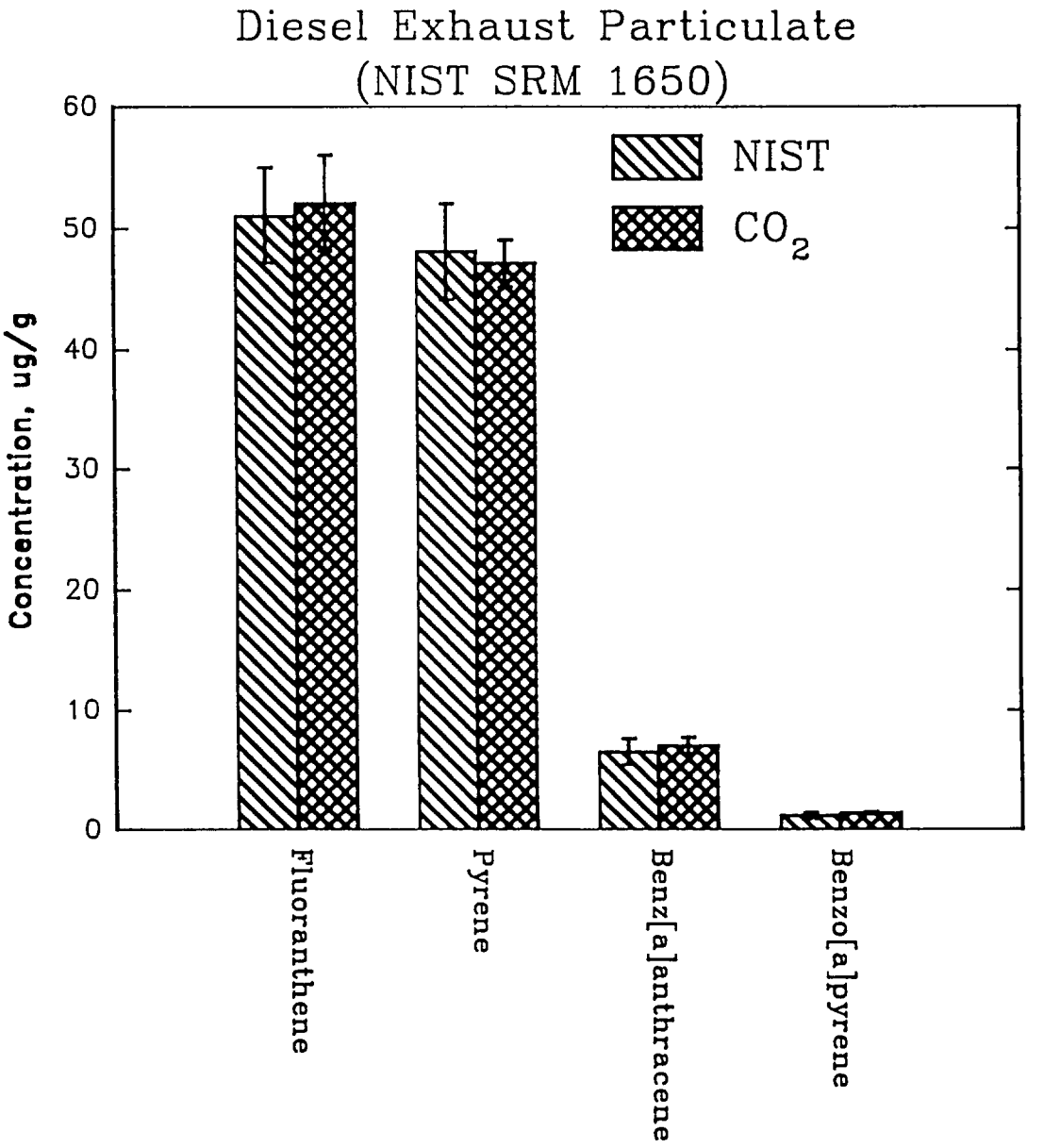


Figure 6: Comparison of NIST certified concentrations of PAHs from diesel exhaust particulate matter (SRM 1650) using conventional liquid solvent extraction (NIST) and off-line SFE. Adapted from reference 3.

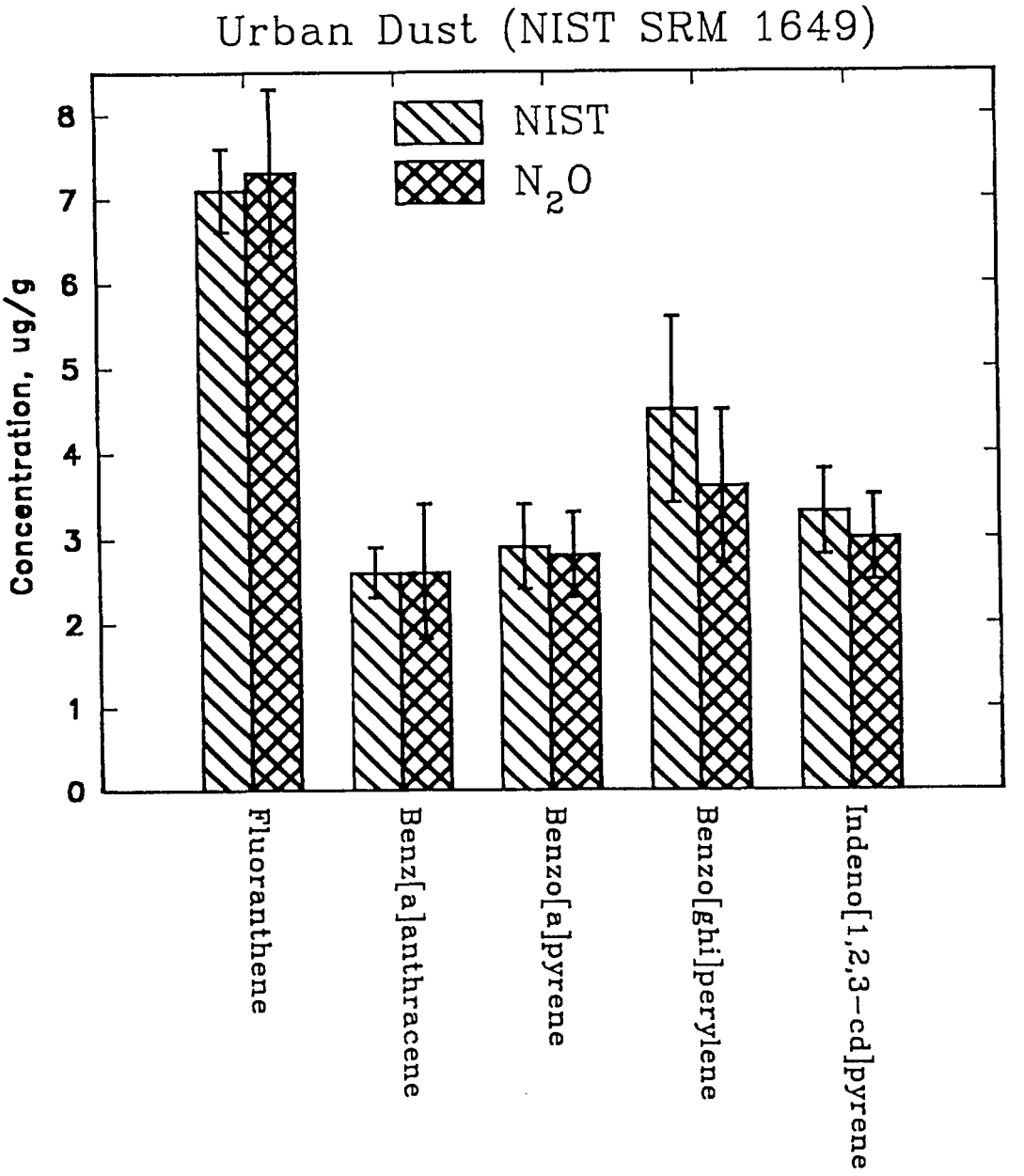


Figure 7: Comparison of NIST certified concentrations of PAHs from urban air particulate matter (SRM 1649) using conventional liquid solvent extraction (NIST) and on-column SFE-GC/MS. Extractions were performed for 20 minutes with 350 atm supercritical $N_2O$. The error bars for the $N_2O$ extractions represent SFE-GC/MS analyses of four replicate samples. Adapted from reference 13.

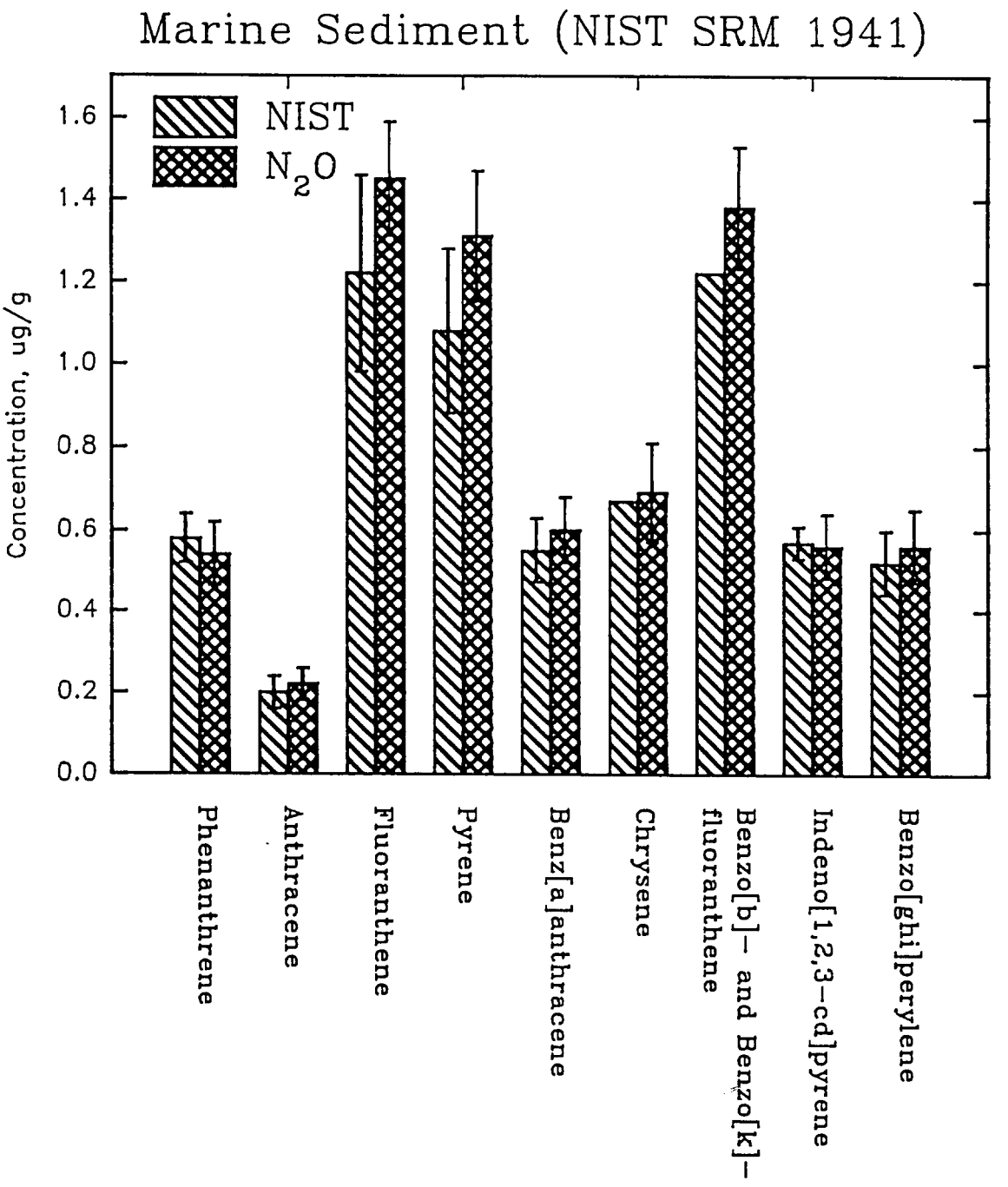


Figure 8: Comparison of NIST certified concentrations of PAHs from marine sediment (SRM 1941) using conventional liquid solvent extraction (NIST) and split SFE-GC/MS. Extractions were performed for 10 minutes with 400 atm $N_2O$ (50 °C). The error bars for the $N_2O$ extractions represent SFE-GC/MS analyses of three samples. Adapted from reference 15.

61

# THE DETERMINATION OF SELECTED PRIORITY POLLUTANTS IN SOIL BY SUPERCRITICAL FLUID EXTRACTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (SFE-GC/MS)

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## ABSTRACT

The supercritical fluid extraction (SFE) of semivolatile organic compounds of environmental significance was studied and compared to conventional liquid extraction methods of soxhlet and sonication. A soil matrix was used as the test substrate and the extracts were analyzed by gas chromatography/mass spectrometry.

Supercritical fluids are attractive as extraction solvents for semivolatile and high molecular weight organic compounds due to the unique properties of these fluids. These include low viscosity, high diffusion coefficients, low toxicity and low flammability. The high vapor pressure of carbon dioxide allows for easy solvent removal and efficient recovery of semivolatile solutes. In addition, solvent power is roughly correlated with pressure so that a certain amount of selectivity may be obtained in the extraction by varying the pressure. SFE may also be coupled with chromatographic systems to take advantage of existing analytical methods.

A set of eighteen environmentally significant compounds, including chlorinated benzenes and phenols, was used in this study. These were spiked on soil at 10-25 ppm levels. SFE was performed with 2% methanol in carbon dioxide at 390 atm. and 80°C. The soxhlet extractions were performed with a 1:1 mixture of acetone and hexane, while a 1:1 mixture of acetone and methylene chloride was used for the sonication extractions. Recoveries of these compounds by SFE averaged 80.2% with a range of 70.4 to 95.1%, while by soxhlet the average recovery was 66.4%, ranging from 53.8 to 81.2%. By sonication the average recovery was 58.6%, and the

individual values ranged from 46.4 to 75.3%. The recovery value for each compound was the average of nine determinations. SFE was found to be more rapid and convenient than the soxhlet or sonication methods.

## INTRODUCTION

Soxhlet and sonication techniques have been widely used for extracting semivolatile organic compounds from solids. Recently, however, supercritical fluid extraction (SFE) has generated considerable interest as a viable analytical technique for extracting semivolatile and high molecular weight organic compounds from a variety of solid matrices. The fundamental concepts of supercritical fluid extraction have been extensively discussed in the literature, therefore this discussion will focus only on those applications which are of environmental importance.

Schantz and Chester (1) reported the extraction of PCBs and PAHs from urban particulate matter and sediments using supercritical $CO_2$ at 40 $^{o}C$ and 345 atm. The extracts were collected on $C_{18}$-bonded phase packed column. Comparable amounts of PCBs and PAHs (except indo[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 and the values obtained for these two compounds by SFE were 30% and 18% higher than the certified values respectively.

Hawthorne and co-workers (2-4) used supercritical fluids to extract PAHs from urban dust, flyash, and river sediments. They reported that supercritical nitrous oxide modified with 5 percent methanol gave recoveries of 100% for fluoranthene and benzo[*a*]anthracene, 85% for benzo[a]pyrene, and slightly more than 50% for indeno[1,2,3-*c,d*]pyrene and benzo[*g,h,i*]perylene from urban dust.

Smith et. al. (5-7) used supercritical fluids to extract high molecular weight organics from a variety of absorbent and particulate matrices. They found that polar organic

compounds were extracted more efficiently with supercritical carbon dioxide containing methanol as a modifier whereas isobutane was more efficient for higher molecular weight and less polar compounds.

Several investigators have reported the extraction of pesticides and other pollutants from soils using supercritical carbon dioxide with or without modifiers (8-11).

Alexandrou and Pawliszyn (12), extracted polychlorinated dibenzo-p-dioxins and dibenzofurans in Municipal Incinerator Fly ash using supercritical nitrous oxide. They obtained better than 90% recovery after one hour of extraction at 400 atm. and 40°C. They reported that pure carbon dioxide does not extract dioxins, therefore it can be used effectively in the cleanup step to remove weakly absorbed organic material.

In this study supercritical fluid extraction was evaluated as an alternative to soxhlet and sonication techniques for the determination of eighteen neutral/acidic pollutants and surrogates in soil. The goal was to establish optimum extraction conditions such as temperature, pressure, solvent composition to recover all of the extracts with minimum losses by volatilization and/or aerosol formation.

## EXPERIMENTAL

### APPARATUS

The supercritical fluid extraction apparatus used in this study has been previously described (13). Briefly, the system consisted of a Varian 8500 syringe pump, a Fiatron CH-30 column heater, and a Lauda RM3 cooling bath. A schematic diagram of the extraction system is shown in Figure 1. An Apple IIe microcomputer was used to control the pump. A micrometering valve (Autoclave Eng.) was placed at the end of the extraction vessel to control the flow to the collection vessel. To improve recoveries of the volatile solutes, a cryogenic trap was installed at the outlet of the collection flask. A 30-cm length of 1/8" o.d stainless steel tubing was placed at the mouth of the collection flask through a rubber stopper. This tube was

jacketed with a 1/4" copper tube through which technical grade carbon dioxide was passed (after expansion from liquid) to achieve cooling temperatures of -50 to -30°C. The tube was oriented downward and condensed extractables and solvent from the collection flask were collected in a small vial at the tube outlet.

Extraction vessels of 1.67- and 10.4-mL capacities were purchased from Keystone Scientific.

Gas chromatography/Mass spectrometry was performed with a HP 5970B model interfaced to a HP-1000 data system for data processing. A 30-m, 0.25-mm ID DB5 capillary column was used.

A HP model 7673A autosampler was used for injecting the samples.

A Computer Chemicals System (CCS) model 3100 Extractor was used for the quality control sample.

MATERIALS

Analytical reference standards were obtained from Chem. Service , Aldrich Chemical Company and Supelco. Stock solutions of 5000 µg/ml of each compound were prepared in acetone. Working calibration standards were prepared in methanol by serial dilution of a composite stock solution prepared from the individual stock solutions.

SFC-grade carbon dioxide was obtained from Scott Speciality Gases.

Soil samples were obtained from Midland county, Michigan.

Quality Control sample was obtained from Environmental Resource Associates.

Glass Beads (80 µm) were obtained from Potters Industries.

## PROCEDURE

### SFE :

SFE extractions were performed with a 1.67-mL or a 10.4-mL extraction vessel. Sample weights ranged from 2 to 10 g of soil. Glass beads were placed at the bottom of the vessel before the soil was loaded. After the soil was loaded into the extraction vessel the appropriate volume of the stock solution described above was added and followed by the addition of another layer of glass beads. The vessel was immediately closed and extracted. The glass beads helped prevent plugging of the extraction vessel outlet frit. For the precision studies, all extractions were performed with a 1.67-mL vessel. After evaluating several collection devices, the one shown in Figure 1 was adopted.

A total of 20 mL of 2% methanol/carbon dioxide (measured as a liquid by pump displacement) was used in a typical extraction of 2 g of spiked soil. The extraction was performed at 80°C and 390 atm. The temperature of the micrometering valve was kept at 35°C during the extraction experiments. Extraction times for this sample size were typically 30 to 40 minutes. After the extraction was complete, the system was vented by opening the micrometering valve and the extraction vessel was removed from the system. The lines and valve were then rinsed with several mL of methylene chloride. The contents of the two collection flasks were combined with the rinsate and the solvent was removed under gentle nitrogen purge until 1 mL remained. A 1-µL aliquot of this solution was injected into the GC/MS.

### Soxhlet:

The soxhlet experiments were performed according to EPA method 3540. Ten grams of soil were loaded and extracted for 16 hours with a 1:1 mixture of acetone and hexane. The spiking level was 100 µg per compound.

### Sonication:

A Heat Systems- Ultrasonics Inc., Model W-385 sonicator was used. The experiments were performed according to EPA method 3550. Ten grams of soil was used, and the spiking

level was 100 µg per compound. The solvent was a 1:1 mixture of acetone and methylene chloride.

## RESULTS AND DISCUSSION

The results of these experiments are summarized in Tables 1-4. Recoveries of the listed compounds by SFE averaged 80.2% with a range from 70.4% to 95.1%, while by soxhlet the average recovery was 66.4% ranging from 53.8 to 81.2%. By sonication it was 58.6%, and the individual values ranged from 46.4 to 75.3%. The recovery value for each compound was the average of nine determinations.

Table 1 shows the recovery as a function of time. In general, most compounds were more than 50% extracted after 15 minutes. Maximum recovery required 30 to 60 minutes. Better flow control would be expected to decrease the extraction times. Carbon dioxide modified with 2% methanol was used after initial studies with unmodified $CO_2$ showed low recoveries for the phenols.

After some initial work the cryotrap was added to the SFE system. This significantly improved the recovery of the volatile chlorinated benzenes as shown in Table 2. The off-line format was preferred in this study because larger sample sizes could be better accommodated in this way to reduce potential errors from sample inhomogeneity.

Recovery precision and range data for the SFE samples are shown in Table 3. Standard deviations averaged approximately 5%, absolute, with few exceptions. This result is typical for determinations of these types of compounds at this level.

The various extraction methods are compared in Table 4. SFE was more efficient than either Soxhlet or sonication for these materials in soil. SFE was also more rapid and convenient than the conventional methods.

The quality control standard was mixed with 80-µm glass beads to prevent plugging of the outlet frit of the extraction vessel. Of the neutral compounds, shown in Table 5, only benzo(*b*)fluoranthene was not recovered, and this could be attributed to its low concentration. Dibenzofuran was not in the calibration standard, therefore it was not

determined. None of the acidic compounds were recovered, partly because they were at or below the detection limit of the method. These are preliminary results and this sample will be investigated further.

## CONCLUSION

Supercritical carbon dioxide modified with 2% methanol was found to be a more efficient than soxhlet or sonication for extracting these compounds from soil. SFE was also more rapid and convenient than conventional methods. Up to 10% moisture did not adversely affect the extraction. More work needs to be done with different types of soils containing varying amounts of moisture. Finally, the collection technology could be improved to minimize losses due to aerosol formation and/or volatilization.

**Table 1. PRECENT RECOVERY OF NEUTRAL/ACIDIC COMPOUNDS FROM SOIL WITH SUPERCRITICAL CARBON DIOXIDE/METHANOL AS A FUNCTION OF TIME**

| COMPOUND | PERCENT RECOVERY[1] | | |
|---|---|---|---|
| | 15 min | 26 min | 34 min |
| Bis(2-chloroethyl)ether | 64 | 66 | 86 |
| Phenol | 62 | 66 | 78 |
| 2-Chlorophenol | 60 | 64 | 82 |
| 1,3-Dichlorobenzene | 64 | 68 | 82 |
| 1,4-Dichlorobenzene | 62 | 66 | 84 |
| 1,2-Dichlorobenzene | 66 | 66 | 80 |
| 2,4-Dichlorophenol | 66 | 70 | 82 |
| 1,2,4-Trichlorobenzene | 72 | 78 | 96 |
| Naphthalene | 66 | 68 | 82 |
| 1,2,4,5-Tetrachlorobenzene | 74 | 78 | 90 |
| 2,4,6-Trichlorophenol | 78 | 82 | 92 |
| Hexachlorobenzene | 60 | 86 | 90 |
| SURROGATES | | | |
| 2-Fluorophenol | 74 | 76 | 88 |
| d5-Phenol | 76 | 76 | 90 |
| d5-Nitrobenzene | 76 | 76 | 92 |
| 2-Fluorobiphenyl | 88 | 92 | 100 |

[1]Extractions were performed at 390 atm. and 80°C. The 2-g soil sample was spiked at the 25 ppm level with each compound. A 1.67-mL extraction vessel was used, and collection was done in 10 mL of methylene chloride with cryogenic trap.

**Table 2. PERCENT RECOVERY OF NEUTRAL/ACIDIC COMPOUNDS FROM SOIL WITH AND WITHOUT CRYOGENIC TRAPPING**

| COMPOUND | PERCENT RECOVERY | |
|---|---|---|
| | Ambient | Cryo. Trap |
| Bis (2-chloroethyl) ether | 67.2 | 75.8 |
| Phenol | 70.4 | 70.4 |
| 2-Chlorophenol | 65.6 | 74.9 |
| 1,3-Dichlorobenzene | 61.5 | 73.8 |
| 1,4-Dichlorobenzene | 45.7 | 76.0 |
| 1,2-Dichlorobenzene | 44.9 | 74.9 |
| 1,2,4-Trichlorobenzene | 58.4 | 82.0 |
| 1,2,4,5-Tetrachlorobenzene | 75.6 | 79.1 |
| Hexachlorobenzene | 89.2 | 86.2 |
| Naphthalene | 62.4 | 74.2 |
| 2,4-Dichlorophenol | 74.8 | 76.4 |
| 2,4,6-Trichlorophenol | 80.4 | 83.1 |
| Pentachlorophenol (me'd)[1] | --- | 84.3 |
| SURROGATES | | |
| 2-Fluorophenol | 72.0 | 82.8 |
| d6-Phenol | 83.6 | 80.4 |
| 2,4,6-Tribromophenol (me'd)[1] | --- | 95.1 |
| d5-Nitrobenzene | 65.2 | 85.3 |
| 2-Fluorobiphenyl | 73.6 | 88.0 |

[1]Pentachlorophenol and 2,4,6-Tribromophenol were analyzed as the methylated derivatives.

[2]These numbers represent averages of 9 determinations. Extraction was performed at 390 atm. and 80°C with supercritical carbon dioxide/2% methanol.
--- = not determined. A 2-g soil sample was spiked at the 25 ppm level.

**Table 3 PERCENT RECOVERIES OF NEUTRAL/ACIDIC COMPOUNDS FROM SOIL WITH SUPERCRITICAL CARBON DIOXIDE MODIFIED WITH 2% METHANOL**

| COMPOUND | RECOVERY[1] | RANGE | SD |
|---|---|---|---|
| Bis(2-chloroethyl)ether | 75.8 | 66-86 | 6.2 |
| Phenol | 70.4 | 64-78 | 4.1 |
| 2-Chlorophenol | 74.9 | 64-82 | 5.2 |
| 1,3-Dichlorobenzene | 73.8 | 68-82 | 4.1 |
| 1,4-Dichlorobenzene | 76.0 | 66-84 | 5.3 |
| 1,2-Dichlorobenzene | 74.9 | 66-80 | 4.4 |
| 2,4-Dichlorophenol | 76.4 | 70-82 | 4.0 |
| 1,2,4-Trichlorobenzene | 82.0 | 76-92 | 4.9 |
| Naphthalene | 74.2 | 68-82 | 4.6 |
| 1,2,4,5-Tetrachlorobenzene | 79.1 | 74-90 | 5.1 |
| 2,4,6-Trichlorophenol | 83.1 | 74-92 | 5.1 |
| Hexachlorobenzene | 86.2 | 80-90 | 4.3 |
| Pentachlorophenol (me'd)[2] | 84.5 | 76-90 | 5.4 |
| SURROGATES | | | |
| 2-Fluorophenol | 82.8 | 76-88 | 6.4 |
| d6-Phenol | 80.4 | 72-90 | 5.6 |
| 2,4,6-Tribromophenol (me'd)[2] | 95.1 | 82-110 | 9.9 |
| d5-Nitrobenzene | 85.3 | 76-92 | 7.0 |
| 2-Fluorobiphenyl | 88.0 | 80-100 | 6.6 |

[1]Data represent average of 9 determinations.
All extractions were performed at 390 atm. and 80°C.
Spiking level was 25 ppm per compound on 2 g of soil.
Extracts were collected in 10 mL methylene chloride with cryogenic trap.

[2]Analyzed as the methylated derivatives.

**TABLE 4. PERCENT RECOVERIES OF NEUTRAL/ACIDIC COMPOUNDS FROM SOIL WITH SOXHLET, SONICATION AND SFE**

| COMPOUNDS | PERCENT RECOVERY[1] | | |
|---|---|---|---|
| | Soxhlet | Sonication | SFE |
| Bis(2-chloroethyl)ether | 67.2 | 50.4 | 75.8 |
| Phenol | 69.0 | 60.0 | 70.4 |
| 2-Chlorophenol | 73.2 | 63.8 | 74.9 |
| 1,3-Dichlorobenzene | 53.8 | 46.4 | 73.8 |
| 1,4-Dichlorobenzene | 54.2 | 49.1 | 76.0 |
| 1,2-Dichlorobenzene | 56.0 | 50.1 | 74.9 |
| 1,2,4-Trichlorobenzene | 59.2 | 53.4 | 82.0 |
| 1,2,4,5-Tetrachlorobenzene | 68.8 | 62.7 | 79.1 |
| Hexachlorobenzene | 73.0 | 75.3 | 86.2 |
| Naphthalene | 57.8 | 53.0 | 74.2 |
| 2,4-Dichlorophenol | 8[illegible].2 | 73.2 | 76.4 |
| 2,4,6-Trichlorophenol | 6[illegible].8 | 69.0 | 83.1 |
| Pentachlorophenol (me'd)[2] | --- | --- | 84.3 |
| SURROGATES | | | |
| 2-Fluorophenol | 62.8 | 56.3 | 82.8 |
| d6-Phenol | 72.4 | 60.6 | 80.4 |
| 2,4,6-Tribromophenol (me'd)[2] | --- | --- | 95.1 |
| d5-Nitrobenzene | 70.4 | 53.3 | 85.3 |
| 2-Fluorobiphenyl | 74.6 | 60.4 | 88.0 |

[1]Data represent average of 9 determinations.
Spiking level was 25 ppm per compound on 2 g soil.

[2]Analyzed as the methylated derivatives.
--- = not determined.

**Table 5 RECOVERIES OF PRIORITY POLLUTANT/CLP ORGANICS IN SOIL QUALITY CONTROL SAMPLE LOT NUMBER 302**

| COMPOUND | ERA CERTIFIED VALUE (µg/kg) | RECOVERY[1] | ADVISORY RANGE |
|---|---|---|---|
| BASE/NEUTRALS | | | |
| Acenaphthene | 4200 | 2000 | 900-5600 |
| bis(2-ethylhexyl)phthalate | 3930 | 2000 | 1100-6200 |
| Nitrobenzene | 9410 | 7000 | 2800-15000 |
| Dibenzofuran | 2110 | --- | 630-3200 |
| 1,2,4-Trichlorobenzene | 7460 | 6200 | 2800-10000 |
| Benzo(b)fluoranthene | 3140 | ND | 650-4900 |
| Naphthalene | 8060 | 8800 | 2800-11000 |
| Isophorone | 10500 | 8000 | 2200-12000 |
| SURROGATES RECOVERIES (%) | | | |
| 2-Fluorophenol | | 98 | |
| d5-Nitrobenzene | | 86 | |
| 2-Fluorobiphenyl | | 100 | |
| d4-Terphenyl | | 74 | |

[1]4.2 g QC sample was mixed with 2 g of glass beads.
Extraction time was 1 hr.
Surrogates were spiked at 25 ppm per compound.
--- = Not analyzed.
ND = Not detected.

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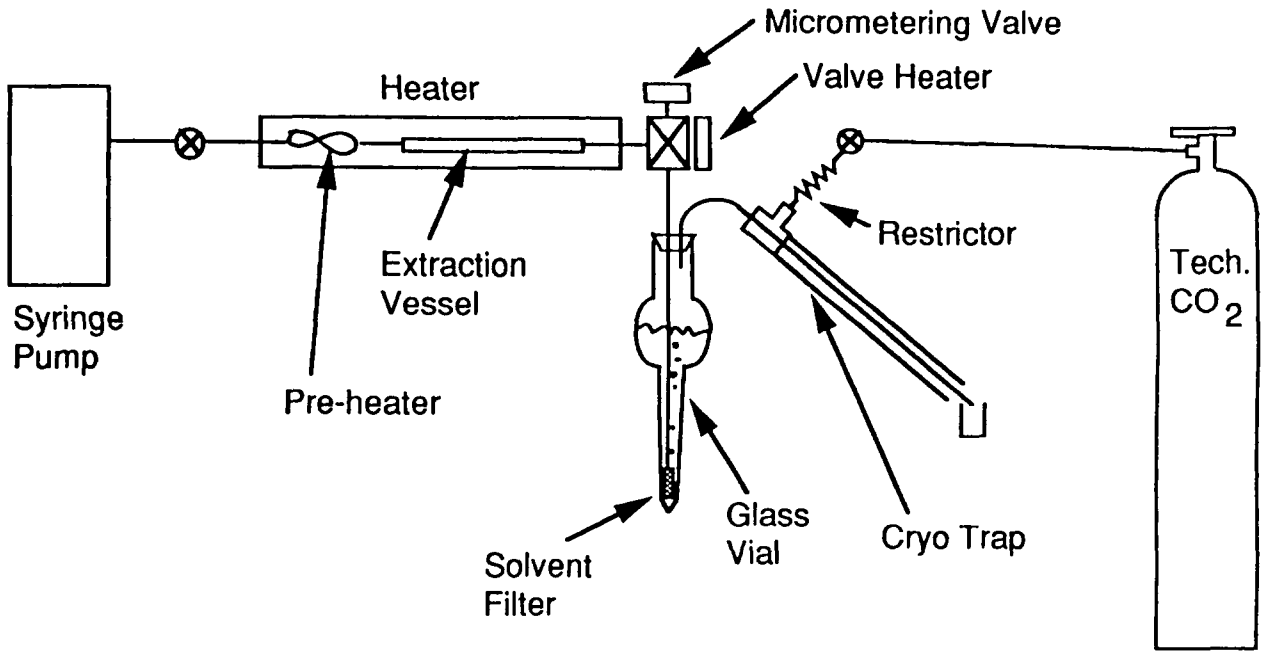
Figure 1. Schematic Diagram of the Supercritical Fluid Extraction Apparatus used in this study.



62

# THE APPLICATION OF SUPERCRITICAL FLUID CHROMATOGRAPHY-MASS SPECTROMETRY TO THE ANALYSIS OF APPENDIX-VIII AND IX COMPOUNDS

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## ABSTRACT

Supercritical fluid chromatographic and mass spectroscopic technology, was used to successfully chromatograph and confirm 200 Appendix VIII and IX compounds on a single column. Chromatographic data, EI quality spectra, mass spectrometer response factors and calibration curves are presented for selected RCRA compounds. The quality of the chromatography and the EI mass spectra clearly show the applicability of SFC-MS as an alternate approach to GC-MS and LC-MS for the quantitative analysis of the broad range of Appendix-VIII and IX organic compounds.

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, 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 SCF-MS technology will both 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, of prime interest to the EPA. The organic compounds cover a broad compositional, polarity, volatility, thermal and hydrolytic stability range. Additionally, there are broad compositional entries such as coal tar, creosote, cresols, PCB'S, 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, containing 12 GC and 4 GC-MS procedures. 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.

In 1989 supercritical fluid chromatographic technology, was used to successfully chromatograph over 270 Appendix VIII and IX compounds using one method, one column, and one eluant within one hour. The work was used as a springboard to mass spectrometric confirmation. Accordingly, an SFC was linked to a mass spectrometer in order to pursue confirmatory analysis.

## PURPOSE

The implementation of the third 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 applicability of supercritical fluid chromatography mass spectrometry as an alternate approach to GC-MS and LC-MS for 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 the analysis of a wider range of compounds than currently practical, and the reduction of the run time enabling more samples to be run daily.

The approach to this work was to use supercritical fluid chromatographic and mass spectrometric instrumentation to generate mass spectra and calibration curve data for a large number of the Appendix VIII and IX materials.

## 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 in 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 AND MOBILE PHASE

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 varying concentrations in appropriate solvents including methanol, acetone, water, toluene, and acetonitrile.

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.

## INSTRUMENTATION

A Lee Scientific, Model-601 SFC, was used for this work consisting of a system controller, syringe pump, chromatograph, biphenyl column, 20 meter, 50 micron, 0.15 micron film thickness, 50 micron frit, and mass spectrometer interface.

A Finnigan INCOS-50 instrument was used for all work.

## EXPERIMENTATION

### Appendix VIII and IX Compound Chromatography

The initial SFC work focused on the generating retention times and response factors for many RCRA compounds on an individual basis. The work is now directed toward generating high quality chromatography for large numbers of RCRA compounds in single injections. Two chromatographic reference blends were prepared containing 130 of the most commonly encountered compounds described in the first four entries of the table on page 1.

### SFC Operating Conditions

Injector Temperature 0°C. Detector Temperature 325°C
Time split injection duration - 0.1 seconds
Injection volume - 40 nanoliters

| Time (min) | Pump Conditions density g/mL | ramp rate g/mL/min | Oven Temperature °Celsius |
|---|---|---|---|
| 0.0 | 0.0700 | | 75 |
| 2.0 | 0.0700 | 0.005 | |
| 28.0 | 0.2000 | 0.02 | |
| 49.0 | 0.625 | 0.0000 | ramp @ 2.5°C |
| 66.0 | 0.625 | | ramp @ 7.5°C |
| 71.0 | | | stop @ 150°C |
| 90.00 | Density and pressure reset to values at time zero within 3 minutes. | | |

### Appendix VIII and IX Compound Mass Spectrometry

The initial SFC-MS work focused on instrument setup and generating spectra comparable to existing EI spectral libraries, which are used for current GC-MS work. The initial work was directed toward determining the quality of the fit between SFC-MS spectra and those in the existing GC-MS library. About 200 reference RCRA compounds were injected, as groups, into the SFC-MS and the resultant spectra compared with those in the GC-MS libraries.

To determine the effectiveness of injecting mixtures, two chromatographic

reference blends were prepared containing 130 of the most commonly encountered RCRA compounds described in the first four entries of the table on page 1.

### SFC-MS Pesticide Calibration Curves

SFC-MS calibration curves were prepared for six pesticides, heptachlor, heptachlor epoxide, lindane, chlordane, endrin and methoxychlor. covering the range of 25 to 350 PPM.

The retention gap technique was used to focus the sample, through the removal of the volatile solvent, to improve the detection limits. One meter of uncoated fused silica tubing was linked in series between the injector and the analytical column. The volatile solvent was swept through the system, leaving the non-volatile analytes in place. Initiating the SFC run transfers the analytes to the column for analysis.

### SFC-MS Operating Conditions

| | |
|---|---|
| Scan Range | 45 - 450 AMU |
| Scan Rate | 1 scan/2seconds |
| Source Temperature | 200°C |
| Interface Temperature | 120°C |
| Transfer Line Temperature | 120°C |
| Nozzle (Tip) Temperature | 350°C |
| Instrument Tuned to PFTBA | |
| Instrument tuneable to DFTPP or BFB criteria | |

## RESULTS AND DISCUSSION

### APPENDIX VIII AND IX COMPOUND CHROMATOGRAPHY

Figures 1 and 2 present the SFC chromatograms of the high and low volatility mixtures used to develop the chromatographic program. This method covers the volatility range of almost all of the Appendix VIII and IX compounds, while representing a broad compound type distribution. In both cases the chromatographic quality is high and baseline resolution of most of the components in the mixture can be obtained. This work represents a significant improvement in the chromatography quality compared to the earlier work presented at the 1989 OSW meeting.

### SFC MASS SPECTRA OF APPENDIX VIII AND IX COMPOUNDS

Figures 3 to 5 present typical SFC-MS total ion chromatograms for three groups of the 200 compounds analyzed on the SCF-MS instrument. The chromatographic quality is high. The peaks are sharp and there is no tailing for polar compounds such as phenols. The quality of fit falls into the range of 800 to 900 for all of the compounds evaluated, demonstrating the instruments confirmatory capabilities. SFC-MS clearly has the ability

to identify a wide variety of RCRA compounds while retaining the chromatographic integrity.

Unique specific ions were generated for all of the 130 RCRA compounds in the mixture represented in Figures 1 and 2. In all cases the primary ion was identical to that ion used for GC-MS analysis, except for those compounds producing a primary ion below a mass of 45. Peak shapes approximated a 20 second peak width, which falls between the 5 and 30 second peak widths experienced with GC-MS and LC-MS respectively. Again, the SFC-MS quality parallels the data quality of currently utilized mass spectroscopy confirmatory techniques.

## SFC MASS SPECTRA OF PCB'S

PCB's are of particular interest because of their occurrence in a broad range of matrices. All eight Arochlor reference materials were analyzed. The total ion chromatogram of a mixture of Arochlors 1232 and 1260 is presented in Figure 6.

A comparison of the SFC-MS heptachlorobiphenyl isomer spectrum and the GC-MS library spectrum is presented in Figure 7. The fitting quality is 976 showing a very good comparison between the actual spectrum and the library reference spectrum, which is equal to that of GC-MS techniques.

Of particular interest is the constancy of the isotope ratios in the chlorine cluster patterns between the reference material and library spectra. This pattern constancy denotes the quality of the SCF-MS spectra and the ease of library matching.

## SFC MASS SPEC CALIBRATION CURVES

The ability to generate calibration curves is illustrated by the response factor data presented in Figure 8. The response factor data clearly show the calibration curve quality. The per cent deviation for the six compounds is about 5%, which is comparable to that obtained by GC-MS. The detection limits for the six pesticides meet the requirements of the regulations, but need to be improved by about a factor of 10 to compare with GC-MS.

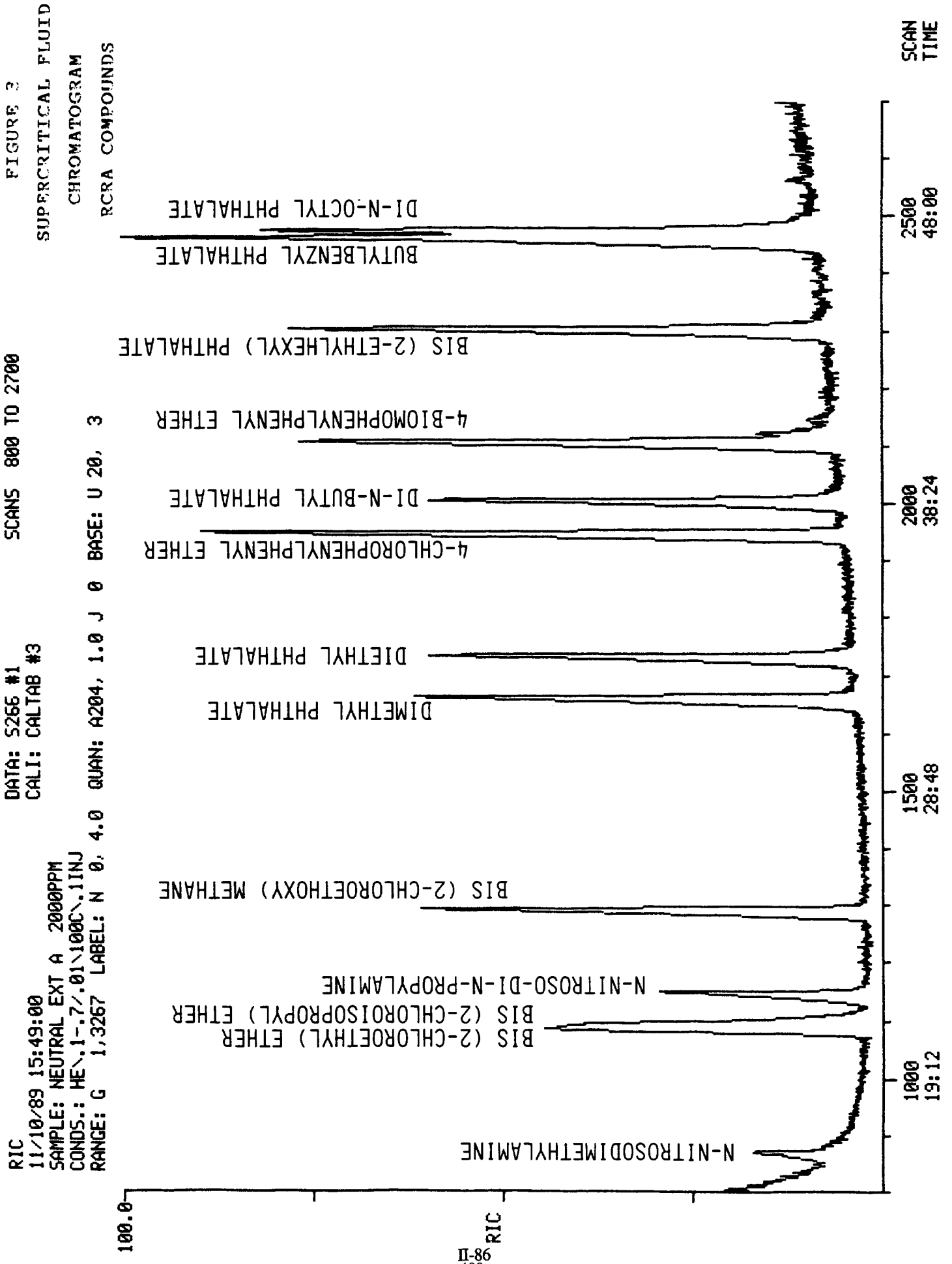
## CONCLUSION

The authors feel that the demonstrated separatory power of supercritical fluid chromatography linked to the confirmatory ability of mass spectrometry will cause this technology to have a very large impact in the area of environmental pollution analysis. This work clearly shows the applicability of SFC-MS as an alternate approach to GC-MS and LC-MS for the analysis of the broad range of Appendix-VIII and IX organic compounds. It is a technology where the phrase "one method fits all", may have real meaning and application.

FIGURE 1
SUPERCRITICAL FLUID CHROMATOGRAM
HIGH VOLATILITY MIXTURE

FIGURE 2
SUPERCRITICAL FLUID CHROMATOGRAM
LOW VOLATILITY MIXTURE

FIGURE 3
SUPERCRITICAL FLUID
CHROMATOGRAM
RCRA COMPOUNDS



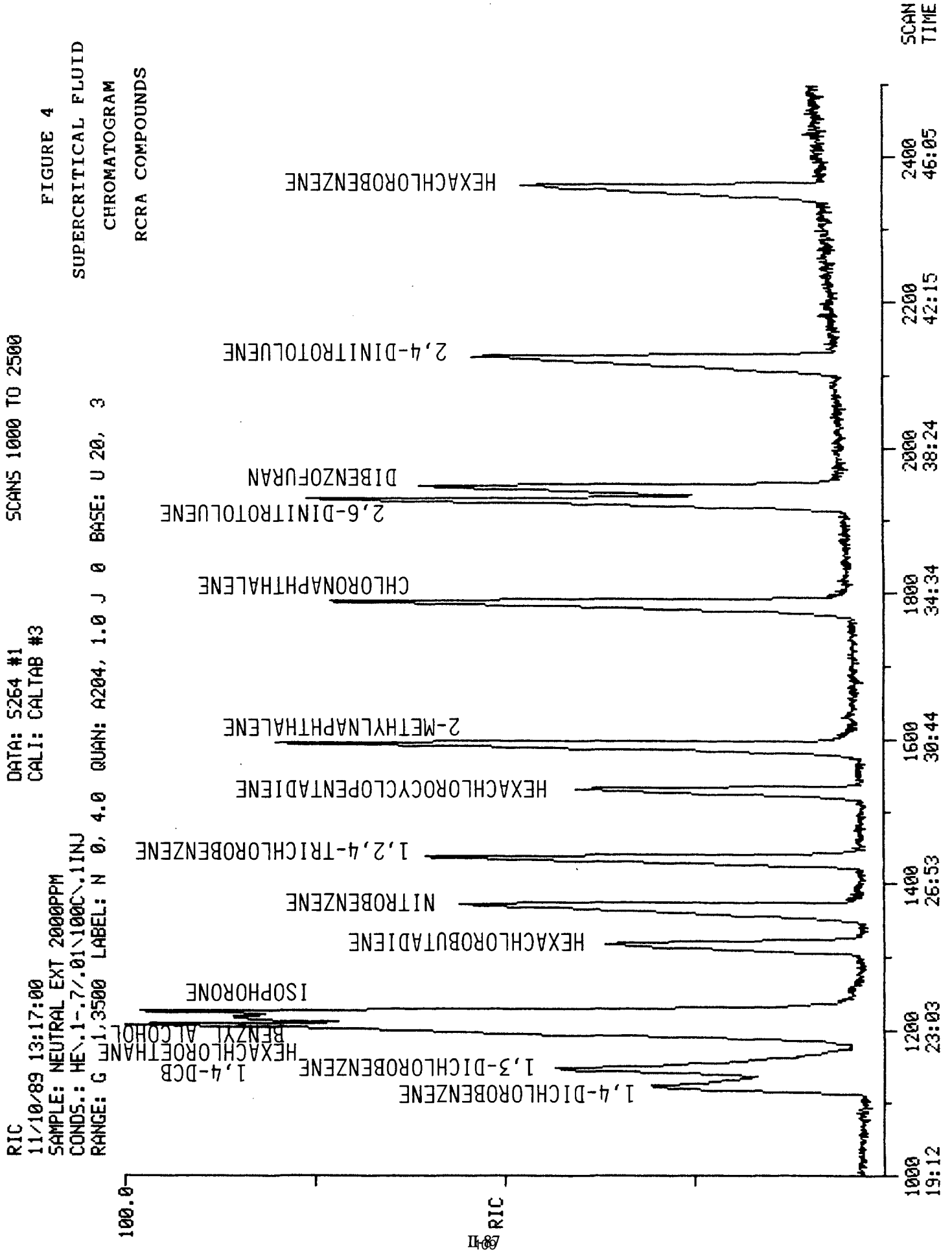


FIGURE 4
SUPERCRITICAL FLUID
CHROMATOGRAM
RCRA COMPOUNDS
RIC
11/10/89 13:17:00
SAMPLE: NEUTRAL EXT 2000PPM
CONDS.: HE\.1-.7/.01\100C\.1INJ
RANGE: G 1,3500 LABEL: N 0, 4.0 QUAN: A204, 1.0 J 0 BASE: U 20, 3
DATA: 5264 #1
CALI: CALTAB #3
SCANS 1000 TO 2500
1,4-DCB
HEXACHLOROETHANE
BENZYL ALCOHOL
1,3-DICHLOROBENZENE
1,4-DICHLOROBENZENE
ISOPHORONE
HEXACHLOROBUTADIENE
NITROBENZENE
1,2,4-TRICHLOROBENZENE
HEXACHLOROCYCLOPENTADIENE
2-METHYLNAPHTHALENE
CHLORONAPHTHALENE
2,6-DINITROTOLUENE
DIBENZOFURAN
2,4-DINITROTOLUENE
HEXACHLOROBENZENE
100.0
RIC
1000 19:12
1200 23:03
1400 26:53
1600 30:44
1800 34:34
2000 38:24
2200 42:15
2400 46:05
SCAN TIME

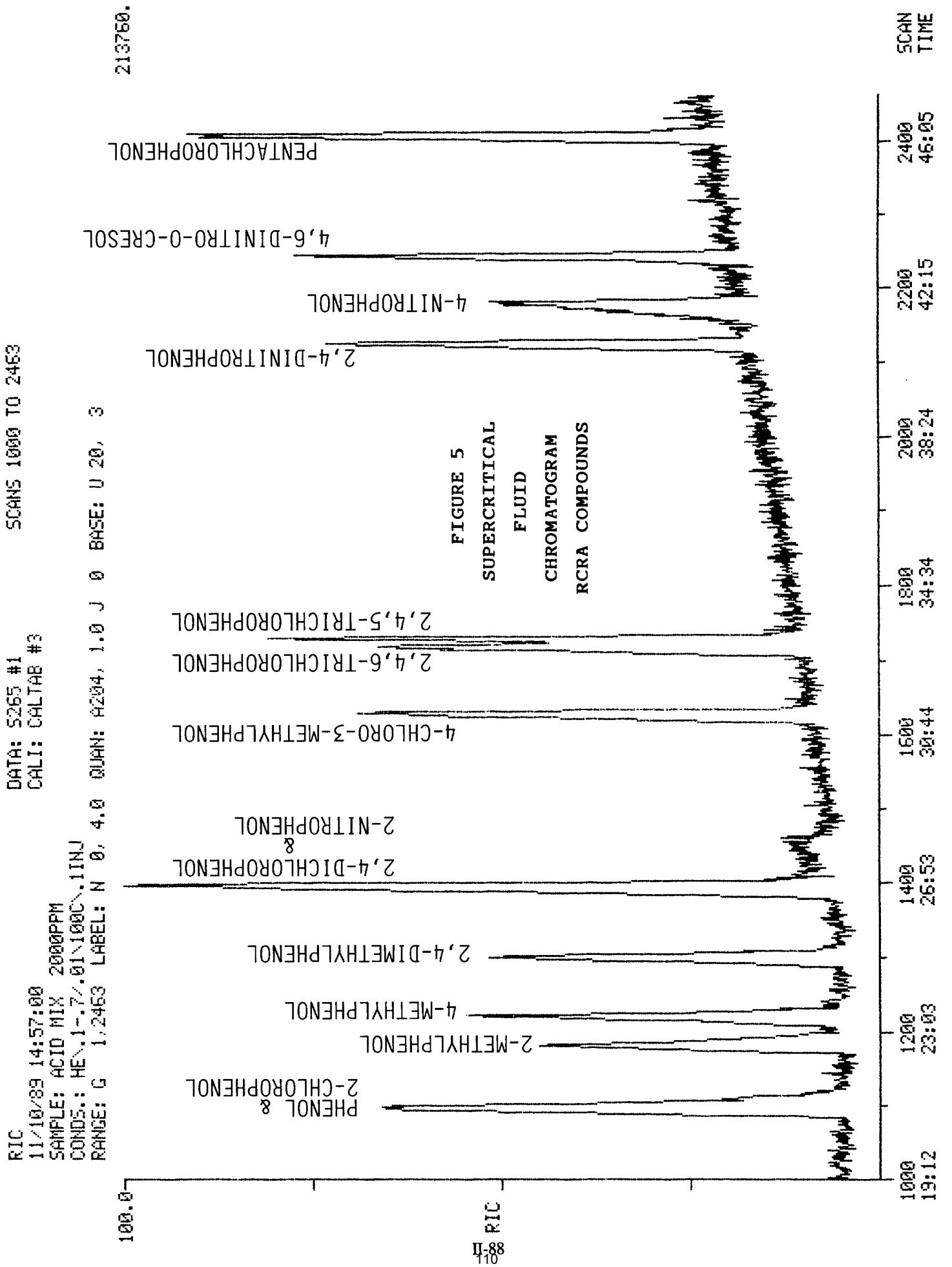



FIGURE 5
SUPERCRITICAL FLUID CHROMATOGRAM
RCRA COMPOUNDS

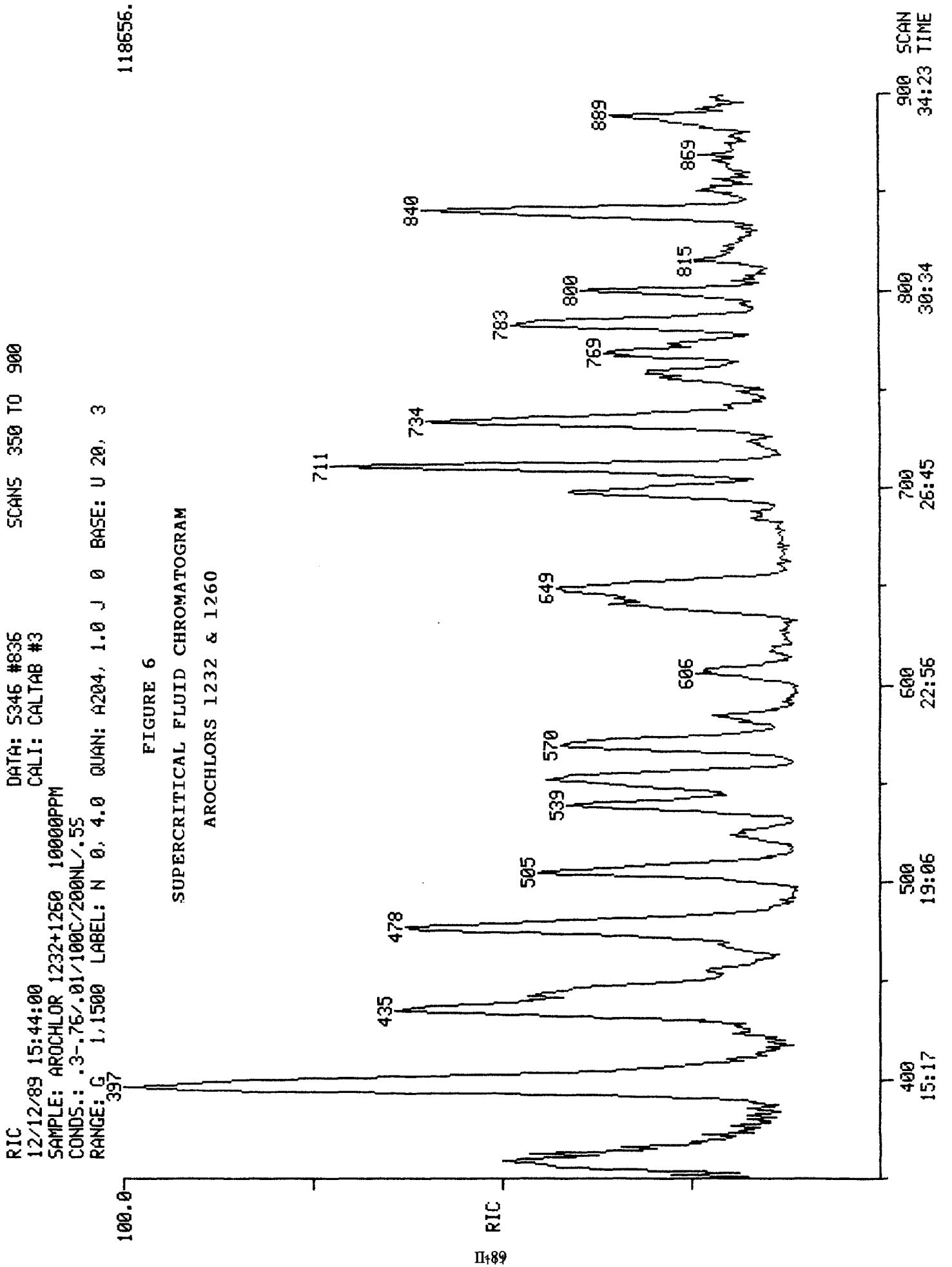



FIGURE 6

SUPERCRITICAL FLUID CHROMATOGRAM

AROCHLORS 1232 & 1260

HEPTACHLORO BIPHENYL

MID LIBRARY SEARCH (LIBRARYNB)
12/12/89 15:44:00 + 32:03
SAMPLE: AROCHLOR 1232+1260 10000PPM
CONDS.: .3-.76/.01/100C/200NL/.5S
# 836 TO # 843 SUMMED - # 847 TO # 853

DATA: S346 # 839
CALI: CALTAB # 3

BASE M/Z: 394
RIC: 246272.

FIGURE 7

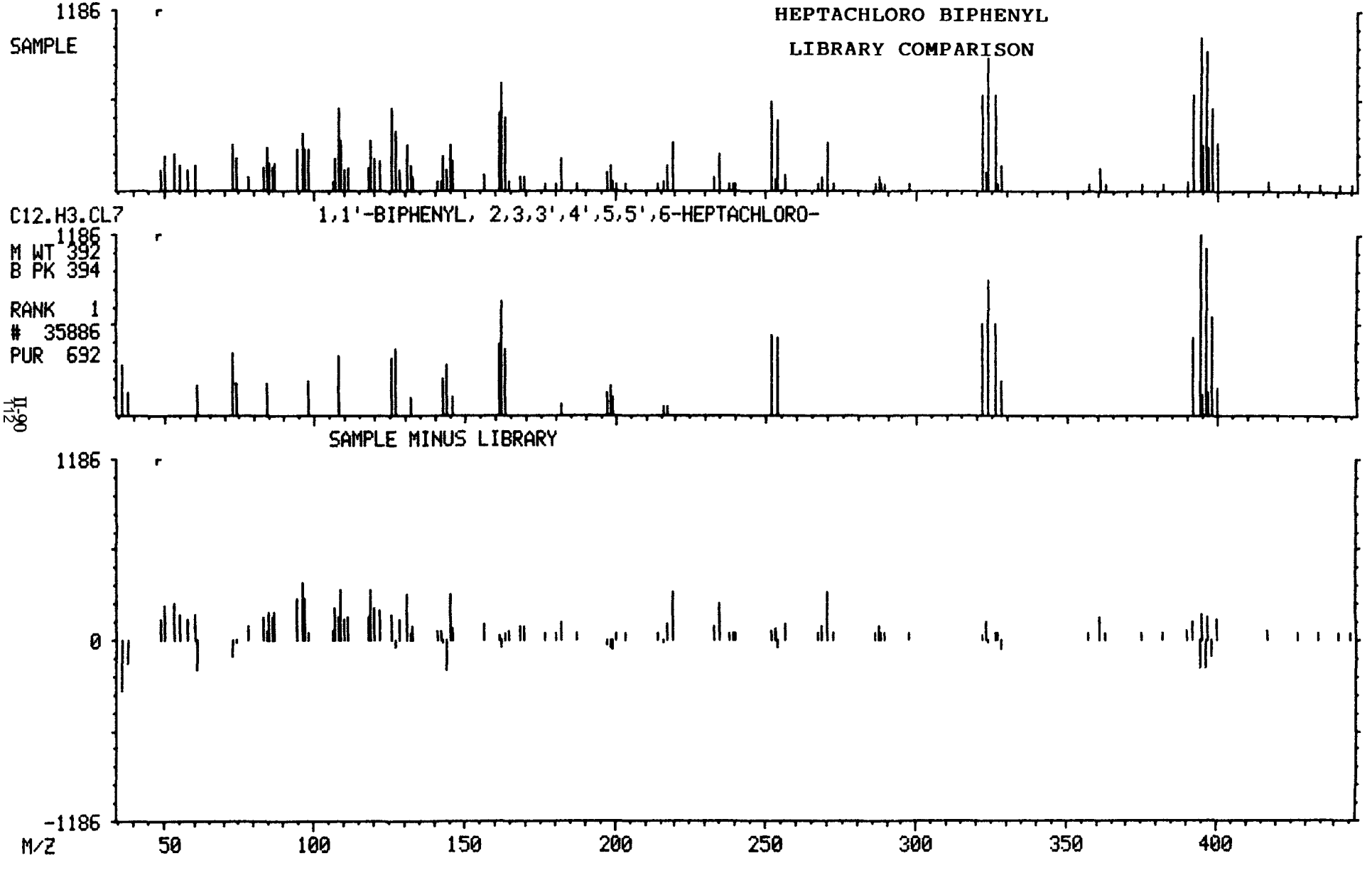
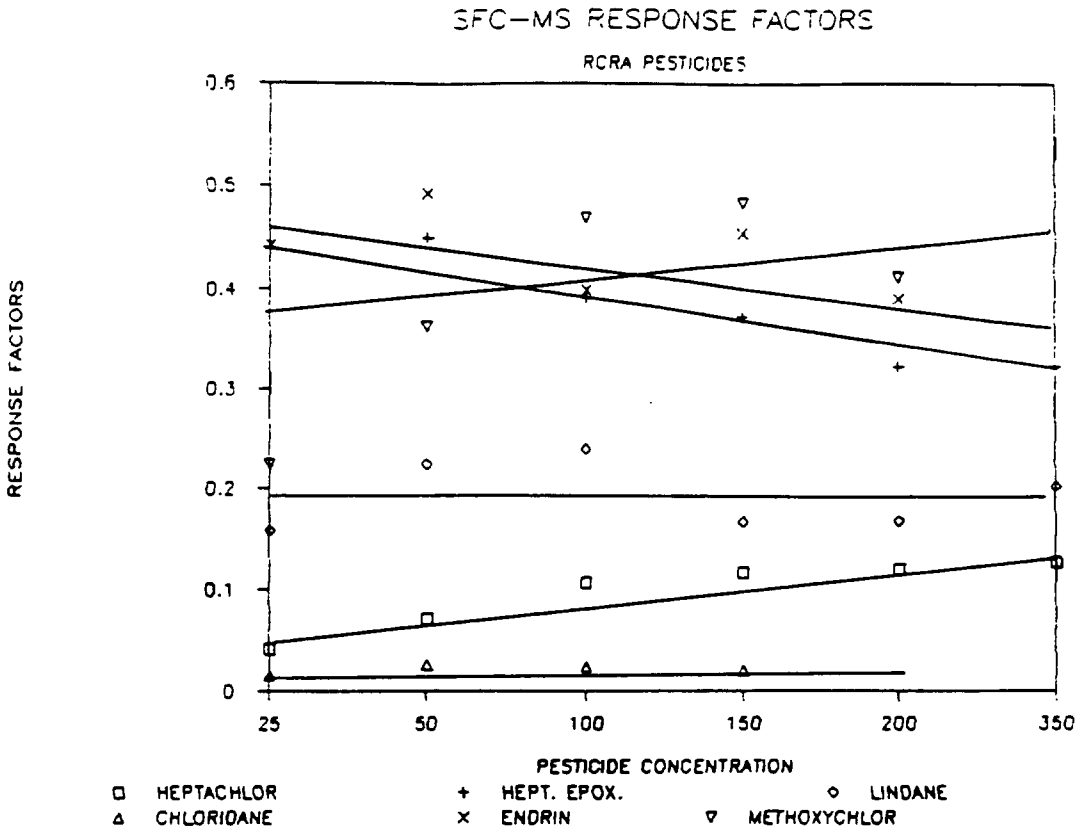


FIGURE 8




SFC–MS RESPONSE FACTORS

| COMPOUND | CONCENTRATION PPM 350 | 200 | 150 | 100 | 50 | 25 | AVERAGE RESPONSE FACTOR | % DEVIATION | ESTIMATED DETECTION LIMIT PPM |
|---|---|---|---|---|---|---|---|---|---|
| HEPTACHLOR | 0.127 | 0.12 | 0.116 | 0.107 | 0.071 | 0.042 | 0.097 | 3.0 | 25 |
| HEPTACHLOR EPOXIDE | 0.321 | 0.321 | 0.371 | 0.391 | 0.45 | 0.441 | 0.382 | 5.1 | 5 |
| LINDANE | 0.202 | 0.168 | 0.166 | 0.239 | 0.224 | 0.158 | 0.192 | 3.0 | 10 |
| CHLORIDANE | 0.021 | 0.024 | 0.026 | 0.016 | | | 0.021 | 0.3 | 100 |
| ENDRIN | | 0.39 | 0.454 | 0.399 | 0.492 | 0.443 | 0.435 | 3.7 | 10 |
| METHOXYCHLOR | | 0.411 | 0.483 | 0.469 | 0.361 | 0.224 | 0.389 | 9.3 | 25 |

63 # AZEOTROPIC DISTILLATION - A CONTINUING EVALUATION FOR THE DETERMINATION OF POLAR, WATER - SOLUBLE ORGANICS

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ABSTRACT. The determination of volatile organic compounds (VOCs) is an important step in the assessment of water quality. Methods for the determination of water-soluble compounds such as ketones, aldehydes, nitriles, and alcohols have not been developed for routine use because of the difficulties in removing and concentrating these compounds from the aqueous matrix. Azeotropic distillation has been evaluated as a possible method for determining the aqueous concentration of selected compounds from the RCRA Appendix VIII, Michigan, and BDAT analytes lists.

An aqueous binary azeotrope is a mixture of an organic compound and water which produces a vapor with the same composition as the liquid when boiled. A minimum boiling azeotrope boils at a lower temperature than either the water or the organic compound, and as such, can be removed from the aqueous sample by careful distillation. Thus, azeotropic distillation can be a viable method for determining the concentration of those compounds which form binary azeotropes with water.

The objectives of this continuing program were to: (1) determine the number of target analytes that could be successfully concentrated by azeotropic distillation, (2) determine the maximum number of analytes that could be chromatographed simultaneously by direct aqueous injection HRGC and (3) determine the overall method performance for each compound. Data from two distillation methods will be presented, namely, trap-to-trap distillation under low vacuum (<0.1 mm Hg) and atmospheric distillation using a modified Nielsen-Kryger distillation head.

The anaytes were tested individually for chromatographic performance on a selection of wide-bore fused silica columns. Direct aqeuous 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 from the distillation, investigations were made into suitable surrogates and internal standards, and precision and accuracy were collected at three concentrations 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.

64

# A METHOD FOR THE CONCENTRATION AND ANALYSIS OF TRACE METHANOL IN WATER BY DISTILLATION AND GAS CHROMATOGRAPHY

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## ABSTRACT

Under the land disposal restriction (40 CFR part 268.41) for spent solvents, methanol has a treatment standard of 0.25 mg/L for wastewaters containing spent solvents and 0.75 mg/L for all other spent solvent wastes in the waste extract using zero headspace extraction. This paper presents the development of an aqueous sample concentration, cleanup and analysis method that surpasses these regulatory treatment standards for methanol. The total sample handling time from the start of distillation to the completion of analysis is less than one hour. The initial experimental parameters were derived from a method for the azeotropic distillation of water soluble volatile organic compounds (1,2). This method uses the principles of distillation and steam stripping. Several modified Nielson - Kryger condenser designs were developed to enrich (relative to the original sample) the resulting distillate in methanol. The distillate is then analyzed by gas chromatography using a DB-WAX capillary column and flame ionization detection. For this application the instrument detection limit was 0.15 ng in a 2 µL injection. With a 40 mL sample, the method detection limit was 0.026 mg/L for reagent water and 0.031 mg/L for ZHE extract.

## INTRODUCTION

The Hazardous and Solid Waste Amendments of 1984 amended RCRA by banning all land disposal of untreated hazardous waste within five and one-half years after passage (May 8, 1990). The basic purpose of the land disposal restrictions is to discourage activities that involve placing untreated wastes in or on the land when a better treatment or destruction alternative exists. Under the land disposal restrictions (40 CFR part 268.41) for spent solvents, methanol has a treatment standard of 0.25 mg/L for wastewaters containing spent solvents and 0.75 mg/L for all other spent solvent wastes in the waste extract using zero headspace extraction (ZHE). The proposed treatment standard for multi-source leachate wastewaters is 0.033 mg/L for methanol. To date there are no EPA approved methods for methanol that have detection limits below these treatment standards. The effect of this situation is that residues from the treatment of solvent wastes and multi-source leachate wastewaters cannot at present be certified to meet the corresponding treatment standards and thus be landfilled.

This paper presents the development of an aqueous sample concentration, cleanup and analysis method with a detection limit lower than the spent solvent treatment standards for methanol. The method also shows promise for meeting the detection limit required for the proposed treatment standard for multi-source leachate wastewaters. The total sample handling time from the start of distillation to the completion of analysis is less than one hour. The initial experimental parameters were derived from a method for the azeotropic distillation of water soluble volatile organic compounds (1,2). This method

uses the principles of distillation and steam stripping. When distilling a 40 mL aqueous sample, or ZHE extract, actual distillation time from the start of visible boiling is 10 minutes or less. GC run time is approximately 17 minutes. A significant advantage is that the distillate is free from nonvolatile organic and inorganic interferences. These nonvolatile components may degrade chromatographic performance and shorten the life of the GC column.

## INSTRUMENTATION, EQUIPMENT AND SUPPLIES

Gas Chromatograph/Data System
  Hewlett Packard 5890 equipped with a flame ionization detector, Macintosh IIci (Apple) with LabView (National Instruments) and GC Integrator & Workmate (WillStein) software.
Columns
  Quantitation: DB-Wax 30m X 0.53mm I.D. 1.0 micron film thickness
  Confirmation: DB-1 30m X 0.53mm I.D. 1.5 micron film thickness
Glassware
  Modified Nielson - Kryger condenser; Ace Catalog # 6555-07, Shamrock Catalog # 6170
  Vigrex columns
    200 mm column (350 mm overall) 24/40 joint Shamrock Catalog # 23202-102
    130 mm column (200 mm overall) 14/20 joint Shamrock Catalog # 23242-106
  Round bottom flasks
    2 L, 500 mL, 100 mL
  Glas-Col Heating Mantles
    2 L flask, 500 watts, Catalog # 04100
    500 mL flask, 270 watts Catalog # TM106
    100 mL flask, 230 watts Catalog # STM400
  Fisher burner
  Prototype Volatile Organic Compound Concentrating Condensers ($VOC^3$)
    Shamrock Glass, Seaford, Delaware
Methanol, B&J Brand Catalog # 232-1, purity 99.9%
Reagent water, deionized, (methanol content must be less than practical quantitation limit)
Glass beads, 5 mm diameter
Boiling chips, VWR Scientific, Inc. Porous Boiling Chips Catalog # 26397-409
Cold water supply, Neslab Coolflow CFT-25

## DISTILLATION PRINCIPLES

Methanol is volatilized from the aqueous sample by boiling. The steam is enriched in methanol relative to the original sample. As the steam passes up through the Vigrex fractionation column it is further enriched in methanol with each plate. The steam is then condensed and collected in a small volume collection chamber in the concentrating condenser. Figure 1 shows the overall distillation system. Once the collection chamber is filled it overflows and methanol enriched water flows back through the lower part of the condenser and the Vigrex column toward the flask. This methanol enriched water comes in contact with additional rising steam. The steam revolatilizes most of the methanol and carries it back to the condenser. When equilibrium is reached most of the methanol has been trapped in the collection chamber. The methanol concentration

enhancement factor is equal to the ratio of the sample volume divided by the collection chamber volume. Figure 2 is a cross section of the main section of the condenser.

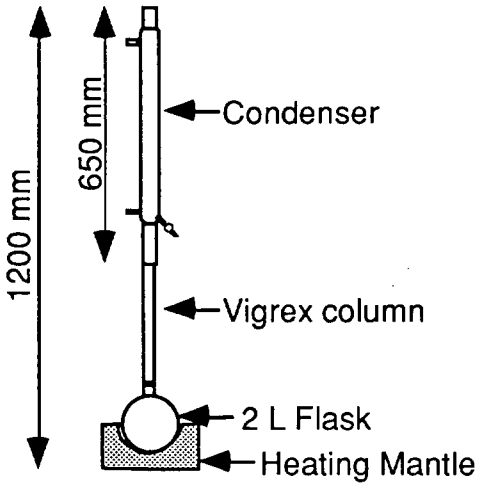


Figure 1
Nielson - Kryger Condenser/Vigrex/Flask/Mantle

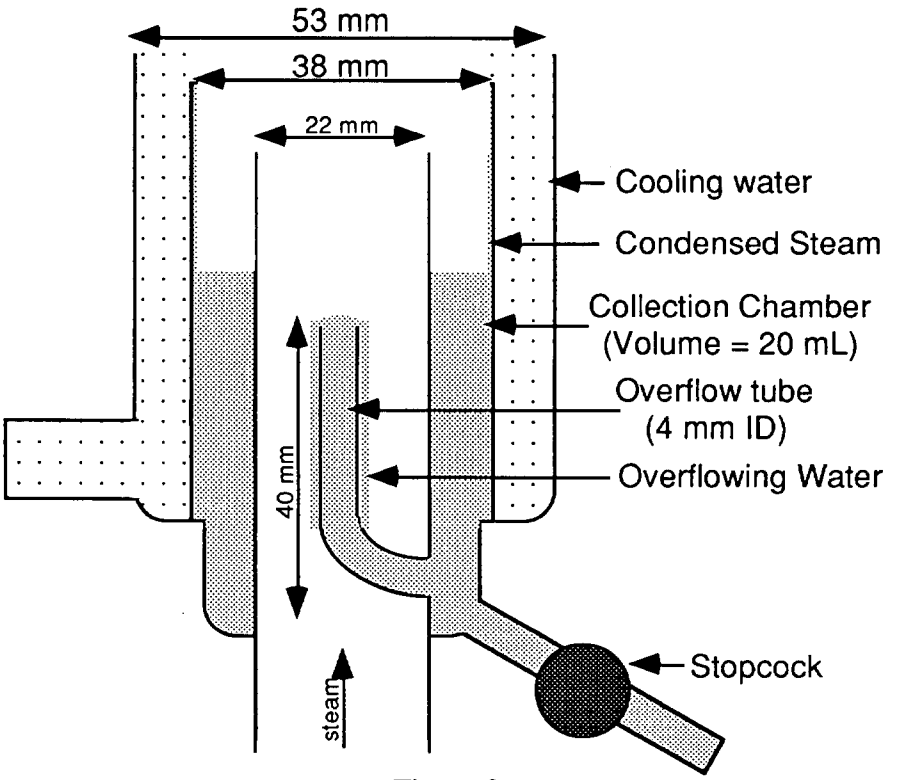


Figure 2
Main section of Modified Nielson - Kryger Condenser

For efficient steam stripping of methanol the overflowing condensed water must flow in a thin layer. If the overflow water layer is thick, methanol is not be able to diffuse to the surface and be revolatilized efficiently by the steam. This situation will occur if large drops form or a *wave* of water is released from the collection chamber. See Figures 4 and 5 for an illustration of this phenomenon. The overflow mechanism must account for this or poor recoveries will result. If the drop or *wave* is large enough it may actually travel all the way down to the flask carrying much of the methanol with it. In addition when the condensed steam flow rate was high and distances between tube walls were small, water bridges formed which also hindered the steam stripping process.

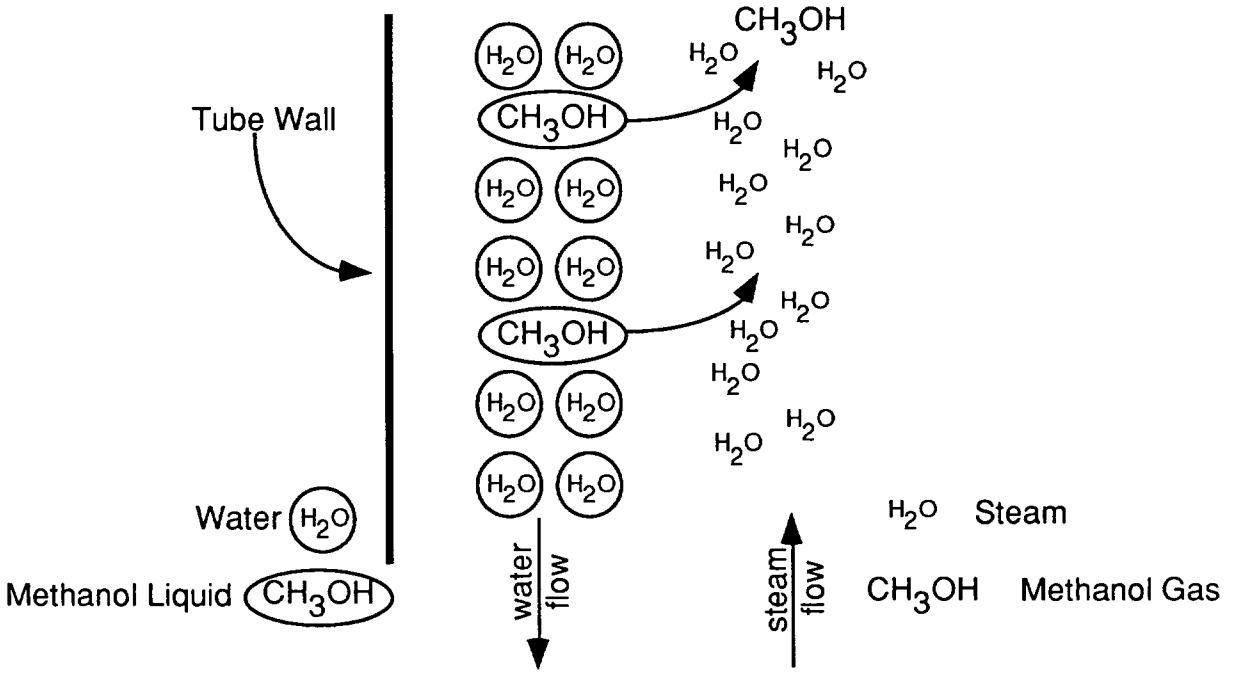


Figure 3
The Steam Stripping of Methanol

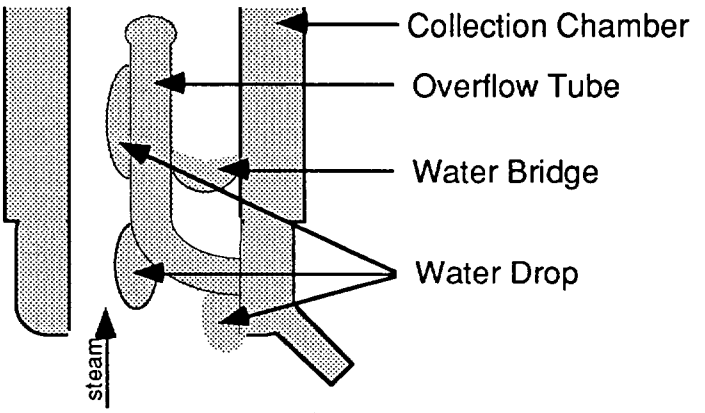


Figure 4
Modified Nielson - Kryger Condenser with Drops and Water Bridges

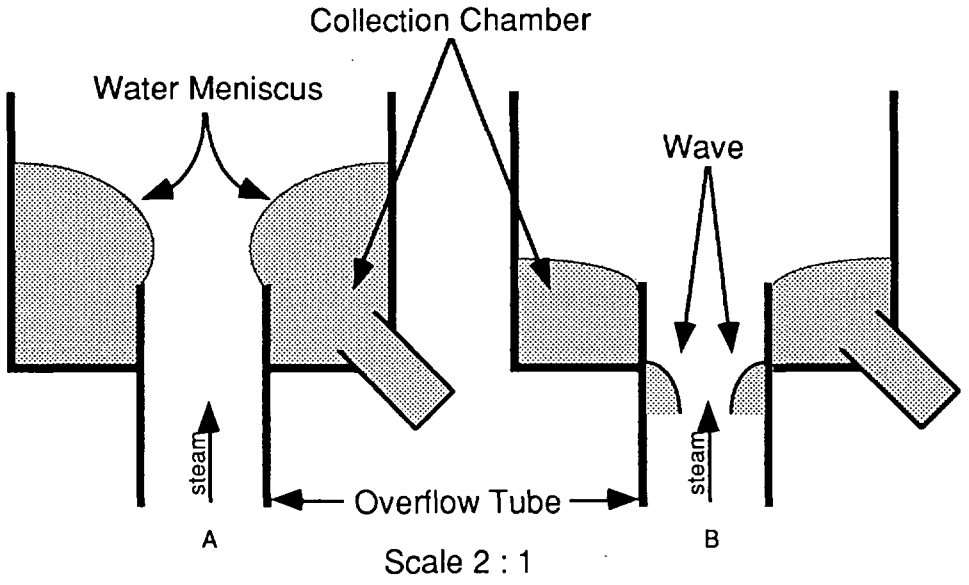


Figure 5
Alternate Design with Waves
{just before the meniscus breaks (A) and shortly after it breaks (B)}

It is desirable for the steam to come in close contact with the overflowing water to volatilize most of the methanol. A narrow condenser neck and overflow tube can accomplish this. But when the inside diameter of these tubes is too small flow problems also result. The size and frequency of the waves as shown in Figure 5 are determined by the flow of condensed water (which is derived from the sample boil/reflux rate), the inside diameter of the overflow tube, the distance between the overflow tube and the collection chamber outside wall and tube materials. If the overflow tube inside diameter and/or the distance to the chamber wall is small the surface tension of water will cause the water level to rise above the top of the overflow tube. Once there is sufficient water pressure on this meniscus it will break and send a *wave* back to the flask. When the *wave* is thick poor methanol recoveries will result. The surface tension/*wave* effect is exacerbated by using nonpolar materials, such as Teflon, for the overflow tube. The surface tension effect can be reduced by notching or flaring the overflow tube. Alternately a wick can be used. But in all cases the water overflow should be smooth and in a thin layer. The sample must boil smoothly as well. If the sample bumps and splatters the overflowing water will reflect this and yield poor recoveries. If the flow rate of steam (sample boil/reflux rate) is too high and the condenser neck is too narrow the *overflowing* water will be blown back into the collection chamber rather than trickling back through the Vigrex column to the flask.

Although this method is applicable to many water soluble volatile organic compounds it was developed and optimized specifically for methanol. Since methanol does not form an azeotrope with water this method is technically not azeotropic distillation even though the basic principles are the same.

## DISCUSSION AND RESULTS

Many parameters were investigated. There are physical parameters such as the sample volume, it's boil/reflux rate and the total distillation time. The physical design characteristics of the condenser itself were examined The most critical of these is the collection chamber volume. Several condenser designs were examined; a commercial modified Nielson-Kryger, and two miniaturized Nielson-Kryger (Peters) systems. Several alternate overflow systems were studied; the straight tube, notched, flared, wick and hoop systems. Two chemical parameters were also studied; methanol concentration and matrix. Table 1 lists the parameters that were studied.

Table 1 Distillation Parameters

| | |
|---|---|
| Physical | |
| sample volume | 40 to 1000 mL |
| boil/reflux rate | 2 to 7 mL/min |
| evenness of boil | glass beads or boiling chips |
| distillation time | 5 to 120 minutes |
| cooling water temperature | 7°C |
| Physical design | |
| Vigrex column | with or without |
| VOC[3] design | |
| collection chamber volume | 1 to 20 mL |
| condenser height | 15 to 60 cm cooling coil, baffles |
| overflow design | Peters/Dow and alternate |
| overflow tube inside diameter | 2 to 10 mm |
| overflow tube height | 2 to 35 mm |
| overflow tube shape (alternate design only) | straight, notched, flared, side drain, wick, hoop |
| Chemical | |
| analyte concentration | detection limit to 10 mg/L |
| matrix | reagent water, ZHE extract |

### MODIFIED NIELSON - KRYGER CONDENSER

Initial experiments used a commercially available Modified Nielson - Kryger condenser from Ace Glass. It uses basically the design described by Peters (2) except that most dimensions are much larger. It is shown as a cross section in Figures 1 and 2. In addition sample removal is through a stopcock rather than with a syringe as described by Peters (2). The collection chamber volume was quite large, 20 mL. This necessitated the use of large sample volumes, 200 to 1000 mL, to achieve the desired concentration factor. Factorial design experiments indicated that 70% recovery and estimated detection limits in the mid ppb range could be obtained with distillation times of one hour. The boil/reflux rate was 5 mL/min. Increasing the sample volume should theoretically lower detection limits but in actual practice the improvement was not as good as expected since the methanol recovery was reduced. Longer distillation times improved recoveries to a point. However sample preparation times of 1 to 2 hours were not desirable.

Several other parameters were also examined. The necessity of smooth or even rolling boil was also noted. Rough boiling or bumping was seen when glass beads were used; but the boiling was much smoother with boiling chips. Any irregularity in the boiling rate was reflected in the steam flow rate which affected the water condensation rate. When the water condensation rate changed rapidly large drops or *waves* of overflow water were seen. As described above this leads to poor recoveries. Acetate buffer solutions were also studied as sample matrixes. No significant difference in recovery was found between reagent water and the acetate buffer. The primary matrix of interest was the ZHE extract . Normally only 200 to 300 mL is available for all of the volatile analyses. After examining all of these factors it was considered necessary to miniaturize the condenser, particularly the collection chamber volume. Miniaturizing allowed for both smaller sample volumes and shorter distillation times.

## PROTOTYPE # 1

The first miniaturized prototype, called a Volatile Organic Compound Concentrating Condenser ($VOC^3$) focused on reducing the collection chamber volume. It is shown in Figure 6. This allowed the use of smaller sample volumes while still maintaining a sufficient concentration factor. The collection chamber volume was reduced to 5 mL. The condenser height was 550 mm. Full and fractional factorial design experiments were used to study many of the parameters. The boil/reflux rate was varied from 1 mL/min. to 5 mL/min. The effect on recovery was very small when distillation times where at least 15 minutes. When sample volume was varied from 40 to 250 mL the recovery was better at the smaller volumes by 20%. Varying the methanol concentration from 0.025 mg/L to 10 mg/L did not produce a significant effect. Adding the ZHE acetate buffer matrix to reagent water improved recoveries up to 10% under some non-optimum conditions but in general had little effect. Distillation times were shortened from 1 hour to 5-10 minutes without sacrificing recovery when the sample volumes were decreased from 250 mL to 40 mL. With a 10 minute distillation time, 4 to 5 samples can be distilled per hour using one distillation system. Experiments were run with and without the Vigrex fractionation column. Average recovery was 90% with and 35% without the column. Thus the fractionation provided by the Vigrex column is necessary.

## ANALYSIS

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

Table 2 Analysis Parameters

| | | | |
|---|---|---|---|
| quantitation column | DB-Wax | external standardization | |
| confirmation column | DB-1 | carrier gas | helium |
| instrument calibration range | 0.2 to 2000 ng | carrier gas flow | 2.5 mL/min. |
| response factor %RSD | <15% | detector | FID |
| response factor %D | <10% | detector temperature | 230°C |
| methanol retention time | 3.56 ± 0.07 min. | hydrogen flow | 37 mL/min. |
| injection volume | 2 uL | air flow | 426 mL/min. |
| injection type | splitless | make-up gas | nitrogen |
| injection port temperature | 180°C | make-up gas flow | 41 mL/min. |
| temperature program | 35°C for 0.0 min., 5°C/min. to 100°C, hold for 2 min. | | |

The instrument detection limit (IDL) was calculated to be 0.15 ng using ten 2 μL injections of a 0.10 mg/L standard.
IDL = $(t_{n-1,99\%})$(Std Dev) = (2.821)(0.0528) = **0.15 ng**.

A special note of caution regarding the GC temperature program is in order. Even though methanol elutes relatively early, the GC temperature must be ramped up high enough and held there long enough to remove any water and other compounds from the capillary column. Retention time shifts may result if the water is not completely eluted from the column.

Since methanol is a common laboratory solvent it is difficult to obtain methanol free water. One deionized lab water system contaminated reagent water with methanol. Also airborne methanol can be absorbed by water in open containers. The concentrator unit appears to be able to extract methanol from the air and contaminate a sample that is undergoing distillation.

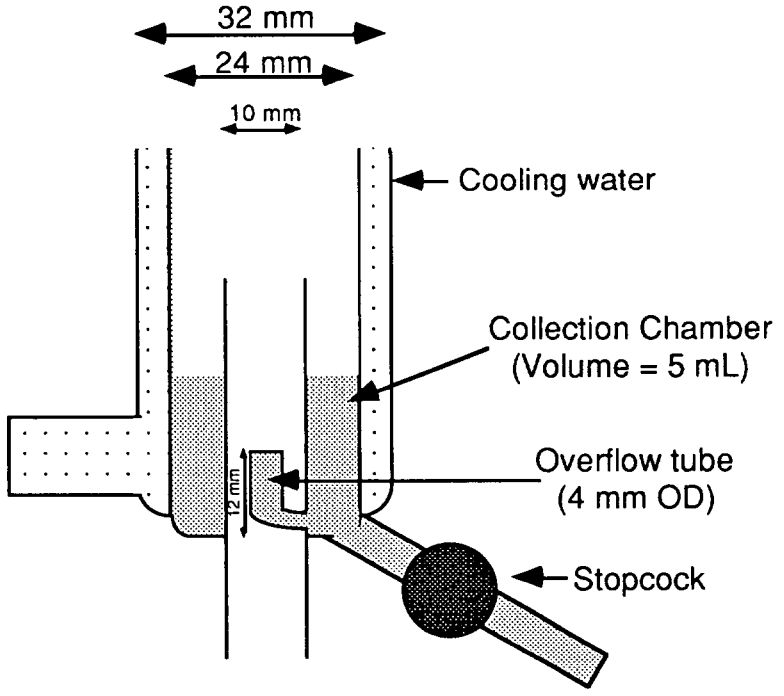


Figure 6
Main section of Prototype #1 Condenser

## METHOD DETECTION LIMIT

Method detection limit studies for reagent water and zero headspace extract were performed. The reagent water detection limit study is summarized in the Table 3.

Table 3 Reagent Water Detection Limit Study

| Replicate # | Total concentration (measured) mg/L | Spiked concentration (measured) mg/L | %Recovery |
|---|---|---|---|
| 1 | 0.042 | 0.023 | 92 |
| 2 | 0.043 | 0.024 | 96 |
| 3 | 0.048 | 0.029 | 116 |
| 4 | 0.041 | 0.022 | 88 |
| 5 | 0.042 | 0.023 | 92 |
| 6 | 0.049 | 0.030 | 120 |
| 7 | 0.065 | 0.046 | 184 |
| Average | 0.047 | 0.028 S.D.=0.0084 | 112 |

The unspiked sample concentration was 0.019 mg/L. The matrix spike added was 0.025 mg/L. The %RSD for the matrix spikes was 31%.
The METHOD DETECTION LIMIT = $(t_{n-1,99\%})$(Std Dev) = (3.143)(0.0084) = **0.026 mg/L**.

The ZHE extract (real sample) method detection limit study is summarized in the Table 4.

Table 4 ZHE Extract Detection Limit Study

| Replicate # | Total concentration (measured) ug/mL | Spiked concentration (measured) ug/mL | %Recovery |
|---|---|---|---|
| 1 | 0.038 | 0.016 | 64 |
| 2 | 0.058 | 0.036 | 144 |
| 3 | 0.062 | 0.040 | 160 |
| 4 | 0.054 | 0.032 | 128 |
| 5 | 0.043 | 0.021 | 84 |
| 6 | 0.044 | 0.022 | 88 |
| 7 | 0.065 | 0.043 | 172 |
| Average | 0.053 | 0.031 S.D.=0.010 | 120 |

The unspiked sample concentration was 0.022 mg/L. The matrix spike added was 0.025 mg/L. The %RSD for the matrix spikes was 35%.
The METHOD DETECTION LIMIT = $(t_{n-1,99\%})$(Std Dev) = (3.143)(0.010) = **0.031 mg/L**.

A ZHE extract from acid stabilized kiln dust sample was spiked with methanol and the recovery calculated. The results are summarized in Table 5.

Table 5 Kiln Dust Matrix Spike

| Spike Added ug/mL | Sample Conc ug/mL | MS Conc. ug/mL | MS %Rec | MSD Conc ug/mL | MSD %Rec | %RPD |
|---|---|---|---|---|---|---|
| 1.0 | 1.6 | 2.32 | 72 | 2.34 | 74 | 1 |

Under normal operating conditions carryover from one sample to the next was minimal. Normal cleaning was to rinse 3 times with 50 mL portions of reagent water. To test the effectiveness of the rinse a system blank was distilled immediately after a 100 mg/L sample. This system blank had a methanol concentration near the method detection limit (0.026 mg/L). This represents about 0.03% carryover from the previous sample.

## OTHER PROTOTYPES

Further miniaturization has been pursued to design a system that provides better enrichment with 40 mL samples or permits work with smaller sample volumes. A smaller glassware system (height of 500 mm) has been designed which is much easier to handle than one that has an overall height of 1000 mm. Figures 7, 9, 10 and 11 show four mini-systems. The condenser height is 150 mm. The first design uses the Peters (2) overflow system while the others have been experiments with other overflow designs. When miniaturizing the following parameters must be taken into account; water surface tension effects, boil/reflux flow rates and steam linear velocity.

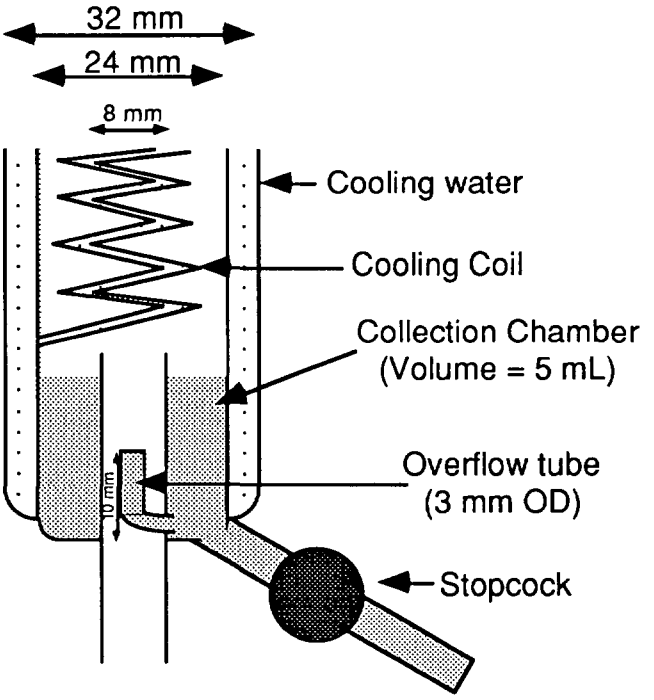


Figure 7
Miniaturized Peter's Overflow System

It is desirable to keep the boil/reflux rate high since the system will come to equilibrium faster and thus keep the sample preparation time to a minimum. The chart below shows that most of the methanol is distilled in the first few minutes. As the boil/reflux rate is increased the methanol distills off in less time. This is shown in Figure 8.

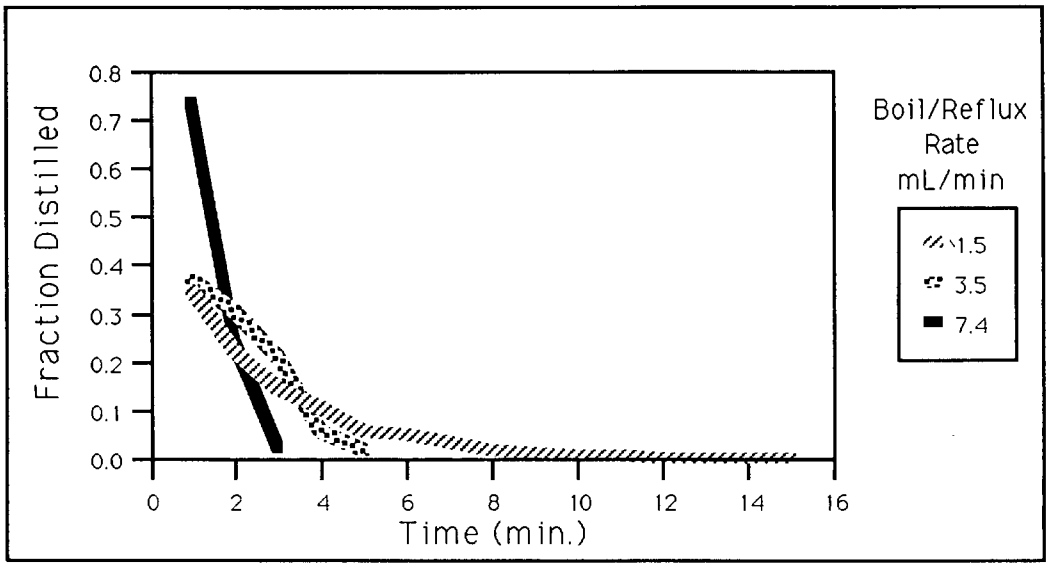


Figure 8
Fraction of Methanol Distilled Off vs Time

The boil/reflux rate must not be so high that the collection chamber overflows in large drops or *waves*. In extreme cases with narrow condenser necks and high steam linear velocities the steam may actually prevent the water from returning to the flask. Thus all condensed water will collect in the condenser and the steam will simply *blow bubbles* in it. As the dimensions of a VOC[3] are reduced surface tension effects become more pronounced. The diameter of the overflow tube and it's distance to the nearest tube wall is important. If this distance is too small a strong water meniscus bridges the gap and disrupts the even flow of water (see Figure 4).

The Peters overflow system is difficult to make in small sizes so alternate overflow systems were investigated. The most successful have been the straight tube overflow, wick and hoop systems. High boil/reflux rates (4 to 7 mL/min) with smooth overflow characteristics have been sustained. Figures 9, 10 and 11 show the alternate overflow systems. It was necessary to have the cooling coils at a steep angle to prevent condensed steam from dripping down the center of the condenser at high boil/reflux rates.

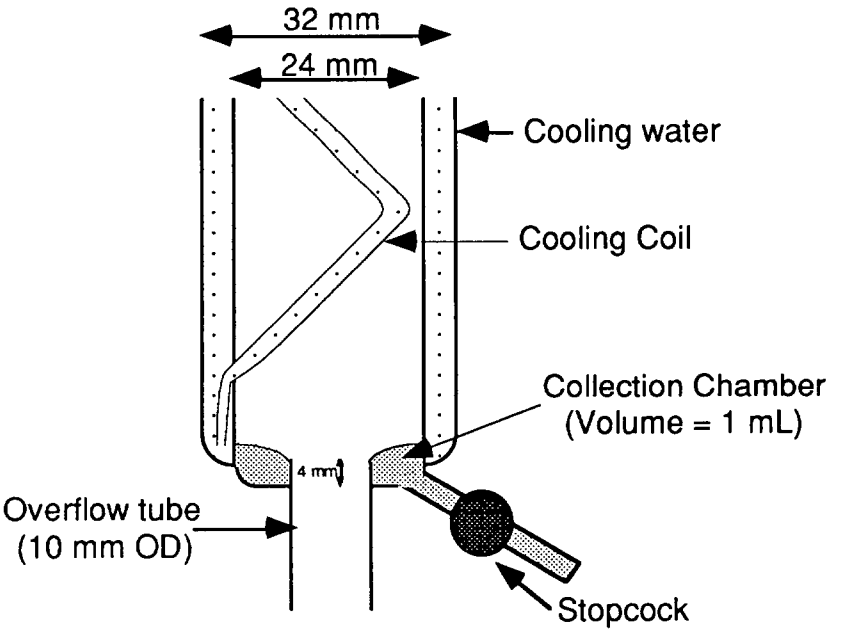


Figure 9
Straight Tube Overflow Condenser

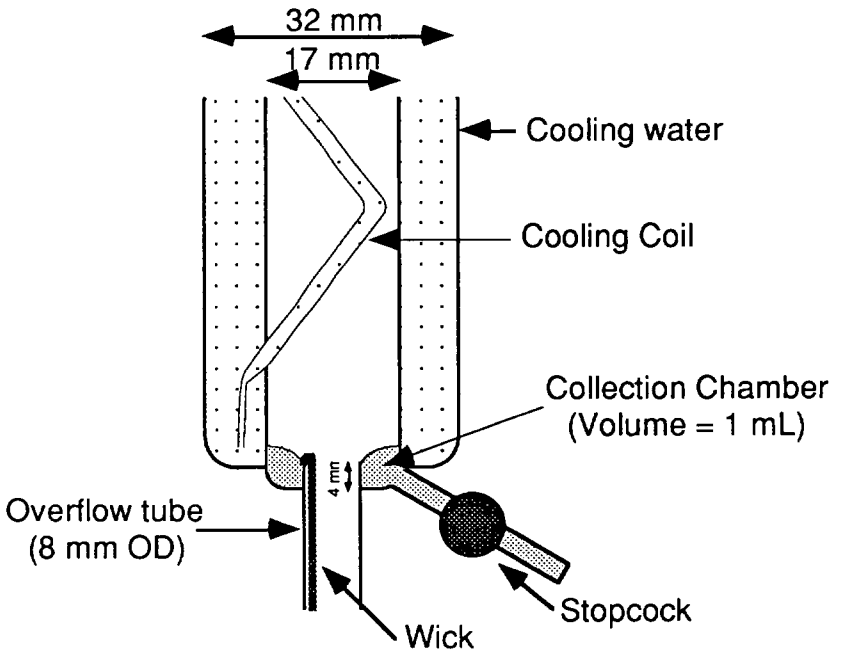


Figure 10
Wick Overflow Condenser

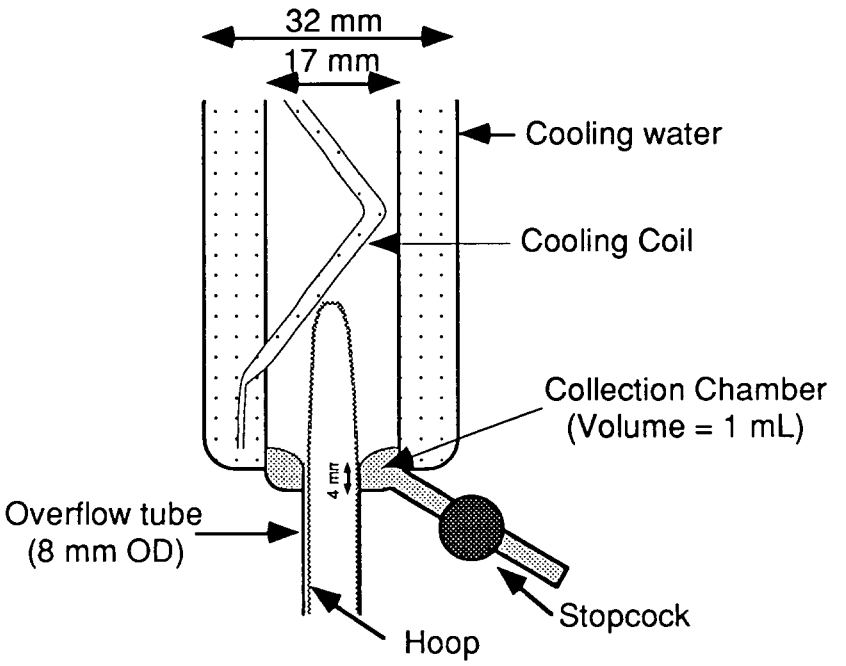


Figure 11
Hoop Overflow Condenser

## SUMMARY

The Volatile Organic Compound Concentrating Condenser ($VOC^3$) has been used to concentrate methanol in aqueous samples to achieve method detection limits well below the current regulatory thresholds (0.75 and 0.25 mg/L) for zero headspace extracts. Enrichment factors of at least 8 with recoveries in the 65-90% range have been routinely achieved. Method detection limits in reagent water and ZHE extract are 0.026 and 0.031 mg/L, respectively, for 40 mL samples. Typical distillation times are 10 minutes. The approximate sample load is 4 to 5 samples/hour for sample preparation per condenser system including cleanup time.

## REFERENCES

1) Report to EPA: Measurement of Polar, Water - soluble, Nonpurgeable VOCs in Aqueous matrices by Azeotropic Distillation - Gas Chromatography / Mass Spectrometry, Midwest Research Institute, September 30, 1989.

2) Peters, Anal. Chem., 1980, 52, 211 - 213, Steam Distillation Apparatus for Concentration of Trace Water Soluble Organics.

65

# ADAPTATION OF SW-846 METHODOLOGY FOR THE ORGANIC ANALYSIS OF RADIOACTIVE MIXED WASTES

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## ABSTRACT

Modifications to SW-846 sample preparation methodology permit the organic analysis of radioactive mixed waste with minimum personnel radiation exposure and equipment contamination. This paper describes modifications to SW-846 methods 5030 and 3510-3550 for sample preparation in radiation-zoned facilities (hood, glove box, and hot cell) and GC-MS analysis of the decontaminated organic extracts in a conventional laboratory for volatile and semivolatile organics by methods 8240 and 8270 (respectively). Results will be presented from the analysis of nearly 70 nuclear waste storage tank liquids and 17 sludges. Regulatory organics do not account for the organic matter suggested to be present by total organic carbon measurements.

## INTRODUCTION

The closure and decommissioning of nuclear waste storage tanks at the Oak Ridge National Laboratory (ORNL) required the chemical, physical, and radiochemical analysis of highly radioactive liquids and sludges to determine their regulatory classifications and to aid in selection of appropriate treatment and disposal methods. A part of this characterization was the analysis of volatile and semivolatile organic compounds in the liquids and sludges.

Approved methodologies for the determination of regulated volatile and semivolatile organic (and other) compounds in wastes are described in the U. S. Environmental Protection Agency (EPA) Solid Waste Manual 846 (SW-846) (1). However, these methods were designed for nonradioactive wastes, and their direct application to radioactive wastes would result in the exposure of laboratory personnel to high radiation fields, and could contaminate personnel, equipment, and instruments with radionuclides.

We find that modifications can be made to SW-846 methods to limit radiation exposure and contamination in keeping with "ALARA" (As Low As Reasonably Achievable) policy, and yet achieve reasonable method performance. Exposures are minimized by traditional radiochemical means of shielding, minimizing the time of exposure to the sample, and maximizing the distance from the sample that the operator conducts the preparation. In addition, sample amounts must be reduced for some preparations.

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*Operated by Martin Marietta Energy Systems, Inc., under U.S. Department of Energy contract DE-AC05-840R21400.

Our approach has been to prepare the samples using modified SW-846 methods in radioactivity zoned facilities such as radiochemical hoods, glove boxes, or hot cells. The organic extracts are effectively decontaminated of the bulk of the radionuclides, and they can be analyzed by SW-846 GC-MS methods in a conventional laboratory.

## EXPERIMENTAL

### Radioactive Waste Samples and Characteristics

The nuclear waste liquids analyzed in this project were collected by suction from underground storage tanks (2), some of which date to the 1940s. Sludges were collected using a coring device (2). Neither sample type was uniform in characteristics from layer to layer or tank to tank, and exhibited considerably diverse properties. The gross alpha activities ranged from <1 to 8.3 x $10^3$ becquerels/mL (Bq/mL) for liquids and to 6.5 x $10^5$ Bq/g for sludges. Gross beta/gamma activities were <20 to 3.6 x $10^6$ Bq/mL for liquids and up to 5.9 x $10^7$ Bq/g for sludges. The major radionuclides were $^{137}$Cs, $^{90}$Sr, and $^{60}$Co. Lesser activities of other radionuclides such as $^{3}$H and $^{233}$U also were present. The sludges were also enriched in $^{244}$Cm, $^{238}$Pu, $^{239}$Pu, and $^{241}$Am. The pH of the liquids ranged from highly acidic (0.2) to highly alkaline (12.7), and total solids ran from 0.3 to 170 mg/mL. The dominant anions were sulfate (to 83,000 mg/L) and nitrate (to 31,000 mg/L). The total organic carbon contents were high: liquids were 10 to 12,000 mg/L and sludges were 4,000 to 28,000 mg/kg.

### Radiochemical Facilities

The radioactivity of the samples required that they be prepared for organic analysis in radioactivity zoned facilities. Health Physics guidelines at ORNL (3) limit the total activity of "very high" radiotoxicity isotopes (such as $^{90}$Sr) to 0.1 microcuries (uCi) for monitored benchtop sample preparation, 10 uCi for radiochemical hood work, and 10 millicuries (mCi) for glove box operations. Benchtop operations are performed in radioactive contamination-zoned laboratories with limited personnel access and periodic health physics monitoring for contamination. Samples, equipment, and staff cannot leave the lab without health physics screening for contamination. The radiochemical hood is located in the contamination-zoned laboratory, and consists of a normal stainless steel fume hood which exhausts through high efficiency particle filters and charcoal filters. Radioactive samples are contained in lead "pigs" when not being processed. The laboratory room air pressure is kept at a slightly lower level than that of surrounding halls or rooms to prevent spread of any airborne contamination. Laboratory room air exhausts through the hood. Glove boxes are located in another contamination-zoned laboratory and they consist of a sealed stainless steel box which is vented to an air exhaust header (also carefully filtered) maintained at lower pressure than the laboratory air. Samples are bagged in and out in such a manner that the glove box atmosphere never is in direct contact with or vents to the laboratory air. Sample manipulations are conducted with the protection of heavy rubber gloves protruding through one wall of the box and below viewing windows. Work with higher activities (>10 mCi) must be performed in hot cells, which have three foot thick concrete walls and remote manipulators. Personnel using all types of facilities wear special coveralls and shoes, and carry radiation dosimeters of several types. Cleanliness and a deliberate, unhurried, and carefully considered work plan are essential to successful operations. As noted in the Results and Discussion section, sample preparation was performed in all three types of facilities at the ORNL High Radiation Level Analytical Laboratory, depending upon the activity of the samples, and the operations performed.

### Methods

The methodology described in this paper is based upon several SW-846 methods: 5030, 5040, and 8240 for volatile organic compounds in aqueous liquids; 3510 or 3550 and 8270 for semivolatile organic compounds in aqueous liquids and sludges (respectively). These methods were approached

as prescribed in the SW-846 manual (1), and the original methods are not described here. Modifications necessary for limiting radiation exposure and contamination are discussed in the text. In some cases, EPA Contract Laboratory Program surrogate standards or matrix spike mixtures were used in method evaluation. Also, a modification was made to method 8015 to permit the direct aqueous injection GC analysis of mg/L concentrations of several alcohols and ketones.

## RESULTS AND DISCUSSION

### Volatile Organics Analysis (VOA) of Aqueous Liquid Wastes

The approach for the VOA entailed an off-line purge and trap (P/T) in a glove box located in a radiochemical laboratory. A glove box operation was required because the whole sample container (250 mL volume) had to be handled for the first opening for VOA. This step was followed by thermal desorption and a second purge and trap and gas chromatography-mass spectrometry (GC-MS) in a separate, conventional GC-MS laboratory. The procedure and apparatus are described in detail elsewhere (4). Briefly, 5 mL of aqueous waste sample and CLP surrogate standards were purged from a 40 mL VOA vial and a specially designed P/T head into a method 624 triple sorbent trap located outside of the glove box using method 5030 purging conditions. We have not detected the transfer into the trap of any radioactivity from waste samples. The internal standard was not added at this step to allow the recoveries of the two P/T stages to be differentiated. Matrix spiked samples and blanks also were prepared with the samples. The traps were screened by standard smear and probe procedures for external contamination, and were then transferred to a conventional GC-MS laboratory. Analysis was conducted by thermally desorbing the traps in a tube furnace at 182°C with a helium flow of 35 mL/min for 11 min. The effluent was bubbled through the Tekmar purging vessel which contained 5 mL of laboratory distilled water and CLP internal standards. This is similar to the desorption of volatile organics sampling train traps in method 5040, except that the internal standard was added to the water, and not swept into the triple sorbent trap prior to thermal desorption. The remainder of the analysis was conducted per method 8240 P/T GC-MS.

We find that this procedure performs quite well for the determination of volatile organic compounds in radioactive aqueous liquids. Keeping the same sample volume as stipulated in SW-846 permits the same reporting limits (i.e., 5-10 $\mu$g/L) as the conventional procedure. Using a VOA vial for the purging chamber allows foam (a problem with high salt content nuclear wastes) to disperse without contaminating the sampling head and transfer lines. A new vial is conveniently used for each analysis, preventing carryover of contaminants and minimizing equipment cleaning operations which are difficult to conduct in a glove box. The performance of the method as gauged by recoveries of surrogate standards and matrix spikes (Tables 1 and 2) is quite reasonable, considering the off-line procedure, two P/T steps, and the hostile sample matrix. The average recoveries generally fall within the QC Acceptance Limits for groundwater (1). The applicability of groundwater limits in methods 5030/8240 to aqueous nuclear wastes by modified 5030/5040/8240 has not been established, but the former are useful for comparison. The reason for the low bromofluorobenzene and chlorobenzene recoveries is not clear, but the similar results for the former in samples and blanks indicates that it is probably a characteristic of the modified apparatus, and not a sample matrix effect. The fact that bromofluorobenzene is the least volatile of the surrogate standards and that chlorobenzene has the highest boiling point of the matrix spiked compounds suggests that the sparging may not have been sufficiently vigorous for optimal recovery. Some of the matrix spike recovery data were discarded from the tabulation in Table 2 because they were inexplicably high (one for benzene, two for toluene, and one for chlorobenzene) or zero when the recoveries of the other matrix spikes were reasonable (two for toluene).

The method blanks were good, and showed only traces of methylene chloride and toluene (<20 μg/L each) and acetone (<40 μg/L). Other volatile organics were occasionally detected at levels of <20 μg/L. As reported elsewhere (4), the main volatile organics found in the samples were acetone (<5-600 μg/L), methylene chloride (8-1,000 μg/L), chloroform (3-400 μg/L), and methyl isobutyl ketone (<5-3,000 μg/L). Lesser concentrations of benzene, toluene, xylenes, trichloroethene, and tetrachloroethane also were determined in some samples.

Major Volatile Organic Compounds in Aqueous Liquids

The VOA was supplemented by a direct aqueous injection GC procedure similar to SW-846 method 8015. This analysis was conducted for two purposes: (a) to determine certain compounds which do not purge and cannot be determined by the VOA, eg, methanol, and (b) to identify aqueous samples which were too concentrated in organic matter to P/T from a 5 mL volume. The latter was to protect the GC-MS from contamination from overloaded traps. A 1.5 mL volume of sample was taken at the time the P/T for VOA was conducted in the glove box, and a 3 μL aliquot of the sample was analyzed before the traps were taken to the GC-MS laboratory. The direct aqueous injection GC was performed using a GC located in a radioactivity contamination-zoned laboratory. The instrument was equipped with the same column packing as the method 8240 GC-MS (i.e., 0.125 in. OD x 8 ft. stainless steel packed with 1% SP-100 on 60/80 mesh Carbopack B), and a flame ionization detector, but was temperature programmed differently (70°C for 2 min, then program to 220°C at 16°C/min and hold at 220°C for 16 min). Three μL were injected using the solvent-flush technique (water), and peaks were identified using retention time. Quantitation was by the method of external standards versus 4 concentration levels of standards ranging from 3 to 40 mg/L.

This supplementary method proved to be quite valuable for the analysis of radioactive aqueous liquids. The method determined several alcohols which the VOA could not analyze, and also provided a better quantitation of ketones at mg/L concentrations which were above the calibration range of the VOA. Methanol and ethanol were found in several samples at concentrations up to ca. 40 mg/L. In two aqueous samples which were overlayered with an organic solvent mixture, was valuable in measuring alcohol and ketone concentrations of 1,000 to 2,000 mg/L. The detection limit of the method was ca. 1 mg/L, and the recoveries of matrix spikes averaged >90% for all analytes except for allyl alcohol (86%), because of peak tailing for the latter.

Semivolatile Organics Analysis (SVOA) of Aqueous Liquid Wastes

This sample preparation was conducted in a radiochemical hood after the sample had been opened, the P/T for VOA completed, and an analysis of gross alpha and beta/gamma activity had been conducted. A 20 mL volume of sample and a 40 mL VOA vial were utilized instead of the 1 L volume and separatory funnel stipulated by SW-846 method 3510 because the radioactivity of the latter was generally too great for a hood, and separatory funnel extractions in a hot cell were considered impractical for extensive numbers of samples. This reduced the reporting limits 50-fold, to 500-2,500 μg/L. The sample was spiked with CLP surrogate standards (and matrix spikes, when required) and three extractions were made with 5 mL of methylene chloride. The initial pH of the sample determined the pH of the first set of extractions. Three distinct cases were observed: pH <2, pH ca. 6-9, and pH >10. When the pH was <2, the sample was extracted as is to recover an acid/neutral fraction, and then the pH was adjusted to >10 with 1 M sodium hydroxide for extraction of the base fraction. When the initial pH was >10, the base/neutral fraction was extracted first, before pH adjustment and recovery of the acid fraction. For samples with pH 6-9, the pH was first adjusted to >10 and treated as noted above. The extractions were performed by gently tumbling the vial ca. 30 times. More vigorous agitation caused emulsion problems. In some cases, emulsions formed in spite of the gentle agitation, and centrifugation was required to break the emulsion. Other types of complicating sample behavior observed with nuclear wastes included evolution of oxides of nitrogen, precipitation, and significant buffering capacity.

Generation of oxides of nitrogen during acidification suggests the presence of nitrite in the samples, and raises the possibility of artifact formation. In a few cases, precipitates formed upon acidification. Also, a few of the initially alkaline samples required up to ca. 7 mL of 12 M hydrochloric acid, versus the 1-2 mL typically needed for adjustment to a pH of <2. The methylene chloride layers were recovered with a Pasteur pipette, and were separated from traces of water by passing through a disposable 10 mL polypropylene syringe fitted with a 0.45 um porosity Acrodisc CR Teflon membrane filter. The fractions were combined, reduced to a 1 mL volume under dry, flowing nitrogen gas, and were then transferred to autosampler vials and the CLP semivolatile organic internal standard solution was added.

Two characterizations were conducted before the SVOA extracts were transferred to the GC-MS laboratory. A GC equipped with an autosampler and a flame ionization detector, located in the contamination-zoned laboratory, was used to prescreen the samples to identify those which did not require GC-MS analysis and also those which required dilution to prevent overloading and organic contamination of the GC-MS. For the aqueous nuclear wastes, the latter was not a problem, and the main use was to screen out samples. The criteria used here was that if the sample did not contain any analyte peaks (different from those in a blank sample) greater than the responses of 4 mg/L (injected concentrations) of CLP Target Compound List (TCL) base/neutral and acid standards, TCL pesticide standards, or other selected Appendix VIII compounds (corresponding to a concentration in the original aqueous sample of 200 $\mu$g/L), then it did not require GC-MS analysis. In practice, less than 20% of the samples were rejected at this point. The SVOA extract also was sampled for gross alpha and beta/gamma activity determination. This characterization was conducted to prevent contamination of the GC-MS laboratory. For aqueous samples, the decontamination factors ranged from 2 to 4 orders of magnitude, and very little radioactivity typically carried over into the SVOA extract. Typically, the samples contained less than 0.01 uCi of radioactivity. In the very few cases where greater activity was observed, a 100 uL aliquot of the SVOA extract or a 1 mL aliquot of a 1:10 dilution (the latter re-fortified with internal standard) were sent to the GC-MS laboratory. It should be pointed out that this reported level of decontamination must never be assumed. The presence of large amounts of chelators or extractants in wastes conceivably could enhance carry-over of radionuclides. The GC-MS analysis was conducted as required by method 8270, except that it was not possible for the base/neutral and acid fractions to be combined and internal standard added at that point.

The modified procedure performed well in comparison with SW-846 QC Acceptance Limits for the conventional procedures. The recoveries of surrogate standards and matrix spikes are listed in Tables 3 and 4. The average recoveries fall well within the QC limits. Although all of the base/neutral compound recoveries were used for the tabulation, some of the acid compound data were deleted because of possible preparation or analysis problems. It is possible that the high initial pH of some samples caused the destruction of the phenolic surrogates and matrix spikes (a matrix effect). Quantitation of at least one phenol, pentachlorophenol historically is difficult. The method blanks were free of TCL compounds, except for traces of the ubiquitous phthalates, di-n-butyl (110 $\mu$g/L) and di-n-octyl (170 $\mu$g/L). Low concentrations (ca. 100-200 $\mu$g/L) of hydrocarbons were observed in all samples and blanks, and were contributed by the Teflon filter assembly. They did not interfere with the identification and quantitation of the TCL compounds. The only SVOA hit exceeding the reporting limit was benzoic acid (2,900 $\mu$g/L). Low levels (ca 20 - 300 $\mu$g/L) of 2-nitrophenol, 2,4-dinitrophenol, 2,4,5-trinitrophenol, and 2-4 ring polycyclic aromatic hydrocarbons also were determined. The main semivolatile organic compound found was the tentatively identified compound tributyl phosphate (2,000-30,000 $\mu$g/L). This compound was not present in the computerized spectral library, and was initially identified manually. It is an important component of the Purex process, and its presence was expected. Dibromonitrophenol also was detected in two samples (700 $\mu$g/L). The obvious generation of oxides of nitrogen during the acidification of some

samples raises the question of at lest some of these nitro-derivatives being artifactual. Our experiences with the SVOA of aqueous liquids are described in more detail elsewhere (5).

SVOA of Sludges

The SVOA of waste tank sludges followed methods 3550 and 8270 with the main exception being the masses extracted. The aliquots varied from ca. 2 to 20 g because of the limited amounts of sample available. The reporting limits accordingly ranged from 500 - 2,500 $\mu$g/kg to 5,000 - 25,000 $\mu$g/kg. The sludge sample extractions with larger masses of sample (10-20 g) or with the highly radioactive samples were conducted remotely in a hot cell, while the smaller masses (eg, 2-5 g) were extracted in a radiochemical hood. The extracts were decanted from ultrasonic extractions conducted in a beaker, and were filtered through a medium porosity sintered glass funnel. Extractions conducted directly in the sintered glass funnel resulted in plugging of the filter. The composited extracts in the hot cell were sampled and analyzed for gross alpha and beta/gamma activity before transfer to a radiochemical hood for volume reduction (with flowing nitrogen gas) to 1 mL, transfer to an autosampler vial, and addition of the CLP SVOA internal standards. The concentrated extracts were sampled for gross alpha and beta/gamma activity and were screened with the GC before transfer to the GC-MS laboratory. In contrast to the behavior with the aqueous liquids, several of the extracts from the more highly radioactive sludges contained appreciable amounts of radioactivity (ca. 0.1 uCi), and 100 uL aliquots were transferred to small-volume autosampler vials to limit the activity taken to the GC-MS laboratory. Also, some of the extracts of the 20 g samples contained too high background levels of chromatographable organic matter, and 1:10 dilutions had to be made before GC-MS. The background was a very complex hydrocarbon mixture.

The performance of surrogate standards in this procedure is shown in Table 5. The recoveries for sludge samples are lower than for the aqueous liquids, and the reproducibilities are poorer. Problems were experienced with the recoveries of acidic compounds, and this undoubtedly was a result of the alkaline nature of the sludges, and the lack of pH adjustment procedures for solid samples in SW-846. Improved methods for semivolatile organics extraction of sludges are needed. The blanks were clean relative to the sludge extracts. the main compounds determined in the sludges were 4-6 ring polycyclic aromatic hydrocarbons (at concentrations of a few hundred to 240,000 $\mu$g/kg), phthalates (eg, bis-[2-ethylhexyl]phthalate at 57,000 $\mu$g/kg in one sludge), and tributylphosphate (2-300 mg/kg). The relative accumulation of polycyclic aromatic hydrocarbons in the sludges probably reflects their low aqueous solubilities and salting-out from the high ionic strength liquids.

Total Organic Carbon (TOC) Accounting

TOC was estimated by another group using method 9060. An important conclusion from the comparison of the TOC data with the regulatory organics analyses is that the latter does not account for the organic matter suggested to be present by the former. For approximately 50% of the aqueous liquid samples, the TOC accounting was < 5%, and for 78% of the samples, the accounting was < 20%. For sludges, the TOC accounting was even poorer for 95% of the sludge samples, the accounting was < 5%. The unaccounted organic matter seems to consist of highly polar, water soluble organics arising at least in part from the degradation of chelators, extractants, and other compounds used in the nuclear industry (2, 6, 7). For example, we have found (2,6) that a simple trimethylsilylation of the regulatory SVOA extract can double the organic matter visualized, and even more can be detected by evaporation and derivatization of the aqueous sample (6,7). Certainly, this is an area for much further work.

## SUMMARY

SW-846 sample methodology can be adapted to radiochemical facility use for the preparation of highly radioactive samples for VOA and SVOA. Analyses of regulated volatile and semivolatile organics can be conducted with minimal personnel radiation exposure and instrument or equipment contamination and with acceptable method performance.

Improvements in instrumental sensitivity are needed to improve the detection limits for SVOA where limited by sample amount. Development of new extraction technology applicable to hot cell or glove box use with larger sample aliquots also would improve SVOA sensitivity. Sludges in particular would benefit from extraction methodology including pH adjustment.

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TABLE 1. RECOVERIES OF VOA SURROGATE STANDARDS FROM RADIOACTIVE AQUEOUS LIQUID WASTE

| Standard[a] | Recovery[b], % Wastes (n = 65) | Blanks (n = 7) | QC Limits |
|---|---|---|---|
| Toluene-$d_8$ | 89 ± 17 | 91 ± 11 | 88 - 110 |
| Bromofluorobenzene | 59 ± 15 | 61 ± 12 | 86 - 115 |
| 1,2-Dichloroethane-$d_4$ | 81 ± 11 | 86 ± 13 | 76 - 114 |

[a] Spiked at concentration of 50 $\mu$g/L
[b] Average ± standard deviations for samples and blanks, and ranges of QC Acceptance Limits.

TABLE 2. RECOVERIES OF VOA MATRIX SPIKES FROM RADIOACTIVE AQUEOUS LIQUID WASTE

| Spike[a] | Recovery[b], % Waste (n = 20)[c] | QC Limits[d] |
|---|---|---|
| 1,1-Dichloroethene | 105 ± 18 | D - 234 |
| Trichloroethene | 87 ± 14 | 71 - 157 |
| Benzene | 89 ± 15[e] | 37 - 151 |
| Toluene | 81 ± 20[f] | 47 - 150 |
| Chlorobenzene | 67 ± 13[e] | 37 - 160 |

[a] Spiked at 50 $\mu$g/L Concentration.
[b] Averages ± Standard deviations for waste and ranges for QC Acceptance Limits.
[c] n = 20 except as noted.
[d] for 20 $\mu$g/L Spikes.
[e] n = 19.
[f] n = 15.

TABLE 3. SVOA SURROGATE STANDARD RECOVERIES FROM RADIOACTIVE AQUEOUS LIQUID WASTES

| Standard[a] | Recovery[b], % Wastes (n = 67) | Blanks (n = 8) | QC Limits |
|---|---|---|---|
| Nitrobenzene-$d_5$ | 70 ± 15 | 65 ± 18 | 35 - 114 |
| 2-Fluorobiphenyl | 64 ± 14 | 58 ± 13 | 43 - 116 |
| Terphenyl-$d_{14}$ | 88 ± 17 | 85 ± 18 | 33 - 141 |
| Phenol-$d_5$ | 53 ± 12[c] | 49 ± 12 | 10 - 94 |
| 2-Fluorophenol | 48 ± 11[c] | 42 ± 8 | 21 - 100 |
| 2,4,6-Tribromophenol | 71 ± 17[c] | 69 ± 14 | 10 - 123 |

[a] Base/neutral and acid compounds spiked at 5 and 10 mg/L concentrations, respectively.
[b] Averages ± standard deviations for wastes and blanks and ranges for QC Acceptance Limits.
[c] n = 63.

TABLE 4. SVOA MATRIX SPIKE RECOVERIES FROM RADIOACTIVE AQUEOUS LIQUID WASTE

| Spike[a] | Recovery[b], % Wastes (n = 14) | QC Limits[c] |
|---|---|---|
| 1,4-Dichlorobenzene | 50 ± 10 | 20 - 124 |
| N-nitroso-di-n-propylamine | 66 ± 10 | D - 230 |
| 1,2,4-Trichlorobenzene | 53 ± 12 | 44 - 142 |
| Acenaphthene | 64 ± 13 | 47 - 145 |
| 2,4-Dinitrotoluene | 71 ± 18 | 39 - 139 |
| Pyrene | 78 ± 12 | 52 - 115 |
| Phenol | 40 ± 9[d] | 5 - 112 |
| 2-Chlorophenol | 43 ± 7[d] | 23 - 134 |
| 4-Chloro-3-methylphenol | 55 ± 19[d] | 22 - 147 |
| 4-Nitrophenol | 69 ± 31[d] | D - 132 |
| Pentachlorophenol | 74 ± 32[e] | 14 - 176 |

[a] Base/neutral and acid compounds spiked at 5 and 10 mg/L concentrations, respectively.
[b] Averages ± standard deviations for wastes and ranges for QC Acceptance Limits.
[c] For 100 $\mu$g/L spikes.
[d] n = 10.
[e] n = 8.

TABLE 5. RECOVERIES OF SVOA SURROGATE STANDARDS FROM RADIOACTIVE WASTE SLUDGES

| | Recovery[b], % | | |
|---|---|---|---|
| Standard[a] | Sludges (n = 19) | Blank (n = 1) | QC Limit |
| Nitrobenzene-$d_5$ | 18 ± 17 | 33 | 23 - 120 |
| 2-Fluorobiphonyl | 37 ± 19 | 35 | 30 - 115 |
| Terphenyl-$d_{14}$ | 66 ± 20 | 99 | 18 - 137 |
| Phenol-$d_5$ | 47 ± 20 | 46 | 24 ± 113 |
| 2-Fluorophenol | 35 ± 19 | 39 | 25 - 121 |
| 2,4,6-Tribromophenol | 37 ± 18 | 92 | 19 - 122 |

[a] Base/neutral and acid compounds spiked at concentrations of 1 and 2 mg/kg (20 g sample) to 10 and 20 mg/kg (2g sample), respectively.

[b] Averages ± standard deviations for sludges, one result for blank, and range for QC Acceptance Limits.

66

# A METHOD TO IMPROVE THE COLUMN CLEANUP EFFICIENCY AND THROUGHPUT OF OILY WASTE SAMPLE EXTRACTS THROUGH A NITROGEN PRESSURIZED ALUMINA COLUMN (A MODIFICATION OF SW-846 METHOD 3611).

by

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## INTRODUCTION

The alumina column cleanup technique that is described as Method 3611 in Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846, 3rd Ed., Vol. 1B, 1986) for the separation of petroleum wastes has one drawback when it is applied to samples that have very high levels of non-target hydrocarbons. The flow of the column frequently becomes obstructed by large molecular weight (non-gas chromatographable) aliphatic hydrocarbons. This obstruction results in very low flow through the column and causes poor separation, breakthrough of non-target aliphatic hydrocarbons, and sometimes even the complete evaporation of the eluting solvent faster than it drips from the column. The time required to perform this cleanup can exceed twenty four hours. A solution to this problem is the addition of nitrogen pressure to the head of the column to maintain the optimum flow through the column. By pressurizing the column, the time required to perform the alumina column cleanup of petroleum wastes is dramatically reduced and the cleanup efficiency is improved. Also discussed will be the amount of material that may be loaded onto the column before cleanup efficiency become impaired.

## EXPERIMENTAL SECTION

### Reagents:

* Methylene chloride, pesticide grade
* Hexanes, pesticide grade
* Alumina, Chromatographic grade 80-325 mesh, EmScience. Activated at 190 degrees centigrade for four hours.

### Apparatus:

A 10 mm i.d. glass column with a 250 mL reservoir is attached to an addition funnel assembly with a ball and socket joint. The addition funnel assembly has a gas inlet port through which nitrogen pressure is applied (See Fig. 1). This procedure employs glassware under pressure, so appropriate safety practices should be followed. These include the use of shields, glassware that is in good condition, and regulating the pressure to less than 20 psi.

Sample Description:

A refinery landfarm soil sample was chosen because it had proved difficult to column clean during its initial analysis. Also, the sample contained several target analytes as well as large amounts of interfering hydrocarbons. A residue determination was performed in order to place a 200 mg equivalent of extractable organics onto the columns. An appropriate amount of the sample was extracted so that all of the experimental cleanups could be performed from a single extract. Surrogate compounds were added to the sample prior to extraction to monitor the preparation quality. The sample was extracted by sonication and then exchanged to hexane using a Kuderna Danish evaporative concentrator with a three ball Snyder column. Two aliquots of the extract were cleaned with gravity flow columns and two aliquots were cleaned using nitrogen pressurized columns.

The columns were packed with 10 g. of alumina and pre-eluted with hexane. The aliquots were applied to the heads of the columns. The base/neutral aliphatic fractions were eluted with 13 mL of hexane and then discarded. The base/neutral aromatic fractions were eluted with 100 mL of methylene chloride.

All of the elution times were recorded. The methylene chloride fractions were then concentrated and the target compounds and surrogates were analyzed according to SW-846 Method 8270. An indication of remaining aliphatics was shown by quantitating mass 57 for the entire chromatogram.

## RESULTS AND DISCUSSION

The elution times of the two pressurized columns were dramatically lower than for the two gravity columns, as shown in Table 1. The total elution time was reduced from more than 24 hours to less than two hours. This is a significant reduction of sample cleanup time and can markedly increase the laboratory's throughput. The flow rate of 2 mL/min. that is specified in Method 3611 can be achieved by regulating the pressure at the head of the column.

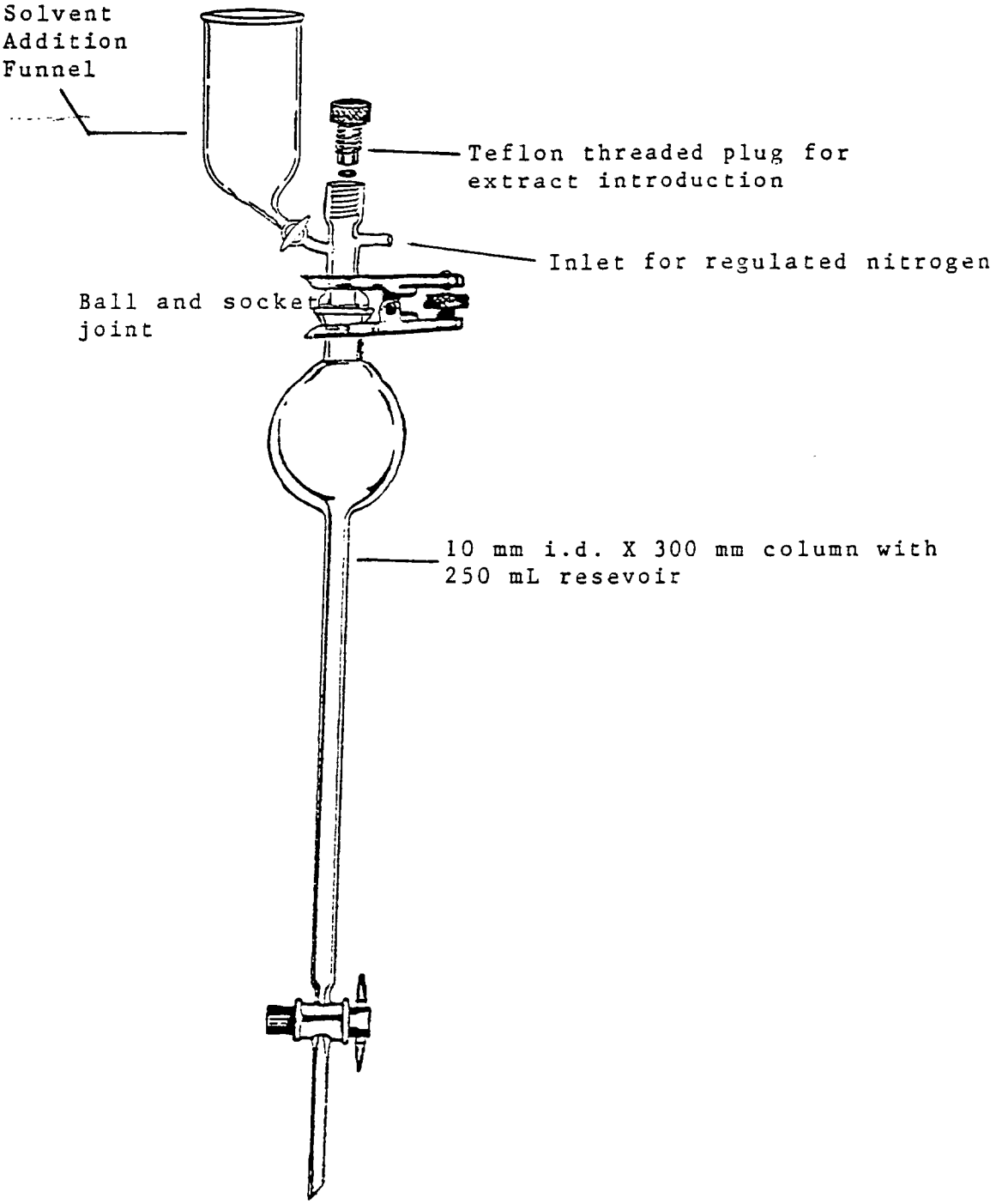
Table 2 contains the surrogate and target compound results. Analyte recoveries for pressurized column cleaned extracts were essentially identical to the recoveries obtained from gravity columns. The surrogates were recovered within acceptable limits in all cases. The total area for the mass chromatogram of mass 57 shows a reduction of an order of magnitude in the amount of aliphatic hydrocarbon interference in the pressure cleaned extracts (see fig. 2).

Some preliminary work has been performed to determine the amount of extractable material that may be placed on the column before the cleanup efficiency becomes impaired. Initial results show that the column may be loaded at up to two or three times the amount recommended in Method 3611. However, difficulties in the extraction and partition processes may prevent the use of these larger sample amounts.

## CONCLUSION

The environmental analytical market is requiring quicker turnaround times and lower limits of detection. These two requirements are frequently at odds. But, with the utilization of this pressurized column technique, the advantages of column cleaning the extracts of samples from difficult matrices can be enjoyed while still maintaining high laboratory productivity.

This technique can also be expanded to include other preparative column cleanup methods that are plagued by slow elution times such as SW-846 Method 3630, the silica gel column cleanup for polycyclic aromatic hydrocarbons.




PRESSURE COLUMN ASSEMBLY

Fig. 1

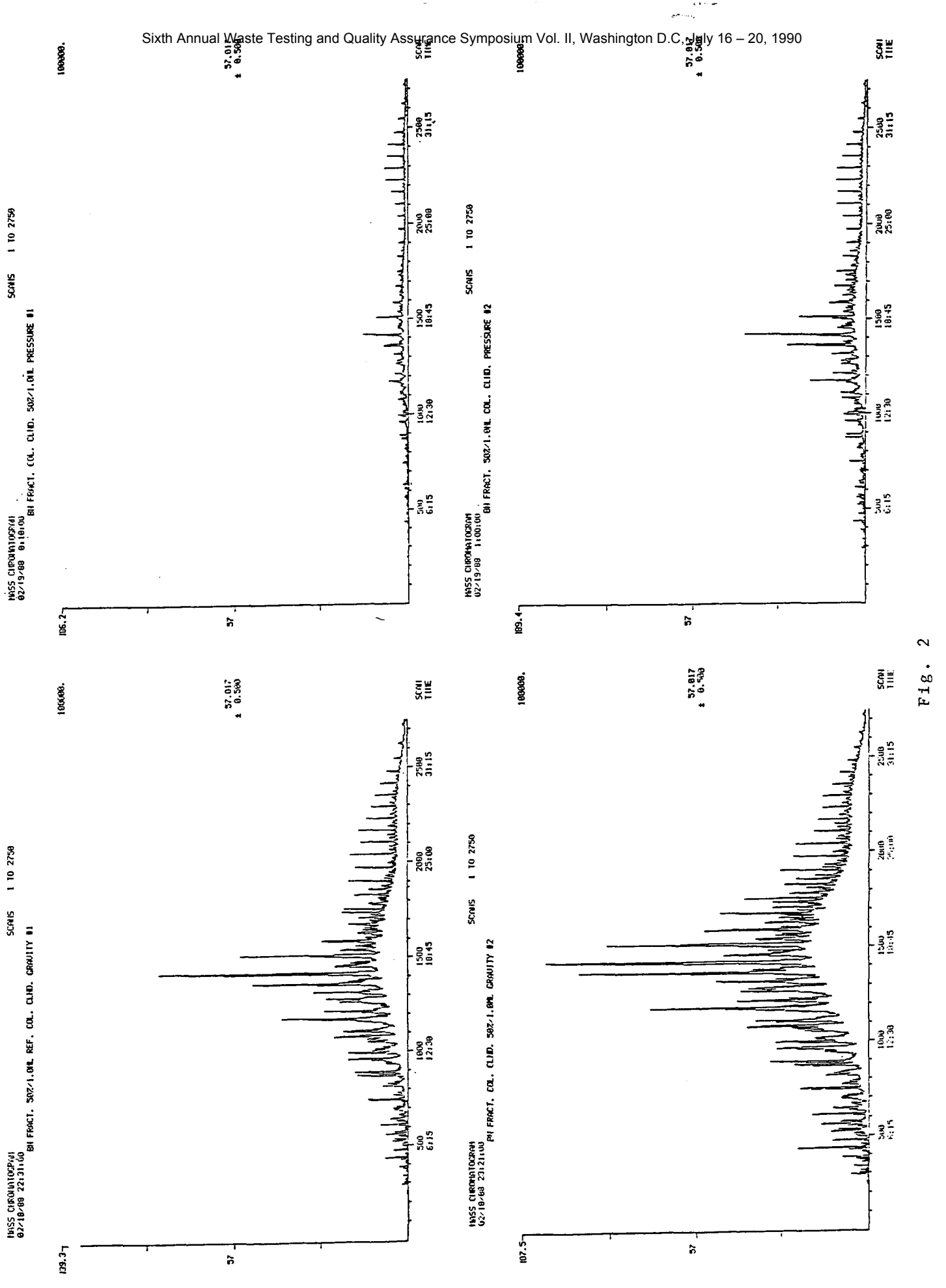

MASS CHROMATOGRAM
02/19/88 0:10:00
BH FRACT. COL. CLID. 502/1.0ML PRESSURE #1
SCANS 1 TO 2750
MASS CHROMATOGRAM
02/19/88 1:00:00
BH FRACT. 502/1.0ML COL. CLID. PRESSURE #2
SCANS 1 TO 2750
MASS CHROMATOGRAM
02/18/88 22:31:00
BH FRACT. 502/1.0ML REF. COL. CLID. GRAVITY #1
SCANS 1 TO 2750
MASS CHROMATOGRAM
02/18/88 23:21:00
PH FRACT. COL. CLID. 502/1.0ML GRAVITY #2
SCANS 1 TO 2750
TIME
SCAN

Fig. 2

## TABLE 1

## ELUTION TIMES
in minutes

| SAMPLE | HEXANE PRE-ELUTION | EXTRACT APPLICATION | HEXANE ELUTION | METHYLENE CHLORIDE ELUTION | TOTAL TIME |
|---|---|---|---|---|---|
| PRESS. #1 | 2.5 | 1.5 | 8.0 | 90 | 104 |
| PRESS. #2 | 3.0 | 1.5 | 10.0 | 95 | 113 |
| GRAV. #1 | 20.0 | 65.0 | 245.0 | 18 HOURS | 24 HOURS |
| GRAV. #2 | 15.0 | 57.0 | 228.0 | 18 HOURS | 24 HOURS |

## TABLE 2

## COMPARISON OF ANALYTICAL RESULTS

| ANALYTE | GRAVITY #1 | GRAVITY #2 | PRESSURE #1 | PRESSURE#2 |
|---|---|---|---|---|
| Naphthalene | 100,000 | 99,000 | 100,000 | 110,000 |
| 1-Methylnaphthalene | 290,000 | 270,000 | 310,000 | 310,000 |
| Phenanthrene | 170,000 | 160,000 | 180,000 | 170,000 |
| Anthracene | 7,900 | 8,500 | 7,400 | 8,300 |
| Fluoranthene | 5,400 | 6,900 | 5,500 | 5,300 |
| Pyrene | 39,000 | 36,000 | 47,000 | 47,000 |
| Benzo(A)anthracene | 25,000 | 24,000 | 26,000 | 25,000 |
| Chrysene | 37,000 | 33,000 | 36,000 | 37,000 |
| Benzo(B)fluoranthene | 9,900 | 9,200 | 9,500 | 9,800 |
| Benzo(A)pyrene | 11,000 | 11,000 | 11,000 | 11,000 |
| Dibenz(A,H)anthracene | 3,700 | 3,900 | 3,500 | 4,200 |

Analyte results in ug/kg

| SURROGATE | GRAVITY #1 | GRAVITY #2 | PRESSURE #1 | PRESSURE#2 |
|---|---|---|---|---|
| D5-Nitrobenzene | 77% | 72% | 76% | 85% |
| 2-Fluorobiphenyl | 83% | 73% | 91% | 96% |
| D14-Terphenyl | 78% | 78% | 89% | 86% |

| COMPOUND NAME | GRAVITY #1 | GRAVITY #2 | PRESSURE #1 | PRESSURE#2 |
|---|---|---|---|---|
| Total Area Mass 57 | 14,000,000 | 26,000,000 | 2,800,000 | 5,500,000 |

67

# A NEW AND IMPROVED TECHNIQUE FOR SPECIATION AND QUANTITATION OF AROCLORS IN HAZARDOUS WASTES

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ABSTRACT

Skilled chemists can usually recognize Aroclor patterns on visible inspection of packed column chromatograms. Identification is difficult or impossible, however, when two or more Aroclors are present, or the PCB residue has been modified by weathering, metabolism or treatment. Quantitation also presents problems for packed column GC methods. In particular, integrating the total area under the pattern is error prone because of interfering compounds in sample extracts.

In an effort to improve PCB analysis in support of hazardous waste regulations, our laboratory has investigated high resolution GC and new approaches to interpreting high resolution GC data. One approach, measurement of selected chlorobiphenyl congeners, has proven useful for reducing data from a 60 meter DB-5 column. Only 12 chlorobiphenyl congeners must be determined, International Union of Pure and Applied Chemistry (IUPAC) Nos. 15, 18, 31, 87, 105, 110, 118, 170, 180, 183, 203 and 206, and from these marker compounds Aroclors 1016, 1254, 1260 and 1268 are estimated. The remaining regulated Aroclor mixtures are also measured by this technique making it suitable for enforcement of existing regulations.

Our laboratory determines an additional 34 chlorobiphenyl congeners which together are the major constituents of the commercial Aroclor formulations, as well as the predominant congeners in the environment. The sum of PCB congener concentrations, "s-PCB", is generally about 70% of the total Aroclor content, and may provide information needed in the future for measuring residues after treatment.

The use of capillary column separations and data reduction procedures described has a number of advantages over packed column GC procedures: 1) data interpretation does not require analyst judgement and can be automated; 2) the techique makes full use of the separation power of capillary columns to minimize interference by pesticides and other sample components; and 3) the technique accurately measures PCBs in samples with more than one Aroclor.

The application of this technique to the determination of Aroclors in auto shredder waste is described and results compared to SW-846 method 8080.

## INTRODUCTION

Much has been written about the problems of identification and measurement of Aroclor mixtures (1,2). Packed column gas chromatography (GC) with an electron capture detector (ECD) has been the preferred analytical technique for PCB analysis for over 25 years. Historically, quarter inch diameter packed columns with chromatographic efficiencies of about 3,500 theoretical plates were operated under isothermal conditions. The detectors with either a tritium or nickel source were readily fouled due to column bleed, and even so-called linearized detectors had linear ranges of less than two decades. This nonlinearity frequently necessitated sample dilution and repeat analysis for accurate quantitation. The Aroclor pattern was typically confirmed by chromatography on a second GC column requiring further analysis time. A major problem discovered early on was that of interferences including pesticides, i.e., DDT (3), phthalates, and other common environmental contaminants. These interference problems were usually solved by adsorption chromatography on silica (3), Florisil (4) or alumina (5).

The limitations of packed column techniques are most apparent when samples contain more than one Aroclor, or the Aroclor pattern has been altered by environmental weathering, metabolism or treatment. The most demanding samples are usually referred to a senior chemist or supervisor, because of the need for a trained eye to properly "judge" the sample contents.

Today, capillary GC is a mature technology due to advancements in microprocessor controls, splitless and cold on-column injection techniques, and computerized data acquisition and processing. The modulated pulsed frequency ECDs have greatly extended the linear dynamic range. Fused silica capillary columns with various bonded and coated stationary phases are available commercially, and these columns deliver efficiencies of 3,000 - 5,000 plates/meter. Since most public health and hazardous waste testing laboratories now have capillary instruments, a need has arisen to develop appropriate tools for data interpretation.

Over the past three years our laboratory has been determining PCBs in sportfish and other marine organisms in order to estimate human health risks to consumers (6). The PCB residues in these organisms may differ from single Aroclor standards due to: 1) weathering in the water column and marine sediments; 2) metabolism at various levels in the food chain; and 3) the occurrance of more than one Aroclor mixture as well as other electron-capturing, halogenated pesticides and metabolites.

We have found that the determination of Aroclors is possible in such samples, but only using capillary GC. When using GC columns with over 200,000 plates, however, data reduction is extremely important as it is not uncommon to have more than 100 peaks in a chromatogram. In the marine studies seven chlorobiphenyl markers were used to estimate Aroclor 1254 and Aroclor 1260 (7), Aroclors for which carcinogenicity potency factors have been estimated. In further developing this technique we find that

all of the regulated Aroclors can be determined in hazardous wastes using data on 12 individual isomers.

The purpose of this paper is to describe the identification and quantitation of Aroclors using selected congener data. The analysis is simplified because all estimates are based on the determination of 12 chlorobiphenyl congeners. Because the procedure is simple and very specific, it is rugged, accomodates a range of operator skills, and is amenable to automated data processing. Application of the method to the analysis of auto shredder waste, a matrix which has proved difficult to analyze by packed column procedures (SW-846 method 8080) is described.

## METHODS AND MATERIALS

Chemicals. Chlorobiphenyl isomer mixtures were obtained from the National Research Council Canada (NRCC), Marine Analytical Chemistry Standards Program (Halifax, Nova Scotia). Individual PCB congeners also are available commercially from several suppliers. Aroclor standards were provided by the U. S. Environmental Protection Agency (Research Triangle Park, NC). Aroclor formulations were diluted to 100 ng/mL and chlorobiphenyl isomers standards were diluted 100-fold using isooctane in both cases.

Nomenclature. The International Union of Pure and Applied Chemistry (IUPAC) numbering system developed by Ballschmiter and Zell (8) and designating all 209 polychlorinated biphenyl isomers is used throughout this report. The sum of all identified chlorinated biphenyl isomers is denoted s-PCB. Similarly, the sum of Aroclor concentrations is referred to as s-Aroclor. To facilitate the interpretation and comparison of congener patterns, PCB data is normalized by dividing the individual isomer concentrations by s-PCB.

Quantitative Analysis of Chlorobiphenyls. Details of the determination of PCB congeners are described elsewhere (7). Briefly, compounds were measured by gas-liquid chromatography on an instrument equipped with a $^{63}Ni$ electron capture detector, an autosampler/injector and a chromatography digitizer/computerized data system. Purged splitless sample introduction, a 60 m X 0.32 mm 0.25 um DB-5 capillary column (J & W Scientific, Folsom, CA) and a 103 min oven temperature program were used.

Extraction and Sample Cleanup. Auto shredder waste samples were extracted using the EPA slurry extraction procedure. Air dried samples (ca. 500 g) were extracted with 3 X 2 L of hexane/acetone on a platform shaker. The extracts were combined, exchanged to hexane, cleaned by partitioning with sulfuric acid, and finally exchanged to isooctane.

## RESULTS AND DISCUSSION

Determination of Chlorobiphenyl Congeners. The analysis of individual chlorobiphenyl isomers, so-called PCB congeners, by gas-liquid

chromatography requires not only high resolution, but also a high degree of reproducibility. The cleanup of sample extracts by partitioning, treatment with acid, and adsorption chromatography eliminates many interferences and improves specificity. However, congener identification is based primarily on gas chromatography retention times ($t_R$).

Much of the early work on capillary chromatography of Aroclors relied on glass columns coated with SE-54, a 5% phenyl-95% methyl silicone stationary phase (8,9). Today fused silica columns and bonded phases have largely replaced coated glass capillary columns because of their durability. The most recent PCB studies (1,10) often use DB-5 columns which have selectivity and retention charactistics equivalent to SE- 54.

The 60 m DB-5 widebore column (0.32 mm i.d., 0.25 micron film thickness) used in this study is very efficient with 3,500 theoretical plates/m according to manufacturer specifications. A number of suppliers provide bonded phase capillaries with efficiencies in the 3,000 to 5,000 plates/m range, and comparable results are expected with any 5% phenyl-95% methyl silicone column with over 200,000 theoretical plates including HP-5, RSL-200, SPB-5 columns and others. The highest efficiencies are obtained with narrow bore columns (0.2 mm i.d.), thinner stationary phases, and efficiency also is proportional the square root of the column length.

The $t_R$ precisions are excellent with modern gas chromatographs. For example, the standard deviation of the $t_R$ for PCB-153 was less than one sec during a 45 h period (6 replicates)(7). With this precision the retention time windows for each congener are narrow, ca. +/- 1.2 sec in a 103 min chromatogram, and the ability to distinquish isomers is improved.

Using the 60 m DB-5 column 46 of the polychlorinated biphenyl congeners in the NRCC standard mixtures were resolved -- their $t_R$ were between 17 and 85 min (**Table 1**). PCB-159/182/187 and PCB-171/202 which are also present in the mixed standards are not adequately separated with this system. The ECD response factors generally increase with chlorine content and the responses are linear over a broad range (7).

Chlorobiphenyl Content of Aroclor Reference Materials. The 46 chlorobiphenyls determined in this study accounted for a very large proportion of each of the regulated Aroclor formulations (**Table 2.**). The only exception was the least chlorinated mixture, Aroclor 1221, where 2,2',5-trichlorobiphenyl (PCB-18), 4,4'-dichlorobiphenyl (PCB- 15), and 2,4',5-trichlorobiphenyl (PCB-31), were the only identified components. For the most widely used Aroclors, 1242, 1254, and 1260, between 73 and 85% of the mixtures were accounted for. Thus, for most of the regulated Aroclors, s-PCB determined by GC-ECD with this group of standards is a good approximation of the Aroclor content. s-PCB, of course, varies depending on congeners determined and for s-PCB to approximate the Aroclor content, the most abundant congeners must be among the target compounds.

Chromatograms for Aroclors 1254, 1260, 1262 and 1268 had peaks with the same $t_R$ as PCB-159/182/187 and Aroclors 1260, 1262 and 1268 also contained the PCB-172/202 peak, but these isomers were not quantitated. The compound coeluting with PCB-77 both in the Aroclor formulations and environmental samples has been unequivocally identified as PCB-110. Accordingly, the sample component is quantified as PCB-77 and corrected for the differential in published detector response factors (7).

Determination of Aroclors Using Selected Congeners as Markers. Without question capillary GC provides a great deal more information than packed-column GC. The problem with identification of Aroclors by capillary GC is one of data reduction. As with any method for estimating Aroclors, a number of assumptions must be made. The present procedure assumes that the composition of each Aroclor does not vary from batch to batch. In other words, all lots have the same congener distribution. Monsanto Company was the sole manufacturer of PCBs in North America. We have not analyzed commercial PCB mixtures manufactured or used on other continents and this assumption may not be universally applicable. The second assumption is that the congener distribution does not change due to selective weathering. In our experience in the analysis of PCBs in marine organisms from California coastal waters (specifically, mussels from inner harbor areas), both assumptions are realistic. With hazardous waste matrices where Aroclors are often at high concentration (e.g., transformer oils) little degradation of the original Aroclor mixtures is expected.

Selection of Aroclor Markers. The selection of marker congeners is straighforward. Chlorobiphenyl markers should be abundant in one regulated Aroclor, but not another. The more prominent the congener is, the lower the detection limit for the Aroclor mixture will be. In the case of Aroclor 1268 there are a number of unique and abundant PCB isomers. In particular, PCB-203, -208, -206 and -209 are abundant and relatively unique to Aroclor 1268 (**Table 2**). For this study, 2,2',3,4,4',5,5',6-octachlorobiphenyl (PCB-203) and 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl (PCB-206) were selected. Aroclors 1254 and 1260 were industrially important in the U. S. (11) and are major environmental contaminants and residues in biota. The pentachlorobiphenyls (PCB-87, -110, -118, and -105) are associated with Aroclor 1254 and the heptachloro compounds (PCB-183, -180, and - 170) are abundant in Aroclors 1260 and 1262 (6)(**Table 2**).

Distinguishing the least chlorinated Aroclors (e.g., 1221, 1232, 1016, 1242, and 1248) is the most difficult because the most abundant congeners are the same in each mixture (**Figure 1**), i.e., 4,4'- dichlorobiphenyl (PCB-15), and two trichlorobiphenyls (PCB-18 and -31) are major constituents of each. Therefore, these three compounds are used as surrogates for all of the low-chlorine-content Aroclors which cannot be distinguished.

Composition Factors. Composition factors define the [Aroclor]:[marker chlorobiphenyl] ratio and are essential for estimating Aroclor

concentrations. Composition factors are equivalent to 100/wt % for any given congener-Aroclor combination. Using the formulation data in **Table 2**, Aroclor 1016 composition factors of 100/15 = 6.7, 100/43 = 2.3, and 100/11 = 9.1 are estimated for PCB-18, -15 and -31, respectively. Composition factors for each of the four measured Aroclors were calculated similarly and appear in **Table 1**.

Calculations. Aroclor concentrations are estimated in a three step process. First, the concentrations of the 12 marker compounds are determined in the sample. Second, the concentration of each marker is multiplied by the appropriate composition factor to give a single Aroclor estimate. Third, the mean Aroclor estimates are calculated and reported.

If the congener pattern in the sample matches the Aroclor reference material, the relative standard deviation (RSD) of Aroclor estimates will be low, generally well below 50%. A graphic example of this is again provided by our recent studies of marine contamination (7). In Mussel Watch samples from throughout California coastal waters, Aroclor 1254 congener profiles were very similar to the U. S. EPA reference material with RSDs of 28 +/- 15%. Even when there are multiple, disperse PCB sources, and residues have been subjected to volatilization, photochemistry, biological and nonbiological tranformations, and partitioning in the environmental compartments, the original pattern of congeners is reasonably well retained. Clearly, the Aroclor mixtures released must have been similar in composition.

Quantitation of the Other Aroclors. The regulation of PCBs in wastes is based on the sum of all commercial Aroclors. To enforce these regulations all Aroclors must be detected and quantified reliably. Analytical methods which overestimate (positive bias) the Aroclor residues are particularly undesirable because enforcement actions must withstand legal challenge. As the present procedure defines and measures all PCB residues as the sum of 4 Aroclor mixtures, it is important to establish how the technique quantifies the other 5 regulated Aroclors.

The accuracy of the procedure is acceptable for all of the regulated Aroclor mixtures except Aroclor 1221 (**Table 3**). Recoveries were between 61 and 135% for all PCB formulations with greater than 30% Cl by weight. For example, 100 mg of Aroclor 1248 is quantified as 90 mg s-Aroclor which is the sum of 55 mg of Aroclor 1016, 43 mg of Aroclor 1254 and 4.7 mg of Aroclor 1260. The major components of Aroclor 1221 are one- and two-chlorine compounds with very low electron-capture detector response factors. The NRCC mixtures contain only one dichloro compound, PCB-15, and no monochlorobiphenyls resulting in a sizable underestimation of Aroclor 1221 by either s-PCB (**Table 2**) or s-Aroclor (**Table 3**). Fortunately, Aroclor 1221 is one of the least toxic and persistent Aroclors, was manufactured in comparatively low volume (11), and is rarely detected in hazardous wastes. In summary, the 12 chlorobiphenyl markers give good estimates of all of the important, regulated Aroclors without any judgement on the part of the analyst as to the Aroclor type. Because the marker chlorobiphenyls are not absolutely specific, there may be some

overestimation, for example, of Aroclor 1254 and 1260. Simple formulas are used to correct these overestimates (7).

If the chemist has additional information about the sample, i.e., the sample originates from electical equipment known to contain a given Aroclor, the selected congener technique is accurate for all of the commercial Aroclors. The appropriate composition factors must be calculated using the formulation data in **Table 2**. PCB-18, -15, and - 31 are markers for the low-chlorine-content PCBs, i.e., those with 21 to 48% Cl by weight. Similarly, PCB-183, -180 and -170 are used as Aroclor 1262 markers with the appropriate composition factors.

PCBs in Auto Shredder Wastes. Auto shredder waste is the residue from metal recovery operations which use discarded automobiles as a metal source. Auto shredder wastes are non-RCRA hazardous wastes which are subject to treatment by chemical stabilization in California prior to disposal because of their heavy metal content (e.g., Zn, Pb, Cd, Cr, Cu, Hg, Ni). The Hazardous Materials Laboratory has had extensive experience in the analysis of autoshredder wastes, not only for regulated inorganic elements, but also for PCB contamination which the laboratory first reported. Auto shredder waste extracts were selected for study here because they contain more than one Aroclor type and are difficult to analyze by packed column methods.

Two auto shredder waste samples were analyzed using the conventional packed column procedure, SW-846 Method 8080. A highly trained and experienced chemist examining the packed column chromatograms identified two Aroclors, 1016 and 1260, in shredder waste extracts. Using the standard quantitation technique (total area), sample No. 1827 was found to contain 43 mg Aroclor 1016/kg and 14 mg Aroclor 1260/kg (dry weight basis). A second auto shredder waste sample, No. 1831, contained 73 mg Aroclor 1016/kg and 20 mg Aroclor 1260/kg.

Almost all of the PCB congeners were detected in capillary chromatograms (**Figure 2**). In sample No. 1827 32 chlorobiphenyls were detected and in No. 1831 34 of the congeners were present (**Table 4**). The twelve chlorobiphenyl markers indicated the presence of three Aroclors, 1016, 1254 and 1260 (**Table 4**). Although small amounts of Aroclor 1268 markers were measured, Aroclor 1268 was not included in s-Aroclor because it did not match the reference material, e.g., the dispersion in Aroclor 1268 estimates was too great with RSDs of 69 and 72%. In contast the three lower chlorinated Aroclors detected in shredder waste extracts matched the reference materials well with RSDs between 11 and 36%.

s-Aroclor concentrations estimated by either 8080 or the congener- based procedure were similar, i.e., 57 vs 99 mg/kg and 93 vs 145 mg/kg for No. 1827 and No. 1831, respectively. On average the relative percent difference for the two methods is less than 50%. However, Aroclor identifications were distinctly different. Aroclor 1254 was not detectable by Method 8080 at the detection limit of 2 mg/kg, yet the

concentrations of PCB-87, -110, -118, and -105 clearly indicated Aroclor 1254 concentrations of 35 (No. 1827) and 52 mg/kg (No. 1831).

Method accuracy was tested by reconstructing the expected congener profiles (using **Table** 2 data) and comparing the predictions with the experimental data. If sample No. 1827 contained 43 mg/kg of Aroclor 1016 and 14 mg/kg Aroclor 1260, a congener profile plotted in **Figure** 3 is expected. Similarly, the congener profile expected for a sample containing Aroclor 1016 (43 mg/kg), Aroclor 1254 (35 mg/kg) and Aroclor 1260 (21 mg/kg) are obtained. The congener profiles clearly demonstrate the presence of Aroclor 1254 in the sample, a fact that is not evident from the packed column data.

This example demonstrates the utility of selected congener data in Aroclor speciation. The capillary chromatograms actually provide a great deal more information in the form of many additional Aroclor 1254-associated peaks. However, data reduction through the use of selected congeners is a much more efficient means for evaluating the raw data.

## CONCLUSION

All of the regulated Aroclor formulations can be determined based on the concentrations of 12 chlorinated biphenyl congeners. Three congeners, PCB-18, -15, and -31, are markers for Aroclors with low chlorine content, pentachlorobiphenyls are markers for Aroclor 1254, heptachlorobiphenyls are markers for Aroclor 1260, and Aroclor 1268 is estimated from PCB-203 and -206.

The advantages of the use of high resolution chromatography and consideration of only selected congeners are the following: 1) the chemist is relieved from "eyeballing" the chromatogram and attempting to interpret patterns; 2) the technique makes full use of the separation power of capillary chromatography and minimizes interferences caused by chlorinated pesticides, pesticide metabolites, chlorinated terphenyls, phthalates, sulfur allotropes, and other electron-capturing coextractives; 3) the technique readily accomodates samples containing more than one commercial Aroclor; 4) multipoint calibration with each congener is less time consuming than multipoint calibration with all 9 regulated Aroclors; and 5) the technique lends itself well to automated interpretation and data processing.

Finally, with little additional effort the number of PCB congeners determined can be increased to over 45 using the NRCC mixtures, or similar mixtures obtained commercially. The determination of these compounds provides a second measure of PCB content, s-PCB, which may be useful for determination of PCB residues after treatment. Some scientists feel strongly that the only valid means for determining PCBs in highly weathered or treated samples is by congener measurement.

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**Table 1.** Typical retention times for chlorinated biphenyl congeners and composition factors for marker chlorobiphenyls.

| Chlorobiphenyl Structure | Chlorobiphenyl IUPAC No.[a] | $t_R$ (min) | RRT[c] | Composition Factor (100/wt % in Aroclor) |
|---|---|---|---|---|
| 2,2',5-Tri | 18 | 17.87 | 0.421 | 6.7 (Aroclor 1016) |
| 4,4'-Di | 15 | 18.06 | 0.423 | 2.3 (Aroclor 1016) |
| 2,2',6,6'-Tetra | 54 | 20.59 | 0.486 | |
| 2,4',5-Tri | 31 | 21.73 | 0.513 | 9.1 (Aroclor 1016) |
| 2,2',5,5'-Tetra | 52 | 25.80 | 0.609 | |
| 2,2',4,5'-Tetra | 49 | 26.38 | 0.622 | |
| 2,2',3,5'-Tetra | 44 | 28.64 | 0.676 | |
| 2,2',3,3'-Tetra | 40 | 31.74 | 0.749 | |
| 2,2',4,5',6-Penta | 103 | 31.84 | 0.751 | |
| 2,3',4,5',6-Penta | 121 | 35.65 | 0.841 | |
| 2,3,4,4'-Tetra | 60 | 37.53 | 0.885 | |
| 2,2',4,5,5'-Penta | 101 | 38.57 | 0.910 | |
| 2,2',3,4,5-Penta | 86 | 41.58 | 0.981 | |
| 2,2',3,4,5'-Penta | 87 | 42.13 | 0.994 | 16 (Aroclor 1254) |
| 3,3',4,4'-Tetra | 77 | 43.36 | 1.023 | 6.3 (Aroclor 1254)[d] |
| 2,2',4,4',5,6'-Hexa | 154 | 43.64 | 1.029 | |
| 2,2',3,5,5',6-Hexa | 151 | 45.07 | 1.063 | |
| 2,3',4,4',5-Penta | 118 | 46.78 | 1.103 | 9.1 (Aroclor 1254) |
| 2,2',3,4,5,6'-Hexa | 143 | 47.65 | 1.124 | |
| 2,3,4,4',5-Penta | 114 | 48.09 | 1.134 | |
| 2,2',4,4',5,5'-Hexa | 153 | 49.61 | 1.170 | |
| 2,3,3',4,4'-Penta | 105 | 49.92 | 1.177 | 30 (Aroclor 1254) |
| 2,2',3,4,5,5'-Hexa | 141 | 51.07 | 1.205 | |
| 2,2',3,4,4',5-Hexa | 137 | 51.86 | 1.223 | |
| 2,2',3,4,4',5'-Hexa | 138 | 52.78 | 1.245 | |
| 2,2',3,3',4,5-Hexa | 129[b] | 53.71 | 1.267 | |
| 2,2',3,4,4',5',6-Hepta | 183 | 55.56 | 1.310 | 18 (Aroclor 1260) |
| 2,2',3,3',4,4'-Hexa | 128 | 56.11 | 1.323 | |
| 2,2',3,4,5,5',6-Hepta | 185[b] | 56.90 | 1.342 | |
| 2,3,3',4,4',5-Hexa | 156 | 59.49 | 1.403 | |
| 2,2',3,3',4,5,6-Hepta | 173 | 60.16 | 1.419 | |
| 2,2',3,3',4,5',6,6'-Octa | 200 | 60.44 | 1.425 | |
| 2,2',3,4,4',5,5'-Hepta | 180 | 62.17 | 1.466 | 9.1 (Aroclor 1260) |
| 2,3,3',4,4',5',6-Hepta | 191 | 63.25 | 1.492 | |
| 2,2',3,3',4,4',5-Hepta | 170 | 67.09 | 1.582 | 19 (Aroclor 1260) |
| 2,2',3,3',4',5,5',6-Octa | 201 | 68.89 | 1.625 | |
| 2,2',3,4,4',5,5',6-Octa | 203 | 69.86 | 1.648 | 5.3 (Aroclor 1268) |
| 2,2',3,3',4,4',5',6-Octa | 196 | 69.99 | 1.651 | |
| 2,3,3',4,4',5,5'-Hepta | 189 | 72.93 | 1.720 | |
| 2,2',3,3',4,5,5',6,6'-Nona | 208 | 76.03 | 1.793 | |
| 2,2',3,3',4,4',5,6-Octa | 195 | 76.18 | 1.797 | |
| 2,2',3,3',4,4',5,6,6'-Nona | 207 | 77.71 | 1.833 | |
| 2,2',3,3',4,4',5,5'-Octa | 194 | 78.88 | 1.860 | |
| 2,3,3',4,4',5,5',6-Octa | 205 | 79.34 | 1.871 | |
| 2,2',3,3',4,4',5,5',6-Nona | 206 | 82.06 | 1.935 | 2.0 (Aroclor 1268) |
| Decachlorobiphenyl | 209 | 84.69 | 1.997 | |

a Structures and IUPAC numbering from Ballschmiter and Zell (8); b The NRCC mixtures contain PCB-159, -182, and -187 which elute between PCB-129 and -183, but these congeners are not adequately resolved by the 60 m DB-5 capillary column, similarly, PCB-171 and -202 elute between PCB-185 and PCB-156; c Retention time relative to 4,4'-DDE; d Composition factor for PCB-110.

**Table 2.** PCB Congener Composition of U. S. Environmental Protection Agency Aroclor Reference Materials.

| | Aroclor Mixture Composition (wt %) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| IUPAC No. | 1221 | 1232 | 1016 | 1242 | 1248 | 1254 | 1260 | 1262 | 1268 |
| 18 | 0.62 | 8.1 | 15 | 14 | 7.4 | | | | |
| 15 | 9.3 | 27 | 43 | 33 | 15 | | | | |
| 31 | 0.85 | 5.9 | 11 | 6.9 | 8.9 | | | | |
| 52 | | 3.9 | 7.6 | 5.7 | 13 | 7.8 | 1.3 | | |
| 49 | | 2.7 | 5.7 | 3.6 | 8.4 | 1.3 | | | |
| 44 | | 2.6 | 5.6 | 3.8 | 8.1 | 2.5 | | | |
| 40 | | 0.65 | 1.3 | 0.89 | 1.8 | | | | |
| 101 | | 0.70 | | 1.5 | 3.8 | 13 | 6.3 | 2.6 | |
| 87 | | 0.38 | | 0.75 | 2.1 | 6.2 | 0.86 | | |
| 110 | | 0.73 | | 1.0 | 5.2 | 16 | 3.3 | 0.80 | |
| 151 | | | | | | 1.5 | 5.2 | 6.0 | |
| 118 | | 0.35 | | 0.91 | 3.5 | 11 | | | |
| 153 | | | | 0.23 | 0.59 | 5.3 | 13 | 11 | |
| 105 | | | | 0.69 | 2.4 | 3.3 | | | |
| 141 | | | | | | 1.5 | 3.3 | 3.0 | |
| 137 | | | | | | 0.54 | | | |
| 138 | | | | 0.28 | 0.75 | 9.5 | 13 | 7.3 | |
| 129 | | | | | | 0.67 | | | |
| 183 | | | | | | 0.49 | 5.5 | 7.9 | |
| 128 | | | | | | 1.6 | 0.77 | | |
| 185 | | | | | | | 0.81 | 1.6 | |
| 156 | | | | | | 1.0 | | | |
| 200 | | | | | | | 0.51 | 1.5 | 2.5 |
| 180 | | | | | 0.70 | 0.93 | 11 | 14 | 1.6 |
| 170 | | | | | 0.40 | 0.86 | 5.3 | 6.3 | |
| 201 | | | | | | | 3.3 | 11 | 32 |
| 203 | | | | | | | | | 19 |
| 208 | | | | | | | | | 18 |
| 195 | | | | | | | 0.66 | 2.3 | |
| 207 | | | | | | | | 0.50 | 5.6 |
| 194 | | | | | 0.22 | | 1.3 | | |
| 205 | | | | | | | | 0.34 | |
| 206 | | | | | | | 0.78 | 3.4 | 49 |
| 209 | | | | | | | | | 11 |
| s-PCB | 10.8 | 52.6 | 89.2 | 73.3 | 82.3 | 85.0 | 76.4 | 79.5 | 139 |

The composition data for Aroclor 1254 and 1260 (congeners eluting between PCB-101 and PCB-205) were published previously (7). Aroclors 1254, 1260, 1262, and 1268 contained congeners coeluting with PCB-159/182/187 which were not resolved on the 60 meter DB-5 column. Aroclors 1260, 1262 and 1268 had peaks corresponding to PCB-172/202, also not resolved. PCB-110 was determined as PCB-77 and corrected (7).

**Table 3.** Estimated Aroclor Content of Nine Regulated Aroclors Based on Content of Selected Congeners

| | Estimated Concentrations of Aroclor 1016, 1254, 1260 and 1268 in 100 pg/uL of Commercial Aroclors (pg/uL) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Marker Chlorobiphenyl | 1221 | 1232 | 1016 | 1242 | 1248 | 1254 | 1260 | 1262 | 1268 |
| 18 | 4.2 | 54 | 101 | 94 | 50 | | | | |
| 15 | 21 | 62 | 99 | 76 | 35 | | | | |
| 31 | 7.7 | 54 | 100 | 63 | 81 | | | | |
| Aroclor 1016 | 11 | 57 | 100 | 78 | 55 | | | | |
| | (81)[a] | (8.1) | (1.0) | (20) | (43) | | | | |
| 87 | | 6.1 | | 12 | 34 | 99 | 14 | | |
| 110 | | 4.6 | | 6.3 | 33 | 101 | 21 | 5.0 | |
| 118 | | 3.2 | | 8.3 | 32 | 100 | | | |
| 105 | | | | 21 | 72 | 99 | | | |
| Aroclor 1254 | | 3.5 | | 12 | 43 | 100 | 8.8 | 1.3 | |
| | | (74) | | (54) | (45) | (0.96) | (120) | (190) | |
| 183 | | | | | | 8.8 | 99 | 142 | |
| 180 | | | | | 6.4 | 8.5 | 100 | 127 | 15 |
| 170 | | | | | 7.6 | 16 | 101 | 120 | |
| Aroclor 1260 | | | | | 4.7 | 11 | 100 | 130 | 5 |
| | | | | | (87) | (39) | (1.0) | (8.6) | (170) |
| 203 | | | | | | | | | 101 |
| 206 | | | | | | | 1.6 | 6.8 | 98 |
| Aroclor 1268 | | | | | | | 0.80 | 3.4 | 100 |
| | | | | | | | (140) | (140) | (2.1) |
| s-Aroclor | 11 | 61 | 100 | 90 | 103 | 111 | 110 | 135 | 105 |

a Numbers in parentheses are relative standard deviations (RSD) for Aroclor estimates based on the markers -- the closer the patterm matches or "fits" the reference standard, the smaller the RSD.

**Table 4.** Polychlorinated Biphenyls and Estimated Aroclor Concentrations in Auto Shredder Waste.

| | mg/kg | | Normalized | | Estimated Aroclor Concentration (mg/kg)[a] | |
|---|---|---|---|---|---|---|
| IUPAC No. | No. 1827 | No. 1831 | No. 1827 | No. 1831 | No. 1827 | No. 1831 |
| 18 | 5.5 | 8.6 | 6.6 | 7.4 | 37 | 58 |
| 15 | 20 | 31 | 24 | 27 | 46 | 71 |
| 31 | 4.9 | 7.9 | 5.9 | 6.8 | 45 | 72 |
| Aroclor 1016 | - | - | - | - | 43(11)[b] | 67(12) |
| 52 | 4.8 | 6.6 | 5.8 | 5.7 | | |
| 49 | 3.1 | 4.2 | 3.7 | 3.6 | | |
| 44 | 3.6 | 4.8 | 4.3 | 4.1 | | |
| 60 | 1.6 | 2.6 | 1.9 | 2.2 | | |
| 101 | 4.9 | 6.8 | 5.9 | 5.8 | | |
| 87 | 1.8 | 2.6 | 2.2 | 2.2 | 29 | 42 |
| 110 | 3.7 | 5.1 | 4.5 | 4.4 | 23 | 32 |
| 151 | 0.83 | 1.2 | 1.0 | 1.0 | | |
| 118 | 4.5 | 6.6 | 5.4 | 5.6 | 41 | 60 |
| 114 | 0.16 | 0.21 | 0.19 | 0.18 | | |
| 153 | 2.3 | 3.3 | 2.8 | 2.8 | | |
| 105 | 1.6 | 2.4 | 1.9 | 2.1 | 48 | 72 |
| Aroclor 1254 | - | - | - | - | 35(31) | 52(35) |
| 141 | 1.2 | 1.1 | 1.5 | 0.94 | | |
| 137 | 0.55 | 0.48 | 0.66 | 0.41 | | |
| 138 | 5.1 | 6.6 | 6.2 | 5.7 | | |
| 129 | 0.60 | 0.37 | 0.72 | 0.32 | | |
| 183 | 0.89 | 0.92 | 1.1 | 0.79 | 16 | 15 |
| 128 | 1.4 | 1.4 | 1.7 | 1.2 | | |
| 185 | 0.081 | 0.059 | 0.098 | 0.051 | | |
| 156 | ND | 0.94 | ND | 0.080 | | |
| 180 | 3.2 | 3.5 | 3.9 | 3.0 | 29 | 32 |
| 191 | 0.39 | 0.013 | 0.47 | 0.011 | | |
| 170 | 0.98 | 1.6 | 1.2 | 1.4 | 19 | 30 |
| Aroclor 1260 | - | - | - | - | 21(32) | 26(36) |
| 201 | 1.9 | 2.2 | 2.3 | 1.9 | | |
| 203 | 0.90 | 0.99 | 1.1 | 0.85 | 4.8 | 5.2 |
| 189 | 0.016 | 0.048 | 0.019 | 0.041 | | |
| 207 | 0.12 | 0.14 | 0.14 | 0.12 | | |
| 194 | 0.96 | 1.4 | 1.2 | 1.2 | | |
| 205 | ND | 0.035 | ND | 0.030 | | |
| 206 | 0.82 | 0.92 | 0.99 | 0.79 | 1.6 | 1.8 |
| Aroclor 1268 | - | - | - | - | 3.2(72) | 3.5(69) |
| 209 | 0.15 | 0.20 | 0.18 | 0.17 | | |
| s-PCB | 82.917 | 116.25 | - | - | | |
| s-Aroclor | - | - | - | - | 99.0[c] | 145.0[c] |

a Aroclor concentrations estimated from the concentration of chlorinated biphenyl congeners. The reported Aroclor concentrations is the mean.

b The number in parentheses is the RSD for Aroclor estimates.

c Because of the poor fit, i.e., RSD >50%, Aroclor 1268 was not included in s-Aroclor.

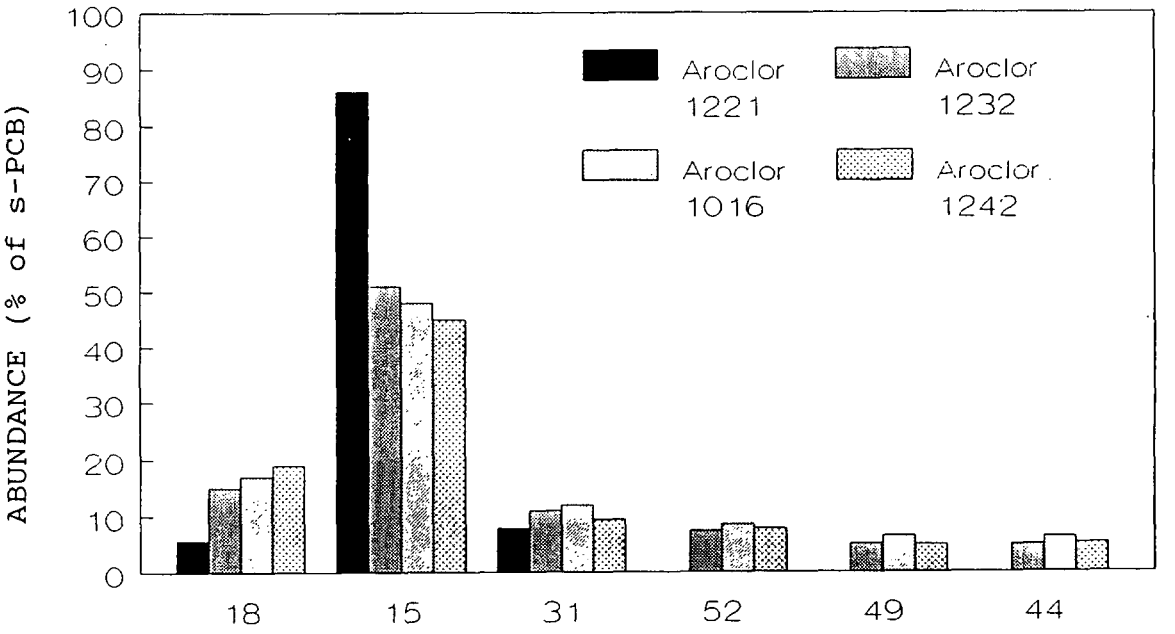


**Figure 1.** Chlorobiphenyl congener content of low-chlorine-content Aroclors. Percent of s-PCB for PCBs 18, 15, 31, 52, 49, and 44 are compared.

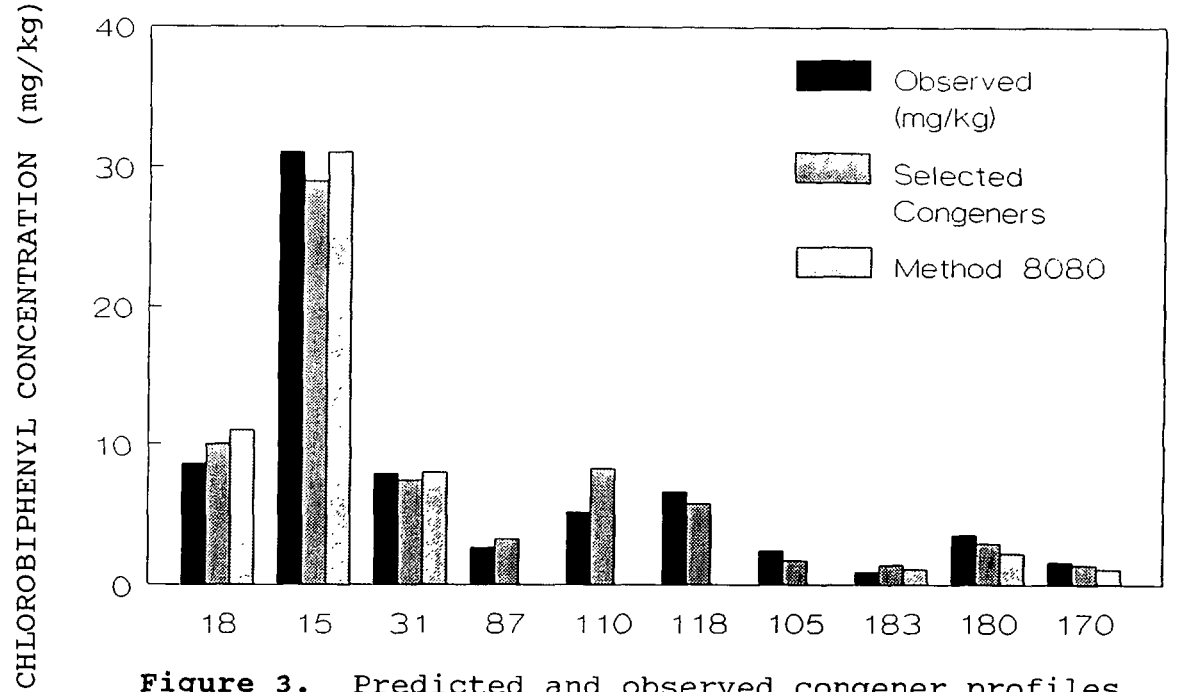


**Figure 3.** Predicted and observed congener profiles (mg/kg) for auto shredder waste sample No. 1831. The profiles are in good agreement except for the Aroclor 1254-associated congeners.

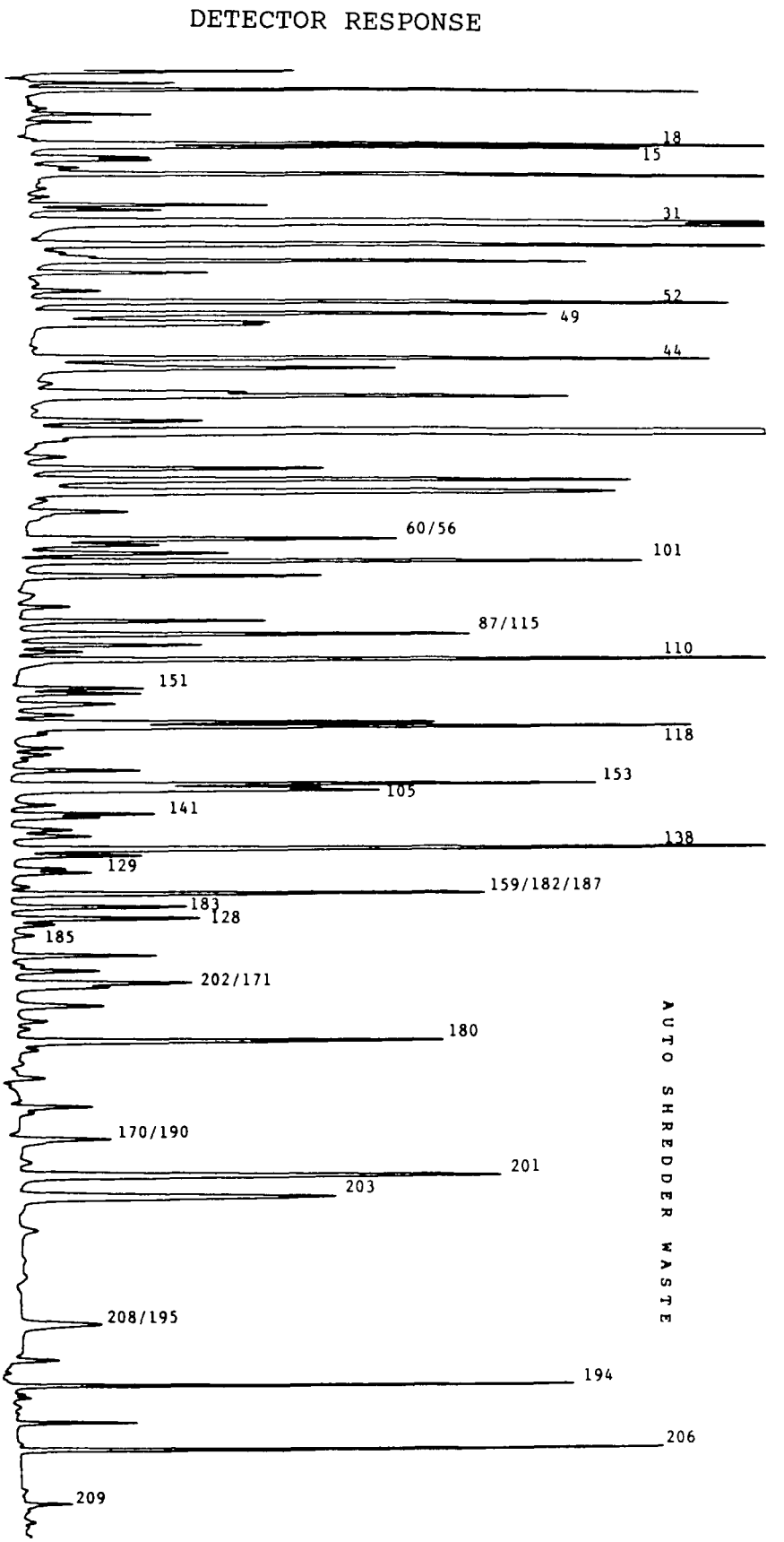


**Figure 2.** Chlorobiphenyl congeners in automobile shredder waste sample extract no. 1824. The chromatogram shows compounds eluting between about 10 and 90 min.

# 68 THE DETERMINATION OF PART PER TRILLION LEVELS OF NITROAROMATICS IN GROUND AND DRINKING WATER BY WIDE-BORE CAPILLARY GAS CHROMATOGRAPHY

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## ABSTRACT

A method has been developed to extract and analyze for selected nitroaromatics at part per trillion levels in ground and drinking water. The compounds included are Nitrobenzene, 1,3-Dinitrobenzene, 2,4-Dinitrotoluene, 2,6-Dinitrotoluene, 2,4,6-Trinitrotoluene and 1,3,5-Trinitrobenzene. The extraction is accomplished using a simple liquid/liquid extraction with toluene. A surrogate, 3,4-Dinitrotoluene, is added to each sample in order to track sample recoveries. The toluene extract is analyzed via a gas chromatograph equipped with a 12 meter DB-210 wide-bore fused silica capillary column and an electron capture detector. Method detection limits of 10 ppt for nitrobenzene; 30 ppt for 1,3-DNB and 2,4-DNT; 6 ppt for 2,6-DNT; and 20 ppt for 2,4,6-TNT and 1,3,5-TNB have been attained using this method.

## INTRODUCTION

Monitoring for nitroaromatics in ground and drinking water is a primary concern of the United States Army. Areas most likely to be contaminated include ballistic test ranges as well as munitions processing and storage sites. This method was developed in response to environmental and state regulatory concerns about possible nitroaromatic contamination of ground and drinking water.

Initial testing performed by other laboratories as part of a preliminary study of one of these areas had indicated trace level contamination of both 2,4-DNT and 2,6-DNT in the ground water. The results however were inconclusive because of possible interferences from the analytical procedure used. In response to the preliminary analysis, geological studies and shallow ground water dye tracing experiments were performed. The results of these experiments indicated that any possible contamination had most likely originated from a former ordnance works.

The method initially chosen for the analysis of these samples was EPA Method 609 because of its' traditional use for the analysis of 2,4-DNT, 2,6-DNT, nitrobenzene and isophorone in municipal and industrial discharges. The methods' stated detection limits are 14 ppb for nitrobenzene, 0.01 ppb for 2,6-DNT and 0.02 ppb for 2,4-DNT. Sample preparation for EPA Method 609 involves the extraction of approximately one liter of sample water with methylene chloride, then solvent exchanging the methylene chloride with hexane, then finally concentrating the sample to ten milliliters or less. Problems encountered using this method included the loss of some of the more volatile nitroaromatics and a concentrating effect of any interferences present in the sample water. In addition, EPA Method 609 does not address the analysis of 1,3-DNB, 2,4,6-TNT or 1,3,5-TNB. In contrast, the simple liquid/liquid toluene extraction described in this presentation offers the advantages of minimal solvent use and no heating, solvent exchange or blowdown.

69

# A PERFORMANCE EVALUATION OF THE CLP HIGH CONCENTRATION ORGANIC PROTOCOL

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Abstract:

The United States Environmental Protection Agency Contract Laboratory Program (CLP) has issued contracts for the gas chromatography/mass spectroscopy analysis of samples containing high concentrations of organic chemicals. It is essential that the data users know the quality of data produced by the method. As this is a new protocol, many of the quality assurance parameters have only recommended control limits. The performance of the method on actual samples will be discussed. The precision and accuracy of the method determined from sample quality assurance data will be presented. Data will be presented on the following quality control parameters with the intent of suggesting acceptability criteria where appropriate: surrogate recovery, retention times, response factors, internal standard area response, control matrix spike recovery and method blanks. The laboratory results obtained on performance evaluation samples will also be discussed.

Notice: Although the research described in this article has been supported by the Environmental Protection Agency under contract 68-03-3249 with Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

70

# OXIDATION OF ACID SURROGATES AND TARGET ANALYTES IN ENVIRONMENTAL WATER SAMPLES USING EPA METHOD 625

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## ABSTRACT

Apart from potentially poor laboratory techniques and occasionally severe emulsion problems during extraction, very low acid surrogate recoveries for environmental water samples using EPA Method 625 are usually caused by the oxidation of the acid surrogates during acid extraction. These very low recoveries are usually accompanied by the presence of iodocyclohexanol in the chromatogram of the sample extracts. Iodocyclohexanol is presumably a reaction product of iodine, generated in the sample from the oxidation of iodide, with cyclohexene which was added by the manufacturer to the methylene chloride as a preservative. Thus, the presence of iodocyclohexanol can be used as a marker for the existence of oxidizing agents in the sample. The oxidation products of the acid surrogates, i.e., 2-fluorophenol, phenol-d5, and 2,4,6-tribromophenol, were identified as fluorobenzoquinone, benzoquinone-d4, and 2,6-dibromohydroquinone, respectively. The presence of these oxidation products can be used to confirm that the low acid surrogate recoveries for a specific sample are due to the oxidation degradation of the acid surrogates. The matrix effects of samples with low acid surrogate recoveries on the recoveries of phenolic target analytes of CLP-HSL compounds were also investigated. The results showed that good recoveries were obtained for phenols with strong electron-withdrawing substituents, while low recoveries were obtained for phenols with electron-donating substituents or with weak electron-withdrawing substituents. The problem of oxidation of acid surrogates and target phenolic analytes can be eliminated by adding a reducing agent such as sodium thiosulfate to the sample before extraction. The problem also can be reduced by adjusting the pH for the extraction. Thus, the sample can be initially extracted at pH 10 to remove 2,4-dimethylphenol, then at pH 7 to partially extract most of the other phenols and finally at pH 2, to extract strong acids such as the nitrophenols and dinitrophenols.

## INTRODUCTION

EPA Method 625(1) is widely used in environmental laboratories for the analysis of semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). In this method, a 1-L aliquot of water is extracted with methylene chloride at pH > 11 and

then at pH < 2. Before extraction, acid and base/neutral surrogate standards are spiked into the water samples to monitor the recoveries of compounds in each sample. If the surrogate recoveries are within established control limits, it is assumed that the method is in control.

In our analyses of thousands of water samples, it was not unusual that we obtained no or low recoveries for acid surrogates (2-fluorophenol, phenol-d5, and 2,4,6-tribromophenol), but good recoveries for base/neutral surrogates in the same sample. This no or low acid surrogate recovery only occurs in the environmental water samples, not in the soil samples nor in the method blanks using HPLC grade water. This suggests that the no or low acid surrogate recoveries observed in the samples were due to matrix effects of the environmental water samples.

## EXPERIMENTAL SECTION

Sample Preparation: Most samples were obtained from our clients and extracted at pH > 11 and then at pH < 2 with methylene chloride according to EPA Method 625(1). Before extraction, each sample was spiked with 1.0 mL of surrogate standard spiking solution which contained 100 ug/mL each of acid surrogates (2-fluorophenol, phenol-d5, and 2,4,6-tribromophenol) and 50 ug/mL each of base/neutral surrogates (nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14). To study the effects of a reducing agent and pH on the recoveries of surrogates and target analytes, a composite sample was prepared in the laboratory by combining field samples which gave no or low acid surrogate recoveries. This composite sample was divided into four equivalent test samples which were all spiked with the surrogates and EPA Contract Laboratory Program (CLP) hazardous substances list (HSL) of 65 semivolatile organic target analytes (2). A sufficient amount of sodium thiosulfate was added to one of the test samples. This sodium thiosulfate treated test sample and an untreated test sample were extracted at pH 12 and then at pH 2. The remaining two test samples were extracted at pH 10 then pH 2 and pH 12 then pH 7, respectively. All methylene chloride extracts were concentrated to 1 ml with a Kuderna-Danish (K-D) concentrator. For the samples obtained from our clients, the base extract and acid extract of each sample are combined and analyzed by GC/MS. For the test samples the two extracts were analyzed separately by GC/MS.

GC/MS Analysis: Samples were analyzed on a HP 5988 GC/MS system. The column used was a 30m x 0.25 mm DB-5 fused silica capillary column (J&W Scientific, Folsom, CA). The column temperature was held isothermal at 40°C for 4 minutes and then programmed at 10°C per minute to 280°C, and held isothermal at this final temperature for 12 minutes. The mass spectrometer was scanned from 35 to 500 amu per half second. CLP-HSL compounds and the surrogate compounds were quantified using multiple internal

standards. The area of the extracted ion current profile at the characteristic m/z of a given analyte was used to calculate the concentration.

## RESULTS AND DISCUSSION

Most of the samples obtained from our clients had good acid and base/neutral surrogate recoveries. However, in some sets of samples, a significant number of samples had low acid surrogate recoveries. A chromatogram of one of these samples is shown in Figure 1.

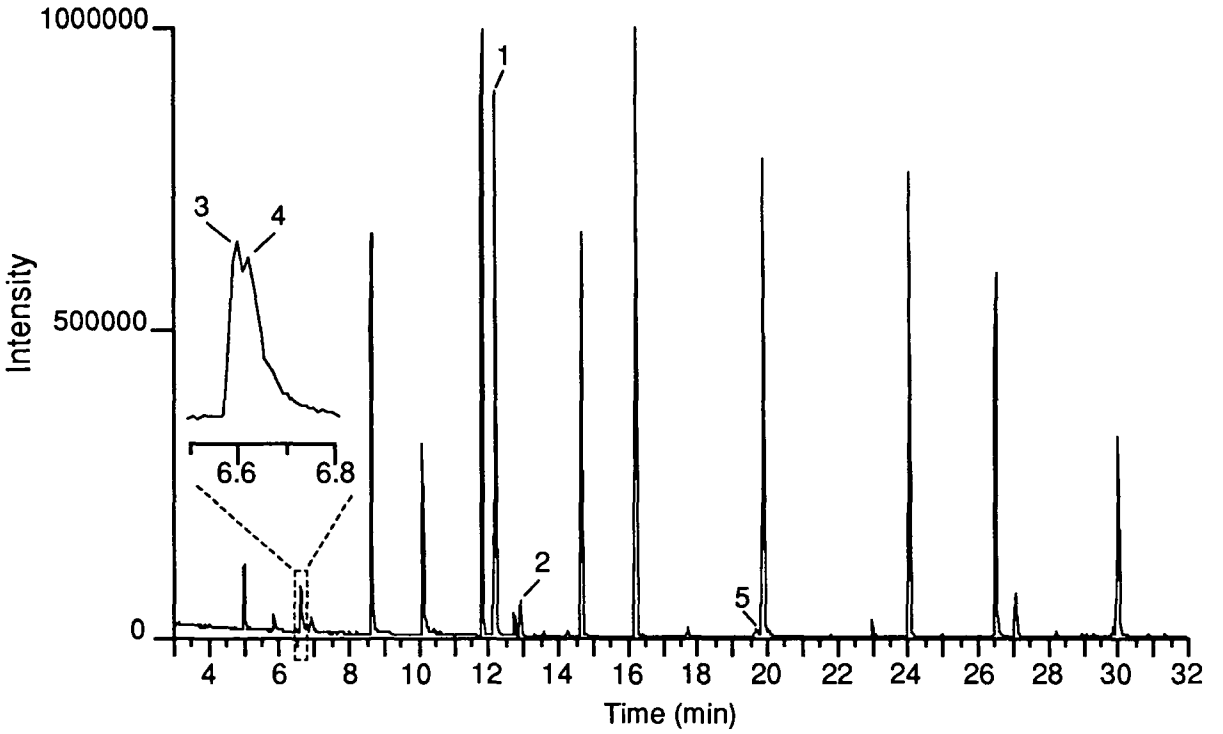


**Figure 1.** Total ion chromatogram of a water sample which has no acid surrogate recoveries. Peaks 1 and 2 are artifacts formed during extraction. Peaks 3, 4, and 5 are oxidation products of surrogates. The large unlabeled peaks are internal standards and base/neutral surrogates.

These samples usually contained iodocyclohexanol (peak 1), and to a lesser extent, chloroiodocyclohexane (peak 2). Iodocyclohexanol, in some cases bromocyclohexanol, and halogenated cyclohexanes are artifacts formed in acidic media during extraction (3,4). Iodocyclohexanol is presumably a reaction product of iodine (generated in the sample under acidic conditions) with cyclohexene. Cyclohexene is added by the manufacturer to the methylene chloride as a preservative and scavenger (3,4). Thus, the presence of iodocyclo-

hexanol in samples suggests that the sample contains an oxidizing agent or agents which oxidize iodide to iodine. Iodine then reacts with cyclohexene in acidic media to from iodocyclohexanol. The presence of iodocyclohexanol can be used as a marker for the existence of oxidizing agents in the sample. In addition to iodocyclohexanol, bromocyclohexanol and halogenated cyclohexanes were observed in some samples. We found large amounts of bromocyclohexanol, iodocyclohexanol, bromochlorocyclohexane, dibromocyclohexane, and chloroiodocyclohexane in high salinity or brine samples.

Examinations of the mass spectra of the small peaks in the chromatograms of samples yielding no or low acid surrogate recoveries resulted in the identification of three oxidation products, one for each of the three acid surrogates. Peaks 3, 4, and 5 in Figure 1 are identified as benzoquinone-d4, fluorobenzoquinone, and 2,6-dibromohydroquinone which are the oxidation products of phenol-d5, 2-fluorophenol, and 2,4,6-tribromophenol, respectively. The presence of these oxidation products can be used as a confirmation that the low acid surrogate recoveries for the samples are due to the oxidation degradation of the acid surrogates. The amount of the three identified oxidation products only accounts for a small percentage of the amount of the acid surrogates spiked into the sample. This may be due to the formation of other intermediate or final oxidation products which are soluble in acidic media and are not extractable by methylene chloride, or to the formation of nonvolatile products, e.g., polymeric oxidation products (5), and are not amenable to analysis by GC/MS.

For the test sample to which no reducing agent was added and was extracted under the normal conditions of the method (pH 12 then pH 7) the recoveries were good only for phenols with strong electron-withdrawing substituents or with strong acidity such as 2,4-dinitrophenol, 2-nitrophenol, 4-nitrophenol, and 4,6-dinitro-2-methylphenol. Low recoveries were obtained for phenols with electron-releasing substituents or with weaker electron-withdrawing substituents. This is in agreement with the results reported by Stone(5) that phenols with electron-withdrawing substituents are more resistant to oxidation than phenols with electron-donating substituents. For the test sample to which sodium thiosulfate was added, good recoveries were obtained for all the phenols because the oxidizing power of the sample had been suppressed. For the sample extracted at pH 7 instead of pH 2, the phenols with medium acidity had reasonable recoveries while the phenols with very weak acidity such as 2,4-dimethylphenol and with strong acidity such as 2,4-dinitrophenol, 4-nitrophenol and 4,6-dinitro-2-methylphenol had very low or no recoveries. The low recovery for 2,4-dimethylphenol can be explained by the fact that it is the weakest acid among the phenols we studied and is most susceptible to oxidation degradation even at pH 7. The reason that no recoveries were obtained for 4-nitrophenol and 2,4-dinitrophenol is

that their acidities are too strong for them to be extracted at pH 7. If the pH was lowered to pH 2, good recoveries for these two compounds would be expected. If the sample was initially extracted at pH 10 even in the presence of oxidizing agents a good recovery was obtained for 2,4-dimethylphenol. This is because at this high pH, the oxidation rate for dimethylphenol proceeds slowly. Our unpublished data show that at pH >10, the recovery for dimethylphenol is lower. This is because at this high pH most of dimethylphenol will be in phenoxide ion form and will not be extracted by methylene chloride. Thus, the sample can be initially extracted at pH 10 to remove 2,4-dimenthylphenol, then at pH 7 to partially extract most of the other phenols, and finally at pH 2 to extract strong acids such as the nitrophenols and dinitrophenols.

## ACKNOWLEDGEMENTS

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71

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The use of high performance liquid chromatography techniques in the screening for priority pollutants.

The pollution of the biosphere is becoming more and more a public and governmental concern, resulting in a growing need for more sensitive and reliable monitoring procedures for a wide range of compounds. Due to the complexity of environmental samples and the growing number of contaminants to be analyzed, the demands on analytical procedures are becoming more and more demanding. High performance techniques, both for analysis as well as sample preparation are required, while automation is desired for obvious reasons.
This paper investigates the use of various HPLC procedures for sample preparation as well as chromatographic analysis of a wide range of compounds.

Firstly a method is shown for the screening of surface- and drinking water for pesticides and their residues, combining off-line preconcentration with gradient reversed phase HPLC.
For the analysis a silica based reversed phase column with polymeric modification is used. This method showed detection limits of sub ppb levels in drinking water for substances like ureapesticides, chlorophenoxyacids, nitro- and chlorophenols

The second method describes the analysis of volatile ketones and aldehydes in air. The off-line sampling procedure incorporates pre-column derivatization with 2,4 dinitrophenylhydrazine. The trapped DNPH-derivatives are extracted and analyzed using RPLC. Limits of detection are in the ppb range.

Thirdly the possibilities of HPLC as sample preparation technique are evaluated. Complex samples are purified using miniature HPLC columns, in multidimensional chromatography approaches.
In the analysis of pesticides and polychlorinated biphenyls HPLC is used successfully to separate the analytes from the matrix. The HPLC column eluate is collected and analyzed using high resolution capillary GC.
In the analysis of poly aromatic hydrocarbons a preconcentration/ sample clean up step is combined on-line with gradient RPLC.

# 72 OPTIMIZATION OF CONTINUOUS LIQUID-LIQUID EXTRACTION PROCEDURES FOR SEMIVOLATILE AND PESTICIDE ANALYSIS

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ABSTRACT. The authors have performed an extensive investigation into the performance and optimization of sample preparation techniques utilizing continuous liquid-liquid extraction for organochlorine pesticide and semivolatile compound analysis of water matrices. The extraction procedures used were based on the EPA CLP Statement of Work 2/88 and SW-846 Method 3520. The analytical procedures used were based on EPA CLP Statement of Work 2/88 for pesticides and semivolatiles. The investigation focused on four topics: (1) optimization of extraction efficiency, (2) determination of the steps in which significant analyte loss may occur, (3) determination of errors and accidents which commonly cause failures, and (4) comparison of the continuous liquid-liquid extraction technique to the separatory funnel shake out technique.

The goal of this investigation was to identify critical parameters in the extraction process and to optimize analyte recovery and process efficiency in a laboratory where over 75 continuous extractors may be in operation at once. This paper presents data from studies conducted by the authors which included the effects of extraction rate, extraction time, extract drying, and errors in Kuderna Danish concentration on analyte recovery. The advantages of continuous liquid-liquid extraction over separatory funnel shake out extraction, such as increased acid fraction recoveries will also be discussed. This paper will present recommendations for the optimum performance of continuous liquid-liquid extraction in an environment requiring high sample throughput.

73

# EXTRACTION OF CONTAMINATED SOILS WITH COSOLVENTS

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## ABSTRACT

The solubilization of hydrophobic compounds in cosolvents was investigated. Soil samples contaminated with wood preserving or utility residues were extracted with aqueous dilutions of methanol and 2-propanol. The resulting extracts were analyzed for polynuclear aromatic hydrocarbons using high performance liquid chromatography. Results of the analyses indicated that the solubility of the compounds tested increased with increasing volume fraction of methanol or 2-propanol and that the increase was semi-logrithmic. The aqueous solubilities of the compounds tested were less than that predicted from crystalline solubility data.

## INTRODUCTION

The University of Texas Environmental and Water Resources Engineering (UT-EWRE) laboratory is conducting research to investigate the solubility of polynuclear aromatic hydrocarbons (PAHs) in solutions of contaminated soils and water, and cosolvents.

Polynuclear aromatic hydrocarbons may be found in soils and in industrial residues as the by-product of activities such as petroleum refining and combustion of fossil fuels. PAH compounds are neutral nonpolar organics consisting of two or more benzene rings arranged in various configurations. Many of these compounds are of concern because of their toxicity or carcinogenicity. Consequently, sixteen of the compounds are regulated as hazardous (40 CFR 261.31-32) by the United States Environmental Protection Agency (US-EPA).

These compounds may be characterized by their low aqueous solubility and their strong sorption to soils and soil organics (Dzombak 1984). Consequently, the solubility and movement of many of these compounds in ground water is low. Solubilization of the compounds is enhanced, however, in solutions containing miscible organics. Chiou (1989) indicated that the presence of a high molecular weight humic material in water can enhance the apparent solubility of hydrophobic solutes. Cosolvents also may enhance the solubility of hydrophobic molecules. The term cosolvent refers to a solution containing a completely miscible, or a partially miscible organic solvent and water. As the concentration of a miscible solvent such as methanol or 2-propanol increases, the hydrophobicity of the solution increases and so does the solubility of hydrophobic compounds in the solution. Fu et al. (1986) reported that hydrophobic aromatic solutes displayed a semi-logrithmic increase in solubility with increasing volume fraction of solvent in cosolvent mixtures. Their results were obtained using soils with low organic carbon content (0.5 to 2.85% by dry weight) and added aromatic solutes. The sorptive capacity of soils decreases in the presence of cosolvents. Rao et al. (1985) presented isotherm data indicating that the sorption of anthracene with uncontaminated soils decreased by 4 orders of magnitude as the volume fraction of methanol in water increased from 0 to 100%.

**Objectives** In this study, the effect of cosolvent solutions on the solubility of PAHs present in soils contaminated with wood preserving and manufactured gas plant (MGP) residues was investigated. The objectives were to: (a) identify the solubilities of the PAHs in various cosolvent fractions and (b) to use these enhanced solubilities to identify relationships which can be used to predict released amounts of constituents if environmental factors and chemical characteristics are known.

## MATERIALS AND METHODS

**Soils** Contaminated soils containing wastes from different sources were used in this study. Descriptions of these soils and wastes are provided below.

(i) Soils Containing MGP Wastes: These soil samples were collected at a site in the northeast at which coal tar was buried in an unconfined disposal pit. The coal tar, a by-product of the MGP process, had been in place for more than 20 years and some migration of the constituents had occurred. Soils from near the source (Site A) and soils downgradient (Site B) were collected and used in this study. The site (A) samples were more heavily contaminated than were the site (B) samples.

(ii) Wood Preserving Wastes: Samples of soil collected from this site (Site C) contained residues of organic chemicals remaining from a midwestern land treatment operation. The land treatment is part of an ongoing program to evaluate the biological treatment of wood preserving wastes containing compounds such as creosote and pentachlorophenol.

(iii) Utility Wastes: This midwestern site contains significant levels of organic compounds remaining from the disposal of MGP wastes. Site (D) samples were collected in an area of actual waste disposal, while the site (E) samples were collected from an area downgradient from the disposal area which was less contaminated.

**Desorption Method** Soils were extracted using water or cosolvent solutions following the procedure in Table 1. Methanol and 2-propanol, used as cosolvents, were supplied by Fisher (Houston, TX) and were HPLC grade. The cosolvents were made by adding deionized-distilled water (Millipore Milli-Q , Bedford, MA) on a volume-volume basis to a sufficient volume of organic solvent. Typical cosolvent percentages ($f_c$) used during the desorption experiments included 0,10,20,30,40,50, and 75 percent. All desorbing solutions contained 0.01 N $CaCL_2$.

**Analytical Methods** High performance liquid chromatography (HPLC) was used to quantify the PAH compounds in the solutions from the desorption studies. Analyses were performed using a Waters HPLC system controlled by an NEC PC running the Maxima 820 software. Operating conditions are shown in Table 2. Samples were injected using a WISP autosampler, and a Waters variable wavelength UV detector was used to detect eluting compounds. Compounds in the samples were quantified using a five-point standard curve and standards were prepared from a commercial stock solution of the 16 PAH compounds (610A, Supelco, Bellefonte,PA).

TABLE 1

PROTOCOL FOR BATCH DESORPTION STUDIES

(a) Sieve wet soil through 2mm sieve. Air dried soil may be used, but the wet soil is preferred to prevent loss of volatile compounds.

(b) Weigh a known amount of soil (approximately 9 grams dry weight) into a centrifuge tube. Repeat for other tubes.

(c) Prepare solutions of the various concentrations of the cosolvent to be studied. For example, 0,10,20,30,40,50 and 75 percent solutions are suggested. All aqueous and cosolvent solutions should contain 0.01 N $CaCL_2$ to facilitate phase separation.

(d) Add a known volume of water or cosolvent solution (approximately 36 mL) into a teflon centrifuge tube containing the soil sample. Prepare triplicate tubes for each concentration of cosolvent.

(e) Place the tubes in a rotary mixer perpendicular to the axis of rotation, and rotate for 24 hours at 30 revolutions per minute.

(f) After mixing, centrifuge the tubes at 10,000 revolutions per minute.

(g) Using a Pasteur pipet, remove the centrifugate from a tube and add to a glass vial equipped with a teflon lined cap. Repeat for the other tubes.

(h) Store the vials at 4° C until ready for HPLC analysis.

TABLE 2

| HPLC OPERATING CONDITIONS | |
|---|---|
| Instrument | Waters Gradient HPLC |
| Initial Solvent Ratio | 35% Acetonitrile and 65% Water |
| Gradient | Linear gradient to 100% acetonitrile in 30 minutes |
| Column | Supelco, Supelcosil LC-PAH reverse phase, 15cm x 4.6 mm |
| Detector | Variable wavelength, operated at 254 nm |

**Solid Phase Extraction**. Quantification of the PAH compounds in the aqueous solutions (zero $f_c$) was difficult because of their low solubilities. Consequently, in these samples, a solid phase extraction/concentration procedure was used to concentrate the target compounds. The concentration was achieved by pumping, with a 10 mL glass syringe, 20

mL of the aqueous sample through a Waters C-18 Sep-Pak cartridge. The PAH compounds retained on the cartridge were eluted with 2 mL of acetonitrile (Fisher Optima) which then was analyzed using HPLC.

## RESULTS AND DISCUSSION

The desorption studies were performed to evaluate the solubility of PAH compounds in cosolvent solutions. Complete results of the desorption experiments with data for each compound in each soil are not shown in this paper because the amount of data generated was prohibitively large. Instead, typical results are presented that are representative of the trends observed. Figures 1 and 2 graphically present the concentration of the respective 3-and 4-ring PAH compounds, anthracene and pyrene, present in the extracting solutions of the MGP high level soil (A). Figures 3 and 4 present similar data for the 4 ring compounds, fluoranthene and pyrene in extracts of the wood preserving soil (C). In each Figure, the $f_c$ values are plotted as the x-axis and the log PAH concentration are plotted as the y-axis. Each point is the average of triplicate analyses, and the best-fit-line as determined by regression analysis is shown in the Figures. The best-fit-line was calculated using:

$$y = ae^{\sigma x} \tag{1}$$

where:

$y$ =PAH Concentration (mg/L),

$a = y$ intercept,

$\sigma = slope$ and $x$ = fraction cosolvent ($f_c$)

The plots indicate that the concentration of compounds present in the cosolvent solutions increased semi-logrithmically as the fraction of organic solvent in solution was increased. This observation is based on the apparent linearity of the data shown. The linear regression for the data presented in Figures 1 to 4 were calculated and equations for the best-fit-lines are shown on the Figures. The $r^2$ values for the lines were near one signalling close agreement of the data to the regressed line. The slopes ($\sigma$) of the regressed lines for these and other desorption analyses (data not shown) are presented in Table 3. The slopes for the data showed a possible trend of increased slope with increasing compound ring number. This trend was most evident for the 2 and 3 ring compounds. This trend is similar to the data presented by Fu et al. (1986) who found that increases of solute solubility in miscible cosolvents were more pronounced for more hydrophobic solutes.

The respective 2-propanol $\sigma$ values in Table 3 are generally larger than the $\sigma$ values for methanol. This indicates that the 2-propanol cosolvents extracted higher concentrations of compound than did the methanol. Decreasing the polarity of the cosolvent may enhance the solubility of hydrophobic compounds, however, the limited miscibility of most hydrophobic solvents would limit their effectiveness as cosolvents.

**FIGURE 1. EXTRACTION OF 3-RING PAHs USING METHANOL-WATER AND 2-PROPANOL-WATER**

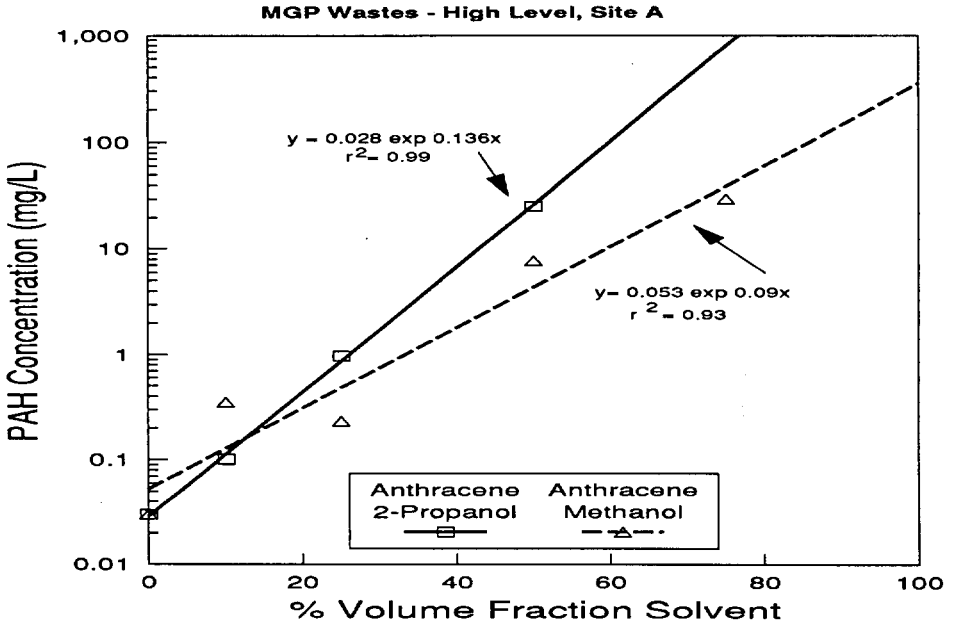


**FIGURE 2. EXTRACTION OF 4-RING PAHs USING METHANOL-WATER AND 2-PROPANOL-WATER**

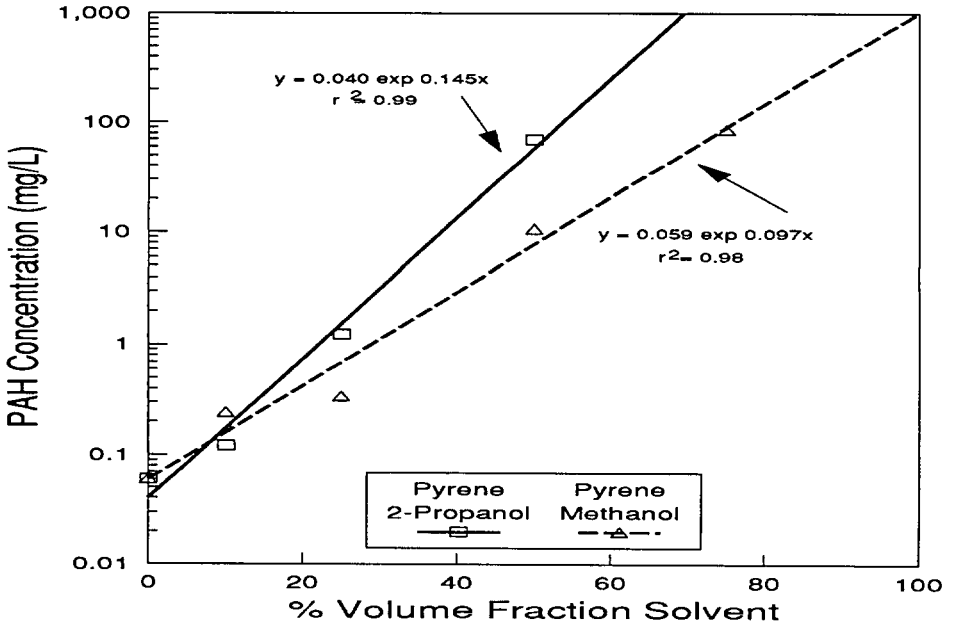

**FIGURE 3. EXTRACTION OF 4-RING PAHs USING METHANOL-WATER AND 2-PROPANOL-WATER**

**Soils with Wood Treating Residues, Site C**

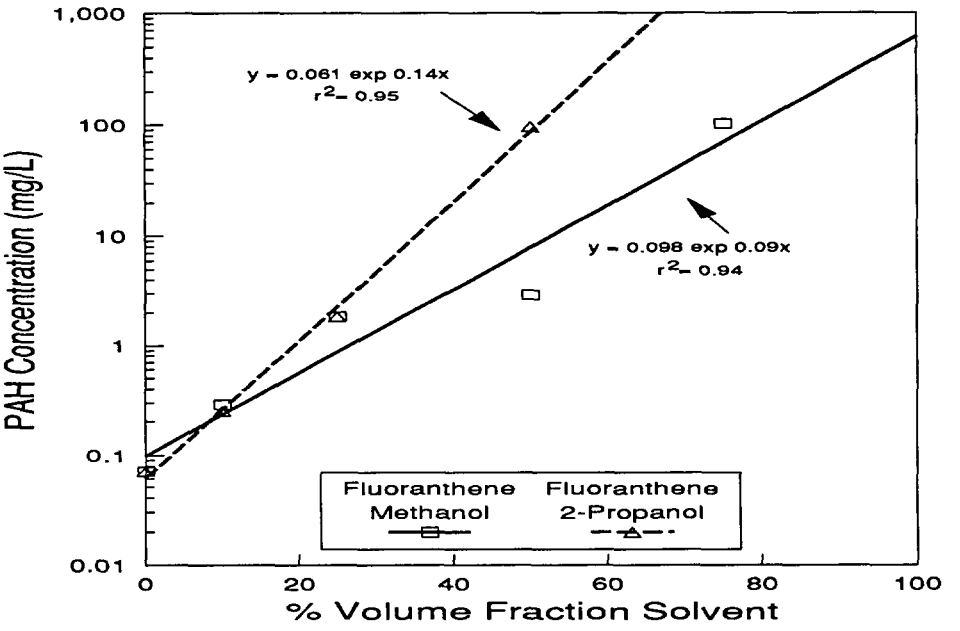


**FIGURE 4. EXTRACTION OF 4-RING PAHs USING METHANOL-WATER AND 2-PROPANOL-WATER**

**Soils with Wood Treating Residues, Site C**

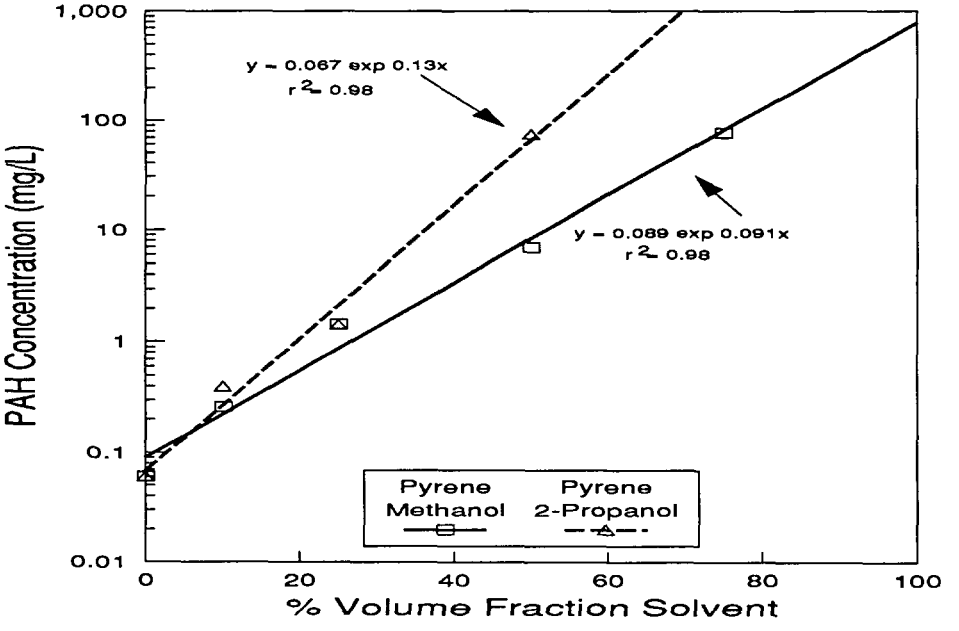

TABLE 3

SIGMA σ VALUES FOR DESORPTION STUDIES, METHANOL COSOLVENTS

| COMPOUNDS | SITES | | | | |
|---|---|---|---|---|---|
| | (A) MGP High | (B) MGP Low | (C) Wood Pr. | (D) MGP High | (E) MGP Low |
| **2-Rings** | | | | | |
| Naphthalene | 0.053 | --(1) | -- | 0.036 | 0.066 |
| **3-Rings** | | | | | |
| Acenaphthylene | 0.068 | 0.053 | -- | -- | 0.092 |
| Acenaphthene | -- | -- | -- | -- | -- |
| Fluorene | 0.085 | 0.084 | -- | -- | 0.037 |
| Phenanthrene | 0.086 | 0.097 | -- | 0.082 | 0.01 |
| Anthracene | 0.088 | 0.110 | 0.074 | -- | 0.002 |
| **4-Rings** | | | | | |
| Fluoranthene | -- | -- | -- | 0.090 | 0.011 |
| Pyrene | 0.097 | 0.088 | 0.083 | 0.077 | 0.009 |
| Benzo(a)anthracene | 0.069 | 0.11 | 0.068 | -- | -- |
| Chrysene | -- | 0.062 | 0.066 | 0.062 | 0.001 |
| **5-Rings** | | | | | |
| Benzo(b)fluoranthene | -- | -- | 0.052 | -- | -- |
| Benzo(k)fluoranthene | -- | -- | 0.029 | -- | -- |
| Benzo(a)pyrene | -- | -- | 0.049 | -- | -- |
| Dibenzo(ah)anthracene | -- | -- | -- | -- | -- |
| **6-Rings** | | | | | |
| Benzo(ghi)perylene | -- | -- | -- | -- | -- |
| Indeno(123-cd)pyrene | -- | -- | -- | -- | -- |

(1)--Compound was below quantitation limit in cosolvent solutions.

TABLE 3 cont.

SIGMA σ VALUES FOR DESORPTION STUDIES, 2-PROPANOL COSOLVENTS

| COMPOUNDS | SITES | | | | |
|---|---|---|---|---|---|
| | (A) MGP High | (B) MGP Low | (C) Wood Pr. | (D) MGP High | (E) MGP Low |
| **2-Rings** | | | | | |
| Naphthalene | 0.059 | --(1) | -- | 0.044 | 0.076 |
| **3-Rings** | | | | | |
| Acenaphthylene | 0.09 | 0.053 | -- | -- | 0.102 |
| Acenaphthene | -- | -- | -- | -- | -- |
| Fluorene | 0.11 | 0.09 | -- | 0.068 | 0.05 |
| Phenanthrene | 0.13 | 0.14 | -- | 0.11 | 0.01 |
| Anthracene | 0.14 | 0.15 | 0.14 | -- | 0.013 |
| **4-Rings** | | | | | |
| Fluoranthene | -- | -- | -- | 0.13 | 0.014 |
| Pyrene | 0.15 | 0.14 | 0.13 | 0.11 | 0.012 |
| Benzo(a)anthracene | 0.12 | 0.23 | 0.12 | -- | 0.005 |
| Chrysene | -- | 0.13 | 0.12 | 0.094 | 0.002 |
| **5-Rings** | | | | | |
| Benzo(b)fluoranthene | -- | -- | 0.13 | -- | -- |
| Benzo(k)fluoranthene | -- | -- | 0.11 | -- | -- |
| Benzo(a)pyrene | -- | -- | -- | -- | 0.007 |
| Dibenzo(ah)anthracene | -- | -- | -- | -- | -- |
| **6-Rings** | | | | | |
| Benzo(ghi)perylene | -- | -- | -- | -- | -- |
| Indeno(123-cd)pyrene | -- | -- | -- | -- | -- |

(1)--Compound was below quantitation limit in cosolvent solutions.

Results similar to these have been described for the solubilization of drugs in cosolvents. Yalkowsky et al. (1981) reported that the solubility of nonpolar compounds in cosolvents ($\log S_m$) increased exponentially with increasing cosolvent composition. If $\sigma$ is defined as the slope of the log $S_m$ versus $f_c$ plot, then the solubility of hydrophobic compounds in cosolvents can be estimated by:

$$\log S_m = \log S_w + \sigma f_c \qquad (2)$$

where:

$S_m$ is the cosolvent solubility,

$S_w$ aqueous solubility and

$f_c$ is the cosolvent fraction

For the soils tested, the aqueous solubilities of the compounds at zero $f_c$ were less than would be predicted based on crystalline solubility data. In Tables 4 and 5 the y-intercepts, which were calculated during the regression analyses, are shown. Also shown are reported solubilities of the pure compounds dissolved in water (Mackay et al. 1977). In some of the soils, one or more of the 16 PAHs were not present in the sample and therefore would not be expected to be found in the zero $f_c$ solutions. To determine which compounds were present in the extracted soil, data from the 75 percent 2-propanol desorption solution were evaluated (Table 6). The 75 percent solution contained a significant fraction of the organic solvent and was effective for extracting the PAH compounds as shown in comparisons with methylene chloride extracts (data not shown). If a particular compound was not present in the 75 percent 2-propanol cosolvent, then it was considered to not be present in the soil and was so indicated in Tables 4 and 5. The quantitation limits (indicated with the less than symbol <) are shown in instances where the compound was present in the soil, but was not detected in a sufficient number of different cosolvent ratios to calculate a value for the y intercept. Compounds such as acenaphthene which were not observed in any of the five soils are not listed in Tables 4 and 5.

The y intercept data, which correspond to the concentration of compound in the zero $f_c$ cosolvent solutions, are estimates of the aqueous solubilities. Actual measured values using zero $f_c$ are shown in Table 7. which were obtained using a Sep-Pak extraction/concentration technique. In most instances the measured values were comparable to the calculated solubilites shown in Tables 4 and 5. Two exceptions were naphthalene and acenaphthylene which were present in the Site (B) and in the Site (E) zero $f_c$ solution respectively, but not in the higher (75% 2-propanol, Table 6) cosolvent solution. These compounds may have been detected in the zero $f_c$ because of the good analytical sensitivity of the Sep-Pak concentration method.

TABLE 4
CALCULATED AQUEOUS SOLUBILITIES FOR METHANOL COSOLVENT DESORPTION CURVES

| COMPOUNDS RECOVERED | SOLUBILITY[1] (mg/L) | SOLUBILITIES (mg/L) FOR SOILS FROM SITES: | | | | |
|---|---|---|---|---|---|---|
| | | (A) MGP High | (B) MGP Low | (C) Wood Pr. | (D) MGP High | (E) MGP Low |
| Naphthalene | 31 | 2.94 | N.R. | N.R. | 13.8 | 0.07 |
| Acenaphthylene | 3.9 | 1.0 | 0.48 | <.08 | N.R. | N.R. |
| Fluorene | 1.98 | 0.45 | 0.24 | <.002 | <0.002 | 0.03 |
| Phenanthrene | 1.29 | 0.25 | 0.12 | <0.004 | 0.009 | 0.01 |
| Anthracene | 0.073 | 0.053 | 0.02 | 0.015 | <0.004 | 0.002 |
| Fluoranthene | 0.26 | <0.002 | <0.002 | 0.098 | 0.01 | 0.01 |
| Pyrene | 0.135 | 0.059 | 0.02 | 0.13 | 0.01 | 0.009 |
| Benzo(a)anthracene | 0.014 | 0.033 | 0.007 | 0.03 | N.R. | N.R. |
| Chrysene | 0.002 | <0.002 | 0.009 | 0.02 | 0.001 | 0.001 |
| Benzo(b)fluoranthene | --[(2)] | <0.007 | <0.007 | 0.02 | N.R. | N.R. |
| Benzo(k)fluoranthene | -- | <0.004 | <0.004 | 0.019 | N.R. | N.R. |
| Benzo(a)pyrene | -- | <0.002 | <0.002 | 0.017 | N.R. | N.R. |

*N.R. Compound not present in soil.
[1] Crystalline solubilities (Mackay and Shiu 1977)
[2] Value not in reference.

TABLE 5
CALCULATED AQUEOUS SOLUBILITIES FOR 2-PROPANOL COSOLVENT DESORPTION CURVES

| COMPOUNDS RECOVERED | SOLUBILITY[1] (mg/L) | SOLUBILITIES (mg/L) FOR SOILS FROM SITES: | | | | |
|---|---|---|---|---|---|---|
| | | (A) MGP High | (B) MGP Low | (C) Wood Pr. | (D) MGP High | (E) MGP Low |
| Naphthalene | 31 | 3.1 | N.R.* | N.R. | 12.0 | 0.08 |
| Acenaphthylene | 3.9 | 0.87 | 0.83 | <0.08 | N.R. | N.R. |
| Fluorene | 1.98 | 0.34 | 0.25 | <.002 | 0.016 | 0.05 |
| Phenanthrene | 1.29 | 0.12 | 0.12 | <0.002 | 0.009 | 0.01 |
| Anthracene | 0.073 | 0.03 | 0.02 | 0.01 | <0.004 | 0.01 |
| Fluoranthene | 0.26 | <.002 | <0.002 | 0.06 | 0.008 | 0.01 |
| Pyrene | 0.135 | 0.04 | 0.04 | 0.1 | 0.008 | 0.01 |
| Benzo(a)anthracene | 0.014 | 0.004 | <0.003 | 0.02 | N.R. | N.R. |
| Chrysene | 0.002 | <.002 | 0.01 | 0.01 | 0.009 | 0.002 |
| Benzo(b)fluoranthene | --[(2)] | <0.007 | <0.007 | 0.006 | N.R. | N.R. |
| Benzo(k)fluoranthene | -- | <0.004 | <0.004 | 0.002 | N.R. | N.R. |
| Benzo(a)pyrene | -- | <0.002 | <0.002 | 0.009 | N.R. | N.R. |

*N.R. Compound not present in soil.
[1] Crystalline solubilities (Mackay and Shiu 1977)
[2] Value not in reference.

TABLE 6
AVAILABLE COMPOUND IN DESORPTION SOLUTIONS[1]
(mg/L)

| COMPOUNDS | SITES | | | | |
|---|---|---|---|---|---|
| | (A) MGP High | (B) MGP Low | (C) Wood Pr. | (D) MGP High | (E) MGP Low |
| Naphthalene | 61 | <.2 | <.2 | 78 | 0.2 |
| Acenaphthylene | 71 | 16 | 19 | <1 | <1 |
| Acenaphthene | <0.2[2] | <0.2 | <0.2 | <0.2 | <0.2 |
| Fluorene | 88 | 40 | 1 | 0.3 | 0.4 |
| Phenanthrene | 76 | 47 | 4 | 0.7 | 0.2 |
| Anthracene | 28 | 19 | 20 | 0.2 | 0.04 |
| Fluoranthene | --[3] | 118 | 200 | 2 | 0.2 |
| Pyrene | 84 | 61 | 164 | 0.9 | 0.1 |
| Benzo(a)anthracene | 15 | 10 | 52 | <0.06 | <0.06 |
| Chrysene | 11 | 6 | 53 | 7 | 0.2 |
| Benzo(b)fluoranthene | 5 | 2 | 32 | <0.14 | <0.14 |
| Benzo(k)fluoranthene | 3 | 2 | 15 | <0.08 | <0.08 |
| Benzo(a)pyrene | 9 | 4.5 | 29 | <0.04 | <0.04 |
| Dibenzo(ah)anthracene | <0.14 | <.14 | <0.14 | <0.14 | <0.14 |
| Benzo(ghi)perylene | <.07 | <.07 | <0.07 | <0.07 | <0.07 |
| Indeno(123-cd)pyrene | 3 | 1 | 6 | <0.06 | <0.06 |

[1] Based upon concentrations recovered from the 75% 2-propanol cosolvent.
[2] Quantitation limit.
[3] Present, but not quantified because of coeluting peaks.

TABLE 7
MEASURED AQUEOUS CONCENTRATIONS

| COMPOUNDS RECOVERED | CONCENTRATIONS (mg/L) FOR SOILS FROM SITES: | | | | |
|---|---|---|---|---|---|
| | (A) MGP High | (B) MGP Low | (C) Wood Pr. | (D) MGP High | (E) MGP Low |
| Naphthalene | 2.3 | 1.4 | N.R. | 12.4 | 0.07 |
| Acenaphthylene | 0.9 | 0.7 | <0.08 | N.R. | 0.1 |
| Fluorene | 0.3 | 0.2 | <.002 | <0.002 | 0.03 |
| Phenanthrene | 0.11 | 0.14 | <0.004 | 0.01 | 0.01 |
| Anthracene | 0.03 | 0.03 | <0.004 | <0.004 | <0.004 |
| Fluoranthene | <.002 | <0.002 | 0.07 | 0.01 | 0.01 |
| Pyrene | 0.06 | 0.09 | 0.06 | 0.01 | 0.01 |
| Benzo(a)anthracene | 0.01 | <0.003 | 0.01 | N.R. | N.R. |
| Chrysene | <0.002 | <0.002 | 0.01 | 0.02 | <0.002 |
| Benzo(b)fluoranthene | <0.007 | <0.007 | 0.01 | N.R. | N.R. |
| Benzo(k)fluoranthene | <0.007 | <0.007 | <0.007 | N.R. | N.R. |

In nearly all cases, the calculated and measured solubilities were lower than that predicted by crystalline solubilities. The decreased solubilities could be the result of unidentified organic solutes from the soil present in solution. The following relation (equation 3) based on Raoult's Law may explain the low solubilities of the compounds in the aqueous samples:

$$S_w = X_i S_i \qquad (3)$$

where:

$S_w$ is the measured aqueous solubility

$X_i$ is the solute mole fraction and

$S_i$ is the ideal solute solubility (Yalkowsky 1980)

The ideal solubility $S_i$ can be calculated from the following equation:

$$\log S_{(i)} = \log S_c + 0.01(MP - 25) \qquad (4)$$

where : $S_c$ = Crystalline Solubility and

$MP$ = Melting Point ($C^0$)

Equation 3 predicts that the aqueous solubility of solutes dissolved in soil organic matter will be influenced by the amount of other organic compounds present in the mixture. As the mole fraction of the solute increases, aqueous solubility will increase to a maximum equal to the crystalline solubility. In complex wastes, where the mole fraction of individual compounds may be small, the aqueous solubilities of the compounds may be less than the respective crystalline solubilities. Validation of this relationship for any soil requires knowledge of the mole fraction of solutes of interest. This information is not readily available because of the many compounds present in these types of wastes. Work, however, is continuing in this research to investigate the appropriateness of using Equation 3 to explain the lowered solubilities.

The solubility data suggest that the aqueous solubilities of compounds emanating from heavily contaminated soils may be less than their respective crystalline solubilities. This may result in inaccurate modelling of pollutant fate and transport in soil water systems. In addition, the aqueous concentrations of hydrophobic compounds, whose source is a contaminated soil, can be difficult to determine because of the low concentrations involved. An alternate approach to quantifying these compounds may involve cosolvents. By analyzing cosolvent extracts of the soil, and plotting these concentrations, the aqueous concentration of material may be estimated by extrapolating to zero cosolvent .

## Conclusions

PAH compounds in a series of soils previously contaminated with coal tar or with creosote were extracted with cosolvents containing methanol or 2-propanol. Data from this work indicate that the solubility of PAH compounds extracted from these soils increases with increasing volume fraction of methanol or 2-propanol, and that the increase is semi-logrithmic. In addition, the aqueous solubility of compounds extracted from heavily contaminated soils may be lower than predicted from crystalline solubility data through the influence of other organic compounds present in the soil.

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74

# HIGH-PERFORMANCE THIN LAYER CHROMATOGRAPHIC ANALYSIS OF ANILINES AND PHENOLS

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Aromatic amines and phenols are of environmental interest because they are commonly found at Superfund sites. They are also found as contaminants in many dyestuffs. Several of these compounds are known to be toxic or carcinogenic.

A rapid, sensitive method has recently been developed for identification and quantitation of aromatic amines and phenols. Mixes of aniline and phenol standards have been separated, identified, and quantitated by high-performance thin layer chromatography (HPTLC). This technique can be used quantitatively if only a few components are to be analyzed, or it can be used as a screening device for several target analytes. Fifteen samples and standards can be applied to a single plate, which allows for high sample throughput. The entire analysis and detection time is usually about one hour per plate. Samples and standards are applied to the same plate so that a direct comparison can be made. Approximate on-plate detection limits are in the 100-nanogram to 1-microgram range.

Individual standards and the mixes are applied to Whatman silica gel 60 $F_{254}$ HPTLC plates with a Camag Linomat IV band applicator. Since the rate of sample application can be varied, samples can be applied from almost any solvent. Volatile solvents such as methanol or hexane are preferred, but even water samples can be directly applied to the plates. All samples analyzed for this work were dissolved and applied to the plate in methanol. Typical volumes spotted were from 5 to 50 microliters.

The plates were developed in classic twin trough TLC chambers. The mobile phase used for separation of the anilines is methylene chloride:methanol (97:3). A slightly less polar solvent system, methylene chloride:hexane (98:2), is used for the phenols analysis. The TLC tanks were allowed to equilibrate with the solvent vapors for at least 30 min before the plates were inserted. The solvent is eluted up the HPTLC plate. The development distance (the distance traveled by the solvent front) was approximately 7 centimeters.

Detection and quantitation are obtained by scanning the plates with UV light using the Camag TLC Scanner II scanning densitometer. The optimum detection wavelengths were determined to be 210 nanometers for phenols and 254 nanometers for anilines. Figure 1 is a HPTLC chromatogram of six phenols that was obtained using the analytical conditions reported above.

Identification of the individual components in a mix is typically obtained by comparing the retention distance of the separated components to the individual standards. UV-visible spectra of individual components can also be obtained with the scanner as an additional identification tool. The retention characteristics of several anilines and phenols are compared in Tables 1 and 2.

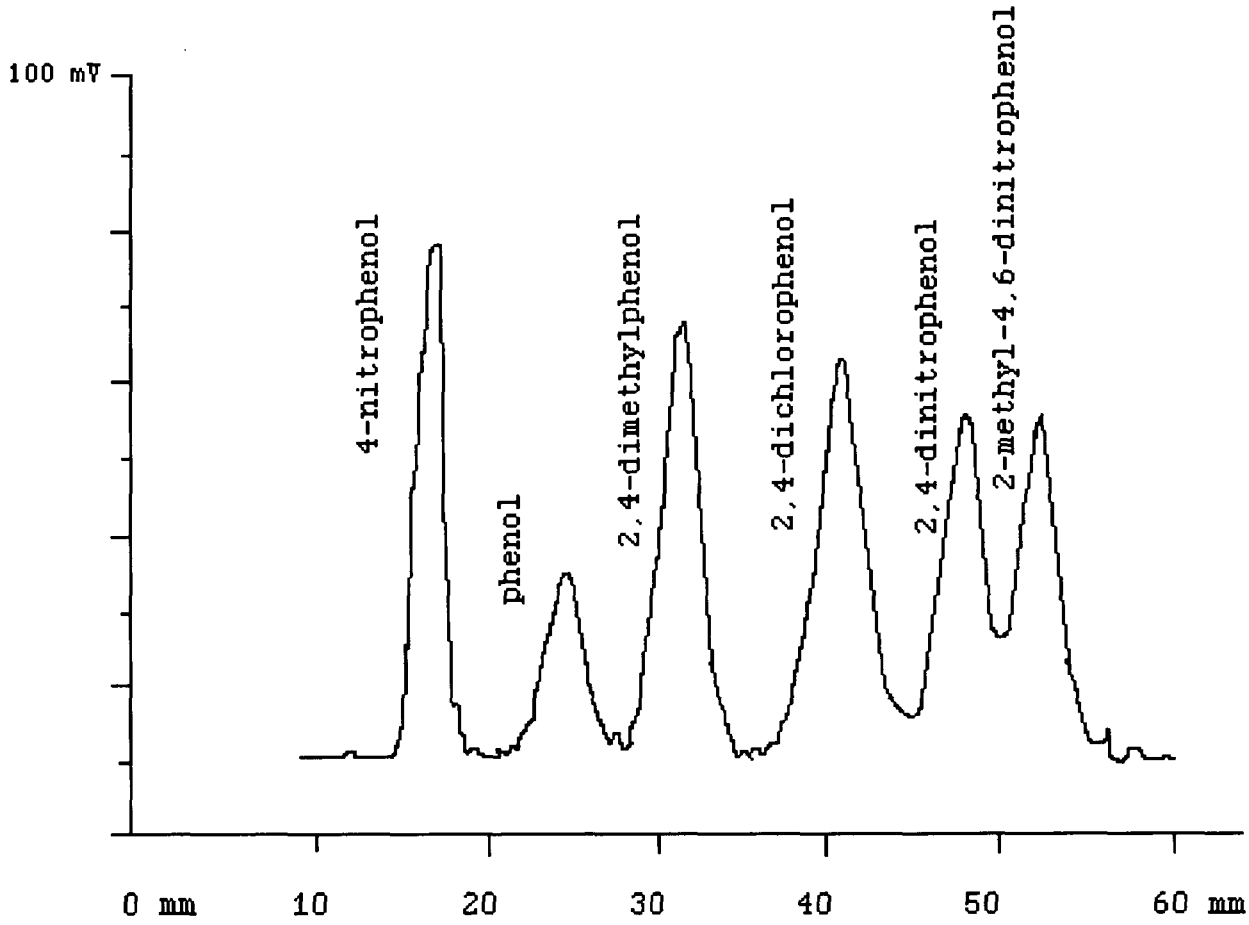


Figure 1: Chromatogram of a Standards Mixture of Six Phenols Separated on an HPTLC Plate (210 nm wavelength detection) The mixture contained 1.25 µg nitrophenol; 2.5 µg phenol 2.5 µg 2,4-dimethylphenol; 2.5 µg 2,4-dichlorophenol 1.25 µg 2,4-dinitrophenol; and 1.25 µg of 2-methyl-4,6-dinitrophenol.

Table 1: Retention Characteristics of Selected Aromatic Amines
Analysis performed on HPTLC plates with a 97:3 methylene chloride:methanol solvent system

| Compound | $R_f$[a] |
|---|---|
| Aniline | 0.59 |
| 2-Methylaniline | 0.66 |
| 3-Methylaniline | 0.60 |
| 4-Methylaniline | 0.56 |
| 2,4-Dimethylaniline | 0.62 |
| *n*-Ethylaniline | 0.76 |
| α-Phenylethylamine | 0.23 |
| *p*-Phenylenediamine | 0.03 |
| Tribenzylamine | 0.88 |
| *p*-Dimethylaminoazobenzene | 0.87 |

[a] $R_f$ = distance traveled by sample/distance traveled by solvent front.

Table 2: Retention Characteristics of Selected Phenols
Analysis performed on HPTLC plates with a 98:2 methylene chloride:hexane solvent system

| Compound | $R_f$[a] |
|---|---|
| Phenol | 0.30 |
| 2-Chlorophenol | 0.66 |
| 2,4-Dichlorophenol | 0.64 |
| 2,4,6-Trichlorophenol | 0.78 |
| Pentachlorophenol | 0.76 |
| 4-Chloro-3-methylphenol | 0.34 |
| 2,4-Dimethylphenol | 0.42 |
| 2-Methyl-4,6-dinitrophenol | 0.81 |
| 4-Nitrophenol | 0.17 |
| 2,4-Dinitrophenol | 0.73 |

[a] $R_f$ = distance traveled by sample/distance traveled by solvent front.

75

# A INTERLABORATORY COMPARISON OF A SW-846 METHOD FOR THE ANALYSIS OF THE CHLORINATED PHENOXYACID HERBICIDES BY LC/MS,

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ABSTRACT

Recently the U.S. Environmental Protection Agency's (U.S.EPA) Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV), working in close cooperation with the Office of Solid Waste (OSW), completed a interlaboratory evaluation of a liquid chromatography/mass spectrometry (LC/MS) method for the analysis of chlorinated phenoxyacid herbicides. This method uses neither hydrolysis nor esterification to prepare samples for analysis. While method performance data was obtained in the study, the focus of this evaluation was to test the intercomparability of LC/MS data. In order to minimize interlaboratory variability due to sample and standard preparation, the sample extracts and a stock standard solution for calibration were prepared by Lockheed Environmental Services Company (LESC) and sent to participating laboratories for LC/MS analysis. Another element of this study was the comparison of data obtained from both types of LC/MS interfaces [i.e. thermospray (TSP) and particle beam (PB)]. The data generated by the study demonstrated that phenoxyacid herbicides can be diagnostic of instrument performance problems. Some characteristics important to instrument performance, particularly for particle beam, were interface temperature and source cleanliness, an increase in thermal degradation ions was observed in the spectra of systems whose performance was not optimum. With thermospray the loss of sensitivity due to high thermospray temperatures can be a diagnostic problem. Those laboratories proficient in LC/MS analysis demonstrated that the limits of detection (LOD's) were comparable between the thermospray and particle beam interfaces for compounds with high molecular

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[1]NOTICE: Although the research described in this article 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 nor recommendation for use.

weight and thermal stability. However, the low molecular weight and thermally labile compounds (e.g. dalapon, dinoseb) were better observed using thermospray.

## INTRODUCTION

Gas chromatography/mass spectrometry (GC/MS) is widely recognized as one of the most powerful techniques in analytical chemistry. Despite its' utility, the application of GC/MS is limited to the following categories of compounds: those that are amenable to solvent extraction, those that can be isolated by purge and trap techniques, and those that are sufficiently volatile to pass through the GC column and yet are resistant to thermal degradation. Unfortunately, A number of compounds of environmental interest, including many on the Resource Conservation and Recovery Act (RCRA) Appendix VIII list, are polar, non-volatile, and/or thermally labile. One important goal of the U.S. EPA methods development efforts has been to develop techniques for compounds that can not be measured by conventional techniques (e.g. GC).

High performance liquid chromatography (HPLC) methods are not subject to the above mentioned analytical limitations, making them suitable for many of the analytes which lie outside the scope of conventional GC. Gradient elution techniques provide analysts with the tools necessary to separate complex mixtures of polar, ionic, and high molecular weight organic materials. However, due to limited types of HPLC detectors (e.g. Ultraviolet/Visible, fluorescent, electrochemical) and their lack of structure confirmation capability, HPLC sacrifices many of the benefits of selective GC and GC/MS analysis.

The logical solution to this dilemma is to couple liquid chromatography and mass spectroscopy to produce a sensitive and reliable technique for identifying and quantitating polar and thermally labile compounds. Examples of environmental organic contaminants which could be analyzed by LC/MS are organophosphorus pesticides[1], triazine herbicides[2], and the chlorinated phenoxyacid herbicides.[3] This latter group of compounds can be analyzed as the free acid, plus the ester form, by LC/MS. The chlorinated herbicides include some of the most widely used herbicides for systemic control of broadleaf herbage for both agricultural and residential usages.

Currently SW-846 methods 8150 and 8151 are approved by the U.S. EPA, for the analysis of chlorinated herbicides in solid waste under the Resource Conservation and Recovery Act (RCRA). These methods specify quantitation by GC with electron capture detector (ECD) and optional GC/MS confirmation. These methods require the use of hydrolysis and subsequent esterification

of the sample extracts before analysis. Sample hydrolysis is a time consuming process and may not always be quantitative. The usual esterification reagent, diazomethane, is a both a potential carcinogen and explosive. Therefore, method accuracy, sample throughput, and laboratory safety, are improved by the elimination of these two steps. The analysis of several chlorinated herbicides (specifically 2,4-D, dicamba, and MCPP) by HPLC using reverse phase column and UV detector has been reported in the literature[4]. A multi-laboratory collaborative study of the HPLC/UV method has been conducted and published[5]. In addition, a ACS monograph and a U.S.EPA internal report have been written on the use of LC/MS for the analysis of these herbicides[3,6]. The use of LC/MS not only eliminates the need for the hydrolysis and esterification steps, but also provides a method for the direct and specific analysis of these compounds, using a mass spectrometer.

Presented in this manuscript are the results of an interlaboratory evaluation of the analysis of chlorinated herbicides and their esters by LC/MS, using two different types of LC/MS interface devices (TSP and PB). Samples were sent to thirteen participating laboratories utilizing thermospray and/or particle beam interfaces originating from several different manufacturers. Statistical analyses were performed on the data (only 7 laboratories returned data) for individual analytes using Statistical Analysis System (SAS) software. The performance of the two interface devices was evaluated in terms of the applicability of each to quantitate these herbicides, as well as, the intra- and inter- laboratory precision and accuracy of these data.

## EXPERIMENTAL

Since the purpose of this study was to compare and evaluate the different LC/MS interface devices for their applicability to the analysis of a particular group of compounds (acid herbicides and their esters), sample extracts, instead of samples, were provided to all the participating laboratories. This not only eliminated any discrepancies in results due to variations in extraction efficiencies by different laboratories, but also reduced the amount of work required for each laboratory.

Duplicate sample extracts, consisting of the eleven analytes in acetonitrile, at four different concentration levels, were sent to each of the thirteen laboratories. Each laboratory was asked to perform triplicate analysis on the four duplicate samples using the equipment available in their laboratory. The laboratories involved utilized approximately equal numbers

of TSP- and PB-LC/MS instruments, and the instruments were manufactured by five different instrument companies.

A concentrated stock standard solution, containing the eleven analytes in acetonitrile at 1000 μg/mL, was sent with each sample set, for instrument calibration and analyte quantitation. The same stock standard was also used for preparation of sample extracts, so that all the chemicals used in this study were traceable to a single original source. It is necessary for all the standards and extracts to be prepared in acetonitrile. The use of methanol could result in the methylation of the free acid herbicides.

A method blank extract was shipped with each sample set. The blank was prepared with a sample of tap water, using the same procedure employed for sample extraction (Method 8150).

For calibration standards a minimum of three concentration levels were specified. The recommended low calibration standard was to be at a level close to the instruments detection limit. The recommended medium and high calibration standards were five times and fifty times higher than the low level calibration standard, respectively. Due to the unstable nature of some of the instruments, no acceptance criteria were required for the calibration factors.

No specific parameters were given to the participants concerning instrument (interface and MS) tuning and calibration. The laboratories were advised to follow the instrument manufacturer's specifications for optimal performance.

Separate HPLC conditions were recommended to laboratories with different instrumentation. Flow rates for those laboratories with TSP interfaces and post-column 0.1 M ammonium acetate additions: flow rate 0.4 mL/min to 0.6 mL/min, with 0.8 mL/min post-column flow. Flow rates for laboratories with TSP interfaces, but without post-column addition: flow rate 1.0 mL/min to 1.2 mL/min. Flow rates for those laboratories with PB interfaces: flow rate 0.4 to 0.6 mL/min. Analytical column: 15 cm x 2.1 mm i.d., C-18, reverse phase, 0.5 μm particle size. Use of a guard column was recommended.

HPLC gradient elution conditions:

| Time (min.) | 1% acetic acid in Water | 1% acetic acid in methanol |
|---|---|---|
| 0 | 50% | 50% |
| 2 | 50% | 50% |
| 12 | 40% | 60% |
| 18 | 0% | 100% |
| 28 | 0% | 100% |
| 33 | 50% | 50% |
| 38 | 50% | 50% |

It is necessary to have 1% acetic acid in the mobile phases in order to keep the acid analytes equilibrated in their acid form.

## RESULTS AND DISCUSSION

Thirteen laboratories were each provided with eight sample extracts, one blank, and one concentrated stock standard for instrument calibration. The eight sample extracts consisted of four duplicate extracts each containing eleven analytes at different concentration levels. In addition, the duplicate samples at each concentration level were treated as individual samples.

Data were received from only seven of the thirteen laboratories. Data were collected by four laboratories using the particle beam interface (two different manufacturers) and by three laboratories using the thermospray interface, (three different manufacturers). These seven data packages were used to evaluate the two main LC/MS interface devices (i.e. TSP and PB) for their applicability and performance in the quantitation of the acid herbicides and their esters.

A SAS software program was employed to perform the comparison of the data for the overall performance between the two interfaces. A probability (P) value[7] was calculated in order to determine if a significant difference exists between the two groups of data. In order for the two data sets to be significantly different with 95% confidence, the P value must be less than 0.05. This comparison was performed on an individual analyte basis at each concentration level. For example, 2,4,5-T at the theoretical concentration of 500 µg/mL, the mean analytical results from the four PB instruments is 543.68 ± 76.24, and the corresponding mean value from the three TSP instruments is 448.985 ± 102.57. The calculated P value is 0.2169, indicating that there is no

significant statistical difference between the two sets of data.

Another objective of this study was to compare the performance of the two LC/MS interface devices made by different instrument manufacturers. The experimental design for making such an evaluation is influenced by the number of participating laboratories and their instrumentations. Because less than half of the expected data packages were returned, some of the comparisons were impossible to perform. However, four sets of PB data, produced by using interfaces made by two different instrument manufacturers, were received. This allows for a limited comparison of PB results obtained from manufacturer **A** and **B**. The P test was again used for this comparison, by combining the data from the two laboratories using PB from manufacturer **A** and comparing it with the combined data from two laboratories using manufacturer **B**. The test was performed on an individual analyte basis, and was done both by considering concentration as a variable (i.e., comparing results from samples at the same concentration level), and by considering the concentration as a non-variable (i.e., comparing results of samples combined from all four concentration levels).

When results of samples from all four concentration levels generated by instrument **A** were combined and compared with the combined results generated by instrument **B**, the statistical test indicated again no significant difference between the two data sets.

Table 1 shows the overall precision and accuracy data from the seven data packages received. Included in this table is the designation of either particle beam, denoted as PB, or thermospray, TS, for interface device.

Initially, the duplicate extracts at the same concentration level were evaluated separately in order to determine if there was any statistical difference in the results between the two samples. SAS analysis of the relative standard deviation (RSD) values from the two duplicate samples, from the same laboratory, indicated that there was no significant difference in the results between the two samples. This was not unexpected, since these two extracts were identically prepared. However, it was important to demonstrate that statistically there was no difference between the samples from duplicate extracts so that triplicate data from each of the two duplicates could be combined for statistical analysis.

SUMMARY

Although the data collected was from a limited data set (i.e. seven laboratories, and one type of extract) the statistical results showed some interesting and informative results, from which a few general and specific conclusions can be extracted.

Dalapon was not detected by PB, presumably because it is too volatile to be transmitted through the PB interface. Dinoseb is a phenol, which respond poorly to PB as a class. Even at the highest concentration level, 500 μg/mL, only one of the four PB laboratories reported values for dinoseb. Dicamba also did not respond well by PB, especially on extracts at the lower concentration levels. None of the four laboratories using PB detected dicamba in the low concentration level extract, 5 μg/mL.

With the exception of dalapon, dinoseb, and dicamba, PB tends to give bias high results, at 500 μg/mL, (average percent mean bias is +16%) and TSP tends to give bias low results (average percent mean bias is -10%) when compared to the true value. The tabulated results for the precision data indicate that PB, at 500 μg/mL, gives better precision (average %RSD is 7%) than TSP (average %RSD is 22%).

At the medium concentration level, 50 μg/mL, there was no clear difference between the results obtained from PB and TSP, except for the previously mentioned compounds, although both are biased low compared to the true value.

Only one of the four PB laboratories, could detect analytes in the low concentration level, 5 μg/mL, extract. This laboratory used a 20 μL injection volume instead of the 4 μL as most other laboratories used. The results reported by this laboratory were at least twice as high s the theoretical value. This strongly indicates that the detection limits for these compounds by PB is at least above 5 μg/mL in the extract (or above 20 ng at a 4 μL injection volume). Two of the three laboratories using TSP, reported values for this low concentration level extract, and these results are in reasonable agreement, with a very low bias (average percent bias is 4%) and an average %RSD of ± 19%, see Table 1. This is a strong indication that TSP provides better sensitivity in detecting low levels of these compounds than PB.

None of the participating laboratories reported any value above the detection limit on the blank sample, indicating no serious contamination problem throughout this study.

PB generally gives better precision than TSP, particularly at the high concentration level (500 μg/mL). This is indicated

by the lower %RSD values, shown in Table 1. Since TSP is more sensitive in detecting these target analytes, the extracts often had to be diluted prior to injection, in order to be within the linear response calibration range of the instrument. Therefore, dilution steps may have contributed partially to the higher %RSD (poorer precision) observed for TSP. However, it can be assumed that the difference in precision in part is due to the fundamental differences in the operating principles of the two interface systems.

Instrument calibration is an important factor in producing accurate data. A uniform calibration method was not used by all of the participants, due to the instabilities of the instruments. This may have contributed to poor accuracy observed in this study.

As far as the results of the comparison between the two PB manufacturers from the four sets of data a couple of conclusions can be drawn. For sample extracts at 500 µg/mL, 250 µg/mL, and 50 µg/mL levels, there is no significant difference between the results obtained by using manufacturer **A** or **B** on all 11 analytes tested. When results of samples from all four concentration levels generated by instrument **A** were combined and compared with the combined results generated by instrument **B**, the statistical test indicated again no significant difference between the two data sets.

Based on the results obtained from this study, LC/MS can be used, and should be the choice of instrument in the future, for the analysis of chlorinated phenoxyacid herbicides. While TSP interfaces provide better sensitivity, PB interfaces tend to provide better precision for a majority of the compounds tested. While PB has the advantage of providing detailed information on the structure of the analytes, it can not detect dalapon, and it responds very poorly to both dicamba and dinoseb.

The choice for which interface to use, TSP or PB, will depend on the type of analytes and the analytical requirements of the data user. From the data obtained in this study one can conclude that for the analysis of low level samples, thermospray, in negative ionization mode, would be preferred for phenoxyacid herbicides. For the analysis of high level samples in which structural confirmation of the analytes is essential, particle beam with electron impact ionization might be preferred.

ACKNOWLEDGEMENTS

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**Table I** - Precision and Accuracy of Interlaboratory Data

| Analytes (500 ug/mL) | Mean | | % RSD | |
|---|---|---|---|---|
| | PB | TS | PB | TS |
| 2,4,5-T | 544 | 449 | 6.27 | 24.5 |
| 2,4,5-T,BUTOXY | 675 | 450 | 11.9 | 22.8 |
| 2,4-D | 556 | 431 | 9.06 | 25.5 |
| 2,4-DB | 602 | 475 | 4.08 | 22.3 |
| DALAPON | . | 415 | . | 36.3 |
| DICAMBA | 473 | 386 | 10.7 | 17.6 |
| DICHLORPROP | 552 | 422 | 5.73 | 18.1 |
| DINOSEB | 317 | 392 | 14.4 | 13.8 |
| MCPA | 553 | 444 | 5.35 | 22.9 |
| MCPP | 533 | 430 | 7.46 | 18.2 |
| SILVEX | 609 | 480 | 5.78 | 20.4 |

| Analytes (50 ug/mL) | Mean | | % RSD | |
|---|---|---|---|---|
| | PB | TS | PB | TS |
| 2,4,5-T | 31.1 | 31.1 | 21.0 | 34.5 |
| 2,4,5-T,BUTOXY | 39.4 | 42.6 | 13.9 | 14.5 |
| 2,4-D | 42.7 | 31.9 | 25.7 | 26.8 |
| 2,4-DB | 35.6 | 51.8 | 12.4 | 18.3 |
| DALAPON | . | 47.0 | . | 22.6 |
| DICAMBA | 36.7 | 45.2 | 23.4 | 16.6 |
| DICHLORPROP | 48.6 | 48.2 | 35.9 | 12.5 |
| DINOSEB | 15.0 | 36.5 | 39.1 | 11.8 |
| MCPA | 52.9 | 47.8 | 41.3 | 5.93 |
| MCPP | 51.0 | 38.2 | 46.5 | 43.1 |
| SILVEX | 35.9 | 32.4 | 27.1 | 29.8 |

| Analytes (5 ug/mL) | Mean | | % RSD | |
|---|---|---|---|---|
| | PB | TS | PB | TS |
| 2,4,5-T | 11.2 | 4.52 | 3.66 | 32.6 |
| 2,4,5-T,BUTOXY | 12.0 | 4.97 | 19.3 | 24.1 |
| 2,4-D | 13.5 | 5.60 | 32.6 | 24.1 |
| 2,4-DB | 10.3 | 4.80 | 14.8 | 7.35 |
| DALAPON | . | 7.48 | . | 19.6 |
| DICAMBA | . | 5.26 | . | 16.8 |
| DICHLORPROP | 16.2 | 5.10 | 34.5 | 15.1 |
| DINOSEB | . | 5.41 | . | 23.3 |
| MCPA | 14.0 | 4.73 | 20.8 | 18.7 |
| MCPP | 14.5 | 4.92 | 18.0 | 14.0 |
| SILVEX | 10.8 | 4.35 | 10.7 | 11.4 |

76

# THE DISTRIBUTION OF TARGET COMPOUND LIST ANALYTES IN SUPERFUND SAMPLES

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ABSTRACT:

The United States Environmental Protection Agency has established a database known as the Contract Laboratory Program (CLP) Analytical Results Database (CARD) to store all of the analytical data reported by CLP laboratories on samples from Superfund sites. This is the first time that all the analytical results and their associated quality assurance data has been assembled in one database. With this enormous database, it is possible to examine many facets of program performance. One area of great interest is the identities of the frequently found compounds at Superfund sites, their concentration levels and their distribution trends. This presentation will describe the frequency, distribution, and concentration of the detected compounds both nationally and regionally. The data will be examined for both geographical trends and possible relationships of compounds that are frequently found together, both within and between analytical fractions. The results will be presented in tabular and graphical formats.

**Notice:** Although the research described in this article has been supported by the Environmental Protection Agency under contract 68-03-3249 with Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

77 DUAL-COLUMN/DUAL-DETECTOR APPROACH TO GAS CHROMATOGRAPHIC ANALYSIS OF ENVIRONMENTAL POLLUTANTS

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Dual-column/dual-detector gas chromatographic procedures using 30-m x 0.53-mm ID fused-silica open tubular columns are being developed in our laboratory for the analysis of compounds of environmental significance. Two columns of different polarities, thus different selectivities toward the target compounds, are connected to an injection tee and identical detectors. This allows the primary and confirmatory analyses to be performed simultaneously. The target compounds include 34 phenolic compounds (as pentafluorobenzyl bromide derivatives), 52 organochlorine pesticides, 42 organophosphorus pesticides, 22 chlorinated hydrocarbons, 16 phthalate esters, and 36 nitroaromatic compounds. Retention times, relative retention times, method reproducibility and linearity, instrument detection limits, and selection of surrogate compounds and internal standards will be discussed for each group of target compounds.

78 OFF-LINE SUPERCRITICAL FLUID EXTRACTION TECHNIQUE FOR DIFFICULT ENVIRONMENTAL MATRICES CONTAMINATED WITH COMPOUNDS OF ENVIRONMENTAL SIGNIFICANCE

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Supercritical fluids have unique properties (their solvent strengths approach those of liquids, their viscosities are low, and solute diffusivities are higher in supercritical fluids than in liquid solvents) which make them very suitable for use in sample preparation. This, and the availability of both off-line and on-line equipment for supercritical fluid extraction (SFE), constituted the driving force behind the evaluation of the SFE technique as an alternative sample preparation technique to the time-consuming Soxhlet extraction or the very nonselective sonication extraction. We are in the process of evaluating the SFE technique with difficult matrices (primarily standard reference materials such as marine sediment, incinerator fly ash, coal tar contaminated soil) and many classes of compounds of environmental significance ( e.g., organophosphorus pesticides, phenolic compounds, chlorinated benzenes, nitroaromatic compounds, and haloethers). The effects of pressure, temperature, sample size, analyte concentration, addition of modifier to the matrix or the carbon dioxide will be discussed. The SFE equipment that allows either single or multiple extractions to be performed in unattended operation was made available to this study by several manufacturers.

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.

79

# A RETENTION INDEX SYSTEM FOR IMPROVING THE RELIABILITY OF GC/MS TENTATIVE IDENTIFICATIONS

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In many, if not all, samples analyzed by GC/MS for volatile and semivolatile organic compounds, significant concentrations of tentatively identified compounds (TICs) are found. A very large percentage (>90%) of these TICs are reported as unknowns. When decisions are made on remedial action steps or cleanup standards, it is becoming increasingly more important to have reliable identification of non-target compounds. Therefore, we have developed a retention index system which can be searched using existing GC/MS data systems to provide additional information on the TICs. The advantages of a retention index are the ability to transfer data between laboratories, as long as the stationary phase is identical, the independence of the retention index and the mass spectrum, and the relative ease of computer searching for matches.

The retention indices were developed as follows. A series of normal hydrocarbons were analyzed along with the internal standards appropriate for the method. The retention index of each internal standard was calculated using the hydrocarbons in the standard fashion. The hydrocarbon spectra were the first additions to the new library. The internal standards were then used to calculate the retention index of non-target analytes. The mass spectra were added to a user-created mass spectral library, while the retention indices were added to a user-created retention library. Therefore, when TICs are found in a sample, they can be searched through both libraries, and a more positive identification can be made.

To date, over 100 compounds have been entered into the new libraries. There are three criteria for selection of compounds to be added. First, compounds which appear on regulatory lists other than the Contract Laboratory Program Target Compound List were added, e.g. Appendix IX compounds. Second, compounds which have had a high frequency of occurrence in samples analyzed in the Contract Laboratory Program program (as provided by the database at the Sample Management Office) were added. Third, compounds which are assumed to be chromatographable under the standard method conditions were added. We are continuing to add compounds to the library at this time.

**80** Refer to paper number 43, Vol. 1 - 297

81

# ON-LINE SUPERCRITICAL FLUID EXTRACTION/GAS CHROMATOGRAPHIC (SFE/GC) METHOD SUITABLE FOR USE WITH MODIFIED CARBON DIOXIDE

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## ABSTRACT

An SFE/GC interface was constructed and studied both with and without an intermediate Tenax-GC adsorption step. Semivolatile pesticides and herbicides were used as test analytes. The addition of the Tenax-GC step allowed for larger extraction volumes than were possible using SFE/GC with analyte transfer directly into the GC column. The intermediate trapping step also improved the chromatographic efficiency relative to direct SFE/GC. Replicate analyses indicated variabilities less than 3% relative standard deviation. This system should allow for on-line analysis of extracts obtained using extraction fluids modified with polar solvents. Experiments to test this with $CO_2$/methanol mixtures are in progress.

## INTRODUCTION

In recent years, chemists have begun to investigate the ways in which supercritical fluids can be exploited to simplify and improve analytical methods. A number of researchers has published on the use of supercritical fluids, such as $CO_2$ and $N_2O$, to extract a wide variety of organic compounds from several different matrices. Through the use of SFE, pesticides, polynuclear aromatic compounds (PNAs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins, dibenzofurans, and phenolic compounds have been recovered from matrices such as soil (1,2), urban dust (3,4), sediment (5), fly ash (6), and polymeric materials such as Tenax-GC (7), polyimides (8), and polyurethane foam (9).

The main benefits of SFE arise from the density-dependent solvation capability that allows some degree of extraction selectivity, the ease with which the extraction solvent can be removed, and the ability to minimize the use of organic solvents, such as dichloromethane, which themselves contribute to the current waste and pollution problems. In addition, supercritical fluids have lower viscosities and higher diffusivitites than liquid solvents. As a result, supercritical fluid extractions can be completed in far less time than is necessary for comparable Soxhlet extractions.

Extractions utilizing supercritical fluids can be performed either off-line or on-line. In off-line methods, the effluent from the extraction cell is expanded into a small volume of receiving solvent. This results

in extracts that are analyzed in the same manner as extracts obtained from Soxhlet extractions. In on-line methods, the entire effluent is directed into the chromatographic system (GC or HPLC) where the analytes are refocused prior to separation. On-line methods offer several advantages. First, better method limits of detection (LODs) are possible because all of the extract is analyzed. Thus, LODs achievable with current methods are possible using on-line SFE methods and smaller samples. Second, the chances of sample contamination are greatly reduced because sample handling is minimized. Third, sample throughput can be increased because extraction and analysis occur in the same step. On-line methods requiring less than one hour for both extraction and GC analysis have been reported (4).

All of the directly coupled SFE/GC methods reported to date have utilized pure $CO_2$ or $N_2O$ as the extraction fluid. There are, however, many instances where $CO_2$ alone is inadequate to recover the analytes of interest (1, 10, 11). Although this might be due, in part, to poor solubility of the analyte in the fluid, there is sufficient evidence to conclude that added modifiers serve to displace solutes from sites on the surface of the matrix (12). In these cases, an organic compound such as methanol is added to the sample in order to improve the recovery of the analyte. Unfortunately, the direct coupling of SFE to GC is not straightforward when modified extraction fluids are used. Methanol added to the extraction fluid will accumulate in the GC column upon expansion of the supercritical fluid and cause poor chromatography. For maximum analytical utility and flexibility, a coupled SFE/GC needs to handle pure and modified supercritical fluids.

An additional constraint on directly coupled SFE/GC systems is the extraction flow rate that can be tolerated. If the flow rate is too fast, poor refocusing of the analytes occurs upon fluid expansion within the column and poor chromatographic peak shapes result (13). If a flow rate is used that results in good peak shape, very long times might be required to completely extract the analytes from the sample. This would be true, for example, if low levels of analyte were to be recovered from a sample volume of several milliliters. Such a situation could be envisioned in the SFE/GC analysis of organic compounds from sorbents (Tenax-GC, XAD, PUF) used for air sampling. Therefore, the research described in this paper has been directed towards the development of an SFE/GC system that would provide flexibility with regard to both extraction flow rate or time and extraction fluid composition.

Earlier research in our laboratory indicated that semivolatile compounds could be recovered easily from Tenax-GC using relatively small volumes of pure supercritical $CO_2$ (7). Because semivolatile compounds should have very large retention volumes on a Tenax-GC cartridge at ambient or near-ambient conditions, this sorbent could be used to retain such analytes after expansion of the supercritical effluent from an SFE cell containing the sample of interest. The analytes would be well-retained on the Tenax-GC independent of extraction flow rate, time or fluid

composition. This would provide a great deal of flexibility in the extraction conditions. The analytes could then be recovered from the Tenax-GC using supercritical $CO_2$ and the effluent from this extraction could be introduced into a GC column. If only small volumes of $CO_2$ are needed for the recovery of analytes from the Tenax-GC, optimal chromatographic performance can be realized in this step by using slow SFE flow rates over a relatively short time. In addition, co-solvents such as methanol will not be well retained by the Tenax-GC (14). Consequently, such compounds could be incorporated into the supercritical fluid used to extract the sample. Upon expansion, the analytes would be retained by the Tenax-GC and the vapor-phase modifier would be poorly retained. The majority of the solvent would quickly break through the cartridge and pass out of the system. The remaining modifier would be swept from the sorbent with either $CO_2$ or helium prior to the transfer of the analytes from the Tenax-GC to the GC column. The volume and dlow rate of supercritical $CO_2$ in this last step would be such that good chromatography would result.

## EXPERIMENTAL

The SFE/GC interface developed during this work is shown in Figure 1. It is shown as configured for analyte deposition onto Tenax-GC for subsequent extraction and deposition onto the GC column (SFE/SFE/GC). For direct SFE/GC operation, the extraction cell (EC) was connected where the Tenax-GC cartridge is shown in the lower half of the Figure. In either configuration, a Valco HPLC injector fitted with a 500 nL rotor (not shown) was placed in-line and before the 0.41 mL SFE cell (EC in Figure 1) which was filled with sea sand and held at 50°C in a modified Lee Scientific Model 501 SFE/SFC system. The valve allowed for the reproducible introduction of a methanol solution of pesticides (approximately 100 ng each) into the pressurized cell so that SFE conditions could be mimicked. The pesticides used were molinate, propoxur, atrazine, $\gamma$-BHC, triallate, terbutyrn, ethyl parathion, $\gamma$-chlordane, and phosmet. The outlet of the SFE cell was directed through a multiport switching valve to an 11 cm x 15 $\mu$m id fused silica restrictor for deposition onto the Tenax-GC ($R_1$) or the GC column ($R_2$). Restrictors $R_1$ and $R_2$ had the same dimensions.

In the SFE/SFE/GC configuration, the system was pressurized to 400 atm ($CO_2$ density = 0.928 g/cm$^3$) with valves 1 and 3 open. The pesticide solution was introduced to the extraction cell, migrated through the cell and expanded through $R_1$ onto the head of a column comprised of a steel tube (6 cm x 4 mm id) with fritted column end-fittings and packed with 0.14 g of Tenax-GC. The Tenax cell was also held at 50°C. Gaseous $CO_2$ passed through valve #3 to vent. The $CO_2$ flow measured at the outlet of valve #3 was 81 mL/min. The length of this first extraction ($E_1$) was varied from 7 to 30 minutes to study possible changes in recovery. At the end of $E_1$, valve #1 was closed and valves 5 and 7 were opened. This introduced a flow of helium through a "T" union near the

end of $R_1$, past the end of $R_1$ and across the Tenax-GC cartridge to remove any residual methanol, if used. After this purge, the multiport switching valve was moved to its other position, valves 5, 7, and 3 were closed, and valves 2 and 6 were opened. In this manner, the Tenax-GC cartridge was back extracted with supercritical $CO_2$ and the effluent was expanded through $R_2$, which passed through a 1/16" cross union, onto the first few cm of the GC column (30 m x 0.32 mm id DB-5, J&W Scientific). Some of the $CO_2$ gas passed through the column and the rest was vented through valve #6 (vent 2). The time of this second extraction ($E_2$) was varied between 4 and 15 minutes. The column temperature during this extraction was maintained at 20°C. After $E_2$ was complete, valve #2 was closed, valve #3 was opened to release the pressure in the Tenax-GC cartridge, and valve #5 was opened to introduce helium into the GC column and to sweep residual $CO_2$ from the cross union. After one minute, valve #6 was closed to purge $CO_2$ from the column and the oven temperature was raised to 180°C for 1 minute and then programmed to 300°C at 5 degrees per minute. Flame ionization detection (FID) was used. During $E_2$, the extraction cell could be cleaned by opening valves 1 and 4.

In SFE/GC operation, the supercritical effluent from the extractiuon cell was expanded through $R_2$ as in SFE/SFE/GC operation. Because $R_1$ and $R_2$ were of the same dimensions, the flows were assumed to be the same. The flows were measured periodically to be sure they had not changed. Times of 7, 10, and 15 minutes for this extraction step were studied. Area ratios relative to $\gamma$-BHC were used to gauge relative recoveries. Separation and detection were performed as for the SFE/SFE/GC experiment. All data were collected using a Nelson Analytical (model 4400, version 7.2) data system.

For comparison, the pesticide mixture was analyzed using 30 s splitless/ split injection on the same GC column.

## RESULTS

The effect of $E_1$ extraction time on the areas measured in the SFE/GC experiment are shown in Table 1. Each entry is the average of triplicate analyses. As the time of extraction increased, the measured areas decreased. This was especially true for terbutryn. Since the extraction flow rates were the same for each time period, the losses are the result of total flow. That is, it appears as if the analytes are deposited into the column then lost from the system. A lower trapping temperature might improve this situation but was not tried because the goal here was to determine if the presence of the secondary Tenax-GC trapping step could minimize the problems associated with longer $E_1$ times.

In the study of the time of $E_2$ in the SFE/SFE/GC experiment, the GC peaks became broader as the time was progressively increased from 4 to 7

to 11 and to 15 minutes. A carryover of 20% was observed for BHC at an $E_2$ time of 4 minutes so an $E_2$ time of 7 minutes was used for the remainder of this work.

Using an $E_2$ time of 7 minutes, the $E_1$ time had little effect on the areas measured when it was varied between 7 and 30 minutes, although better recoveries were observed for phosmet using a 15 minute extraction time. These results indicate that the analytes do not break through the Tenax-GC column, at least up to times of 30 minutes. This allows for a great deal of flexibility in the selection of the $E_1$ time as long as the analytes of interest are well-retained by the Tenax-GC. For compounds of relatively low volatility, this should not be a problem.

The SFE/SFE/GC chromatogram obtained using an $E_1$ time of 15 minutes and an $E_2$ time of 7 minutes is shown in Figure 2. A gas chromatogram of the test compounds obtained using conventional splitless/split injection is shown in Figure 3 for comparative purposes. Although some broadening of the chromatographic peaks is seen in the case represented in Figure 2, relative to Figure 3, the efficiencies of the SFE/SFE/GC separation are certainly adequate for most purposes and could probably be improved by careful optimization of flow rate and column temperature during $E_2$. Replicate analyses using SFE/SFE/GC provided area precision of less than 3% RSD.

Table 2 shows a comparison of the chromatographic peak area to height ratios for each of the analytes for both SFE/GC and SFE/SFE/GC. This ratio is indicative of chromatographic efficiency, with a low ratio reflecting a higher efficiency. The extraction times for both SFE/GC ($E_1$) and SFE/SFE/GC ($E_2$) were 7 minutes at the same extraction flow rate, and thus differences reflect the effect of the Tenax-GC on the system performance. It can be seen that in all cases the presence of the Tenax-GC resulted in sharper peaks. This is presumably due to the accumulation of the analytes at the head of the Tenax-GC cartridge. When the Tenax-GC is back extracted, the analytes are introduced into the column as a tight band. In SFE/GC, the analytes were introduced into the column over a longer time because of the band spreading that occurred during the migration through the sand. Such an effect would be expected to be more pronounced in an actual extraction where desorption of the analytes from the matrix might take place over a longer time with the result that they would be spread out even more. The use of a secondary sorbent can minimize this effect.

A study of the performance of the SFE/SFE/GC system when methanol-modified $CO_2$ is used as the extraction fluid is currently in progress.

## SUMMARY

The use of the secondary sorbent Tenax-GC in an on-line SFE/GC analysis scheme (SFE/SFE/GC) can provide greater flexibility in the extraction of the sample than can direct SFE/GC for analysis of semivolatile organic

compounds. The use of on-line SFE/GC methods has the potential to allow for the collection of smaller samples (smaller air sampling volumes) and, because the entire extract is analyzed, to lower the limits of detection of the analytical method.

ACKNOWLEDGEMENT

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TABLE 1. EFFECT OF FIRST EXTRACTION TIME (E1) ON RECOVERIES IN SFE/GC

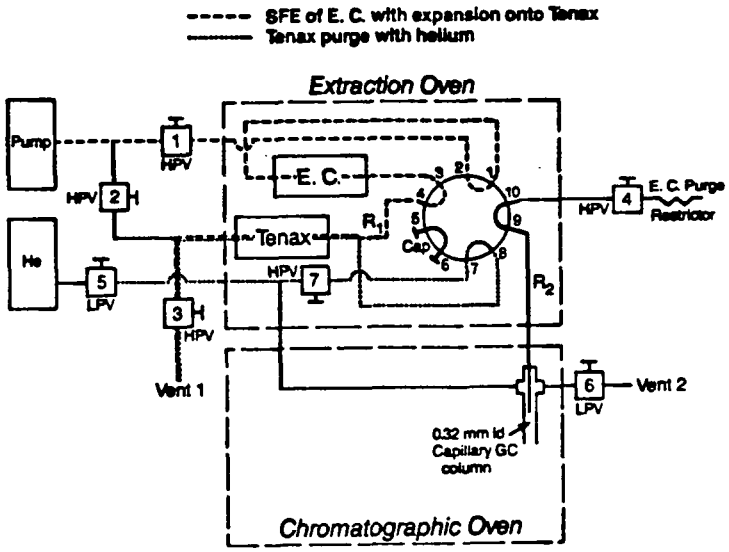
| | Chromatographic Peak Areas | | |
|---|---|---|---|
| Compounds | $E_1$ = 7 min Average Area (n=3) | $E_1$ = 10 min Average Area (n=3) | $E_1$ = 15 min Average Area (n=3) |
| Molinate | 149527 | 142925 | 123094 |
| Propoxur | 123733 | 117224 | 101087 |
| Atrazine | 84996 | 68710 | 66362 |
| γ-BHC | 73335 | 70537 | 60252 |
| Triallate | 107195 | 103578 | 89790 |
| Terbutyrn | 31662 | 12248 | 17006 |
| Ethyl parathion | 97223 | 93410 | 81241 |
| γ-Chlordane | 92127 | 87681 | 77910 |
| Phosmet | 62853 | 60652 | 51310 |

TABLE 2. CHROMATOGRAPHIC EFFICENCY OF PESTICIDE SEPARATION AS REFLECTED BY AREA/HEIGHT RATIOS

| Compound | SFE/GC[a] (%RSD) | SFE/SFE/GC[b] (% RSD) |
|---|---|---|
| Molinate | 7.4 (3.9) | 5.4 (4.9) |
| Propoxur | 7.6 (4.7) | 5.4 (7.5) |
| Atrazine | 8.2 (1.2) | 5.8 (6.5) |
| γ-BHC | 8.4 (3.8) | 6.2 (7.4) |
| Triallate | 7.4 (5.6) | 5.7 (6.3) |
| Terbutyrn | 8.5 (4.2) | 5.8 (1.0) |
| Ethyl parathion | 8.3 (5.7) | 6.0 (5.8) |
| γ-Chlordane | 8.9 (4.3) | 6.3 (6.0) |
| Phosmet | 12.8 (3.7) | 8.8 (1.3) |

[a] Extraction time of 7 minutes; triplicate analysis.
[b] Extraction of sand for 15 minutes followed by 7 minute extraction of Tenax-GC; triplicate analysis.

A.




B.

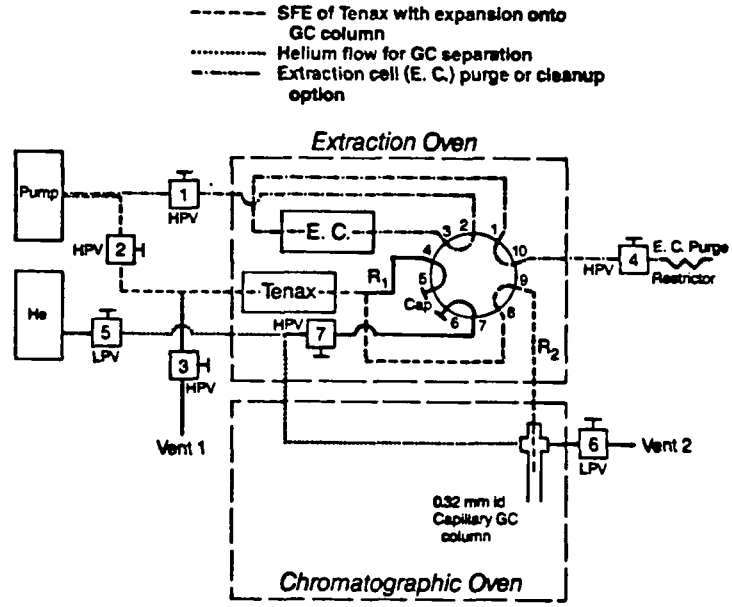



Figure 1. SFE/SFE/GC interface shown with flow paths for A) transfer of extracted components from extraction cell to Tenax-GC, and B) transfer of analytes from Tenax-GC to capillary GC column.

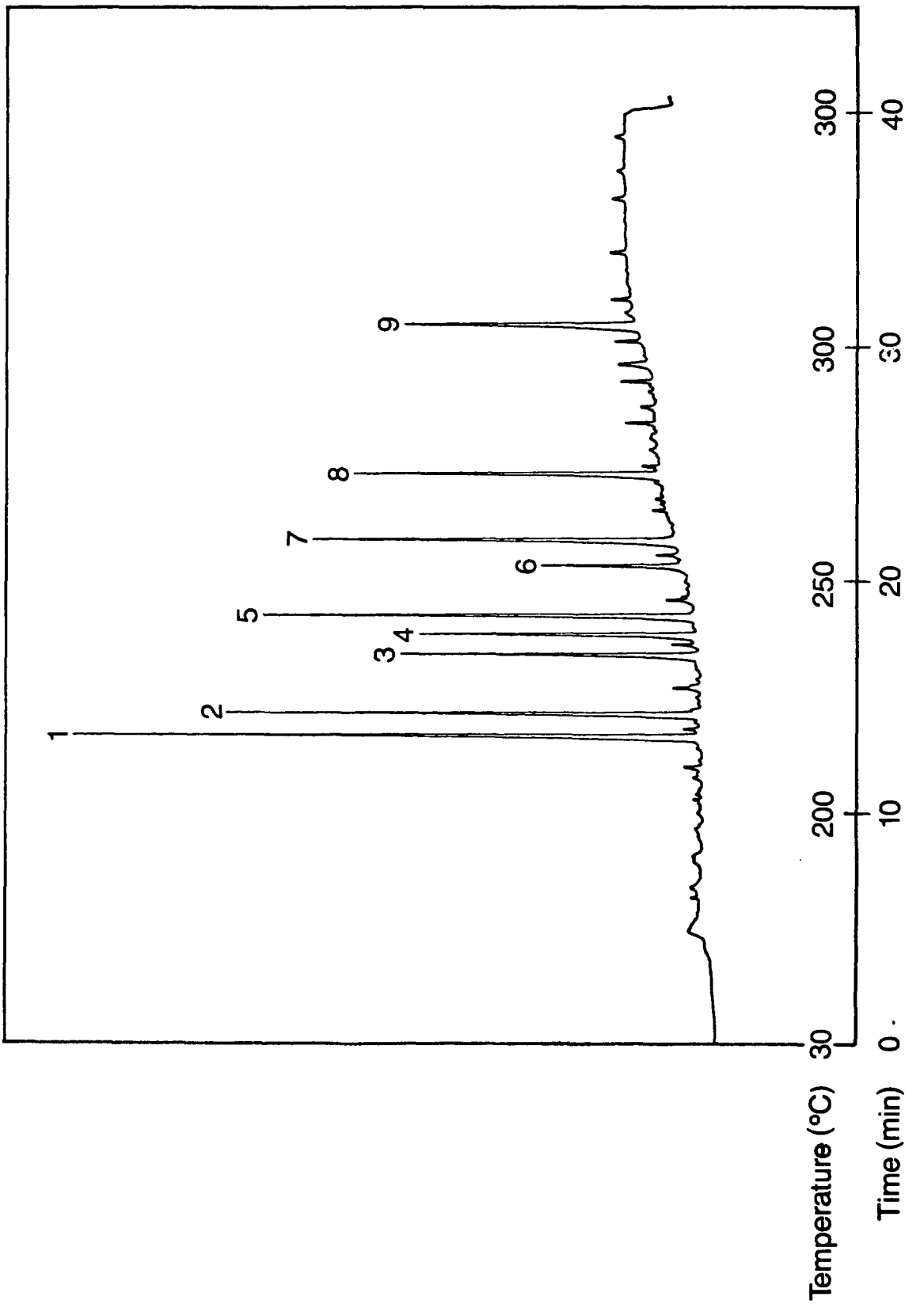



Figure 2. SFE/SFE/GC chromatogram of pesticide test mixture. Compound identifications are (1) molinate, (2) propoxur, (3) atrazine, (4) γ-BHC, (5) triallate, (6) terbutryn, (7) ethyl parathion, (8) γ-chlordane, (9) phosmet. Conditions as described in the text.

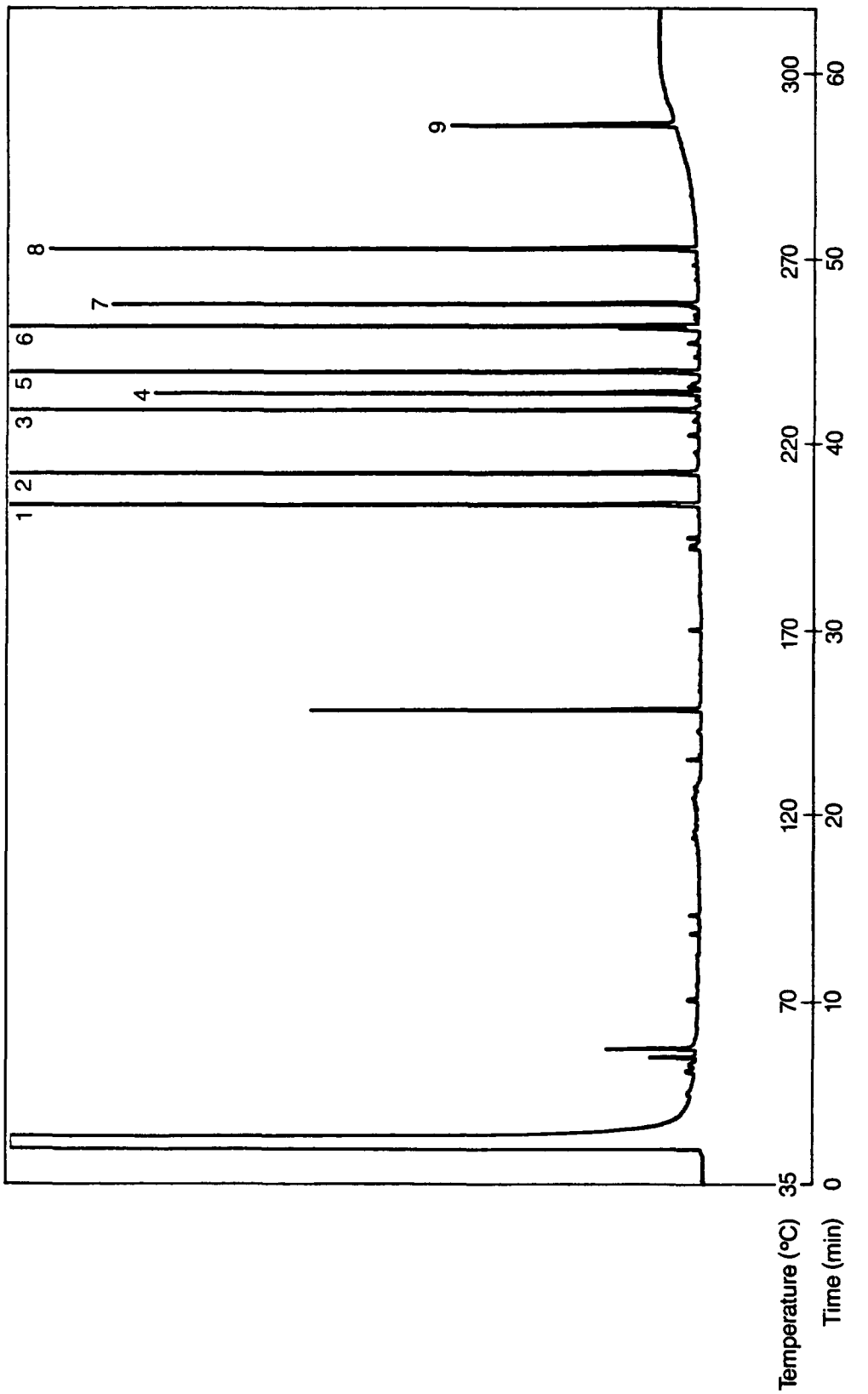



Figure 3. GC chromatogram of the pesticide test mixture after splitless/split injection. The large peak before molinate is either an impurity or thermal decomposition product of propoxur.

82 Refer to paper number 55, Vol. II - 32

83 Refer to paper number 42, Vol. I - 286

84

# MULTILABORATORY VALIDATION STUDY OF PCBs IN SOILS USING SOXTEC® EXTRACTION TECHNIQUE (METHOD 3541)

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# MULTILABORATORY VALIDATION STUDY OF PCBs IN SOILS USING SOXTEC® EXTRACTION TECHNIQUE (METHOD 3541)

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## ABSTRACT

The Oak Ridge National Laboratory has evaluated a multilaboratory Soxtec® PCB extraction study and has compiled the data from the eight participating laboratories. The experiment required each laboratory to extract PCB aroclor 1254 and 1260 from 10-g samples of Fuller's earth on 3 non-consecutive days. Each sample was to be spiked at a concentration level of 5 ppm or 50 ppm. The average for all PCB percent recovery values is 88%, with a 95% confidence interval of (82%, 93%). The estimated standard deviation for a single measurement within a laboratory is 19%.

## INTRODUCTION

In 1987 the Oak Ridge National Laboratory (ORNL) submitted laboratory data to the Environmental Protection Agency (EPA) supporting an alternative method to EPA 3540 and EPA 3550 for the rapid and quantitative extraction of polychlorinated biphenyls (PCBs) in soils. The new procedure for PCB extraction was developed for Tecator's Soxtec® System HT and reduced the extraction time from 16-17 hours to 2 hours. The laboratory data for the Soxtec® extraction procedure showed that about 82.0% of PCBs can be recovered in soil and clay for a concentration range of 5 to 50 ppm. The recovery percentages may vary with concentration level and day-to-day operations. For a single PCB extraction, the recovery percentage will vary about 13.0%, with a 95% confidence interval on the variance of $(9.93)^2 \leq$ Variance $\leq (16.29)^2$.

Subsequently, EPA gave ORNL a single-site approval to use the Soxtec® extraction procedure. EPA indicated that a blanket approval would be given for all laboratories if at least six additional facilities could successfully use the detailed procedure and obtain PCB recovery percentages equivalent to the existing SW846 Method 3540. EPA said that this validation could be done more simply than a formal petition for each site.

In 1988 ORNL sent EPA a statistically designed experiment to demonstrate the capability of a laboratory to use the Soxtec® extraction procedure. This designed experiment required each laboratory to extract PCB aroclors 1254 and 1260 from 10-g samples of Fuller's earth on 3 non-consecutive days. Each sample was to be spiked at a concentration level of 5 ppm or 50 ppm. The 12 samples extracted were then sent to ORNL for analysis by gas chromatography procedure EPA Method in SW846. The analytical data from the multilaboratory experiment were sent to EPA for comparison with recovery percentages equivalent to the existing SW846 Method 3540. EPA has approved the new Soxtec® extraction method and has integrated it into SW846 as Method 3541.

## MATERIALS AND METHODS

Method 3541 was developed to extract PCBs [*1*] from soil, sediment, sludges, and waste solids. The method uses a commercially available, unique three-stage extraction system to achieve comparable PCB recovery with method 3540 but in a much shorter time. The two differences between this proposed method and Method 3540 are stages (1) and (3). In the initial extraction stage, the specimen-loaded extraction thimble is immersed into the boiling solvent. This stage ensures very rapid intimate contact between the specimen and solvent, with subsequent rapid recovery of the PCB. In the second stage, the thimble is elevated above the solvent and is rinse-extracted as in Method 3540. In the third stage, the solvent is evaporated, as would occur in the Kuderna/Danish (K/D) step in Method 3540. The concentrated specimen is then ready for measurement of the PCB concentrations, as in SW 846, Method 8080.

After air-drying of the specimens, following EPA Method 600/4-81-055, interim methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue (Step 3.1.3), the specimen is ground to 100-200 mesh (840 $\mu$m) using a Fisher Cyclotec 1093 grinder (or equivalent). The powdered specimen is extracted using a 1:1 acetone/hexane mixture as the extraction solvent. The extract is then concentrated and exchanged into pure hexane prior to final gas chromatographic PCB measurement.

A Tecator's Soxtec® System HT extraction system with controlled heated oil bath and multiples of six extraction modules was used for this work. The apparatus is used in a hood. PCB contamination-free cellulose extraction thimbles (Fisher catalog 1522-0018 or equivalent) are used. If the sample does not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it is processed into a homogeneous sample that meets these requirements. Fisher Cyclotec Model 1093, Fisher Mortar Model 155 Grinder, Fisher scientific Co., Catalog Number 8-323, or equivalent brands and models are recommended for sample processing. These grinders will handle most solid samples, except gummy, fibrous, or oily materials. These types of specimens may be mixed with anhydrous sodium sulfate to improve grinding efficiency.

Sediment/soil samples were processed as follows. Any water layer is decanted and discarded. The sample is thoroughly mixed, especially composite samples. Any foreign objects, such as sticks, leaves, and rocks, are discarded. The specimen is air-dried at room temperature for 48 hours in a glass tray or on hexane-cleaned aluminum foil.

A sufficient amount of dried specimen is ground to yield 20 g of powder, using the Cyclotec 1093 sample mill. The mesh size is typically 100-200 mesh (840 $\mu$m). Ten grams of specimen is weighed into the extraction thimbles. The thimbles are placed in the device with 50 mL solvent (acetone/hexane, 1/1).

The extraction is carried out by immersing the sample thimble in boiling solvent for 60 minutes. The sample is then raised above the solvent and rinsed for an additional 60 minutes. Finally, the solvent is evaporated, and the extract volume is reduced. The evaporated solvent is collected, and the extraction is stopped when the desired concentration factor (1-2 mL remaining extract) is

collected. The extract can be analyzed directly, carried through a cleanup procedure, or solvent exchanged, depending on the requirements of the measurement method.

For the analysis of PCBs, the extracted and hexane-exchanged specimens are prepared for Method 8080, *Determination of Polychlorinated Biphenyls (PCB) by Gas Chromatography*. If further cleanup is necessary, the Florisil® and/or sulfur procedures may be employed. In such cases Method 3620 is carried out, followed by Method 3660, if necessary, using the 10-mL hexane extracts obtained. Following cleanup, the extracts are analyzed by electron capture GC, as described in the previous paragraphs and in Method 8080.

## MULTILABORATORY EXPERIMENT

Eight laboratories agreed to participate in a multilaboratory experiment to verify Method 3541 for the PCB extraction procedure developed for Tecator's Soxtec® System HT. The experiment for each laboratory consisted of 12 samples of Fuller's earth spiked with either 5 ppm or 50 ppm and either aroclors of 1254 or 1260. The laboratories were responsible for spiking the samples. These samples were to be extracted by the proposed PCB extraction procedure over 3 nonconsecutive days. The experimental factors and their levels are listed in Table 1.

Table 1. Experimental factors and their levels for the PCB extraction multilaboratory experiment.

| | Levels | | |
|---|---|---|---|
| Factors | Low | Middle | High |
| 1. Aroclor | 1254 | | 1260 |
| 2. PCB Level in Fuller's earth (ppm) | 5 | | 50 |
| 3. Days | Day 1 | Day 2 | Day 3 |

Each laboratory was to extract 4 Fuller's earth 10-g samples per day for 3 nonconsecutive days for a total of 12 experimental runs. The experimental design randomly assigned the order of extracting the PCB-spiked samples for each day. All 4 daily samples can be extracted concurrently by a multi-unit Tecator's Soxtec® Systems (e.g., HT6, HT12). For each day, the experimental design is a two-level factorial ($2^2$) for the aroclor- and spike-level factors. The percent recovery was evaluated for each sample and calculated by:

$$\text{Percent Recovery} = 100\% \times (\text{mg of PCB found})/(\text{mg of PCB spiked}).$$

Slight deviations from the planned experiment occurred which influenced the results. Two laboratories, No. 2 and No. 5, didn't interpret our spiking instructions correctly and used 50 and 500 ppm, rather than 5 and 50 ppm. Replicate samples for each extraction were sent to ORNL by laboratories No. 2 and No. 4. Replicate samples are one extraction that was divided into two vials. Laboratory No. 6 repeated two conditions (day = 2, PCB level = 50 ppm, aroclor = 1260 and

day = 3, PCB level = 50 ppm, aroclor = 1254) but didn't do two other conditions (day = 2, PCB level = 50 ppm, aroclor = 1254, and day = 3, PCB level = 5 ppm, aroclor = 1254).

The PCB extracts were sent to ORNL for chemical analysis after the completion of the extraction procedure. A single Analytical Chemistry Division staff member analyzed the entire series of submitted PCB extracts, using a single electron-capture gas chromatograph to minimize personnel and equipment variability.

## RESULTS AND DISCUSSION

The PCB percent recovery (%) results for the multilaboratory experiment are averaged over the 3 days and presented in Table 2. The PCB percent recovery averaged over all laboratories and factor levels is 88%, with a 95% confidence interval of (82%, 93%). The sources of experimental variation were investigated using the method of analysis of variance (ANOVA) [2]. Only data from the five laboratories were included that followed the planned experiment (No. 1, No. 3, No. 4, No. 7, and No. 8). The average of the replicate samples for laboratory No. 4 was used for the ANOVA. The estimated variance from different sources is measured by the mean square. The mean squares are illustrated in Fig. 1 for the following sources of variations: (Lab) differences among laboratories, (Arcolor) differences between aroclor types within each laboratory, (Level) differences between spike levels within each laboratory, (A X L) interaction differences between aroclor types and spike levels within each laboratory, and (Error) experimental error due to differences among days.

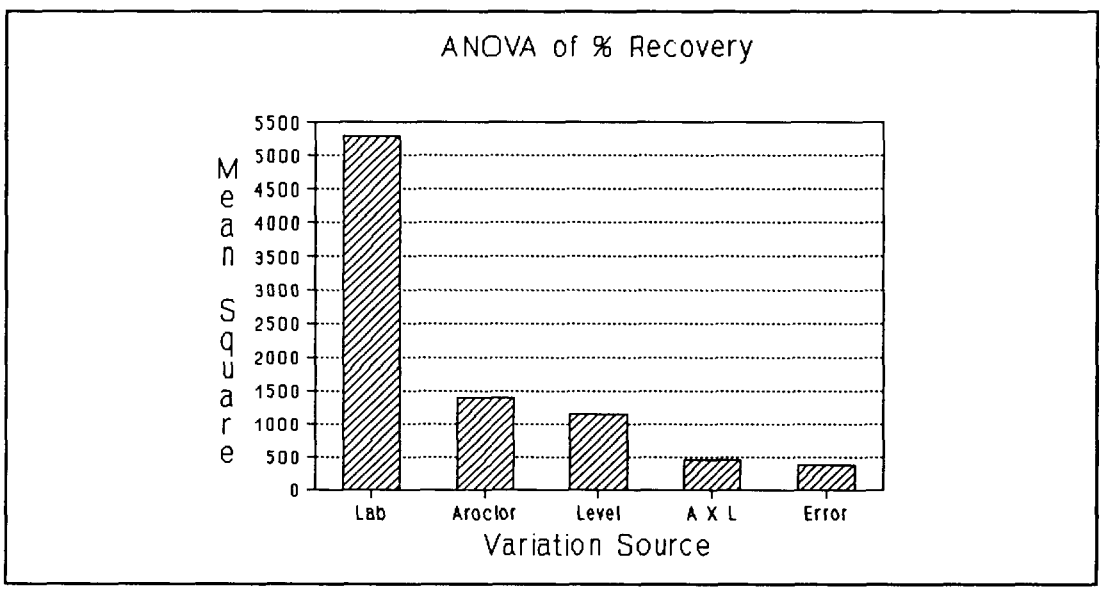


Fig. 1. ANOVA mean squares for percent recovery sources of variation.

Table 2. Summary statistics for PCB percent recovery (%) extracted by Tecator's Soxtec® System HT.

| | | Aroclor | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1254 | | | 1260 | | | |
| | | PCB Level | | | PCB Level | | | All |
| Laboratory | Statistics | 5 | 50 | 500 | 5 | 50 | 500 | Levels |
| No. 1 | Number | 3 | 3 | | 3 | 3 | | 12 |
| | Average | 101 | 74 | | 84 | 79 | | 84 |
| | St Dev | 35 | 42 | | 7 | 8 | | 26 |
| No. 2 | Number | | 6 | 6 | | 6 | 6 | 24 |
| | Average | | 57 | 67 | | 70 | 57 | 67 |
| | St Dev | | 7 | 15 | | 15 | 10 | 13 |
| No. 3 | Number | 3 | 3 | | 3 | 3 | | 12 |
| | Average | 73 | 63 | | 71 | 57 | | 66 |
| | St Dev | 11 | 8 | | 3 | 6 | | 9 |
| No. 4 | Number | 6 | 6 | | 6 | 6 | | 24 |
| | Average | 113 | 144 | | 100 | 85 | | 111 |
| | St Dev | 18 | 30 | | 13 | 4 | | 29 |
| No. 5 | Number | | 3 | 3 | | 3 | 3 | 12 |
| | Average | | 97 | 80 | | 80 | 77 | 84 |
| | St Dev | | 9 | 5 | | 3 | 9 | 10 |
| No. 6 | Number | 2 | 3 | | 3 | 4 | | 12 |
| | Average | 141 | 128 | | 138 | 106 | | 125 |
| | St Dev | 4 | 15 | | 15 | 8 | | 18 |
| No. 7 | Number | 3 | 3 | | 3 | 3 | | 12 |
| | Average | 100 | 123 | | 82 | 94 | | 100 |
| | St Dev | 18 | 15 | | 8 | 5 | | 19 |
| No. 8 | Number | 3 | 3 | | 3 | 3 | | 12 |
| | Average | 65 | 38 | | 93 | 52 | | 62 |
| | St Dev | 16 | 22 | | 37 | 13 | | 29 |
| All Laboratories | Number | 20 | 30 | 9 | 21 | 31 | 9 | 120 |
| | Average | 99 | 93 | 71 | 96 | 79 | 75 | 88 |
| | St Dev | 29 | 43 | 14 | 25 | 18 | 10 | 30 |

The sources of variation are tested to be significantly different from zero by comparing the ratio of the mean squares for the sources of variation with the mean square for the experimental error using an F-statistic. This F-test at the 5% significance level shows significant variation for laboratories, aroclor type within laboratories, and spike level within laboratories, but not for the interaction between aroclor type and spike level within laboratories. The estimated standard deviation for a single measurement within a laboratory is 19%.

ORNL speculates that the major source of variation of the percent recovery among different laboratories is caused by the shipping method for samples. The instructions requested that the

concentrated extract be sealed in septum-capped gas chromatographic vials and sent to ORNL. These vials were to contain the 10-mL hexane extracts; however, some vials had less then 10 mL when they arrived at ORNL. Hexane was added to those vials to bring the total volume to 10 mL. This volatilization may account for differences in ORNL results and those results measured at other laboratories. For example, ORNL found about a 67% recovery rate for samples from laboratory No. 2, but this laboratory has indicated that they found about a 90% recovery rate for the same samples. Other shipping methods were also used. For example, laboratory No. 7 evaporated the samples to dryness for shipping, and 10 mL of hexane was added to the samples at ORNL. In retrospect, this shipping method would be the preferred method.

## NOTES

Soxtec® is a registered trademark of Tecator, Inc., Herndon, Virginia, and is distributed by Fisher Scientific.

Florisil® is a registered trademark of U.S. Silica Co., Berkeley Springs, West Virginia.

## ACKNOWLEDGEMENTS

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# INORGANICS

85

# PRE-CONCENTRATION TECHNIQUES FOR TRACE METALS

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Virtually all trace metal analyses of hazardous wastes are currently performed by graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES). Recently, environmental applications of inductively coupled plasma-mass spectrometry (ICP-MS) have appeared in the literature. Each of these techniques has certain limitations when applied to hazardous waste analysis. GFAAS and ICP-MS provide very low detection limits, but they are prone to serious spectral and physical-chemical interferences in complex matrices. While ICP-AES is more robust, it often does not possess adequate detection limits.

This presentation will demonstrate the application of trace element pre-concentration (TEP) to ICP-MS and ICP-AES, as well as to ion chromatography (IC). The TEP methods are based on a commercially available device, with some modifications necessitated by the specific measurement systems. After adjusting the sample pH to about 5.4, trace metals are pre-concentrated on a column packed with a macroporous iminodiacetate-functionalized resin. The alkali and alkaline-earth metals, as well as residual concomitant anions, such as sulfate and phosphate, are removed by flushing the column with ammonium acetate. The trace metals are then eluted

with nitric acid directly to the instrumentation used for quantitation.

TEP-ICP-MS can be applied to samples such as brines and caustics, since the trace metals are separated from the sample components which cause interferences in conventional ICP-MS. TEP improves the detection limits of ICP-AES for nine analytes by a factor of 10 to 100, depending on the volume of sample pre-concentrated. Finally, both the sensitivity enhancement and the matrix elimination aspects of TEP allow the analysis of hazardous waste digests by IC. TEP-IC instrumentation is rugged and potentially field-portable.

The analytical performance of the various TEP-hyphenated techniques will be documented by specific applications. Limitations of the methods will be discussed. Finally, current work on extending TEP to more analytes will be described.

NOTICE: Although the research described in this abstract 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, and no official endorsement should be inferred.

86

# ANALYSIS OF WATER AND WASTES USING ICP-AES WITH ULTRASONIC NEBULIZATION

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## ABSTRACT

An ultrasonic nebulizer was used to lower the detection limits of pollutant metals in water and waste samples. Procedures described in the USEPA Method 200.7 were followed to demonstrate its capability for routine ICP analysis. Statistical and control data showed that the ultrasonic nebulizer provided comparable accuracy and better precision than the pneumatic nebulizer.

## INTRODUCTION

The methods for metal analysis in water and waste samples, currently approved by the United States Environmental Protection Agency (USEPA), include flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry, and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Among the three techniques cited, the ICP-AES method is preferred because of its capability of fast, multielement analysis.

Most commercial ICP spectrometers utilize pneumatic nebulizers such as the concentric, the cross-flow, and the Babington-type nebulizers. In the past 20 years, laboratory-built ultrasonic nebulizers have been used successfully to enhance the detecting power of ICP-AES [1]. Detection limits for most elements in aqueous solutions obtained with an ultrasonic nebulizer are generally 5 to 25 times better than those achieved with a pneumatic nebulizer.

Taylor and Floyd at the USEPA [2] reported the use of a water-cooled ultrasonic nebulizer for ICP analysis of environmental samples. Pollutant metal analysis using the ultrasonic system was not affected by the presence of organic pollutants or moderately high salt contents. Correspondingly, no nebulizer plugging problems were encountered, no interferences due to desolvation were noticed, and no problems with sample memory were observed.

Despite the advantages of ultrasonic nebulization, poor system design often led to short transducer life, short-term instability, long-term signal drift, and severe memory effect. Recently, a new air-cooled ultrasonic nebulizer [3] was introduced for routine analysis in ICP-AES. This system overcame the shortcomings mentioned above.

In this study, an air-cooled ultrasonic nebulizer was used to aspirate water and waste samples. The ICP-AES technique was able to determine pollutant metals below their regulated levels when an ultrasonic nebulizer was utilized. Quality assurance and quality control procedures described in the USEPA Method 200.7 [4,5] were followed to demonstrate the capability of this methodology for routine analysis of water and wastes.

## EXPERIMENTAL

A simultaneous and a sequential ICP spectrometer were used in this study. The pneumatic nebulizers on both systems were replaced with the air-cooled ultrasonic nebulizers. Table 1 shows the operating conditions for the ICP spectrometers and the ultrasonic nebulizer. A conventional torch and a low-gas-flow torch were used for the simultaneous and the sequential spectrometer, respectively. The ICP operating conditions for the ultrasonic nebulizer were similar to those for the pneumatic nebulizer.

Multielement solutions were prepared from their 1000 mg/L reference standard solutions. Unless otherwise stated, all standard, blank, and sample solutions were acidified with 5% HCl and 1% $HNO_3$. Sample preparation and experimental procedures described in Method 200.7 [4,5] were followed whenever possible.

## RESULTS AND DISCUSSION

The operating principle of the air-cooled ultrasonic nebulizer has been described elsewhere [3]. Table 2 lists the analytical wavelengths and instrumental detection limits for the ICP spectrometers. Comparable results were achieved with both systems, regardless of the difference in torch type. In general, these detection limits are factors of 5 to 25 better than those obtained with a pneumatic nebulizer.

A major problem in ICP analysis of wastes is spectral interference. Typical spectral interferences on pollutant metals such as As, Pb, Se, and Tl are caused by the presence of large amounts of Al and Fe in the samples. Since the ultrasonic nebulizer has a higher nebulization efficiency than the pneumatic nebulizer [1], larger amounts of analytes and interferents are introduced into the plasma. Unless the interferent peak is extremely close to the analyte peak and the resolution of the spectrometer is relatively low, a lesser extent of spectral interference is expected for the ultrasonic nebulizer, as demonstrated by the results shown in Table 3. The interference information is expressed as analyte concentration equivalents arising from 100 mg/L of the interferent elements. The extent of spectral interference greatly depends on the choice of analytical wavelengths and their corresponding off-line background correction positions. Negative values are due to spectral interferences near the background correction positions rather than at the analyte peaks. It is important to note that some of the analytical lines used in this study (Table 2) are different from those listed in Method 200.7 [4]. In general, the analyte concentration equivalents obtained with the ultrasonic nebulizer in this study are either comparable to or smaller than those obtained with the pneumatic nebulizer [4].

In the appendix to Method 200.7 [5], a preconcentration procedure was described to lower the method detection limits for the analysis of drinking water. The modified procedure also provided improved accuracy and precision by concentrating the analytes four-fold prior to pneumatic aspiration into the plasma. Table 4 compares the ICP method detection limits obtained with ultrasonic nebulization, pneumatic nebulization, and pneumatic nebulization with 4-fold preconcentration. Detection limits achieved with the ultrasonic nebulizer are much lower than those obtained with the pneumatic nebulizer, and are well below the maximum contaminant levels set by the National Primary and

Secondary Drinking Water Regulations [6,7]. The accuracy and precision data for As and Pb are compared in Table 5. As clearly indicated, the accuracies of determination are comparable for all systems. Among the procedures listed, direct analysis with ultrasonic nebulizer yielded the best precisions at the maximum contaminant levels (MCL).

Table 6 lists precision and accuracy data for deionized water spiked with contaminants at low concentration levels. Superior precisions were obtained with the ultrasonic nebulizer. Except for Cr and Zn, the recoveries of all elements are acceptable at such low concentrations. The relatively poor recoveries for Cr and Zn at these concentrations were attributed to the considerable amounts of impurities found in the nitric acid.

Tap water samples from Omaha, Nebraska were spiked with contaminants at their respective MCL and 1/2 MCL, Table 7. Results obtained with both spike levels are similar. The standard deviations for the measurements are less than those obtained with a pneumatic nebulizer [5]. As compared to the results in Table 6, the recovery of Cr in Table 7 has been improved. Because the spike concentration of Zn was quite high in the tap water, the level of contaminant in the nitric acid could not significantly affect its recovery. Further investigation revealed that the signal suppression was due to ionization interference [1] caused by the presence of Na (about 100 mg/L) in the tap water. The ionization effect can be corrected by buffering the sample, by matrix matching, or by standard addition procedures [4].

A major concern for the analysis of water and waste samples is quality assurance and quality control. Preliminary analysis of a USEPA ICAP-23 water pollution quality control sample revealed that only half of the results were within +/- 5% of the true value listed, Table 8. A new solution was prepared and aspirated with the pneumatic nebulizer. Data obtained with the pneumatic nebulizer are primarily the same, except that the standard deviations are higher. The relatively poor recoveries for Al, Ba, Ca, K, Na, and other elements might be due to contamination from the glassware, especially the ampul which was used to store the concentrated ICAP-23 quality control sample. It is also interesting to point out that the ampul contained slightly less than 20 mL of the concentrated sample rather than the stated amount of 23 mL.

Figures 1 to 3 show the control charts for routine monitoring of waste effluents. As illustrated in Figure 3, the mean value, the upper control limit, and the lower control limit (95% confidence interval) are represented by horizontal grids on each control chart. The true value of concentration is shown in parentheses. These data were obtained through an extended period of time by a technician. Figure 1 shows the control charts for As, Cd, Cr, Cu, Ni, and Zn in the USEPA WP-287 water pollution quality control sample. Excellent recoveries were obtained for all elements including Cr and Zn. Most of the data are within the control limits of the true values. Control charts for the USEPA ICAP-19 water pollution quality control sample are compared for the ultrasonic and the pneumatic nebulizers, Figure 2. The dates listed indicate the change of sample introduction system for routine ICP analysis. Obviously, the capability of ultrasonic nebulization for routine water and waste analysis is clearly documented. Finally, the advantage of low-level detection is demonstrated for the determination of As in the USEPA WS-378 (Conc. 18) water supply quality control sample, Figure 3. The mean value of

0.053 mg/L (Std Dev = 0.003) for 20 measurements in 5 months compares favorably with the true value of 0.051 mg/L (Std Dev = 0.004). These data collectively suggest that the ICP-AES method with ultrasonic nebulization is an excellent alternative for the determination of metals in water and wastes.

## SUMMARY

In conclusion, the air-cooled ultrasonic nebulizer significantly improved the detection limits of pollutant metals in water and waste samples. Comparable accuracy and better precision were obtained when the pneumatic nebulizer of the ICP-AES system was replaced with the ultrasonic nebulizer. The ultrasonic nebulization system was applicable to both the conventional torch and the low-gas-flow torch. Prior to the use of ultrasonic nebulizer, trace-level analysis of pollutant metals including As and Pb had to be performed on a graphite furnace atomic absorption spectrometer. The ICP-AES method with ultrasonic nebulization significantly improved laboratory productivity by minimizing the usage of graphite furnace atomic absorption.

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7. National Secondary Drinking Water Regulations, 40 CFR 143, USEPA.

TABLE 1. Experimental Facilities and Operating Conditions

Simultaneous ICP Spectrometer (System I)

| | |
|---|---|
| Model | : ICAP 61 |
| Manufacturer | : Thermo Jarrell Ash Corporation |
| ICP torch | : Conventional torch |
| Operating conditions | : Forward power 1.1 kW |
| | Outer gas flow rate 16 L/min |
| | Intermediate gas flow rate 0.5 L/min |
| | Injector gas flow rate 0.7 L/min |
| | Observation height 15 mm above load coil |
| | Integration time 4 s |

Sequential ICP Spectrometer (System II)

| | |
|---|---|
| Model | : 3410 ICP |
| Manufacturer | : Applied Research Laboratories, Inc. |
| ICP torch | : Low-gas-flow, mini-torch |
| Operating conditions | : Forward power 0.65 kW |
| | Outer gas flow rate 7.5 L/min |
| | Intermediate gas flow rate 0.8 L/min |
| | Injector gas flow rate 0.8 L/min |
| | Observation height 9 mm above load coil |
| | Integration time 1 s |

Ultrasonic Nebulizer (For Systems I and II)

| | |
|---|---|
| Model | : U-5000 |
| Manufacturer | : CETAC Technologies, Inc. |
| Transducer | : Air-cooled piezoelectric, 1.4 MHz |
| Operating conditions | : Current 5 A |
| | Heating temperature 140 $^{o}$C |
| | Cooling temperature 5 $^{o}$C |
| | Sample uptake rate 2.5 mL/min |

Table 2. Analytical Wavelengths[a] and Instrumental Detection Limits (ug/L)[b]

| | System I, USN | | System II, USN | |
|---|---|---|---|---|
| Element | Wavelength | IDL | Wavelength | IDL |
| Ag | 328.068 | 0.07 | 328.068 | 0.1 |
| Al | 396.152 | 0.2 | 396.152 | 0.5 |
| As | 193.696 | 1 | 193.696 | 2 |
| Ba | 493.409 | 0.2 | -- | -- |
| Be | 234.861 | 0.03 | 234.861 | 0.01 |
| Ca | 317.933 | 0.3 | -- | -- |
| Cd | 228.802*2 | 0.1 | 214.438 | 0.2 |
| Co | 228.616 | 0.3 | 237.862 | 0.4 |
| Cr | 205.552*2 | 0.5 | 267.716 | 0.3 |
| Cu | 324.754 | 0.06 | 324.754 | 0.5 |
| Fe | 259.940 | 0.2 | 259.940 | 0.2 |
| Ga | 417.206 | 0.4 | -- | -- |
| K | 766.491 | 10 | -- | -- |
| Mg | 279.553 | 0.03 | -- | -- |
| Mn | 257.610 | 0.03 | 257.610 | 0.07 |
| Mo | 202.030 | 0.3 | -- | -- |
| Na | 588.995 | 0.4 | -- | -- |
| Ni | 231.604*2 | 0.8 | 231.604 | 0.7 |
| Pb | 220.353 | 1 | 220.353 | 1 |
| Sb | 217.581 | 3 | -- | -- |
| Sc | 361.384 | 0.02 | -- | -- |
| Se | 196.026 | 2 | 196.026 | 3 |
| Sn | 189.989 | 2 | -- | -- |
| Sr | 421.552 | 0.1 | -- | -- |
| Tl | 190.864*2 | 3 | -- | -- |
| V | 292.402 | 0.1 | 311.071 | 0.2 |
| Zn | 213.856 | 0.07 | 213.856 | 0.05 |

[a] *2 means second order.
[b] IDL=3*Std Dev, based on 10 measurements of a blank solution.

Table 3. Analyte Concentration Equivalents[a] (mg/L) Arising from Interferents at the 100 mg/L Level

| | Interferent | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | Al | Ca | Cr | Cu | Fe | Mg | Mn | Ni | Ti | V |
| Al | -- | -- | -- | -- | 0.02 | -- | -- | -- | 0.02 | -- |
| Sb | 0.04 | -- | -- | -0.05 | -0.03 | 0.03 | 0.03 | 0.10 | -0.06 | 0.21 |
| As | -0.09 | -- | 0.07 | -- | -- | -- | -- | 0.23 | -0.03 | 5.04 |
| Ba | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Be | -- | -- | -- | -- | 0.02 | -- | -- | -- | -- | -- |
| Cd | -- | -- | -- | -- | -- | -- | -- | -0.01 | -- | 0.01 |
| Ca | -- | -- | 0.12 | -- | 0.02 | -- | 0.05 | -- | 0.07 | 0.04 |
| Cr | -- | -- | -- | 0.02 | 0.01 | -- | 0.01 | 0.21 | 0.03 | -- |
| Co | -- | -- | -- | -- | -- | -- | -- | 0.10 | 0.31 | -- |
| Cu | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Fe | 0.03 | -- | -- | -- | -- | 0.02 | 0.03 | -- | 0.03 | 0.07 |
| Pb | -0.01 | -- | 0.05 | 0.03 | 0.02 | -- | -- | 0.04 | -- | 0.01 |
| Mg | -- | 0.01 | -- | -- | -- | -- | -1.03 | -- | 0.02 | -- |
| Mn | -- | -- | -- | -- | 0.15 | -- | -- | -- | -- | -0.01 |
| Mo | -- | -- | 0.01 | -- | -- | -- | 0.01 | -0.01 | -- | -0.02 |
| Ni | -- | -- | -- | -- | 0.01 | -- | -- | -- | 0.01 | -- |
| Se | -- | -- | -- | -- | -- | -- | 0.04 | -- | -- | 0.04 |
| Na | -- | -- | -- | -- | -- | -- | 0.02 | -- | 0.02 | -- |
| Tl | 0.03 | -- | 0.11 | -- | 0.18 | -- | 0.27 | -- | 0.03 | 1.38 |
| V | -- | -- | 0.01 | -- | 0.03 | -- | -0.02 | -- | 0.14 | -- |
| Zn | -- | -- | -- | 1.18 | 0.02 | -- | -- | 0.40 | -- | -- |

[a]ICP System I with USN was used.

Table 4. Comparison of Maximum Contaminant Levels (mg/L) and ICP Method Detection Limits[a] (mg/L) for National Primary and Secondary Drinking Water Regulations

| | | Method Detection Limit | | |
|---|---|---|---|---|
| | | USN | PN | PN 4X |
| Element | MCL | (System I) | (Ref 5) | (Ref 5) |
| Ag | 0.05 | 0.0002 | 0.0028 | 0.0013 |
| As | 0.05 | 0.0017 | 0.0157 | 0.0030 |
| Ba | 1 | 0.0002 | 0.0013 | 0.0004 |
| Cd | 0.01 | 0.0002 | 0.0013 | 0.0006 |
| Cr | 0.05 | 0.0007 | 0.0031 | 0.0006 |
| Pb | 0.05 | 0.0009 | 0.0157 | 0.0046 |
| Cu | 1 | 0.0002 | 0.0028 | 0.0007 |
| Fe | 0.3 | 0.0004 | 0.0063 | 0.0037 |
| Mn | 0.05 | 0.00003 | 0.0003 | 0.0002 |
| Zn | 5 | 0.0001 | 0.0019 | 0.0010 |

[a]MDL=3.143*Std Dev, based on 7 measurements of a low-level spiked solution.

Table 5. Comparison of Precision and Accuracy Data[a] (mg/L) for As and Pb

| Method | Element | MCL Spike | Determined Accuracy & Precision: Mean | Std Dev | 95% Confidence Interval | Percent Recovery: Range | Mean |
|---|---|---|---|---|---|---|---|
| USN | As | 0.05 | 0.052 | 0.0008 | 0.051 - 0.053 | 101 - 106% | 104% |
| (System I) | Pb | 0.05 | 0.053 | 0.0002 | 0.053 - 0.054 | 106 - 107% | 107% |
| PN | As | 0.05 | 0.050 | 0.007 | 0.036 - 0.064 | 84 - 108% | 99% |
| (Ref 5) | Pb | 0.05 | 0.050 | 0.006 | 0.038 - 0.062 | 88 - 106% | 100% |
| PN 4X | As | 0.05 | 0.051 | 0.001 | 0.048 - 0.052 | 98 - 102% | 101% |
| (Ref 5) | Pb | 0.05 | 0.050 | 0.002 | 0.046 - 0.054 | 96 - 102% | 99% |

[a]Based on 7 measurements of a single aliquot.

Table 6. Precision and Accuracy Data[a] (mg/L) for Deionized Water

| Element | Spike | USN (System I): Mean | Std Dev | Recovery | PN 4X (Ref 5): Mean | Std Dev | Recovery |
|---|---|---|---|---|---|---|---|
| Ag | 0.0020 | 0.0018 | 0.0001 | 89% | 0.0021 | 0.0002 | 105% |
| As | 0.0100 | 0.0100 | 0.0001 | 100% | 0.0107 | 0.0012 | 107% |
| Ba | 0.0025 | 0.0026 | 0.0001 | 103% | 0.0028 | 0.0002 | 108% |
| Cd | 0.0025 | 0.0024 | 0.0001 | 97% | 0.0024 | 0.0002 | 96% |
| Cr | 0.0025 | 0.0011 | 0.0003 | 43% | 0.0027 | 0.0002 | 108% |
| Cu | 0.0020 | 0.0021 | 0.0000 | 105% | 0.0018 | 0.0002 | 90% |
| Fe | 0.0160 | 0.0153 | 0.0003 | 95% | 0.0170 | 0.0006 | 107% |
| Mn | 0.0025 | 0.0023 | 0.0000 | 92% | 0.0025 | 0.0001 | 100% |
| Pb | 0.0100 | 0.0100 | 0.0004 | 100% | 0.0097 | 0.0013 | 97% |
| Zn | 0.0040 | 0.0033 | 0.0001 | 84% | 0.0044 | 0.0006 | 110% |

[a]Based on 7 measurements of a single aliquot.

Table 7. Precision and Accuracy Data[a] (mg/L) for Omaha Tap Water

| Element | MCL Spike | Average Recovery Mean | Average Recovery Percent | Std Dev | 95% Confidence Interval |
|---|---|---|---|---|---|
| Ag | 0.05 | 0.0490 | 98% | 0.0003 | 0.0484 - 0.0496 |
| As | 0.05 | 0.0497 | 99% | 0.0011 | 0.0475 - 0.0519 |
| Ba | 1 | 0.945 | 95% | 0.005 | 0.935 - 0.955 |
| Cd | 0.01 | 0.0093 | 93% | 0.0001 | 0.0091 - 0.0095 |
| Cr | 0.05 | 0.0384 | 77% | 0.0005 | 0.0374 - 0.0394 |
| Cu | 1 | 0.941 | 94% | 0.005 | 0.931 - 0.951 |
| Fe | 0.3 | 0.285 | 95% | 0.002 | 0.282 - 0.288 |
| Mn | 0.05 | 0.0459 | 92% | 0.0003 | 0.0453 - 0.0465 |
| Pb | 0.05 | 0.0474 | 95% | 0.0008 | 0.0458 - 0.0490 |
| Zn[b] | 1 | 0.901 | 90% | 0.004 | 0.894 - 0.909 |

| Element | 1/2 MCL Spike | Average Recovery Mean | Average Recovery Percent | Std Dev | 95% Confidence Interval |
|---|---|---|---|---|---|
| Ag | 0.025 | 0.0245 | 98% | 0.0001 | 0.0243 - 0.0247 |
| As | 0.025 | 0.0248 | 99% | 0.0005 | 0.0238 - 0.0258 |
| Ba | 0.5 | 0.467 | 93% | 0.003 | 0.460 - 0.474 |
| Cd | 0.005 | 0.0047 | 93% | 0.0001 | 0.0045 - 0.0049 |
| Cr | 0.025 | 0.0204 | 82% | 0.0004 | 0.0196 - 0.0212 |
| Cu | 0.5 | 0.467 | 93% | 0.0025 | 0.462 - 0.472 |
| Fe | 0.15 | 0.142 | 94% | 0.001 | 0.139 - 0.144 |
| Mn | 0.025 | 0.0230 | 92% | 0.0001 | 0.0228 - 0.0232 |
| Pb | 0.025 | 0.0231 | 92% | 0.0007 | 0.0217 - 0.0245 |
| Zn[c] | 0.5 | 0.451 | 90% | 0.004 | 0.444 - 0.458 |

[a]Based on measurements of 7 aliquots.
[b]Spike level for Zn is 1/5 of the MCL.
[c]Spike level for Zn is 1/10 of the MCL.

Table 8. Analysis[a] of USEPA ICAP-23 Water Pollution Quality Control Sample (mg/L)

| Element | True Value | USN (System I) Mean | USN (System I) Std Dev | USN (System I) RSD | PN (System I) Mean | PN (System I) Std Dev | PN (System I) RSD |
|---|---|---|---|---|---|---|---|
| Al | 1.0 | 1.631 | 0.009 | 0.5% | 1.532 | 0.024 | 1.5% |
| As | 1.0 | 1.004 | 0.002 | 0.2% | 0.936 | 0.011 | 1.1% |
| Ba | 1.0 | 1.291 | 0.008 | 0.6% | 1.289 | 0.009 | 0.7% |
| Be | 1.0 | 1.083 | 0.005 | 0.5% | 1.065 | 0.003 | 0.3% |
| Ca | 1.0 | 1.118 | 0.006 | 0.6% | 1.089 | 0.004 | 0.3% |
| Cd | 1.0 | 1.038 | 0.003 | 0.3% | 0.958 | 0.004 | 0.4% |
| Co | 1.0 | 1.010 | 0.008 | 0.8% | 1.009 | 0.007 | 0.7% |
| Cr | 1.0 | 1.089 | 0.009 | 0.8% | 1.033 | 0.011 | 1.1% |
| Cu | 1.0 | 1.101 | 0.004 | 0.4% | 1.073 | 0.015 | 1.4% |
| Fe | 1.0 | 1.038 | 0.008 | 0.7% | 1.041 | 0.005 | 0.5% |
| K | 10.0 | 9.131 | 0.054 | 0.6% | 9.416 | 0.476 | 5.1% |
| Mg | 1.0 | 1.033 | 0.007 | 0.7% | 1.016 | 0.006 | 0.5% |
| Mn | 1.0 | 1.008 | 0.007 | 0.7% | 0.993 | 0.004 | 0.4% |
| Mo | 1.2 | 1.142 | 0.009 | 0.8% | 1.140 | 0.004 | 0.3% |
| Na | 1.0 | 1.863 | 0.014 | 0.7% | 1.783 | 0.079 | 4.4% |
| Ni | 1.0 | 1.013 | 0.007 | 0.7% | 1.018 | 0.006 | 0.6% |
| Pb | 1.0 | 1.136 | 0.004 | 0.4% | 1.027 | 0.012 | 1.1% |
| Sb | 1.0 | 1.113 | 0.003 | 0.3% | 1.026 | 0.016 | 1.5% |
| Se | 1.0 | 1.117 | 0.004 | 0.3% | 0.981 | 0.016 | 1.6% |
| Tl | 1.0 | 0.963 | 0.016 | 1.7% | 1.051 | 0.026 | 2.4% |
| V | 1.0 | 1.032 | 0.007 | 0.7% | 1.024 | 0.005 | 0.5% |
| Zn | 1.0 | 1.084 | 0.006 | 0.6% | 1.027 | 0.006 | 0.5% |

[a]Based on 7 measurements of a single aliquot.

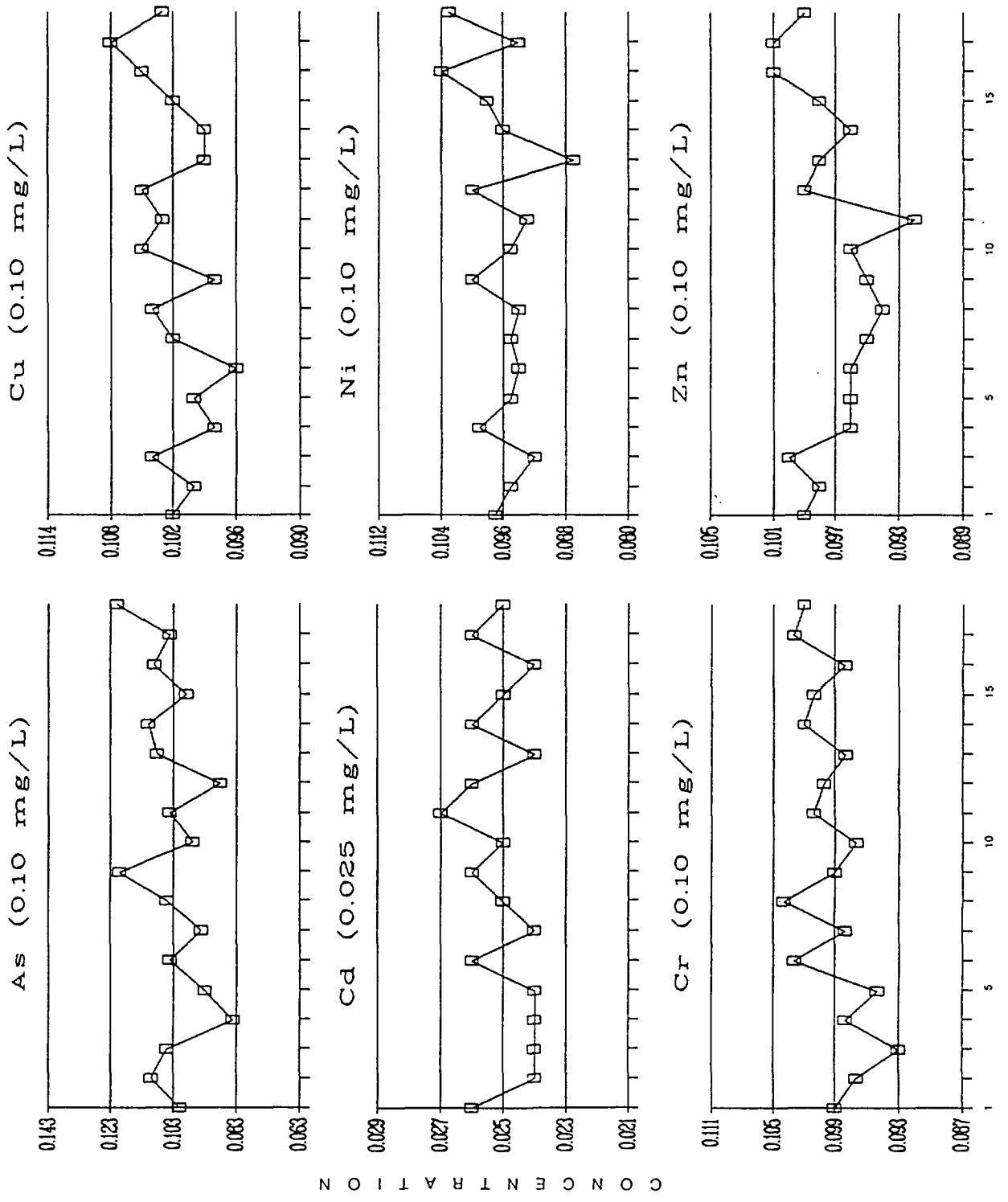


Figure 1. Control Charts for WP-287 (USN, ICP System II)

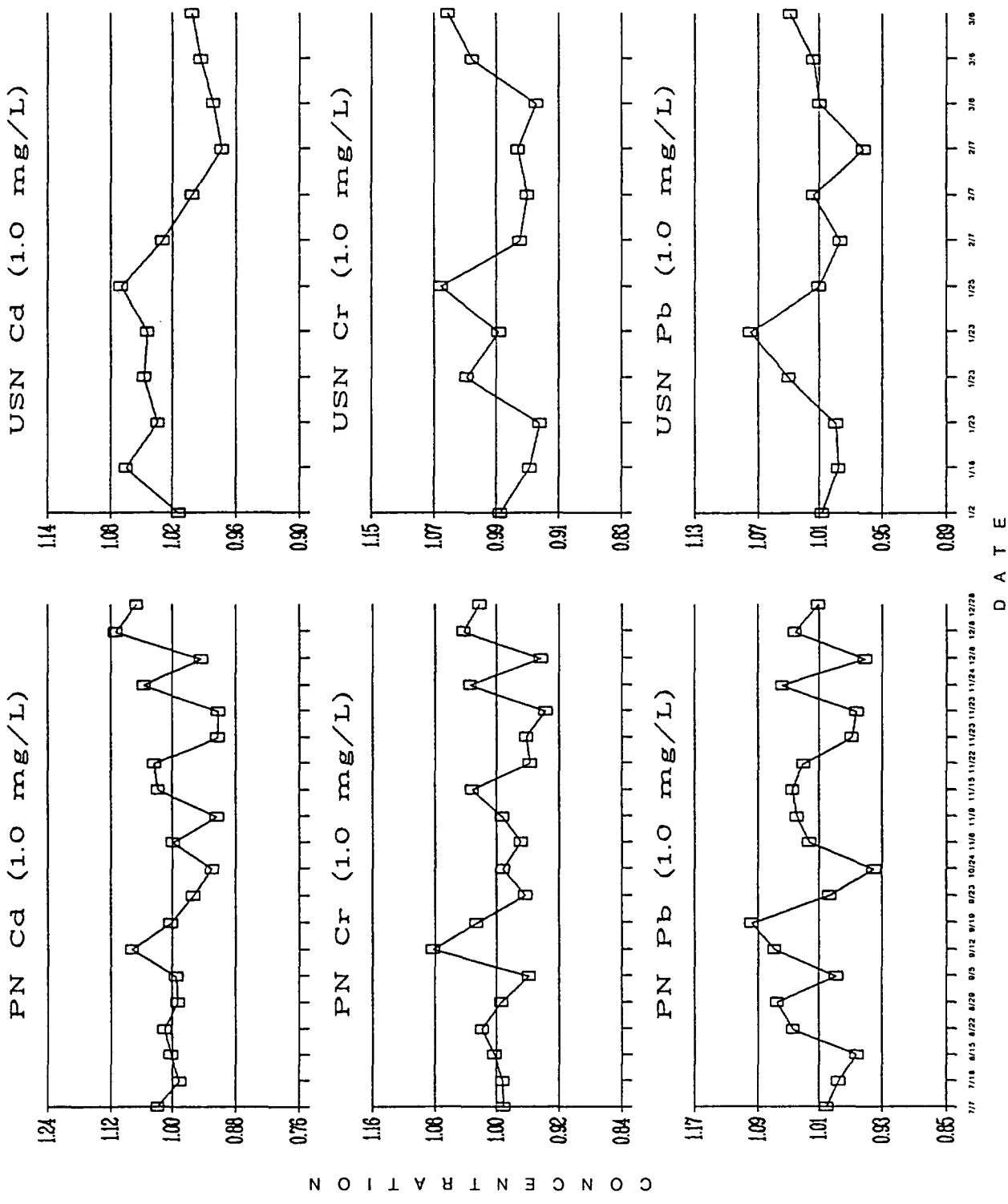


Figure 2. Comparison of Control Data (ICAP-29) for Pneumatic and Ultrasonic Nebulizer (ICP System II)

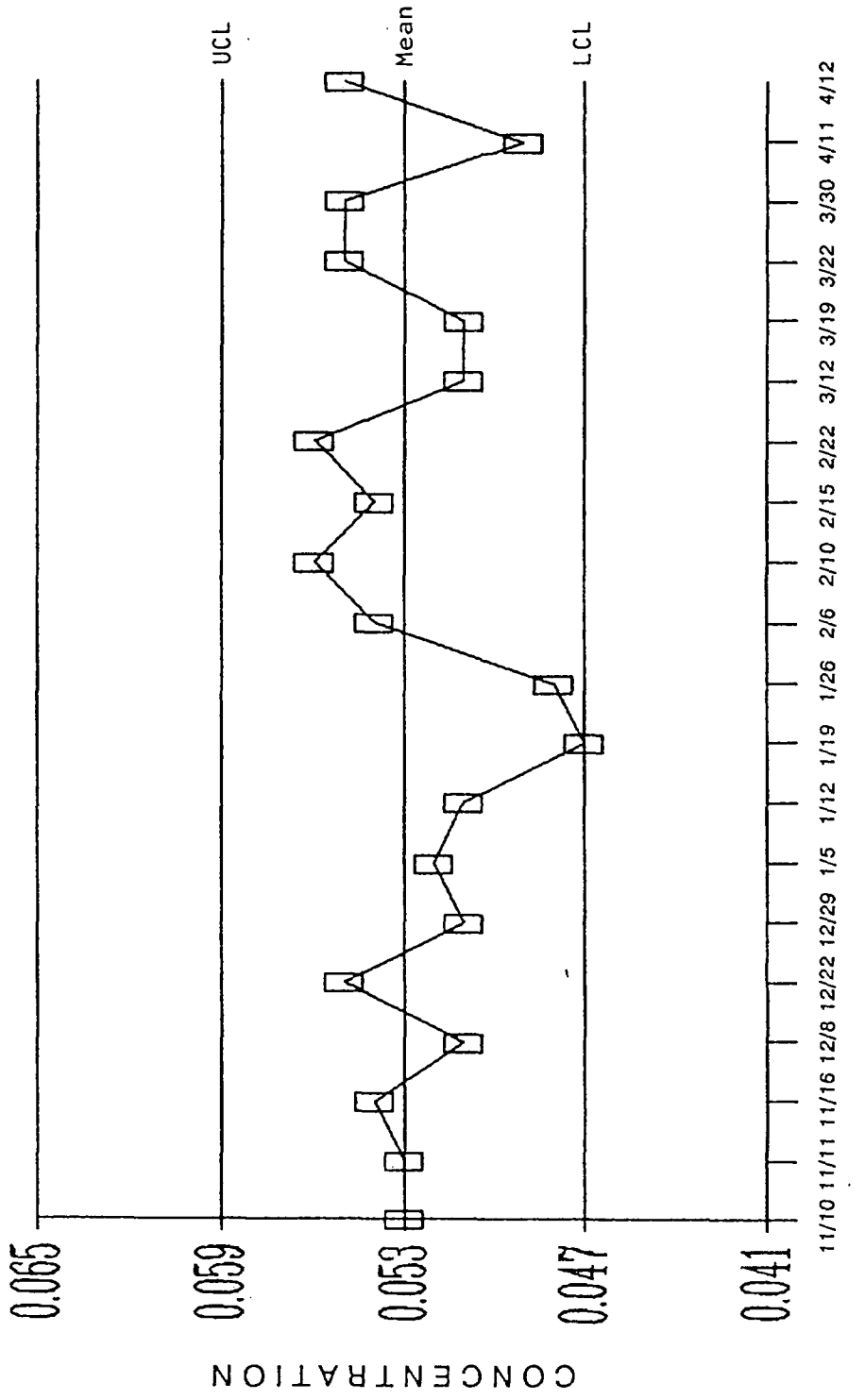


Figure 3. Control Chart for As in WS-378 (USN, ICP System II)

87

# A STUDY OF THE LINEAR RANGES OF SEVERAL ACID DIGESTION PROCEDURES

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## ABSTRACT

The analysis of solid matrices (sediments, sludges, soils, and solid wastes) for the presence of regulated elements is most commonly performed using an acid digestion procedure. The acids destroy the matrix and react with the elements of interest to form water soluble compounds. When the digestion is complete, it is usual to add water, forming a liquid which can then be analyzed by a variety of analytical instruments. Implicit in most published methods is the belief that elements will be solubilized in direct proportion to the concentration of the element in the matrix at any concentration or in any molecular form. However, previous studies[1,2,3] have shown this is not always the case.

The purpose of this study is to examine some of the factors that affect the linear range of commonly regulated elements. Five factors will be examined: 1) the total amount in micrograms of the analyte in a two gram sample; 2) The solubility of the compound in which the element is bound; 3) The vigor of the acid cocktail; 4) the effect of other target elements in the sample on solubilization and/or co-precipitation of the element under consideration; 5) concentration of hydrochloric acid.

Four methods, EPA 3050, SCL, ASTM 9.3.4 (a nitric acid/hydrogen peroxide digestion modified for solids analysis), and the digestion described in EPA draft Method 6020 will be compared.

## INTRODUCTION

The determination of the concentration of regulated elements in solid matrices (sediments, sludges, soils, and solid wastes such as spent catalysts, press cakes, slags, powders, etc.) is generally performed using acid digestion procedures. The purpose of the acid digestion is to solubilize all the elements of interest. To do this, a digestion procedure must perform two distinct tasks: 1) It must decompose the sample matrix to expose the entire mass to the acid cocktail. 2) It must react with the elements of interest to form water soluble compounds. If the elements are already in a soluble state, then this task is not necessary. When the digestion is complete, it is usual to add water to form a solution that is suitable for analysis by a variety of analytical instruments (typically Flame Atomic Absorption Spectrophotometry (FAA) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) but also Graphite Furnace Atomic Absorption Spectrophotometry (GFAA) and Inductively Coupled Plasma Mass-Spectroscopy (ICP-MS)) . If the digestion is successful, the amount of the element in the solution is equal to the

amount of the element in the sample matrix. Ideally, a digestion procedure should be able to solubilize any amount of the elements of interest in the matrix, irrespective of the molecular state, so that a graph of concentration found versus concentration of analyte in matrix would be **linear**. Previous studies have shown that this is not always the case[1,2,3]. There is a limit to the range of matrix concentrations that will yield a linear relationship, for a given digestion procedure. This is called the **linear range**. Above or below this range, the amount of analyte in solution is significantly lower than the amount in the sample matrix.

There is no data available on the linear ranges for most published acid digestion procedures. Therefore, analysts and review personnel have no guide for evaluating the data obtained from these methods. Linear ranges for target elements vary from element to element, and exhibit several different types of relationships between the concentration in solution and the concentration in the sample matrix.

This study will examine the factors that determine the type and length of the linear ranges of antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, molybdenum, nickel, selenium, silver, thallium, vanadium, and zinc (hereafter referred to as the "target elements") by four published methods. These include EPA SW 846 (3rd Edition) method 3050 (Version 1), an alternative method from the Southern California Laboratory (SCL) of the California Department of Health Services (DOHS), hereafter referred to as the SCL method, the EPA draft method 6020 for ICP-MS, and ASTM method 9.3.4 modified for solids, was also compared (this method is very similar to EPA SW 846 method 3050 for GFAA). This list of regulated elements is based on California Administrative Code Title 22[4] which is similar to Federal regulations[5,6].

Five factors that contribute to linear range will be examined: 1) the total amount in micrograms of the analyte in a two gram sample; 2) The solubility of the compound in which the element is bound; 3) The vigor of the acid cocktail, i.e., the power of the cocktail to oxidize the target elements; 4) the effect of other target elements in the sample on solubilization and/or co-precipitation of the element under consideration; 5) the amount of hydrochloric acid present.

## EXPERIMENTAL SECTION

### A) Study Design.

The first factor is the amount of analyte in a sample. To examine this, all sixteen target elements were digested by all four methods, EPA SW 846 method 3050, the SCL method, EPA draft method 6020, and ASTM 9.3.4 over a range of concentrations from about 100 ug/g to 1,000,000 ug/g for a two gram sample size (with the exception of method 6020 where one gram samples were used).

Initially, three solid materials were spiked with all sixteen elements at different concentrations from 100 ug/g to 10,000 ug/g (these three materials were analyzed by 10 different laboratories by the SCL method and method 3050. See reference 2). Elements that showed linear behavior in this range were digested individually at concentrations of 25%, 50%, and 100% (by weight) using reagent grade compounds that were, where possible, water soluble. Elements that showed non-linear behavior were then spiked into solid matrices at concentrations that seemed to bracket the transition region from linearity to non-linearity. This process was repeated using less soluble compounds. In this way it was possible to separate the power of the acid cocktail to decompose a sample matrix from its ability to react with target elements to form water soluble compounds. For each element and method linear range curves were prepared for each type of compound. Finally, eleven samples from industrial sites were analyzed by all four methods.

**B) Digestion Procedures**

**(1) EPA SW 846 method 3050**[7] was used as designated. It directs that 1.00-2.00 grams of sample be digested first with 10 mL 1:1 (v/v) nitric acid at 95°C for 15 minutes, then 5 mL conc. nitric acid is added and is refluxed for 30 minutes. This step is repeated until the sample no longer changes in appearance. The digestate is then concentrated to 5 mL. The sample is treated with no more than 10 mL of 30% hydrogen peroxide. Finally, 5 mL of conc. hydrochloric acid and 10 mL of de-ionized water are added and the sample is refluxed for 15 minutes. The sample is then either filtered (Whatman 41 or equivalent) or centrifuged (2-3,000 rpm for 10 min) and the filtrate (or supernatant) is collected in 100 mL volumetric flask and analyzed by either FAA or ICP.

**(2) The SCL method**[1,2] calls for 1.00 - 4.00 grams of sample to be digested in a mixture of 10 mL conc. hydrochloric acid and 2.5 mL of conc. nitric acid at ambient temperature. The sample and reaction mixture are slowly heated to 95°C to prevent an overly vigorous reaction. The digestion is continued until the disappearance of $NO_2$ (reddish brown) fumes and no more change in appearance. The digestate is then filtered (Whatman 41 or equivalent) and collected in a 100 mL volumetric flask. The filter paper is washed with no more than 5 mL hot (95°C) conc. hydrochloric acid, and then 20 mL hot de-ionized water, all of which is collected into one flask (this will be referred to as the primary filtrate). The filter paper and residue are placed back in the digestion vessel, 5 mL conc. hydrochloric acid are added and refluxed at 95°C until the filter paper disintegrates (approx. 10-15 min.) The disintegrated paper is then washed with de-ionized water and again filtered (this filtrate will be referred to as the secondary filtrate.) The filtrates should be allowed to come to room temperature before bringing to volume. These filtrates are then analyzed by either ICP or FAA. The results are combined as follows:

$$(X_1 + X_2) * V/w = X_t * V/w = C$$

(EQUATION 1)

$X_1$ = concentration of element x in primary filtrate
$X_2$ = concentration of element x in secondary filtrate
$X_t$ = total concentration of element x = $X_1 + X_2$
V = volume of volumetric flask used for both primary and secondary filtrate.
w = weight of sample taken
C = concentration of element x in sample.

If a precipitate forms on the bottom of either the primary or secondary filtrate flasks after the flasks have cooled, then add up to 10 mLs of conc. HCl to the flasks. The additional acid will either 1) dissolve the precipitate or 2) more precipitate will form. If the latter occurs: a) Decant the liquid portion and filter through a Whatman 41 or equivalent and collect the filtrate in a new flask marked "filtrate" (either primary or secondary). Place the original flask with the precipitate under this same funnel and wash the filter paper with hot HCl until all precipitate in filter paper has dissolved. Then add enough conc. HCl to the flask as needed to dissolve the remaining precipitate on the bottom. This flask is marked as either primary or secondary "residue". The primary concentration is then equal to the filtrate plus the residue, as is the secondary concentration. (NOTE: This method is an updated version of previously published versions)

3) **A.S.T.M. Method 9.3.4** calls for 2.0 grams of sample digested with 10 mL of conc. $HNO_3$ and swirl and allow it to sit until any frothing subsides. Heat to 95° C and allow refluxing for 30 minutes. The digestion cover is then removed and the sample is brought to near dryness (this step is modified from the published method that calls for taking the sample to dryness). 5 mL of conc. $HNO_3$ is then added. 30% Hydrogen peroxide is then added drop-wise until the solution cease to change color. The sample is then evaporated to about 3 mL and filtered through a Whatman 41 filter paper and collected in a 100 mL volumetric flask.

4) **EPA Draft Method 6020 (CLP-M) Version 3.4 SAS** calls for 1.0 grams of samples digested with 2 mL of (2+3) $HNO_3$ and 10 mL of (1+4) HCl. The slurry is heated to 95° C and refluxed for 30 minutes. The sample is then filtered and brought to volume with ASTM type I water to 200 mL.

C) **Instrumentation and Analysis.** The digestates were analyzed on a Perkin-Elmer 5500 ICP-AES by EPA SW 846 method 6010 and in a few cases on a Varian Video 12 FAA by EPA SW 846 methods 7090, 7130, 7760.

D) **Materials.** Three solid phase samples were prepared for the study. The solid phase samples were designated from D to F. Samples D, E, and F were spiked samples with all the target elements in each sample. Each analyte was spiked at three different concentrations, designated low, middle, and

high. These materials were spiked and homogenized in the laboratory. The concentrations in these samples are referred to as the "true" value (for a more detailed description of these materials see reference 1). All materials with concentrations above 200,000 ug/g were neat reagent grade chemicals.

## RESULTS

Table I lists the linear ranges for all the target elements for each digestion procedure. Of the four digestions, the SCL method had the fewest limitations on its linear ranges, there were only four elements that could not be solubilized up to 2 grams, while method 3050 had six, ASTM had seven, and method 6020 had 10, depending on the state of the element.

Table II lists the results from each method for eleven different field samples. Sample A is a spent catalyst, sample B is spent catalyst mixed with soil, samples C through G are materials from battery recovery plants, H is a mixed non-petroleum waste from an oil refinery possibly including spent catalyst, I and J are materials from a solid waste refinery, and sample K is a press cake mixed with petroleum products. All of these samples were dried, milled, and sieved through a U.S. standard #10 sieve.

Table III shows the distribution of elements solubilized in water and the amount trapped in the filter paper and residue using the SCL method. For comparison, the results from method 3050 are listed next to the primary filtrate results.

Four types of relationships were observed between the concentration of target elements in the sample matrix and the amount of target element in solution:

**1) Direct Linear Relationship.** Most elements showed a direct linear relationship between the concentration in the solid matrix and the concentration solubilized in the liquid from a concentration of 100 ug/g to 1,000,000 ug/g for all four methods. This means that if the element was in a water soluble form, all of it can be held in solution. For example, all four methods completely solubilized, as little as 130 ug/g up to 1,000,000 ug/g, of chromium, when it was present in either the form of potassium dichromate or chromium trioxide.

**2) Asymptotic Relationship.** Several elements were solubilized in a direct linear fashion at low concentrations but due to limited solubilities the element either did not solubilize or was precipitated out at higher concentrations so the graph curved asymptotically to a maximum concentration. As concentration in the sample matrix increases above the linear range, the amount in solution did not proportionally increase. A good example of this phenomena is the analysis of lead using digestion method 3050. Seven materials were prepared from a local soil and lead nitrate to yield matrix concentrations from 260 ug/g to 120,000

ug/g. These spiked soil samples were digested using method 3050, the results yielded part of Graph I: At concentrations below 40,000 ug/g, all the lead in a two gram sample will be solubilized. Above this concentration, the number of micrograms of lead in the sample will no longer equal the number in solution, although it will increase up to about 60,000 ug/g. The remaining lead is insoluble and remains either at the bottom of the digestion beaker or trapped in the residue in the filter paper (see table III). Using other compounds of lead, metallic lead, lead sub-oxide, lead oxide, and lead dioxide, the curve was still asymptotic but the point of deviation from linearity is dependent on the chemistry of the compound under consideration (see table II).

**3) Sigmoidal Relationship.** Antimony methods 3050 and 6020 and thallium by ASTM 9.3.4 were accurate and linear at middle concentrations but inaccurate and non-linear at low and high concentrations. This is a result of two factors: a) a fixed amount of the element is trapped in the filter paper and residue. As the matrix concentration increases, the amount trapped is fixed and a greater proportion of the element present in the matrix is solubilized. At low concentrations, the amount trapped can be significantly more than 25% of the total present and so the curve is inaccurate. At higher concentrations this fixed amount can become insignificantly small and so the curve is effectively linear, albeit slightly displaced on the lower side. b) At even higher concentrations, the digestate becomes saturated and can solubilize no more and the curve becomes asymptotic. This creates a curve that is somewhat S-shaped or sigmoidal. The degree of curvature can depend on which compound is present e.g., if elemental antimony is present the curve will be strongly sigmoidal. Using potassium antimony tartrate the curve is only slightly sigmoidal at the low end (Graph II).

**4) Non-Linear Relationship.** The element is either simply not soluble or only partially soluble. Antimony digested by ASTM method 9.3.4 is a good example (see Table II).

## DISCUSSION

1) All of these method can solubilize up to 1,000,000 ug/g of any of these elements, provided it is in a soluble form, with only four exceptions. Lead cannot be solubilized by hydrochloric acid above the low percent range, from 6% to about 25%, depending on solubility and reactivity of the compound of lead. Chlorides of lead have only a limited solubility in HCl.

Antimony and its salts cannot be solubilized by nitric acid in any significant proportion since nitric acid reacts with antimony to produce $Sb_2O_5$[8,10], which is insoluble in nitric acid. Barium salts have extremely variable solubilities in nitric acid while they will react with HCl to form $BaCl_2$, which is somewhat soluble in HCl. Silver also has a limited linear range for all the methods for similar reasons to barium, AgCl forms easily with and is soluble in HCl. Most of the AgCl is lost when water is

added[9]. For these elements there are inherent limitations on the linear range using $HNO_3$ or HCl digestions. These elements either do not go into solution at all, or once in solution, they precipitate. As a result, they become trapped in the filter paper and residue, or if they have temperature dependent solubilities, they settle to the bottom of the flask (see Table III).

2) The solubility of the compound in which the element is bound can have an effect on the linear ranges if the digestion procedure is not vigorous enough. This is a problem especially for method 6020 but all the methods have it to one degree or another. This is illustrated by the nickel data for method 6020 (Graph III). Virtually no metallic nickel can be solubilized by method 6020 but up to 1 gram of nickel in the form of $Ni(NO_3)_2 \cdot 6H_2O$. In contrast, the other three methods were able to oxidize metallic nickel into a soluble compound. What was true for nickel was also true for antimony, chromium, molybdenum, and selenium. Method 6020 was able to oxidize up to 1 gram of elemental cobalt, copper and zinc.

3) The vigor of the acid cocktail is crucial to a good linear range. Since it is impossible to predict the molecular forms of the elements present, we cannot predict the solubility of the elements in water. Thus, a digestion should be vigorous enough to change the molecular form of the element so that it can be solubilized in water. By far the most vigorous digestion is the SCL method since aqua regia has four active species, $HNO_3$, HCl, NOCl, and $Cl_2$. As a result, the SCL method had the longest linear ranges for the most elements.

4) Co-precipitation is mainly a problem with large quantities of lead and to a far lesser extent, silver. When the other target elements were present in quantities in excess of their linear range, they became trapped in the filter paper and residue. Lead and silver have temperature dependent solubilities and will pass through filter paper and then precipitates in the flask as the solution cools. During the crystallization process, other elements can become trapped in the lattice, lowering the effective linear range of the other elements. This can be seen on table III.

5) The importance of the concentration of hydrochloric acid varies with the element and its molecular form. For some elements it makes no difference how much HCl is used, such as, arsenic, cadmium, chromium, cobalt, copper, nickel, selenium, and zinc. The results for these elements were same for the ASTM method, which employed no HCl, and the SCL method, which uses mostly HCl. For a number of elements, however, the amount of HCl used was of critical importance. These include antimony, barium, lead, molybdenum, silver, thallium, and vanadium. For these elements, the ASTM method performed the most poorly and the SCL method performed best, having the longest linear ranges. Method 3050 also performed better than the ASTM method but not as well as the SCL method due the much larger amount of HCl used in the SCL method.

## SUMMARY AND RECOMMENDATIONS

None of these acid digestion procedures have completely linear ranges for all the target elements and their various compounds. In fact, the linearity not only varied from method to method and element to element, but in some cases they also varied widely from compound to compound. This wide variability does not even begin to take into account the effect of matrix on linear range. This violates one of the basic assumptions on which most acid digestions are based, an infinite linear range for all elements and for all of their compounds. Without this assumption, much of inorganic data generated by hazardous materials laboratories becomes questionable. Most "high" results, especially those involving antimony, barium, molybdenum, lead, silver, and vanadium may well be highly inaccurate.

A quality control procedure that might take into account the limited linear ranges would be running duplicates of different mass e.g., a 2.0 g and a 1.0 g duplicates. If the second duplicate is significantly higher than half of the first, there is a strong indication that the linear range has been exceeded.

The data above, especially the antimony data, also suggests that the existing methods for determining "less than" values are inadequate. The majority of these methods are based solely on instrument performance and assume 100% extraction efficiency. This assumption is false since it has been shown that the filtration step actually removes analytes from solution. Therefore, if small amounts of a given analyte are present in the sample matrix, they may not make it through the filtration step and into the filtrate. No matter how sensitive the instrument, if the analyte cannot find its way into solution, the instrument cannot see it. Furthermore, the common practice of increasing sample size to lower method detection limits may have entirely the opposite effect. By increasing the sample size, one has increased the amount residue left by the digestion. This residue can act like a ion-exchange resin. Thus an increased sample size can reduce the amount of analyte in the filtrate.

It should not be assumed by laboratories and regulators that an acid digestion procedure that can solubilize an element at one concentration can solubilize that element at all concentrations nor in all matrices. Laboratories must take into consideration studies on the effective linear range for methods they are using and for each element of interest. Published methods should list the approximate linear range for the covered elements. At the very minimum, we recommend that SW 846 method 3050 should be amended in the method performance section to note that it has only a limited linear range for antimony, barium, lead, and silver. We recommend that the SCL method be adopted as an accepted alternative to method 3050 for soils, sediments and sludges. However, method 3050 should not be used for solid wastes with high concentrations of target elements. Method 6020 should definitely not be used for solid wastes due to the large number of elements with compromised linear ranges.

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TABLE I
LINEAR RANGES in µg/g

| Element | 3050 | SCL | 6020 | ASTM 9.3.4 |
|---|---|---|---|---|
| Ag ($AgNO_3$) | 50 - 150 | 50 - 700 | NL | NL |
| Ba ($BaOH_2$) | 50 - 700 | 50 - 2500 | NL | NL |
| Cr (Elemental) | L | L | 200 - 250,000 | L |
| Mo ($MoO_3$) | 50 - 60,000 | L | 200 - 60,000 | 50 - 500 |
| Ni (Elemental) | L | L | 200 - 100,000 | L |
| Pb (Elemental) | 50 - 200,000 | 50 - 50,000 | 200 - 10,000 | L |
| Pb ($Pb(NO_3)_2$) | 50 - 40,000 | 50 - 120,000 | 200 - 40,000 | L |
| Pb ($Pb_2O$) | 50 - 250,000 | 50 - 120,000 | 200 - 100,000 | L |
| Pb (PbO) | 50 - 60,000 | 50 - 120,000 | 200 - 20,000 | L |
| Pb ($PbO_2$) | 50 - 60,000 | 50 - 250,000 | 200 - 20,000 | L |
| Sb (Elemental) | 5,000 - 20,000 | 50 - 50,000 | 3,000 - 20,000 | NL |
| Sb(K(SbO)Tartate) | 5,000 - L | L | 3,000 - L | NL |
| Se (Elemental) | L | L | 50 - 20,000 | L |
| Tl ($Tl_2SO_4$) | L | L | L | 3,000 - 10,000 |
| V ($NH_4VO_3$) | 50 - 250,000 | L | 200 - 250,000 | 50 - 1,000 |

$As_2O_3$, $BeSO_4$, Cd, Co, $CoCl_2.6H_2O$, $CrO_3$, $K_2Cr_2O7$, Cu, $CuSO_4$, $(NH_4)6Mo7O_{24}$, $4H_2ONi(NO_3)_2.6H_2O$, $H_2SeO_3$, and Zn were all analyzed and found to be linear for all four methods.

L = 50 - 1,000,000 µg/g

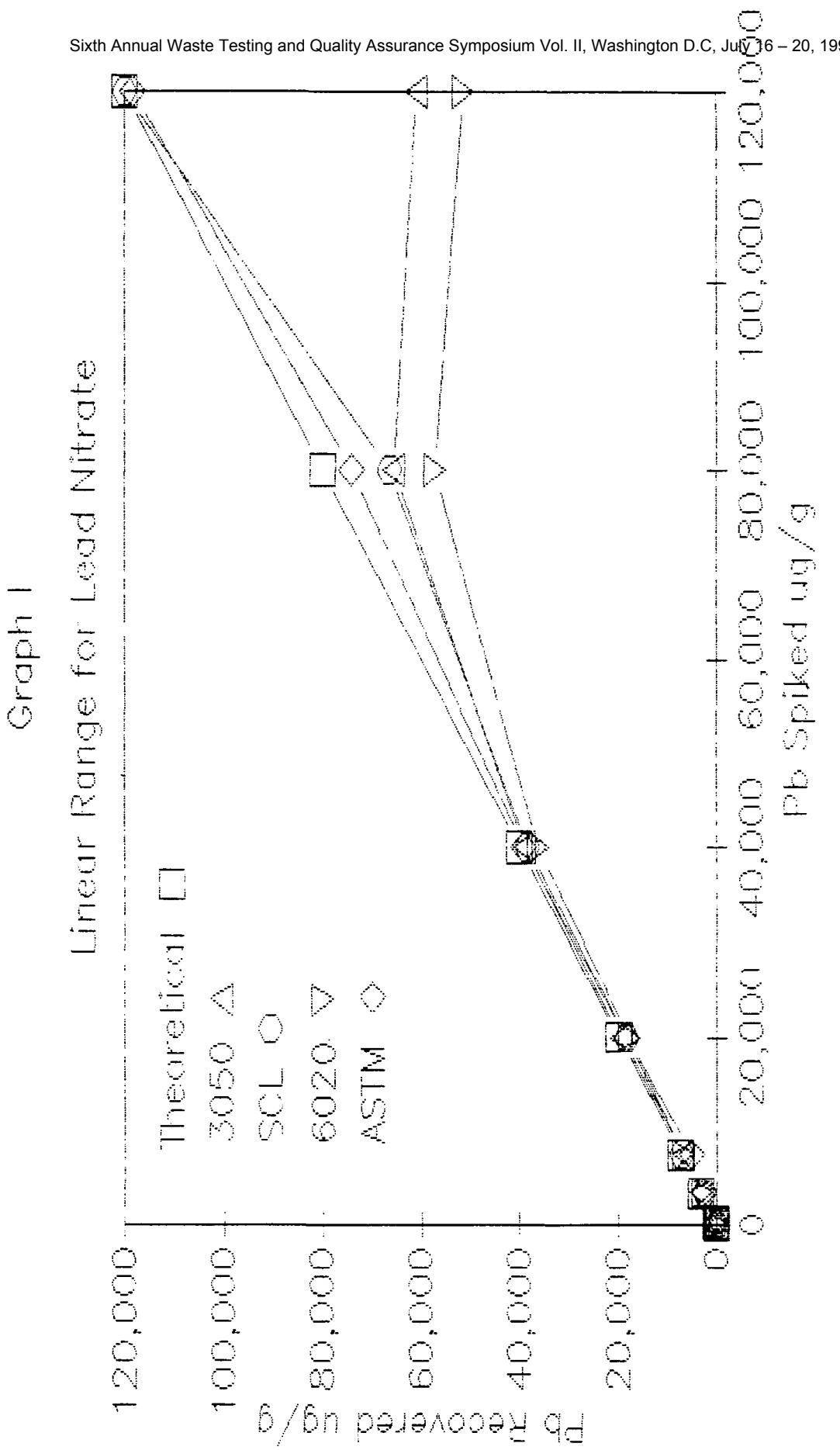
NL = Not Linear

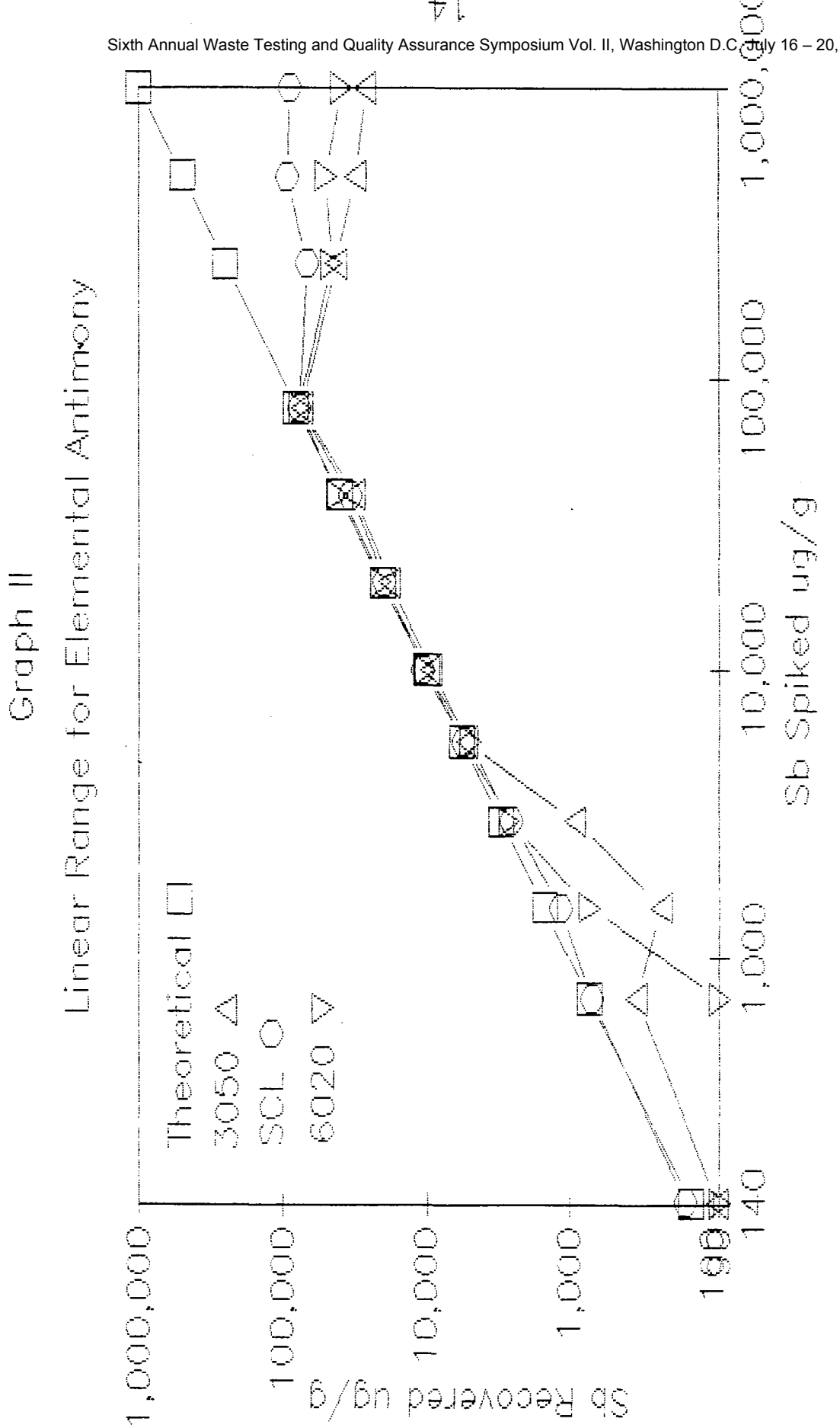
**TABLE II**
**RESULTS FROM FIELD SAMPLES in μg/g**

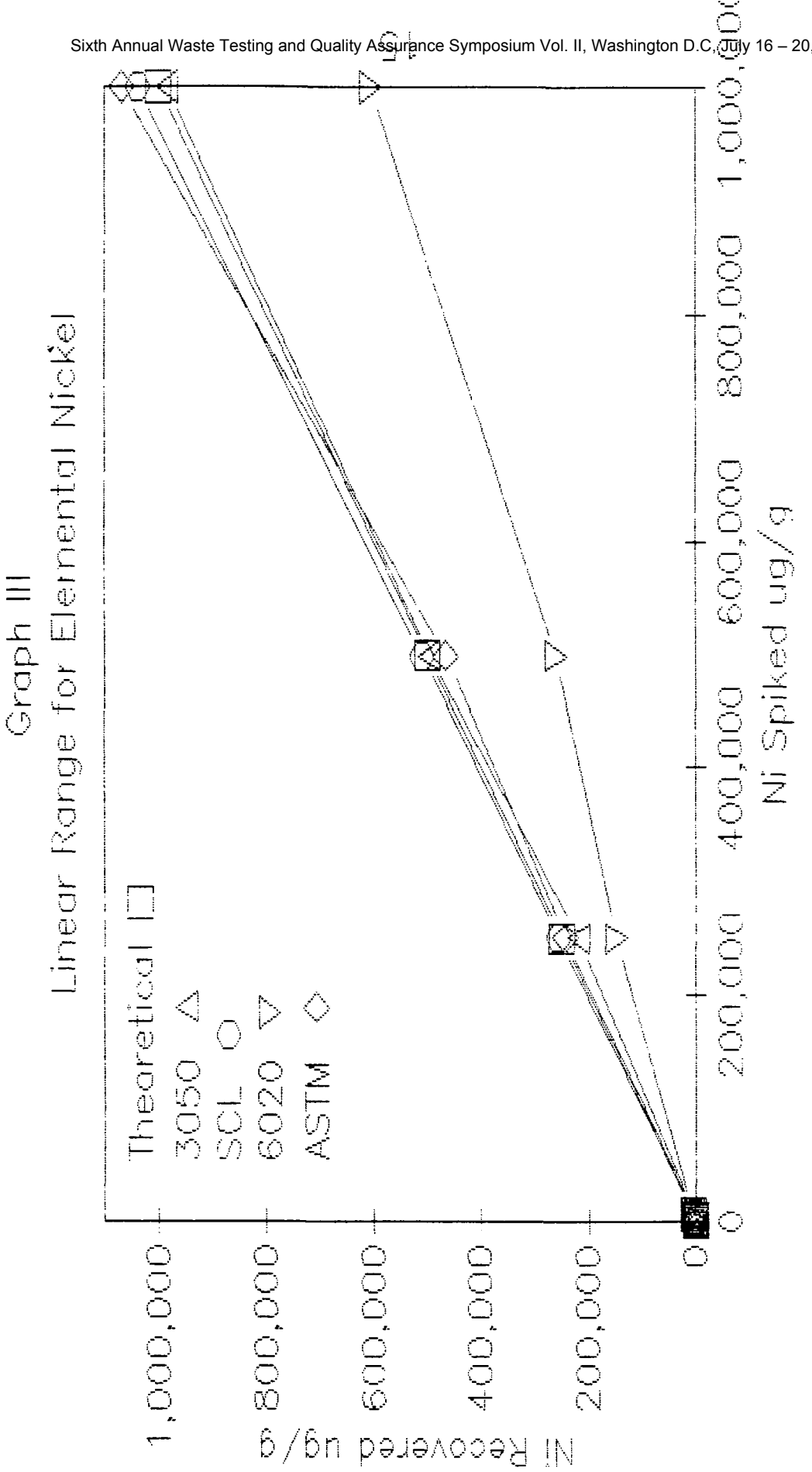
| Sample | Element | 3050 | SCL | 6020 | ASTM 9.3.4 |
|---|---|---|---|---|---|
| A | V | 31,000 | 31,000 | 29,000 | 19,000 |
| B | NI | 270 | 310 | 210 | 230 |
| | V | 28,000 | 32,000 | 28,000 | 19,000 |
| C | BA | 340 | 510 | <200 | 220 |
| | CU | 1200 | 1100 | 1500 | 930 |
| | PB | 340,000 | 110,000 | 140,000 | 880,000 |
| | ZN | 140 | 93 | <200 | 88 |
| D | AS | 280 | 400 | <200 | 120 |
| | BA | 210 | 310 | <200 | 97 |
| | CR | 300 | 260 | <200 | 290 |
| | CU | 1300 | 1200 | 1600 | 670 |
| | PB | 280,000 | 140,000 | 150,000 | 430,000 |
| | SB | 1200 | 1300 | 510 | <50 |
| | ZN | 1200 | 1100 | 620 | 940 |
| E | PB | 130,000 | 140,000 | 150,000 | 380,000 |
| | SB | 2600 | 5300 | 2400 | <50 |
| F | AS | 330 | 330 | <200 | <50 |
| | CU | 800 | 730 | 1300 | 970 |
| | PB | 220,000 | 110,000 | 90,000 | 800,000 |
| | SB | 23,000 | 97,000 | 13,000 | 690 |
| G | AG | <50 | 230 | <200 | <50 |
| | CD | 1600 | 2000 | 1800 | 1600 |
| | CU | 6600 | 4400 | | |
| | NI | 280 | 370 | 390 | 390 |
| | PB | 280,000 | 110,000 | 99,000 | 230,000 |
| | ZN | 1400 | 1500 | 1600 | 1200 |
| H | CO | 610 | 460 | 690 | 91 |
| | CR | 6000 | 9000 | 8000 | 9100 |
| | CU | 470 | 680 | 670 | |
| | MO | 2300 | 3200 | 2400 | 3200 |
| | NI | 13,000 | 16,000 | 13,000 | 16,000 |
| | PB | 190 | 350 | 450 | 280 |
| I | AG | <50 | 10,000 | <200 | 290 |
| | BA | 260 | 250 | <200 | 140 |
| | CR | 1000 | 500 | 340 | 680 |
| | CU | 17,000 | 17,000 | 12,000 | 18,000 |
| | NI | 600 | 550 | 350 | 610 |
| | PB | 3100 | 5300 | 2600 | 3800 |
| | ZN | 4100 | 3900 | 2700 | 4100 |
| J | AG | <50 | 11,000 | <200 | 23,000 |
| | BA | 170 | 530 | <200 | 190 |
| | CD | 310 | 280 | 230 | 350 |
| | CU | 5100 | 3200 | 3000 | 8900 |
| | PB | 18,000 | 18,000 | 14,000 | 20,000 |
| | ZN | 44,000 | 42,000 | 42,000 | 51,000 |
| K | AG | 87 | 140 | <200 | <50 |
| | BA | 1300 | 1300 | 320 | 890 |
| | CR | 750 | 1300 | 520 | 960 |
| | CU | 1900 | 3700 | 2400 | 2700 |
| | MO | 81 | 230 | <200 | <50 |
| | NI | 410 | 760 | 430 | 490 |
| | PB | 21,000 | 19,000 | 18,000 | 21,000 |
| | ZN | 5300 | 4900 | 5300 | 5500 |

## TABLE III
## DISTRIBUTION OF ELEMENTS IN SCL & 3050 DIGESTION PROCEDUREIN TOTAL MICROGRAMS

| Sample | Element | 3050 | Primary Filtrate | Primary Residue | Secondary Filtrate |
|---|---|---|---|---|---|
| A | V | 62,000 | 61,000 | 510 | |
| B | NI | 540 | 610 | <100 | |
| | V | 56,000 | 64,000 | 790 | |
| C | BA | 680 | 743 | 280 | |
| | CU | 2400 | 1700 | 410 | |
| | PB | 680,000 | 57,000 | 166,000 | |
| | ZN | 280 | 180 | <100 | |
| D | AS | 560 | 800 | <100 | |
| | BA | 420 | 370 | 260 | |
| | CR | 600 | 520 | <100 | |
| | CU | 2600 | 2100 | 390 | |
| | PB | 560,000 | 220,000 | 53,000 | |
| | SB | 2400 | 2600 | 130 | |
| | ZN | 2400 | 2200 | <100 | |
| E | PB | 260,000 | 231,000 | 53,000 | |
| | SB | 5200 | 11,000 | 130 | |
| F | AS | 660 | 670 | <100 | <100 |
| | CU | 1600 | 1450 | <100 | <100 |
| | PB | 440,000 | 149,000 | 6200 | 63,000 |
| | SB | 46,000 | 180,000 | 6200 | 10,000 |
| G | AG | <100 | 460 | <100 | |
| | CD | 3200 | 4000 | <100 | |
| | CU | 13000 | 12500 | 690 | |
| | NI | 580 | 750 | <100 | |
| | PB | 560,000 | 170,000 | 230,000 | |
| | ZN | 2800 | 3100 | <100 | |
| H | CO | 1200 | 920 | <100 | <100 |
| | CR | 12,000 | 17,000 | 350 | 350 |
| | CU | 940 | 1400 | <100 | <100 |
| | MO | 4600 | 6000 | 290 | 140 |
| | NI | 26,000 | 29,000 | 1300 | 810 |
| | PB | 380 | 760 | <100 | <100 |
| I | AG | <100 | 12,000 | 8500 | |
| | BA | 420 | 400 | <100 | |
| | CR | 2000 | 1500 | <100 | |
| | CU | 33,000 | 33,000 | 240 | |
| | NI | 1200 | 1100 | <100 | |
| | PB | 6200 | 11,000 | 640 | |
| | ZN | 8200 | 7900 | 1500 | |
| J | AG | <100 | 18,000 | 3500 | |
| | BA | 340 | 420 | <100 | |
| | CU | 10,000 | 7300 | 250 | |
| | PB | 38,000 | 36,000 | 640 | |
| | ZN | 88,000 | 82,000 | 1500 | |
| K | AG | 170 | 280 | <100 | |
| | BA | 2600 | 1500 | 1000 | |
| | CR | 1500 | 2500 | <100 | |
| | CU | 3800 | 7300 | 7300 | |
| | MO | 160 | 460 | <100 | |
| | NI | 820 | 1500 | <100 | |
| | PB | 42,000 | 38,000 | 820 | |
| | ZN | 11,000 | 9600 | 210 | |


Graph 1
Linear Range for Lead Nitrate
Theoretical □
3050 △
SCL ○
6020 ▷
ASTM ◇
Pb Recovered ug/g
120,000
100,000
80,000
60,000
40,000
20,000
0
Pb Spiked ug/g
0
20,000
40,000
60,000
80,000
100,000
120,000


Graph II
Linear Range for Elemental Antimony
Theoretical □
3050 △
SCL ○
6020 ▽
Sb Recovered ug/g
Sb Spiked ug/g
1,000,000
100,000
10,000
1,000
140
1,000,000
100,000
10,000
1,000


Graph III
Linear Range for Elemental Nickel
Theoretical □
3050 △
SCL ○
6020 ▽
ASTM ◇
Ni Recovered ug/g
Ni Spiked ug/g
0
200,000
400,000
600,000
800,000
1,000,000

88

# THE "ART" OF SUCCESSFUL ANALYSES OF INORGANIC CLP PERFORMANCE EVALUATION SAMPLES

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Most environmental laboratories view the passing of the EPA Contract Laboratory Program [CLP] Performance Evaluation [PE] QA/QC sample analysis as an almost impossible task. More laboratories today are required to pass the CLP PE QA/QC analysis to bid on jobs submitted by clients. There are strong indications that SW-846 regulations will require CLP type QA/QC protocols to be followed for inorganics analysis. Therefore, instituting CLP QA/QC protocols for inorganics analysis is of interest to non CLP environmental laboratories.

We have assisted numerous laboratories in instituting CLP QA/QC protocols where we have stressed increased productivity through a minimum of errors (1). This paper will detail our experience in assisting laboratories to institute CLP QA/QC protocols for inorganics analysis and discuss the common errors that lead to failure prior to our on-site training support.

The analysis of the CLP PE samples for inorganics requires an ICP, a Furnace AA and a cold vapor mercury analyzer. It will be assumed for this paper that the methods for these systems have been developed properly. This is not always the case as many laboratories approach ICP from an AA background and fail to account for ICP interferences or attempt to standardize the ICP with too many calibration standards. As for Furnace AA analyses, many laboratories accept the method of standard additions as a necessary evil and employ it routinely which greatly reduces productivity. We always set up modern Furnace AA systems to avoid the method of standard additions (2).

The first common error made is in sample preparation. Consider that the analyses of three CLP PE samples (blank, water and soil) requires the digestion of 26 samples using the hot plate methodology (Figure 1). Consider that the digested samples require pre-digestion spikes at the ppb level and that the soil samples require separation of the solids from the digestate liquid following digestion. This requires a level of organization and reduction of contamination that many laboratories are not used to meeting. We will discuss the use of a very simple acid washing protocol to reduce contamination and the use of multi-element trace metal standards, designed by SPECTRA, to easily add the required pre-digestion spike standards with fixed volume automatic pipets.

The most recent CLP inorganics statement of work issued in April 1990 (3) has approved closed vessel microwave digestion for the preparation of waters and soils. This has reduced the amount of digestions required from 26 for hot plate (Figure 1) to 13 for microwave (Figure 2). The reason for this is that the hot plate technique requires a separate digestion based on analyses by ICP ($HNO_3/H_2O_2/HCl$) or by

Furnace AA ($HNO_3/H_2O_2$). The microwave technique uses only $HNO_3$ and is divided into Water and Soil categories since the Water digestion requires 5 ml $HNO_3$ and the Soil digestion requires 10 ml $HNO_3$. Therefore, laboratories should convert from hot plate digestions to closed vessel microwave digestions.

The preparation of standards for CLP inorganic analyses is a major source of lowered productivity. Different multi-element standard mixes are required for each CLP QA/QC requirement including ICP calibration, Furnace AA calibration, ICP Initial and Continuing Calibration Verification, Furnace AA Initial and Continuing Calibration Verification, ICP Pre-Digestion Spikes, Furnace AA Pre-Digestion Spikes, Furnace AA Post-Digestion Spikes, ICP Interference Check, ICP Inter-Element Correction and ICP 2xCRDL analyses.

SPECTRA developed the first set of CLP standards to meet the entire CLP QA/QC requirements for ICP and Furnace AA in 1986 (4). Our newest standards designed for the 7/87 and 7/88 CLP Statement of Work can also be used for the 4/90 ILM01.0 Statement of Work for both hot plate and microwave digestion. The standards are designed around the use of automatic pipets which greatly increases productivity and decreases contamination errors. Figure 3 outlines the use of the SPECTRA CLP QA/QC multi-element standards for pre-digestion spiking of waters and soils based on the 4/90 Statement of Work requirements for hot plate and microwave digestion.

Examples of increasing productivity for both ICP and Furnace AA analyses of CLP PE samples will be discussed.

## REFERENCES

(1) Tatro, M.E., Teaching the art of environmental analysis, Environmental Laboratory, 1(5), 32 (1989).

(2) Tatro, M.E., Meeting Furnace AA CLP QA/QC Requirements For Inorganics Analyses, American Environmental Laboratory, 2(1), 44 (1990).

(3) USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Document Number ILM01.0 (April 27, 1990).

(4) Tatro, M.E., Methods Development Logic for CLP Inorganics Analyses, American Laboratory, 20(12), 48 (1988).

**HOT PLATE DIGESTION SET UP FOR INORGANIC CLP P-E SAMPLES**

**ICP**

Water
Water Duplicate
Water + Pre-Digestion Spike
Water Preparation Blank
Aqueous Laboratory Control Sample

Blank
Blank Duplicate
Blank + Pre-Digestion Spike

Soil
Soil Duplicate
Soil + Pre-Digestion Spike
Soil Preparation Blank
Solid Laboratory Control Sample

**FURNACE AA**

Water
Water Duplicate
Water + Pre-Digestion Spike
Water Preparation Blank
Aqueous Laboratory Control Sample

Blank
Blank Duplicate
Blank + Pre-Digestion Spike

Soil
Soil Duplicate
Soil + Pre-Digestion Spike
Soil Preparation Blank
Solid Laboratory Control Sample

Total Digestions = 26

FIGURE 1. Required preparations using hot plate digestion.

**MICROWAVE DIGESTION SET UP FOR INORGANIC CLP P-E SAMPLES**

**WATER**

Water
Water Duplicate
Water + Pre-Digestion Spike
Water Preparation Blank
Aqueous Laboratory Control Sample

Blank
Blank Duplicate
Blank + Pre-Digestion Spike

**SOIL**

Soil
Soil Duplicate
Soil + Pre-Digestion Spike
Soil Preparation Blank
Solid Laboratory Control Sample

Total Digestions = 13

FIGURE 2. Required preparations using closed vessel microwave digestion.

**USE OF SPECTRA CLP QA/QC MULTI-ELEMENT STANDARDS FOR HOT PLATE AND MICROWAVE PRE-DIGESTION SPIKES**

**HOT PLATE**

| SPIKE REQUIREMENT | ml ADDED |
|---|---|
| ICP - WATER | 1.0 |
| ICP - SOIL | 2.0 |
| FURNACE AA - WATER | 1.0 |
| FURNACE AA - SOIL | 2.0 |

**MICROWAVE**

| | |
|---|---|
| WATER | 0.5 |
| SOIL | 1.0 |

FIGURE 3. Additions of Pre-Digestion Spike Standard using the SPECTRA CLP QA/QC Multi-Element Kit for both hot plate and microwave digestion procedures.

89

# STATE-OF-THE-ART SAMPLE PREPARATION METHODS FOR ENVIRONMENTAL INORGANIC ANALYSIS

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The weak link in atomic spectroscopy analysis continues to be sample preparation. The EPA Contract Laboratory Program [CLP] has recently approved closed vessel microwave digestion for the preparation of waters and soils prior to ICP and Furnace AA analysis (1). However, microwave digestion has not yet been approved by NPDES and SW-846 regulations. Therefore, most environmental laboratories still must resort to antiquated hot plate methods for the preparation of samples for inorganics analysis.

ICP analysis is far more productive than Furnace AA for trace metal analysis. However, analysts are forced to use Furnace AA to meet required detection limits not attainable by ICP. If samples were concentrated prior to analysis to increase the analyte concentrations, then analysts could use the more productive ICP technique. At this time, EPA approves only evaporation of liquid samples to concentrate samples. Evaporation techniques lead to contamination from the atmosphere and also concentrate ICP interfering elements such as Na, K, Ca and Mg.

The ICP and Furnace AA analysis of metals in oil need not be digested if the oil is in a liquid state. A simple dilution with xylene or kerosene is that is needed to dissolve the oil sample prior to analysis. This "dilute and shoot" technique is favored over digestion, since it leads to a minimum of contamination and a minimum of analyte loss.

This paper will discuss three techniques of sample preparation that are state-of-the-art. The first technique, closed vessel microwave digestion, will be presented as adopted by CLP. The logic of developing a closed vessel microwave digestion method will be shown from our development of a microwave digestion method for the preparation of sewerage sludge prior to ICP analysis (2). The need to characterize the sludge sample by hot plate digestion prior to microwave digestion to obtain the "true" values of analytes extracted by the EPA approved hot plate technique will be stressed. The advent of pressure control microwave digestion techniques will also be addressed.

The use of the Trace-Con automated extraction/concentration system developed by Knapp (3) will be discussed as it applies to the concentration of waters prior to ICP analysis. The Trace-Con is a computer controlled solid phase ion-exchange resin prepared from either oxine/cellulose or EDTrA/cellulose that is designed to automatically concentrate transition elements while allowing alkali and alkaline-earth elements to pass through the ion exchange material.

Elution of the ion-exchange resin with a small volume of acid provides a concentrated sample suitable for ICP analysis. The mechanism of the Trace-Con as well as real world applications will be presented.

The "dilute and shoot" technique of inorganic analysis where sample preparation is avoided will be discussed using an application developed by SPECTRA for the Furnace AA analysis of copper in jet fuel oils. The method will demonstrate the need for computer graphics to identify optimum conditions of analysis.

REFERENCES

(1) USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Document Number ILM01.0 (April 27, 1990).

(2) Tatro, M.E., Sample Preparation: The Weak Link in Atomic Spectroscopy, Spectroscopy, 5(3), 14 (1990).

(3) Tatro, M.E., Sample Preparation Techniques for Inorganic Environmental Analyses, American Environmental Laboratory (in press).

90

# ANALYSIS OF ARSENIC, SELENIUM, AND MERCURY IN TCLP EXTRACTS OF STABILIZED HAZARDOUS WASTE BY HYDRIDE GENERATION/MULTI-ELEMENT ICP OPTICAL EMISSION SPECTROSCOPY

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## ABSTRACT

Hydride Generation-Inductively Coupled Plasma (HG-ICP) analysis of Landban TCLP extracts makes possible the simultaneous analysis of arsenic, selenium, and mercury, at the ppb levels, with only a single sample preparation. HG-ICP analysis streamlines the overall analytical procedure, greatly reduces the time required for analysis, and reduces analytical and capital equipment costs.

TCLP extracts of stabilized hazardous wastes are an excellent matrix for this technology since they generally contain only low concentrations of transition metals, which can cause interferences with the hydride generation chemistry. The vapor generation device can be quickly and easily connected to the ICP sample introduction system and fully automatic operation, with an autosampler, is possible.

## INTRODUCTION

The analytical sensitivity requirements for arsenic, selenium, and mercury analysis, as set forth by the Landban legislation, are given in Tables I, II, and III. Graphite Furnace Atomic Absorption Spectroscopy (GFAA) is usually the method of choice for the analysis of arsenic and selenium, while Cold Vapor Generation Atomic Absorption (CVAA) Spectroscopy is used for mercury. These methods provide adequate sensitivity, accuracy, and precision for most purposes, but are very expensive in terms of capital equipment investments, labor costs, and analytical time.

Generation of volatile hydrides, by reaction with sodium tetraborate ($NaBH_4$), is commonly used for sensitivity enhancement in either the atomic absorption or ICP analysis of many metalloid elements. Hydrides of elements from Groups IVA (Ge, Sn, and Pb), Group VA (As, Sb, Bi), and VIB (Se, Te) can all be produced under appropriate conditions. Mercury doesn't form a volatile hydride like the metalloids, but can be reduced to the volatile metallic state with $NaBH_4$.

Hydride Generation Atomic Absorption (HGAA) methods for arsenic and selenium are given in either SW-846[1] or Standard Methods of the Examination of Water and Wastewater[2], however there are problems with these methods. The SW-846 use of metallic tin for arsenic or selenium hydride generation makes automation virtually impossible. The Standard

Methods required sulfuric acid fuming also causes selenium volatilization losses.

The use of $NaBH_4$ instead of metallic tin, to produce arsenic and selenium hydrides and to reduce mercury to the metallic state, makes automation of the hydride generation step easy. Chemical interferences in the hydride generation step, arising from high concentrations of transition and noble metals can be a problem, but careful sample type choice, and if necessary the use of up to 50% HCl solutions to complex the metals, can make this problem manageable.

Using a combined nitric and hydrochloric acids for digestion eliminates the need for a separate mercury digestion and analyzing arsenic from the $As^{5+}$ state, instead of the $As^{3+}$ state, eliminates the need for a sulfuric acid fuming.

Combining hydride generation with Multi-Element Inductively Coupled Plasma-Optical Emission Spectroscopic (HG-ICP) provides a means for a more rapid analysis of these three elements than with atomic absorption instruments. ICP analysis, therefore, greatly reduces sample analysis time, reduces the need for for atomic absorption equipment, reduces the number of QC samples that must be run, and reduces labor costs.

## THEORY

### Arsenic

Arsine ($AsH_3$) is generated very rapidly from arsenic in the $As^{3+}$ state by reaction with $NaBH_4$. Borohydride can also generate arsine from $As^{5+}$ by first reducing it to $As^{3+}$, however this reaction is much slower, generally resulting in a lower efficiency of arsine production and a loss of analytical sensitivity. Pre-reduction of $As^{5+}$ to $As^{3+}$, by reaction with NaI or KI, can be used to obtain maximum arsenic analysis sensitivity, however iodide salts interfere with selenium and mercury hydride reductions. Arsine generation interference can also occur when residual $NO_3^-$, from the nitric acid used for sample digestion, reacts with iodide to form $NO_2$, which then reoxidizes $As^{3+}$ to $As^{5+}$.

Even though arsine generation from $As^{3+}$ is more efficient, there are advantages to performing the analysis with arsenic in the $As^{5+}$ state. Digestion of the samples with nitric acid conveniently insures that all the arsenic present in the sample solution is present in the plus five oxidation state and the elimination of the iodide reduction simplifies the sample preparation and eliminates the $NO_2$ interference. Arsenic sensitivity can also be largely restored, without interfering with the production of hydrogen selenide and mercury vapor, by the use of a flow injection hydride generator with a reaction coil before gas liquid separation.

## Selenium

Hydrogen selenide production is only possible from the $Se^{4+}$ state, however selenium may exist as elemental selenium ($Se^{0}$), $Se^{2-}$, $Se^{4+}$, and $Se^{6+}$ in samples. Satisfactory analysis of selenium can be achieved by first oxidizing of all the selenium in the samples to the $Se^{6+}$ state by using a nitric acid digestion and then reducing the $Se^{6+}$ to the $Se^{4+}$ state by adding hydrochloric acid and boiling gently for about 30 minutes. Deterioration of the samples, with slow oxidation of the $Se^{4+}$ back to $Se^{6+}$, has been reported, however, Se standards have been found to be stable for at least a week with concentrations of 10% nitric and 10%, or more, hydrochloric acids. Samples, treated as described above and with final concentrations of 10% nitric and hydrochloric acids, have also been found to be stable for several days, however storage time should be minimized after the hydrochloric acid reduction step.

## Mercury

The high vapor pressure of mercury first lead to its determination in air by Muller[3] and Woodson[4] in 1930 and 1939. Poluektov et al.[5], in 1964, first noted an enhancement in the flame atomic absorption determination of mercury in liquid samples when stannous chloride was present. This work, later, lead to the development of the mercury cold vapor atomic absorption analysis method, which uses stannous chloride to reduce $Hg^{2+}$ to volatile metallic mercury prior to its being swept out of the solution and into the absorbance cell by a stream of gas. Schlesinger et al.[6] reported that sodium borohydride effected the reduction of a variety of metal ions, including mercury in 1953, but it wasn't until 1971 that Braman[7] reported using it for the determination of mercury in samples.

## Interferences

The hydride generation technique is prone to several types of interferences that can occur in either the hydride production or transportation stages. Since the study, by Smith[8], of the effects of 48 different elements on the hydride determination of antimony, arsenic, bismuth germanium, selenium, and tin, a large number of papers have been published concerning interferences and their control.
The most important interferences to the determination of As, Se, and Hg by hydride generation are those caused by transition or noble metals, those caused by volatile nitrogen oxides or chlorine, and physical interactions between the sample vapors and the apparatus. Concentrations of interfering metals above approximately 1 to 100 ppm, depending on the metal, can interfere in the hydride production step, causing a lowering of sensitivity. If the metal is in sufficiently high concentration, it can even be reduced to the metallic state which then can react with mercury vapor, arsine, or hydrogen selenide to form an intermetallic compound, causing severe loss of sensitivity and carry over. Metal interferences can be largely controlled by the use of low borohydride concentrations, high concentrations of HCl, and masking

agents. Unfortunately, while a masking agent such as L-Cysteine works well for arsenic, it interferes in the determinations of selenium and mercury. The primary means of controlling metals interferences are, therefore, to keep the metals concentrations as low as possible, use low borohydride concentrations, and use higher concentrations of HCl (up to 50%) to tie up the metals as chloro-complexes.

As described above, reactions between the volatile nitrogen oxide $NO_3^-$ and $I^-$ leads to the production of $NO_2$ which reoxidizes $As^{3+}$ to $As^{5+}$, which results in reduced sensitivity when the analysis is performed with arsenic in the $As^{3+}$ state. This problem is easily controlled by performing the analysis with arsenic in the $As^{5+}$ state. $NO_3^-$ is also eliminated during the selenium reduction step when the sample, after addition of HCl, is boiled. The addition of another reactant such as sulfamic acid[9] or urea, which react with $NO_3^-$, can also be used to reduce or eliminate this interference.

If hydrogen peroxide, $H_2O_2$, is used in the digestion, care must be taken to completely destroy or eliminate all traces of this reagent prior to adding HCl and heating otherwise dissolved chlorine gas $Cl_2$ is produced. This $Cl_2$ gas then slowly reoxidizes $Se^{4+}$ to $Se^{6+}$, which in unreactive with borohydride. This slow reoxidation causes a loss of sensitivity which increases with time. This problem is most easily avoided by using a nitric acid/hydrochloric acid digestion instead of a nitric acid/hydrogen peroxide one.

As described above, when high concentrations of interfering metals are used, especially copper or noble metals, plating out of the metal on the reaction device surfaces can occur, producing interferences by the production of inter-metallic compounds. Mercury also has a tendency to adsorb or plate out on parts of the reaction apparatus or the gas/liquid separator, especially if the parts are dry, when the Hg vapor concentration is high, and then revolatilize when the vapor concentration is low. This leads to severe problems of carry over and drift. Hydrogen selenide also seems to readily dissolve in this mercury film, possibly being reduced to metallic Se at the same time, leading to a very large and irrecoverable loss of sensitivity. These problems are controllable by making all samples, standards, and the rinse solution a mixture of nitric and hydrochloric acids and using the nebulizer as the gas liquid separator. The $HNO_3$/HCl mixture prevents any mercury plating out in the reaction portions of the hydride generator and the constant spraying of this mixture by the nebulizer seems to prevent any plating out in the spray chamber or torch.

## EXPERIMENTAL SECTION

### Apparatus

The hydride vapor generator can be constructed, using a 4 roller peristaltic pump and a manifold assembled according to Figures 1 and 2, or a commercial system such as the Varian VGA-76 may be used. If the

VGA-76 is used the sample and drain pump tubes should be placed on inside position of rollers and the sample pump tube on the outside. (Varian, Instrument Group, 220 Humboldt Court, Sunnyvale, CA 94089, (800)231-8134.)

A Leeman Labs Plasma-Spec I sequential Inductively Coupled Plasma, equipped with a Thermo Jarrell Ash fixed cross-flow nebulizer, was used for all sample analysis work (Leeman Labs, Inc., 600 Suffolk St., Lowell, MA 01854, (508)454-4442 and Thermo Jarrell Ash Corporation, 8 East Forge Parkway, Franklin, MA 02038-9101, (508)520-1880.)

Reagents

Reagent water, defined as water in which an interferant is not observed at, or above, the methods detection limit of the analyte(s) of interest was used throughout. Typically this water was equivalent to ASTM Type I water. All reagents used were ACS reagent grade or better.

Sample Preparation

If the TCLP extract of the stabilized waste contains undissolved solids, the extract must be well shaken prior to analysis. A 50 mL sample aliquot is transferred to a 125 mL Erlenmeyer flask.

When all samples are transferred, add 5 mL of concentrated $HNO_3$ and 5 mL of concentrated HCl to the flasks, hang a glass hook on the lip of the flask to speed up evaporation, and cover them with a reflux cap. Place the samples on a hot plate and, with gentle refluxing, evaporate them to near dryness, making certain that the samples are not allowed to go completely dry. Cool the flasks and, if the digestion is not complete, add additional 3-mL portions of concentrated $HNO_3$ and HCl. Return the samples to the hot plate for continued refluxing and evaporation.

Continue the heating, with additional acids being added as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate the sample to near dryness and cool. Add 5 mL of HCL, 10 mL of reagent water, and 1 g or urea. Remove the glass hook and heat, at a gentle simmer, for 30 minutes to dissolve any precipitate or residue resulting from evaporation and to reduce the selenium to the $Se^{4+}$ state for analysis. Cool and add additional $HNO_3$ to bring the total $HNO_3$ to 5 mL (about 2-3 mL).

Transfer the digested sample to a 50 mL volumetric flask. Wash the digestion flask and reflux cap carefully into the volumetric flask to insure that sample transfer is quantitative. After dilution to volume, if necessary, filter the sample (Whatman #1 filter paper or equivalent) to remove any undissolved particles that might clog the ICP nebulizer. The sample is now ready for analysis. Because of the potential for degradation of the sample, samples should be analyzed as soon as

possible after the final heating and dilution. Maximum storage time before analysis should be less than 48 hours.

Connection of Hydride Generator to ICP

Minor modifications are made to the Thermo Jarrell Ash fixed cross flow nebulizer and to the Leeman ICP spray chamber to facilitate switching between normal sample nebulization and hydride generation. With these modifications, switching between the sample input devices will not require shutting down the ICP or making any changes in operating conditions.

A section of Leeman sample pump tubing about 3/16" long is used to attach about 8" of the 1/16" O. D. Teflon™ tubing to the sample inlet of the nebulizer. This tubing extends outside the torch box where it is connected to either the Leeman sample pump tubing or the reaction coil of the hydride generator. By turning off the nebulizer argon gas flow for only a few seconds it is possible to switch between the Leeman sample pump tubing or the reaction coil of the hydride generator.

About 8" of the 1/8" O. D. Teflon™ tubing is attached to the Leeman spray chamber drain and extended outside the torch box where it is connected to either the Leeman drain pump tubing or the hydride drain pump tubing.

Operating Conditions

Hydride Generation-Multi/element Inductively Coupled Plasma-Optical Emission Spectroscopy instrumentation and operating conditions are given in Table IV.

Calibration

A linear calibration is typically obtained with four standards and the range limited to a maximum of 100 ppb to insure greatest accuracy in the low ppb range. Typical calibration curves are shown in Figure 3. With the use of quadric fitting, the calibration range can be extended to 500 to 1000 ppb, however carry over between samples or standards becomes a significant problem.

Analytical Results for Undigested Standards

Leeman ICP Sample trays containing 40 alternating blanks and standards, containing 25 ppb of As, Se, and Hg and 2500 ppm of Ca to matrix match the TCLP extracts, were analyzed on 5 different days. The 25 ppb level was chosen for the standard to match the lowest regulation levels for TCLP extracts for Se and Hg. The daily and overall average results are shown in Table V. These results indicate that the Instrument Detection Limits (IDL's) for the three elements are between 2 and 2.5 ppb, the Per Cent Relative Standard Deviation (%RSD) at 25 ppb is between 3% and 7%, and that an accuracy of ±20% at 25 ppb is possible at the 50 ppb level.

## Analytical Results for Digested Standards

Twenty 50 mL aliquots of a mixed standard, containing 50 ppb of As, Se, and Hg and 2500 ppm of Ca to matrix match the TCLP extracts, were prepared according to the sample preparation method given in this report. These 20 standards aliquots were then placed in a Leeman autosampler tray, alternating with 20 blanks, and analyzed. Over three sets of analysis of these digested standards 42 results for As and 52 results for Se and Hg were obtained. The results, shown at the bottom of Table V, are similar to those for the undigested standard and show that the %RSD's range between about 3% and 7% with an accuracy of about 20%.

## CONCLUSIONS

1. Hydride Generation/Multi-Element ICP Optical Emission Spectroscopy can be shown to provide sufficient sensitivity, accuracy, and precision to allow analysis of arsenic, selenium, and mercury in TCLP extracts of stabilized hazardous wastes at the ppb levels.

2. Multi-Element Hydride Generation/ICP Optical Emission Spectroscopy is much more rapid than single element atomic absorption analysis, requiring only 4 minutes of instrument time instead of about 20 minutes.

3. Additional time savings are achieved since all QC samples need only be run once, not three times.

4. Sample digestion with combined nitric and hydrochloric acids can be shown to produce excellent recoveries of arsenic, selenium, and mercury.

5. The need of a separate sample digestion for mercury can be eliminated by the use of a combined nitric and hydrochloric acids digestion.

6. By using existing ICP equipment, the purchase of additional atomic absorption can be avoided, reducing capital equipment costs.

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## TABLE I

### ARSENIC HAZARDOUS WASTE CODES AND TREATMENT STANDARDS

| WASTE CODE | WW/NWW[2] | TREATMENT STANDARD | | CCW/CCWE[1] | REGULATION SOURCE[3] | |
|---|---|---|---|---|---|---|
| CALIF | LIQ | 500. | ppm CCW | | CALIF | |
| D004 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| K031 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| K048 | NWW | 0.004 | ppm | CCWE | 1st | 3rd |
| K049 | NWW | 0.004 | ppm | CCWE | 1st | 3rd |
| K050 | NWW | 0.004 | ppm | CCWE | 1st | 3rd |
| K051 | NWW | 0.004 | ppm | CCWE | 1st | 3rd |
| K052 | NWW | 0.004 | ppm | CCWE | 1st | 3rd |
| K084 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| K101 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| K102 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| LEACHATE | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| P010 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| P011 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| P012 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| P036 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| P038 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| U136 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| D004 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| K031 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| K084 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| K101 | WW | 2. | ppm | CCW | 1rd | 3rd |
| K101 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| K102 | WW | 2. | ppm | CCW | 1rd | 3rd |
| K102 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| LEACHATE | WW | 1.39 | ppm | CCW | 3rd | 3rd |
| P010 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| P011 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| P012 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| P036 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| P038 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| U136 | WW | 0.79 | ppm | CCW | 3rd | 3rd |

[1] Constituent Concentration in Waste (CCW) or Constituent Concentration in Waste Extract (CCWE).
[2] Waste Water (WW) or Non-Waste Water (NWW).
[3] California Listed Waste (CALIF) or 1st, 2nd, or 3rd third of Landban.

**TABLE II**

SELENIUM HAZARDOUS WASTE CODES AND TREATMENT STANDARDS

| WASTE CODE | WW/NWW[2] | TREATMENT STANDARD | | CCW/CCWE[1] | REGULATION SOURCE[3] | |
|---|---|---|---|---|---|---|
| CALIF | LIQ | 20. | ppm CCW | | CALIF | |
| D010 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| K048 | NWW | 0.025 | ppm | CCWE | 1st | 3rd |
| K049 | NWW | 0.025 | ppm | CCWE | 1st | 3rd |
| K050 | NWW | 0.025 | ppm | CCWE | 1st | 3rd |
| K051 | NWW | 0.025 | ppm | CCWE | 1st | 3rd |
| K052 | NWW | 0.025 | ppm | CCWE | 1st | 3rd |
| LEACHATE | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| P103 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| P104 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| U204 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| U205 | NWW | 5.6 | ppm | CCWE | 3rd | 3rd |
| D010 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| LEACHATE | WW | 0.82 | ppm | CCW | 3rd | 3rd |
| P103 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| P114 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| U204 | WW | 0.79 | ppm | CCW | 3rd | 3rd |
| U205 | WW | 0.79 | ppm | CCW | 3rd | 3rd |

[1] Constituent Concentration in Waste (CCW) or Constituent Concentration in Waste Extract (CCWE).
[2] Waste Water (WW) or Non-Waste Water (NWW).
[3] California Listed Waste (CALIF) or 1st, 2nd, or 3rd third of Landban.

## TABLE III

### MERCURY HAZARDOUS WASTE CODES AND TREATMENT STANDARDS

| WASTE CODE | WW/NWW[2] | TREATMENT STANDARD | CCW/CCWE[1] | REGULATION SOURCE[3] |
|---|---|---|---|---|
| D009 | NWW[4] | RORTIN[5] | MOT6 | 3rd 3rd |
| K071 | NWW[4] | RORT7 | MOT | 3rd 3rd |
| K106 | NWW[4] | RORT | MOT | 3rd 3rd |
| U151 | NWW[4] | RORT | MOT | 3rd 3rd |
| | | | | |
| CALIF | LIQ | 20. ppm CCW | | CALIF |
| D009 | NWW | 0.025ppm | CCWE | 3rd 3rd |
| K071 | NWW | 0.025ppm | CCWE | 1st 3rd |
| K071 | NWW | 0.025ppm | CCWE | 3rd 3rd |
| K106 | NWW | 0.025ppm | CCWE | 3rd 3rd |
| LEACHATE | NWW | 0.2 ppm | CCWE | 3rd 3rd |
| U151 | NWW | 0.025ppm | CCWE | 3rd 3rd |
| D009 | WW | 0.03 ppm | CCW | 3rd 3rd |
| K071 | WW | 0.03 ppm | CCW | 1st 3rd |
| K101 | WW | 0.027ppm | CCW | 1st 3rd |
| K101 | WW | 0.082ppm | CCW | 3rd 3rd |
| K102 | WW | 0.027ppm | CCW | 1st 3rd |
| K102 | WW | 0.082ppm | CCW | 3rd 3rd |
| K106 | WW | 0.03 ppm | CCW | 3rd 3rd |
| LEACHATE | WW | 0.15 ppm | CCW | 3rd 3rd |
| P065 | WW | 0.03 ppm | CCW | 3rd 3rd |
| P092 | WW | 0.03 ppm | CCW | 3rd 3rd |
| U151 | WW | 0.03 ppm | CCW | 3rd 3rd |
| | | | | |
| P065 | NWW[8] | INRORT9 | MOT | 3rd 3rd |
| | | | | |
| P092 | NWW10 | INRORT | MOT | 3rd 3rd |

[1] Constituent Concentration in Waste (CCW) or Constituent Concentration in Waste Extract (CCWE).
[2] Waste Water (WW) or Non-Waste Water (NWW).
[3] California Listed Waste (CALIF) or 1st, 2nd, or 3rd third of Landban.
[4] High Mercury Subcategory
[5] Roasting or retorting; or incineration followed by roasting or retorting as a method of treatment.
[6] Method of Treatment (MOT).
[7] Roasting or retorting as methods of treatment.
[8] Mercury Fulminate.
[9] Incineration followed by roasting or retorting as a method of treatment.
[10] Phenyl Mercury Acetate.

## TABLE IV

Instrumentation

| Component | Model/size | Manufacturer |
|---|---|---|
| ICP (Sequential) | Plasma-Spec I | Leeman Labs, Inc. Lowell, MA |
| Nebulizer | Fixed Cross-flow | Thermo Jarrell-Ash Franklin, MA |
| Vapor Generator | VGA-76 | Varian Instruments Sunnyvale, CA |
| or | | |
| Peristaltic Pump | Rabbit or Rabbit Plus | Rannin Instrument Woburn, MA |
| Hydride Manifold | 99-100399 (or lab. constructed) | Varian Instruments Sunnyvale, CA |

Emission Wavelengths

| Leeman ICP Line | Wavelength |
|---|---|
| As3 (with Background Position B1) | 234.984 nm |
| Se1 (with Background Position B1) | 203.985 nm |
| Hg1 (with Background Position B1) | 253.652 nm |

Operational Parameters

| Component | Setting |
|---|---|
| Power (@ 0.5 amps) | 1000 Watts |
| Outer Torch Flow | 12 L/minute |
| Intermediate Torch Flow | 0 L/minute |
| Sample Torch Flow (@ 37.5 psig) | 0.5 L/minute |
| Sodium Borohydride (1% w/V) | 1 mL/minute |
| Sample (10% $HNO_3$/10% HCl) | 8 mL/minute |
| Wavelength Update (between each sample) | 3 minutes |
| Rinse Time | 99 seconds |
| Delay Time | 60 seconds |
| Update Frequency (U1 and U2) | 10 samples |
| Analysis Times: | |
| As and Hg | 3 x 3 seconds |
| Se | 3 x 6 seconds |

## TABLE V

### ANALYTICAL RESULTS FOR UNDIGESTED STANDARDS

CALIBRATION BLANKS

| Date | As(ppb) | Se(ppb) | Hg(ppb) |
|---|---|---|---|
| 3/13/90 | -3.16 ± 0.43 | -1.7 ± 0.77 | -5.55 ± 1.16 |
| 3/14/90 | -1.73 ± 0.71 | 1.68 ± 0.83 | -2.50 ± 0.93 |
| 3/15/90 | -2.15 ± 0.94 | -0.11 ± 0.56 | -3.51 ± 0.60 |
| 3/16/90 | -0.53 ± 1.20 | -0.56 ± 0.65 | -0.01 ± 0.30 |
| 3/19/90 | -1.54 ± 0.84 | -0.12 ± 0.70 | -2.31 ± 0.62 |
| Average | -1.54 0.84 | -0.12 0.70 | -2.31 0.62 |
| IDL (3 Std. Dev.) | 2.5 ppb | 2.1 ppb | 1.9 ppb |

UNDIGESTED 25 ppb MIXED STANDARD CONTAINING 2500 PPM Ca

| Date | As(ppb) | Se(ppb) | Hg(ppb) |
|---|---|---|---|
| 3/13/90 | 21.9 ± 1.28 | 21.2 ± 1.60 | 21.4 ± 0.73 |
| 3/14/90 | 22.6 ± 0.78 | 23.6 ± 1.25 | 23.6 ± 1.02 |
| 3/15/90 | 22.4 ± 1.57 | 23.8 ± 0.78 | 23.0 ± 0.49 |
| 3/16/90 | 21.6 ± 2.35 | 25.8 ± 1.07 | 24.2 ± 0.43 |
| 3/19/90 | 24.8 ± 1.11 | 29.7 ± 0.89 | 24.8 ± 0.31 |
| Averages | 22.7 1.42 | 24.8 1.12 | 23.40 0.60 |
| %RSD's | 6.3% | 4.7% | 2.6% |

DIGESTED 50 ppb MIXED STANDARD CONTAINING 2500 PPM Ca

| Date | As(ppb) | Se(ppb) | Hg(ppb) |
|---|---|---|---|
| 4/6/90 | 44.6 ± 4.11 | 42.6 ± 2.29 | 42.8 ± 0.92 |
| 4/9/90 | 54.8 ± 4.83 | 47.2 ± 1.78 | 43.0 ± 1.10 |
| 4/9/90 | 47.1 ± 2.87 | 47.3 ± 1.97 | 43.1 ± 0.91 |
| Averages | 48.8 ± 3.94 | 45.7 ± 2.01 | 43.0 ± 0.98 |
| %RSD's | 6.8% | 4.4% | 2.3% |

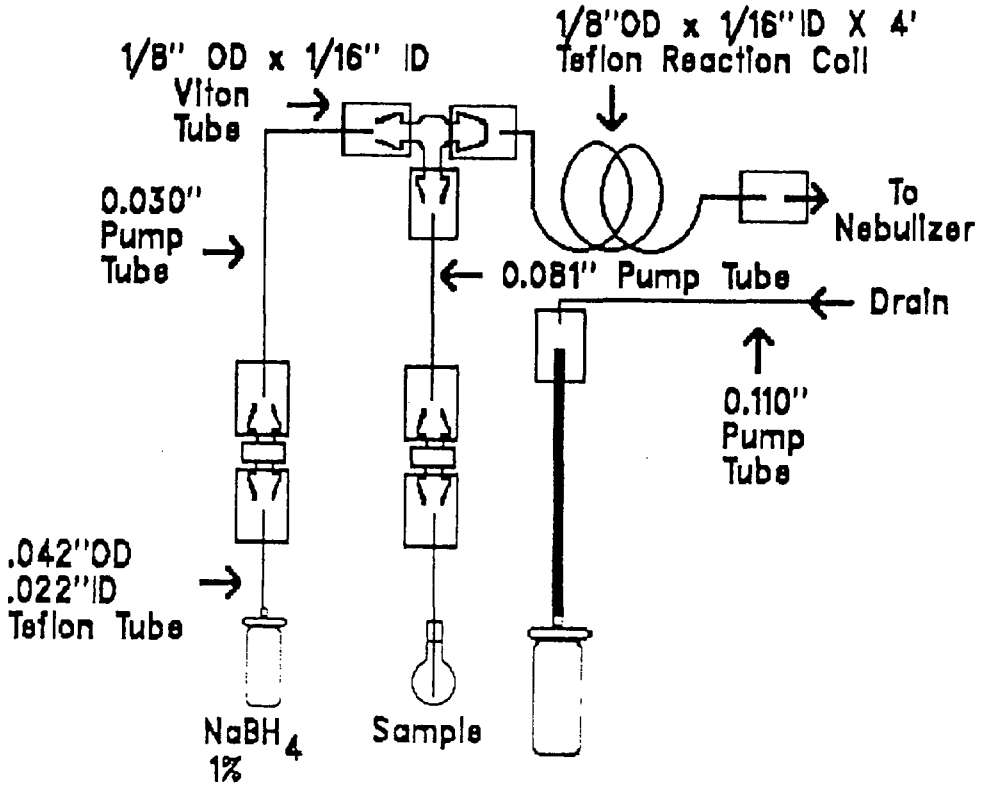


FIGURE 1. HYDRIDE GENERATOR MANIFOLD

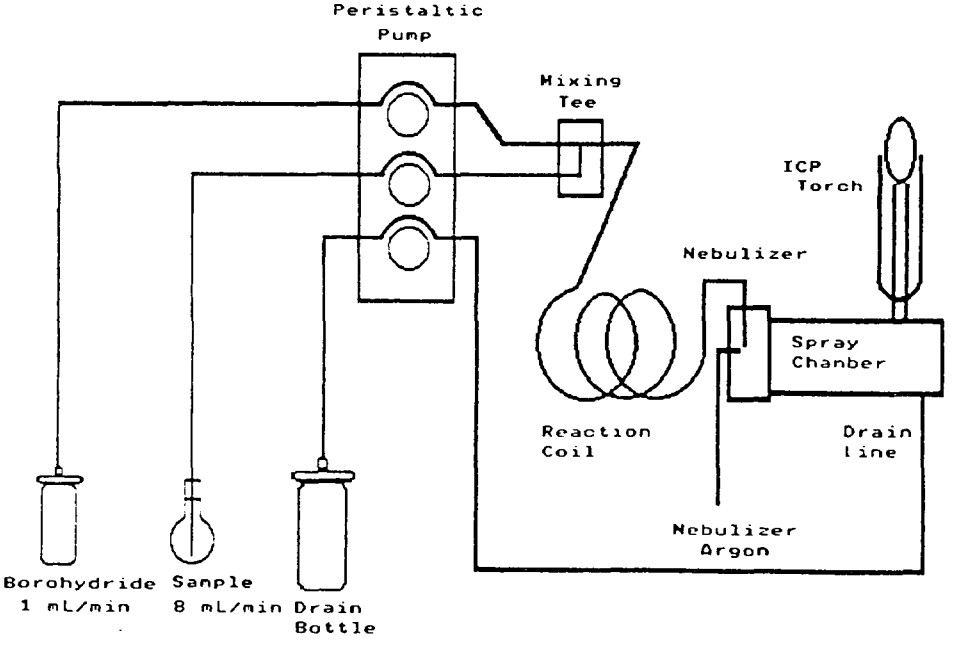


FIGURE 2. HYDRIDE GENERATION - ICP ASSEMBLY

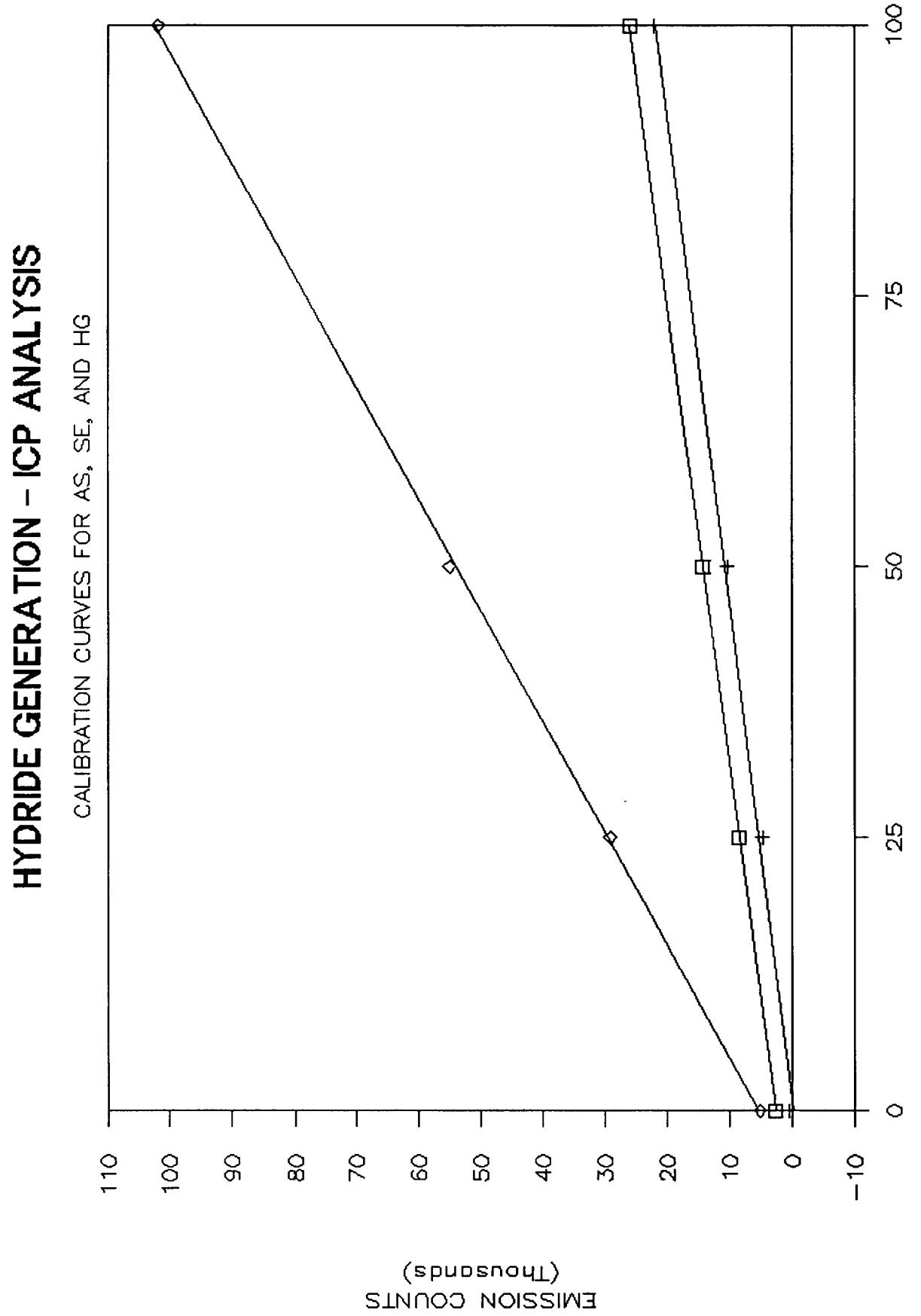
HYDRIDE GENERATION – ICP ANALYSIS
CALIBRATION CURVES FOR AS, SE, AND HG
EMISSION COUNTS
(Thousands)
110
100
90
80
70
60
50
40
30
20
10
0
−10
0
25
50
75
100
CONCENTRATION (ppb)
As
Se
Hg

FIGURE 3.

91

# X-RAY FLUORESCENCE SPECTROSCOPY IN HAZARDOUS WASTE AND CONTAMINATED SOIL ANALYSES

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## ABSTRACT

X-Ray fluorescence (XRF) spectroscopy has a number of advantages which recommend it for the determination of toxic metals in wastes and soils. Salient features of the instrumentation will be described. Laboratory XRF instruments can make precise, rapid measurements, and, if properly calibrated, accurate ones. Portable instruments can find hot spots at waste sites and aid in designing a sampling plan. The determination of lead, arsenic, cadmium and other metals in contaminated soils will be described. The fundamental parameters approach to "standardless" analysis is very promising for the semiquantitative (within 50%) determination of metals in completely unknown and unspecified matrices. The ease of sample preparation for XRF spectroscopy and the ability to deal with problem matrices is illustrated by the analysis of waste oil.

## INTRODUCTION

X-ray fluorescence (XRF) spectrometry has an important role in the analysis of hazardous wastes. Its potential is still being developed, and there are many elemental analysis problems involving hazardous waste in which more consideration should be given to XRF.

XRF spectrometry has long had an important niche in industrial chemical analysis. Steel mills, foundries and non-ferrous metal smelters use XRF for rapid, precise and unbiased analyses. The mining industry uses XRF in all aspects of its work from prospecting to assaying the finished products. The petroleum industry uses XRF to accurately determine metals in petroleum products.

XRF could be almost as useful to those doing hazardous waste analyses, if it were properly understood and more widely available. Environmental analyses require great sensitivity and XRF does not always offer sufficient sensitivity, as detection limits are in the 1 to 100 ppm range. However, hazardous waste analysis is very different from measuring natural levels in the environment, and is in many ways more akin to the analysis of commercial materials. For those analyses in which significant concentrations of heavy metals

or other target elements are present, conventional XRF instrumentation very often has sufficiently low detection limits.

Once it is established that XRF has sufficient sensitivity for a particular hazardous waste analysis, the many advantages of XRF determinations can be appreciated. Often very little sample preparation is needed. Solids or liquids can simply be placed in disposable cups with an X-ray transparent window and analyzed directly. Viscous waste oils and paint sludges can be characterized without problematic digestions such as those required by AA or ICP. The easy sample preparation makes XRF spectrometry ideal for rapid qualitative analysis.

XRF instrumentation is usually quite trouble free and easily maintained. It is very stable and holds calibration well. The precision of repeated measurements is usually very good. It is multielement, in either a simultaneous or rapid sequential fashion. Computer controlled spectrometers with sample changers can analyze many samples while unattended. A wide variety of quantitative methods are available. Often methods developed for industrial materials can be adapted to hazardous wastes. The above factors combine to make XRF very useful for efficiently analyzing a large number of similar samples, such as determining toxic metals in a large number of soil samples or used oil samples.

The remainder of the paper describes some applications of XRF spectrometry to hazardous waste analysis. The advantages of XRF and areas in which it is particularly useful are illustrated.

## FUNDAMENTALS

X-rays are a form of radiation more energetic and of shorter wavelength than visible and ultraviolet light. The wavelengths of X-rays are traditionally measured in Angstroms (1 Angstrom equals $10^{-10}$ meters), although the more correct metric unit is nanometers (10 Angstroms equals 1 nanometer). The shorter the wavelength of an X-ray, the higher the energy. X-ray energies are measured in kiloelectron volts (keV). Dividing 12.4 by an energy in keV gives the wavelength in Angstroms. Of course, dividing 12.4 by a wavelength in Angstroms gives the energy of the X-ray in keV. Analytically useful X-rays are in the range from about 0.2 to 20 Angstroms or from about .6 to 60 keV. For example, the K alpha emission of sulfur is at 5.373 Angstroms (2.31 keV), the K alpha emission of cadmium is at 0.54 Angstroms (23.0 keV) and the L beta emission of lead is at 0.98 Angstroms (12.7 keV).

The X-ray emission spectrum of an element is relatively simple compared to ultraviolet and visible emission spectra (which are used in ICP). A regular pattern is followed. Within a given series, such as the K lines, the emission energy increases with increasing atomic number (the wavelength gets shorter).

When X-rays irradiate a material, they can be either absorbed, scattered or transmitted. Absorbed X-rays lead to fluorescence or emission of characteristic X-rays. Scattered X-rays contribute to the background. The amount and type of scattering is a source of information about a sample. Absorption and scattering coefficients are well known for almost all elements. It is possible to use these values in calculations of matrix effects which greatly reduce the need for matrix matching of samples and standards. Such calculations are known as fundamental parameters methods and are described more completely in the section on standardless analysis.

XRF spectrometry is an elemental technique. The results determined by XRF are the total amount of a particular element present in a sample, regardless of what compound contains the element. This is an advantage when total amounts are of interest, as there is no digestion to cause incomplete recoveries. It is a disadvantage if the concern is with amount extractable by a certain digestion.

INSTRUMENTATION

There are two types of X-ray fluorescence spectrometers, energy dispersive and wavelength dispersive. The classification is based on the method by which the X-rays are detected. Wavelength dispersive spectrometers have been in analytical laboratories for a longer time, and use a high powered X-ray tube to irradiate a sample with X-rays. The fluorescent X-rays, which are characteristic of the elements present in the sample, are dispersed by the analyzing crystal, where Bragg diffraction separates X-rays by wavelength. In a sequential spectrometer the detector and analyzing crystal are moved in concert so that each wavelength is individually focused on the detector. The detector, either a scintillation or a proportional counter, counts all the X-rays which reach it. In a simultaneous spectrometer there is a separate crystal and detector for each element of interest. A typical wavelength dispersive sequential spectrometer will cost about $150,000 and a simultaneous spectrometer over $200,000.

One product of research on radioactivity and transuranic elements is the energy dispersive detector, a lithium drifted silicon semiconductor (the SiLi detector). This detector produces a current proportional to the energy of an X-ray which strikes it. It can resolve the characteristic X-rays of the elements and is used in energy dispersive spectrometers as both the dispersive element and the detector. As in wavelength dispersive instruments, the sample is irradiated by X-rays produced by an X-ray tube. The SiLi detector is placed close to the sample and receives X-rays of all energies. X-rays are counted and sorted by energy. A multi-channel analyzer accumulates the counts to produce a spectrum. An energy dispersive spectrometer is naturally multi-element, although to collect a complete spectrum several sets of excitation conditions may be used. An energy dispersive XRF spectrometer suitable for laboratory use costs $50,000 to $125,000.

Portable XRF spectrometers can be used in the field at waste sites and to survey quite large areas for soil contamination. In their current state of development, they have much poorer resolution and considerably less sensitivity than laboratory instruments. Most of them employ a rather crude energy dispersive detector. They work best with a known, unchanging sample matrix. Matrix matching of standards is highly desirable, perhaps obtained by using an alternative technique to analyze preliminary samples from a site. The best use for these portable instruments is for finding hot spots and for providing a large number of semiquantitative results as an aid in sampling. It should be remembered that the overall error from such field measurements is no better than the sampling error.

A few generalizations which compare energy dispersive and wavelength dispersive instruments will be given. The treatment is far from exhaustive, but serves to contrast relative strengths and weakeners. It should be noted that there is a considerable body of knowledge on XRF methods, and the literature should be consulted when new problems are approached.

Wavelength dispersive spectrometers are ideal for studies which involve determining 5 to 10 elements in a large number of samples. Such an effort would justify the preparation or purchase of a suitable number of matrix matched standards and careful calibration of the instrument. A typical measurement scheme would use about one minute per element per sample for trace elements. This one minute includes both peak and background measurement. The calculation of

the final concentrations would be almost instantaneous and would be available as soon as each sample was completed.

Since energy dispersive instruments are inherently multielement, hey are ideal for the qualitative and semiquantitative analysis of complete unknowns and one of a kind samples, such as might be found at an abandoned drum site. Energy dispersive instruments are also well suited for all types of quantitative analyses. It may be necessary to employ several excitation conditions to achieve optimum results. For instance, chromium, lead and cadmium are far enough apart in the periodic table to usually require different operating conditions for the instrument. Because the deconvolution of complex spectra is often necessary, data processing can consume a significant portion of the analysis time. All in all, energy dispersive spectrometers can make the same quantitative measurements as the more expensive wavelength dispersive instruments.

## SOILS CONTAMINATED WITH HEAVY METALS

The contamination of soils by toxic metals is a serious environmental problem, which often involves large areas. It is important that the contaminated area be well defined. After remedial actions, careful measurements must be made in order to certify the success of the abatement process. X-ray fluorescence spectrometry is an effective way to meet the analytical challenges posed by this type of problem. XRF has several advantages over AA or ICP. It is less operator dependent and has a much simpler sample preparation.

Prior to laboratory measurements, portable XRF equipment can be used to perform a preliminary survey of a site. The main sampling can be better planned and executed if some basic facts about the site are known. A preliminary survey with a portable XRF spectrometer can set the boundaries of the contaminated area, find hot spots, and establish gradients. This type of information will greatly increase the likelihood that the principal sampling will be proper and valid.

Soil or rock samples can be analyzed as ground powders, after drying and then grinding them to a uniform size. This, of course, should be done no matter what analytical technique is applied. A five to ten gram portion of the sample is then placed in a disposable plastic cup with a thin mylar or polypropylene window, which is X-ray transparent. The XRF analysis is done on this sample, non-destructively, and can easily be repeated.

Obtaining suitable standards is the main difficulty with XRF measurements of contaminated soils. The most accurate calibrations are done with standards which closely match the samples. Ideally, the standards should span the concentration range of the analytes and the major elements in the standards should match those in the samples. The parameters in the calibration equations, which may contain interelement corrections, are adjusted by least squares techniques to fit the standards. In order to accurately determine the parameters, there should be many more standards than parameters. Several standards should be left out of the calibration and then used to test the final fit.

One approach is to take samples from a similar project or from a previous sampling of the target site as calibration standards. They can be prepared and analyzed by several techniques until the results are self-consistent. Another possibility is to add known amounts of an element, as a solution, to a base material. This is followed by drying and mixing. A third approach is to use certified reference materials such as those from NIST or the Canadian Certified Reference Material Project (Canadian Centre for Mineral and Energy Technology, Ottawa, Ontario).

The need for matrix matching is reduced by using scattered radiation as an internal standard. As discussed previously, the composition of the matrix determines the scattering of X-rays. By measuring the scattering for all standards and samples, and by correcting for differences in scattering, it is possible to significantly improve accuracy. This technique can compensate for differences between samples and standards. Andermann and Kemp (1958) were some of the earliest investigators to use scattered X-rays as internal standards. Reynolds (1963) was an early user of Compton scattering as an internal standard. Since absorption is roughly inversely proportional to scattering, these investigators found that by ration the intensities of characteristic lines to scattered intensities they could compensate for varying absorption by different matrices. A common choice is the Compton peak of one of the characteristic lines of the X-ray tube. Scattering is used as an equivalent to an internal standard, attempting to compensate for inadequacies in empirical calibrations. More recent applications of this technique have included trace elements in geological materials (Feather and Willis, 1976 and Giauque et.al, 1977).

The needs of the study, the availability of standards, and the time available all affect the calibration. Usually, environmental studies can be done with a basic set of standards with scattering corrections used to compensate for

matrix matching problems. Care in XRF calibrations is well worth the time and effort. XRF instruments are very stable and hold calibration well. Once calibrated, analyses proceed quickly.

One of the few interference problems of any consequence in XRF spectrometry is the almost exact coincidence of the lead L alpha line and the arsenic K alpha line. Lead can be measured just as well using the L beta line, but the alternative isn't as good for arsenic. To avoid the interference from lead, arsenic can be measured using the K beta line, which is not as intense as the K alpha line. Using the K beta line of arsenic raises the detection limit by a factor of four or five. An alternative suitable for some situations is to measure the combined line from lead and arsenic. The presence of either or both is a concern. When assessing a clean-up, both must be removed and this can be checked with the combined line. A potential disadvantage can be turned to good use.

## SEMIQUANTITATIVE ANALYSIS "WITHOUT" STANDARDS

An energy dispersive X-ray fluorescence spectrometer can produce spectra covering all elements from sodium to uranium in about ten minutes. This permits a rapid analysis of an unknown with detection limits for most elements of less than 100 ppm. A rapid, multielement qualitative analysis can be of great utility. In our laboratory, qualitative XRF analysis is used as a screening technique. Screening means initial, preliminary analyses which serve to direct subsequent analyses. If no toxic or priority pollutant metals are found in a sample, then it may be possible to eliminate additional metals analyses. Difficult samples such as sludges, paint wastes and used oils can be checked for the presence of toxic metals. If none are found, further work is not necessary.

The principal difficulty with the quantitative analysis of hazardous wastes by XRF spectrometry is calibration. Although the best XRF work is done with an empirical calibration, one which uses standards which closely match the samples, this type of approach is not possible with most hazardous wastes. A laboratory at a treatment and disposal facility, an enforcement laboratory or a laboratory at a remedial action site often does not know what will be in the next waste it encounters. While XRF is ideal for qualitatively analyzing such wastes, as described earlier, quantitative analysis is not so straightforward. However, it is now possible to analyze samples by XRF spectrometry with only minimal standardization. A few standards are used

to calibrate the sensitivity of the spectrometer, but there is no need for close matrix matching of standards to unknown wastes.

Although empirical calibrations are still the most accurate and precise, great progress is being made in standardless analyses. These methods offer the possibility of quantitative analysis of hazardous wastes with acceptable accuracy. For most wastes, sampling is the source of the largest error. This is particularly true for solids, soils and viscous liquids. If the analytical error is kept under 20%, then the sampling error will be the dominant contribution to the overall error. Accuracies of 20% or better are possible with standardless calibration procedures.

Methods which rely on few standards, but instead are based on the fundamentals of X-ray physics, are called fundamental parameters methods. These methods take advantage of the well known behavior of X-rays and their interactions with matter. Using a few parameters such as the X-ray tube voltage, current and anode material, it is possible to predict the output of the tube. For each X-ray photon of a particular energy which strikes a particular atom in the sample, the probabilities of scattering or absorption are well known. The fluorescent yield of those atoms excited by the incident X-rays can also be predicted. Absorption or scattering of the emitted X-rays must also be considered. By integrating the above factors for the whole sample, the complete emission spectrum of any material can be predicted by calculation. It is more usual that the emission spectrum is measured and the composition of the sample is sought. This too can be done. With a given set of experimental conditions and an observed spectrum, the sample composition can be varied until the predicted spectrum matches the observed spectrum. Fundamental parameters methods rely on accurate data for fluorescent yields, absorption cross-sections, etc. and on only a few experimental parameters. These include geometric factors for instrumental design and some measure of detector sensitivity.

The basis for these methods has been understood for a long time. Development of practical fundamental parameters procedures has required the availability of extensive computer power and the talent of many researchers (Jenkins et.al, 1981). One of the more influential computer programs implementing the fundamental parameters approach was developed at the Naval Research laboratory (Criss et.al, 1978). This program required a mainframe computer, but similar programs have been written for personal computers. Programs such as these generally require that one

measurement for each element of interest be made from standards, which may be pure elements or compounds. They require that at least one emission line be measured for each element in the sample (except that one element can be determined by difference) and allow specification of a particular compound for a given element (such as an oxide). Fundamental Parameters programs have been shown to work well on such materials as metal alloys and the major elements in rocks.

There is one major limitation preventing the application of the fundamental parameters approach described above to the XRF analysis of hazardous wastes. Wastes often contain significant amounts of organic material, which, because of its light element nature, is not directly observed by conventional XRF spectrometers. The composition of the light element part of the sample matrix must be known if the fundamental parameters approach to quantification is to be successful. Fortunately approaches have been developed which allow estimation of the light element nature of a sample.

When X-ray photons impinge upon a sample, they are either transmitted, absorbed or scattered. There are two types of scattered radiation. Rayleigh (or coherent) scattering does not cause a change in wavelength. Compton (or incoherent) scattering produces scattered radiation which is of longer wavelength or less energy than the incident radiation. Each element is characterized by a different ratio between scattering and absorption and by a different ratio between Compton and Rayleigh scattering. Light elements scatter the most, and heavier elements absorb a higher proportion of incident X-rays. Thus the scattered X-rays contain information about the composition of the whole matrix, including the light element content.

A combination of the above approaches promises to provide standardless analysis for any sample. Characteristic line spectra are used to identify and quantify the heavier elements (sodium and above), and the scattered radiation is used to determine the nature of the light elements. The light elements are determined by comparing the measured scattered radiation with the calculated contribution to the scattering of the heavier elements. A fundamental parameters approach is used to adjust the sample composition until the calculated spectrum matches the experimental spectrum, including the scattered radiation. Since basic physical constants are used to account for absorption, scattering and fluorescence of each element, there is no need for standards which closely match the sample. A few standards, perhaps pure elements or standard reference

materials, are used to calibrate geometric factors and detector sensitivities.

Fundamental parameters programs which include scattering calculations to account for the light elements have been implemented by several investigators. Nielson (1977 and 1983) used the ratio of the incoherent scatter to the coherent scatter to characterize the light elements of the sample. This is done by using the scatter ratio to select two light elements whose concentrations are adjusted to give the appropriate light element atomic number, absorption and scattering. The program iteratively adjusts the sample composition, both light and heavy elements, until self-consistency is achieved and the calculated spectrum matches the observed spectrum. The spectrometer was calibrated with multielement thin films. The procedure was used to analyze coal, NBS orchard leaves, a soil and a ground rock with excellent results. Measured values were within two standard deviations of the reference values for most elements, which included major and trace elements. This type of procedure seems ideal for hazardous waste analysis because it does not require similar standards.

A similar approach has been implemented by Van Grieken and colleagues (Van Grieken et. al 1979; Van Dyck and Van Grieken, 1980). The ratio of coherent to incoherent scattered radiation was used to characterize the light elements. For a number of standard reference materials the absorption coefficients determined by this method were within 5% of the values calculated from the known compositions. Good results were obtained in the analysis of several reference materials. Calibration of the spectrometer was done with commercially available thin metal or compound films. There was no need for soil, rock or organic calibration standards to match the reference materials analyzed.

The preceding section has outlined the potential of fundamental parameters methods to provide virtually standardless analysis of a wide variety of materials. This potential has yet to be realized in the analysis of hazardous waste. However, the basis exists for the development of XRF methods for the quantitative analysis of hazardous wastes. In addition to programs developed by independent investigators, such as those mentioned above, some instrument vendors have developed similar programs. With the necessary computer programs becoming increasingly available, the tools for the development of standardless XRF analysis of hazardous waste are available. It should soon be possible to place a small subsample of any hazardous waste in an XRF spectrometer and within a few minutes know

its composition with an accuracy of 10 to 20% with limits of detection of about 10 ppm.

USED OIL

A very large amount of used oil is produced every year from vehicles and industrial sources. Much of it is burned as fuel, including a significant amount burned in small commercial and residential boilers. This large amount of used oil in commerce and its use as a fuel make it a convenient receptacle for hazardous waste. Spent halogenated solvents, often from degreasing, can be present in used oil. Sometimes this is inadvertent and sometimes intentional. The EPA assumes that if more than 1000 ppm chlorine is present in used oil, then halogenated solvents have been added to the used oil and the mixture is a hazardous waste. The mixture must be treated as a hazardous waste fuel. This presumption can be rebutted if the generator can show that the chlorine is not from chlorinated solvents. Another concern is the presence of toxic metals in used oil. Lead is often found in used automotive oil, although the amount has decreased over the last several years as the amount of lead in regular gasoline has decreased. If used oil contains more than 100 ppm lead or 4000 ppm chlorine, it is off specification used oil, and is subject to regulation. Burning oil high in chlorine will produce hydrochloric acid, which can cause corrosion in boilers. Lead in used oil which is burned can lead to hazardous emissions.

Thus there is a need to determine lead and total chlorine in used oil. Measuring total chlorine should be much easier than measuring individual chlorinated solvents by gas chromatography/mass spectrometry. The reference method for determining chlorine in oil should be combustion of the oil in an oxygen bomb followed by ion chromatographic analysis of the chloride in the combustate. This technique is slow and requires a skilled operator.

XRF analysis of used oil for lead and chlorine has much to recommend it. Little sample preparation is needed; the sample need only be placed in a disposable plastic cup, perhaps preceded by dilution. X-ray fluorescence spectrometry is an ideal way to determine chlorine in new oil, and is perhaps the method of choice because of its accuracy and precision. Indeed, ASTM has a XRF method for sulfur in oil (ASTM D-2622), and sulfur is similar to chlorine in XRF analyses. Used oils present a much tougher problem. Two principal reasons are sediment and water. Sediment is often present in oil, as a product of combustion or as particulates from machining. Since almost all XRF

spectrometers irradiate the bottom of the sample, sediment which settles to the bottom of the sample is a problem. If it contains the analyte, it will increase the reported concentration. In any event, the sediment is not representative of the oil matrix, and it will absorb X-rays emitted by chlorine in the oil matrix. Water can also be a problem. Used oil tanks often have considerable amounts of very dirty water on the bottom. Also, some cutting oils are water based with water miscible oils. Water can be a problem because it presents a substantially different matrix from the oil matrix used in calibration standards. An analyst may unknowingly attempt to analyze a very dirty water sample or a two phase sample with water on the bottom. Another problem is the often messy nature of used oils. The viscosity may reach that of a sludge. Three phases may be present; oil, water and sediment. Large amounts of sediment may be present, including some that settles very slowly. All these factors make oil analysis a problem. However, these factors complicate all analytical methods for used oil. XRF, if used properly, still has much to recommend it.

The most suitable methodology for the determination of chlorine in used oil by XRF is not yet completely defined, but the following describes possible techniques. Calibration should be done using a suitably spiked oil matrix. Mineral spirits, mineral oil, or a similar chlorine free material should be used. A readily available chlorinated hydrocarbon, such as 1-chlorodecane (available from Aldrich) is added. In the preparation of standards volatile compounds should be avoided in order to produce stable standards. Standards which include the range from 1000 to 4000 mg/kg should produce a linear calibration curve. Samples high in chlorine should be diluted to the linear portion of the curve. Of course, the K alpha peak of chlorine would be measured and suitably background corrected.

The main area of concern is whether the sample matrix matches the matrix of the standards. When it does XRF will give excellent results. The analyst should check this by preparing spiked samples. A spiking solution can be prepared in the same way as the calibration standards. If spike recoveries are not at least 85%, then the results for that sample should not be accepted. It is sometimes possible to improve results by diluting samples with mineral spirits. Dilution reduces the influence of X-ray absorbing sample constituents. In our laboratory used oil samples are often diluted by a factor of five. Until experience is acquired, it is best to treat each sample or type of sample separately, and spike them all.

XRF analysis is even more suitable for the determination of lead. This is because the X-rays emitted by lead are more energetic and penetrating than chlorine K alpha emissions, and thus less affected by the sample matrix. XRF is widely used to determine a wide variety of metals in petroleum products. XRF spectroscopy has been used for the determination of wear metals in used lubricating oil (Liu et. at 1986). Determining lead in all types of used oil is a similar measurement. The determination of lead can be done similarly to the XRF analysis of oil for chlorine. Standards containing lead in oil are available from Conostan (Conoco, Ponca City, Oklahoma). Detection limits for lead in oil are on the order of 10ppm, so at the regulatory limit of 100 ppm lead can be accurately determined. Our laboratory has had success using XRF to determine lead in used oil. Since preparation of oil samples for AA or ICP is a difficult task, additional development of XRF methods is well warranted.

## SUMMARY

The analysis of hazardous wastes is a complex and difficult task. Hazardous wastes are of widely varying chemical composition and physical characteristics. Improved accuracy and increased efficiency in their analyses are needed. Elemental analyses by X-ray fluorescence spectrometry have much to offer and should be considered as an alternative. XRF spectroscopy is an ideal way to determine toxic metals in contaminated soils, particularly when there are a large number of samples. It is now practical to semiquantitatively (within 25%) determine metals in waste samples with unknown or unique matrices. The theoretical calibration approach, fundamental parameters, can produce such results with minimal use of standards. Waste oils are a large volume waste stream particularly amenable to XRF analyses.

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92

# RECENT ADVANCES IN MEASURING MERCURY AT TRACE LEVELS IN THE ENVIRONMENT

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## ABSTRACT

The environmental significance of Mercury and numerous methods for measuring mercury have long been known. This paper will review and compare existing methods, then summarize recent advances in mehtodology including Cold Vapor Atomic Fluorescence. Emphasis will be placed on accuracy, sensitivity, practicality for routine operation and level automated through-put.

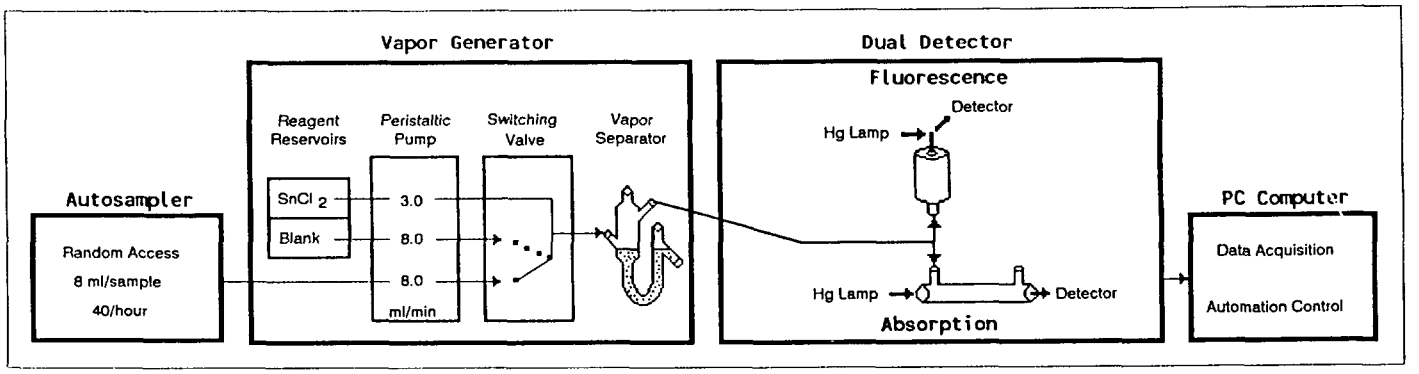
Methodology for a complete system will be described based on selected sample preparation, introduction and detection techniques. Sample preparation techniques include manual water bath digestions, automated flow-through heating bath digestions with heating coils and autoclaved batch digestions. Each is considered for accuracy, sample through-put, sample size, reagent conservation and labor requirements. Cold Vapor Sample Introduction techniques include manual batch generation, automated continuous generation and continuous generation with gold or silver amalgamation. Mercury detection methods include various configurations of Atomic Absorption and Atomic Fluorescence.

## INTRODUCTION

The determination of ultratrace concentrations of mercury by cold vapor atomic absorption and most recently, atomic fluorescence, has become widely accepted. Various techniques for both the continuous generation of mercury vapor and its detection have been reported. Nearly all of the methods are based on the reduction of mercuric ions to elemental mercury with $SnCl_2$, separation of elemental mercury from solution as a "cold vapor" and determination with a mercury specific spectrometer. There is still a need for a method that readily lends itself to routine operation, (excessive performance for practical usage). It would be a combination of techniques that are widely accepted yet flexible enough to incorporate the most recent advances. Routine methods should be EPA approved, simple and automated. These traits must be implemented without affecting sensitivity and accuracy. A method that addresses itself to these questions is presented in this paper.

## APPARATUS

A system was assembled with four common components; an autosampler, vapor generator, dual detector, and an industry standard computer (Figure 1). Automation is accomplished by continuous pumping of reagents and computer instrument control. A flow control valve alternates the reaction mixture between $SnCl_2$ plus Blank and $SnCl_2$ plus Sample. Mercury is then removed from the reaction mixture as a "cold vapor" by continuous aeration with a carrier gas. The detector has been specifically designed for conveniently interchanging atomic absorption and atomic fluorescence optics modules, both techniques are readily available to operate. Data acquisition and storage are handled by "Touchstone" (a unique software package), and a PC compatible computer.




## DISCUSSION

The reaction mixture, vapor-liquid separator and dual detector were designed for optimal performance. The reaction mixture ($SnCl_2$ plus Blank to $SnCl_2$ plus Sample) forms from a fixed ratio rates of 3 ml/min of $SnCl_2$ to 8 ml/min of blank or sample. The reaction mixing and aeration times are operator selected and valve controlled to allow for flexibility of sample types and concentration ranges.

The atomic absorption optics module was specifically designed and optimized for cold vapor mercury determination as described by EPA method 245.2. The atomic fluorescence module reflects the latest technique of mercury detection by EPA method 245.2. The atomic fluorescence module reflects the latest technique of mercury detection by emission rather than absorption. Since emission is inherently more sensitive than absorption, mercury detection at ppt levels becomes possible.

## Conclusion

For those operations which require measurement under EPA Method 245.2, the atomic absorption optics provides a detection limit well within the required minimum detection level of 0.2ppb. The fluorescence detection with detection limits well below 0.01ppb is then used to corroborate the AA results. Together they provide verified results which can withstand legal scrutiny.

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93

# The USE of ION CHROMATOGRAPHY in SOLID WASTE MATRICES;METHOD 300

John D. Pfaff and Carol A. Brockhoff

## Introduction:

The Environmental Protection Agency approved the use of method 300 for the analysis of nitrate in drinking waters in 1984. This constituted the first approved method for the use of ion chromatography to analyze drinking waters and/or wastewaters. The Environmental Monitoring Systems Laboratory (EMSL) in Cincinnati, Ohio has revised method 300 to bring current equipment into the method . Additionally matrices were investigated to extend the methods usefulness. This paper will cover the findings of the effort to use this method in matrices of interest in the solid waste field. The analysis of solid materials, groundwaters and leachates were investigated and single laboratory precision and bias data produced. The method has been sent to the Office of Solid Waste with EMSL's recommendations for acceptance as an approved method to be published in the Test Methods for Evaluating Solid Waste, SW846.

## Experimental:

In general, Method 300 is used to analyze the following common anions; fluoride, chloride, bromide, nitrate, nitrite, ortho phosphate and sulfate. Since these anions are extremely soluble in water it was felt that they could easily be extracted from solid materials and then analyzed through the use of ion chromatography. If this were shown to be the case the use of Method 300 could be extended into solid matrices.

Groundwater is also of great interest in the protection of the environment from solid wastes. Material disposed of on the surface or buried in the earth can migrate by percolation into aquifers or through a leaching technique by surface waters which then, in turn, contaminate groundwaters.

The method described here uses a chemically suppressed ion chromatograph with conductometric detection. The AG4A guard and the AS4A separator columns were used with the micro membrane suppressor. These items are produced by the Dionex Corp. The eluant used was 1.7 mM sodium bicarbonate ($NaHCO_3$) and 1.8 mM sodium carbonate ($Na_2CO_3$).

The author contacted the producers of standard reference materials but found no solid materials which had a known anionic content. Consequently an EPA quality control sample of shale (WP 386) was used. The material was first extracted with each technique under investigation to produce a background value. To produce a solid with all the anions of interest a volume of reagent water which had been fortified with the anions of interest was added to the solid and thoroughly mixed. The slurry was placed on a magnetic stirrer/hot plate and heated at a medium heat while stirring taking care not to let the mixture boil.

This was continued until little water was left. Then the slurry was transferred to an oven, heated at 95°C overnight and stored in a desiccator. Enough of the material was produced to allow all analyses needed in the study. Separate portions of the well mixed material was used to investigate recovery of the anions.

Solid Materials Extraction Technique:

The unfortified shale solid was used to evaluate the extraction techniques. Three techniques were evaluated, first; a volume of reagent water ten times the weight of solid material used was added to the solid . This slurry was then mixed on a magnetic stirrer for ten minutes then filtered and analyzed.

Secondly; again the ten times ratio of reagent water to solid was used. This time the slurry was sonicated for ten minutes then filtered and analyzed.

Thirdly; the same water ratio was used and heated to 60 C then placed in a sonicator while still hot and sonicated for ten minutes then filtered and analyzed.

The results of these extractions and analyses are shown in Table 1. Three anions were found in the unspiked shale;fluoride,chloride and sulfate. Each technique was carried out with four repetitions and the results compared. One gram of solid was used with ten milliliters of reagent water. The large concentration of sulfate present made comparison difficult and the values are suspect. However the fluoride and chloride values showed that the first extraction technique gave not only the higher recovery weights but also the most consistent and lowest standard deviation values. Consequently, this extraction technique was chosen and used to produce the remaining values.

The amount of solid used was investigated using weights of one, two and five grams of the spiked shale solid. The spike used was the same in all cases and consisted of the anions and

concentrations shown in Table 2. Each weight used was run twice and the average values compared. These values are shown in Table 3. It can be seen that for weights of 1 or 2 grams the value remains constant showing good extraction. Five grams of solid extracted may have overtaxed the volume of water used and gave poor comparison values.

The spike recovery values were obtained using weights of 2 and 5 grams of solid material. These values are shown in Table 4. It can be seen that values for fluoride are not usable. It is felt that two conditions contribute to these values. First, fluoride elutes in an area affected by the" water dip". This area is the result of the negative response to the reagent water which has less conductance than the eluant. Thus the positive fluoride peak fall in an area of negative background. Secondly, all retained anions elute in this area and add to the response of the fluoride peak making quantitation extremely difficult. The high concentration of fluoride in the blank makes the differentiation of 1 mg/liter of fluoride difficult to detect. Because of these effects it is felt that this method cannot at this time be recommended for the analysis of fluoride.

Although the solid shale was fortified with orto phosphate and sulfate the very high concentration of sulfate caused an overlape of the sulfate and ortho phosphate peaks and made quantitation difficult. Inorder to quantitate ortho phosphate and sulfate the concentration of sulfate that interfers with ortho phosphate will have to be determined. EMSL intends at a later date to investigate other solid materials which, hopefully, will have

lower background concentrations of sulfate and will allow further investigation of ortho phosphate and sulfate.

A chromatogram of the spiked shale solid extract is shown in Figure 1.

Leachates:

Inorder to mimic the effects of water percolating through a solid waste and then further into the ground EPA developed the Leachate technique. This technique utilizes a 24 hour extraction with water and the possible addition of 0.5 N acetic acid to adjust the ph. The technique stipulates that no more than 4 mL of acetic acid be used for each gram of solid material used. After the extraction is carried out the total volume of the liquid extract should be adjusted to 2000 mL. If 100 grams of solid material is used that would mean that a maximum acetic acid used would be 20 mL of 0.5 N acetic acid per 100 ml of water.

This same volume of acetic acid was added to reagent water and injected into the ion chromatograph. The resulting off scale peak has been superimposed onto a typical chromatogram of a spiked solid shale extract inorder to show which peaks would be lost if the maximum acetic acid is used in the leachate procedure. This is shown in figure 2. It can be seen that all anions from fluoride to bromide could not be detected.

Groundwaters:

The only precaution that should be taken prior to the analysis of a groundwater is to filter the sample if any

particulate material is present. This is to protect the columns of the chromatograph which cannot tolerate solids. With this exception a groumdwater would be the same as any other aqueous sample.

Summary:

Ion chromatography can be used to analyze anions in solids if preceded by a simple extraction technique. A solid sample, that is of a fine consistency, and weighing about 1 or 2 grams is extracted with a volume of reagent water ten times the weight of the solid material used and stirred on a magnetic stirrer for ten minutes. The resulting slurry is filtered and injected into the ion chromatograph. The resulting analysis can be used for chloride, nitrite, bromide, nitrate, ortho phosphate and sulfate.

Leachates that have not used acetic acid to adjust the pH can be analyzes after filtration. If acetic acid has been used the analyst can determine if any anions can be quantitated by putting the same concentration in reagent water and running it to see what area is covered over by the acetic acid peak.

Groundwater should not pose any problems for analysis by ion chromatography after filtration. This method has been published by the Environmental Monitoring Systems Laboratory, 26 W. M.L.King Drive, Cincinnati, Ohio 45268 as method 300.0, Revised 12/89.

Table 1: COMPARISON OF THE EXTRACTION TECHNIQUES

| Anion | Technique 1 10 min stir mg/L | | | | Technique 2 10 min sonicate mg/L | | | | Technique 3 Heat-sonicate mg/L | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| F | 6.3 | 6.4 | 6.5 | 6.5 | 4.7 | 4.8 | 4.2 | 4.0 | 1.9 | 4.3 | 5.1 | 5.2 |
| Cl | 10.6 | 9.6 | 9.8 | 10.5 | 10.0 | 10.1 | 9.1 | 8.4 | 7.4 | 9.4 | 8.9 | 8.7 |
| SO | 977 | 956 | 1014 | 1012 | 814 | 831 | 716 | 660 | 440 | 674 | 750 | 806 |
| | F | Cl | SO | | F | Cl | SO | | F | Cl | SO | |
| X | 6.4 | 10.2 | 990 | | 4.4 | 9.4 | 756 | | 4.1 | 8.6 | 667 | |
| Sd | 0.10 | 0.51 | 28.1 | | 1.54 | 0.87 | 161 | | 1.54 | 0.87 | 161 | |

TABLE 2 SPIKE USED

| Anion | Conc.(mg/L) |
|---|---|
| F | 1 |
| Cl | 10 |
| $NO_2$-N | 5 |
| Br | 5 |
| $NO_3$-N | 10 |
| $HPO_4$-P | 10 |
| $SO_4$ | 20 |

TABLE 3 COMPARISON of CHLORIDE for VARIOUS AMOUNTS of SOLID

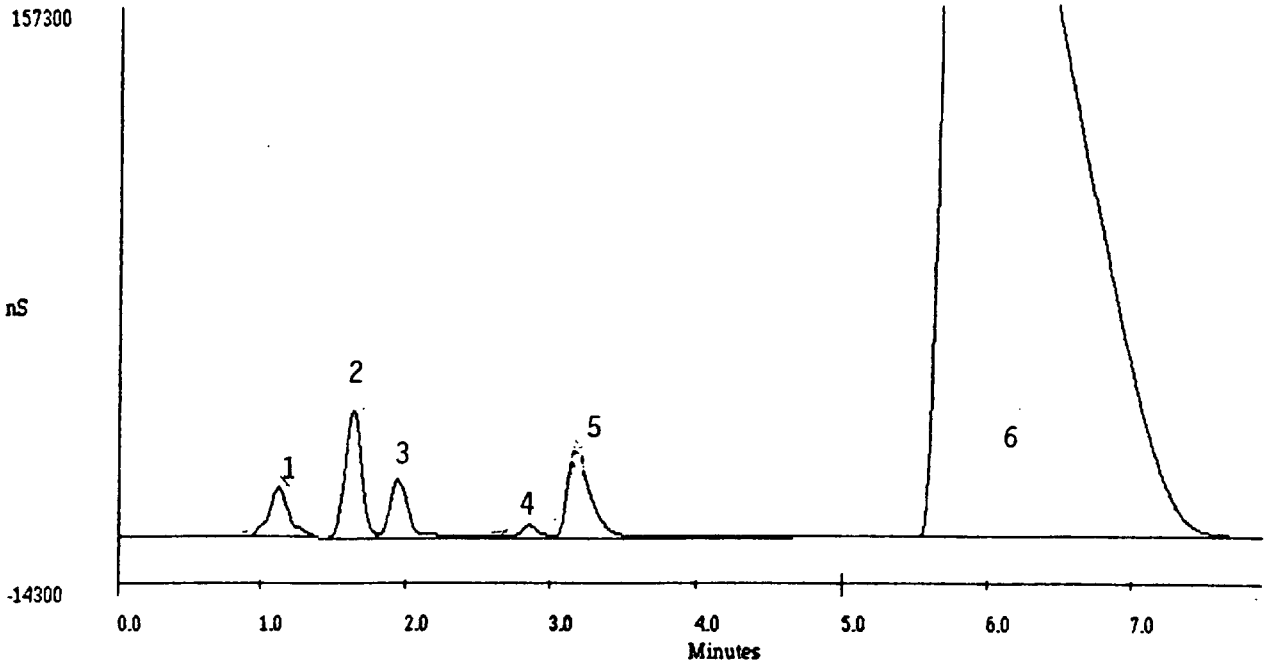
| Anion | Wt. of Solid grams | Recovery mg's | Water Used mL's |
|---|---|---|---|
| Cl | 1 | 10.1 | 10 |
| | 2 | 10.2 | 20 |
| | 5 | 8.5 | 50 |

TABLE 4 RECOVERIES of SPIKES

| Anions | Solid Used grams | Spike mg/L | Am't Found mg/L | Blank mg/L | % REC. |
|---|---|---|---|---|---|
| | 2 | | | | |
| F | | 1 | 4.5 | 6.5 | 0 |
| Cl | | 10 | 15.4 | 10.2 | 52 |
| $NO_2$ | | 5 | 3.7 | -- | 74 |
| Br | | 5 | 5.3 | -- | 106 |
| $NO_3$ | | 10 | 7.5 | -- | 75 |
| | 5 | | | | |
| F | | 1 | 6.3 | 6.5 | 0 |
| Cl | | 10 | 15.6 | 8.5 | 71 |
| $NO_2$ | | 5 | 2.8 | -- | 56 |
| Br | | 5 | 4.2 | -- | 84 |
| $NO_3$ | | 10 | 6.4 | -- | 64 |

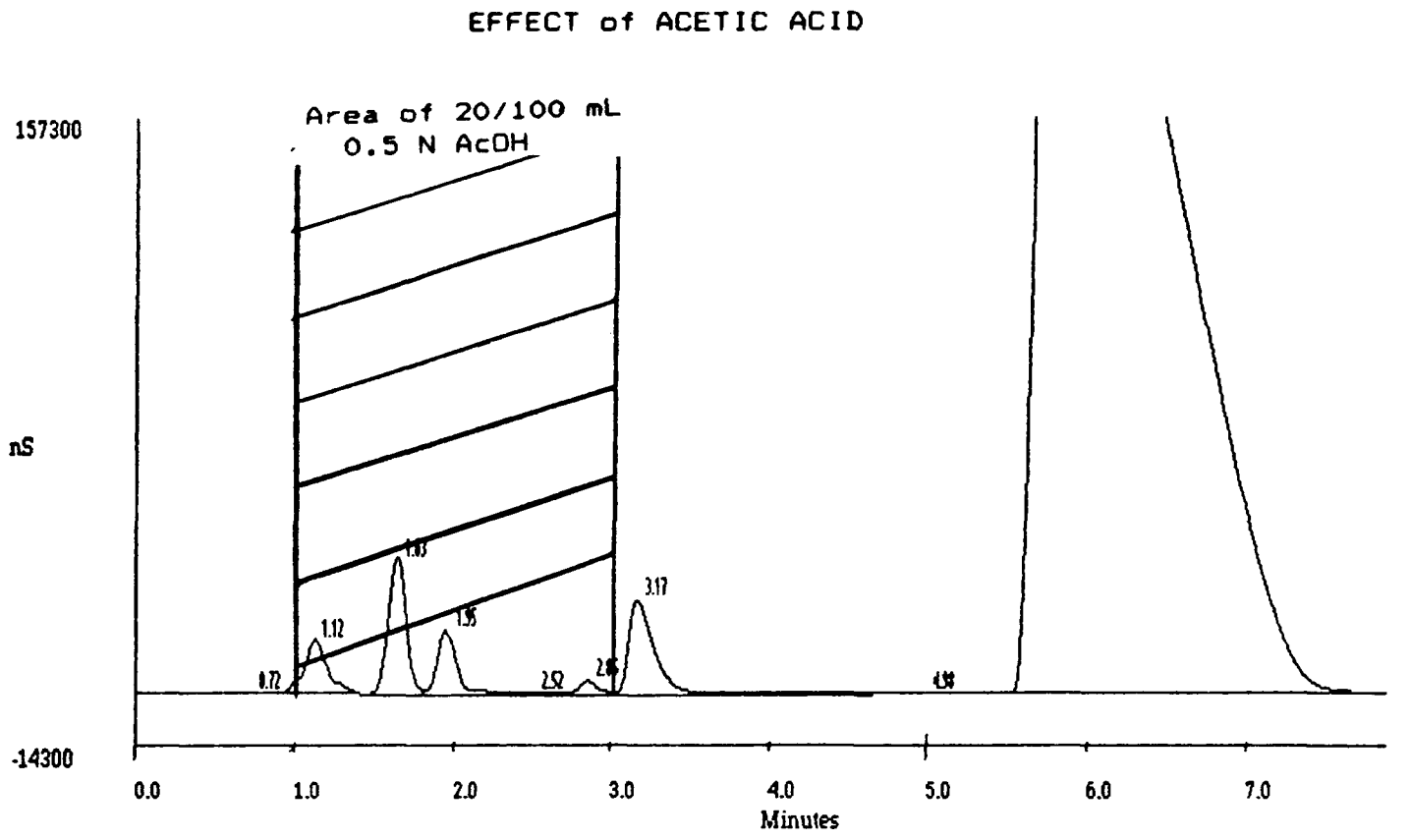
**Figure 1**

METHOD 300 EXTRACTION of SPIKED SHALE




| Anion | Peak Num. | Retention Time(min.) | % Rec. |
|---|---|---|---|
| F | 1 | 1.1 | 0 |
| Cl | 2 | 1.6 | 72 |
| $NO_2$ | 3 | 1.9 | 56 |
| Br | 4 | 2.9 | 84 |
| $NO_3$ | 5 | 3.2 | 64 |
| $SO_4$ | 6 | 5.4 | -- |

**Figure 2**


EFFECT of ACETIC ACID
Area of 20/100 mL
0.5 N AcOH
157300
nS
-14300
0.72
1.12
1.83
1.95
2.52
2.85
3.17
4.98
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Minutes

94

# THE DETERMINATION OF THE EFFECTS OF PRESERVATION ON NITRITE AND NITRATE IN THREE TYPES OF WATER SAMPLES UTILIZING TRAACS 800 AUTOANALYZER AND SINGLE COLUMN ION CHROMATOGRAPHY

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**ABSTRACT** Nitrite and nitrate are important parameters in ground water analysis. Excessive amounts of nitrates has been shown to increase the methemoglobin in the blood of infants. A 35-50% increase causes headaches, a 70% increase is lethal. Nitrite in acidic solutions forms nitrous acid which can react with secondary amines to form nitrosoamines, many of which are carcinogenic.

The 1989 EPA Federal Register states that unpreserved samples to be analyzed for nitrite and nitrate are to be kept at 4°C and analyzed within 48 hours. However, if samples are to be tested after 48 hours, the procedure states that the samples should be preserved with $H_2SO_4$ to pH<2 and stored at 4°C. Under these conditions, the samples have been allowed a 28 day holding time. Some states recommend acidification while others do not. Early indications in our lab suggested that nitrite was not stable in acidic solutions and was, in fact, converted to nitrate over time.

This paper describes the effects of preservation on nitrite and nitrate in ground, leachate and surface waters.

**INTRODUCTION** The stability of nitrite and nitrate in acidified and unacidified water were determined using a colorimetric method and ion exchange chromatography. The colorimetric method measures nitrite, after reaction to form a color complex, at 520 nm. Nitrate is reduced to nitrite and the combined nitrate plus nitrite is measured. The concentration of nitrate is determined by difference. Nitrite and nitrate separates on an ion exchange column using 2.5mM lithium hydroxide as the eluent. The separated ions are measured by UV detection at 214nm.

Tests were run on unpreserved reagent grade water and reagent grade water acidified to pH=2 and pH<2 with $H_2SO_4$. Acidified and unacidified water were spiked with nitrite at the following levels: 0.5, 1.0, 2.0 and 5.0 mg/L. Ground, leachate and surface water samples were run unpreserved and preserved, at pH=12, with NaOH. The three types of water samples, unpreserved and preserved, were spiked at the following levels: 0.5 and 1.0 mg/L nitrite for analysis on the TRAACS 800 and 10.0 and 50.0 mg/L nitrite for analysis using Waters Ion Chromatograph. Prior to analysis on the IC, samples were diluted 10-fold and filtered through a 0.45 micron filter. Samples for the colorimeteric method were filtered through a 0.45 micron filter prior to analysis.

**Experimental:**

Apparatus: The colorimetric instrumentation used was a Bran & Luebbe TRAACS 800 AutoAnalyzer segmented flow system with the following components:

- .Random Access Autosampler sampling at 120 samples/hour.
- .Multi-test cartridge for nitrite.
- .Multi-test cartridge for nitrate + nitrite.
- .Reagent Sequencer.
- .IBM PC PS/2 30 data system.
- .UV/VIS Detector @ 520nm.

The chromatographic instrumentation used was a Waters Single Column Ion Chromatography system with the following components:

- .510 Pump, flow rate @ 1.2ml/min.
- .712 WISP Autosampler, 100ul loop.
- .IC-Pak Anion Column
- .In-line Precolumn Filter
- .441 UV Detector @ 214nm
- .840 Data Handling System

In the colorimetric reaction nitrate, which has undergone reduction to nitrite, and nitrite originally present reacts with sulfanilamide to form a diazonium salt. This couples with N-(1-naphtha)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured at 520nm.

In the chromatographic system, 2.5mM lithium hydroxideis used as the eluent and the species monitored using UV detection at 214nm.

**Reagents and Chemicals:**

Colorimetric Method:

- .Cupric Sulfate ($CuSO_4.5H_2O$)
- .Brij-35, surfactant.
- .Hydrazine Sulfate ($N_2H_4.H_2SO_4$)
- .Hydrochloric Acid (HCl)
- .N-1-Naphthylethylenediamine dihydrochloride. ($C_{12}H_{14}N_2.2HCl$)

.Phosphoric Acid, conc. ($H_3PO_4$)

.Potassium Nitrate ($KNO_3$), standard

.Sodium Hydroxide (NaOH)

.Sodium Nitrite ($NaNO_2$), standard

.Sulfanilamide ($C_6H_8N_2O_2S$)

Ion Chromatography Method:

.Eluent
- $LiOH/H_2O$
- Boric Acid
- D-Gluconic Acid
- Glycerin
- Acetonitrile

.Wescan 200 ppm Nitrite Standard

.Wescan 200 ppm Nitrate Standard

## RESULTS AND DISCUSSION

Reagent grade water spikes stored at $4^oC$ and unpreserved showed no deterioration of nitrite or nitrate during a thirty day test period. Water samples (ground, leachate and surface) stored at $4^oC$ and unpreserved showed stable nitrite concentrations from 14-37 days. The surface water showed some deterioration of the nitrite after 14 days. This is believed to be caused by conversion of nitrite to nitrate by bacteria present in the surface water. (Fig.1-4)

Reagent grade water spikes stored at $4^oC$ and acidified with $H_2SO_4$ showed immediate deterioration of nitrite to nitrate while nitrate remained stable. This would explain the poor nitrite spike recoveries experienced in the lab during routine analysis. Total conversion of nitrite to nitrate in 14 days was seen in water preserved to pH<2. (Fig.5-6)

The water samples referred to above stored at $4^oC$ and preserved with NaOH to a pH=12 showed excellent stability of nitrite out to 37 days. No conversion of nitrite to nitrate was seen during this test period.It is believed that at this high pH, bacteria that effects nitrite conversion was not present. Nitrate was seen to be stable in both acidic and alkaline conditions. (Fig.7-9)

**SUMMARY**

Past practices of acid preservation will not allow for accurate nitrite determination due to conversion of nitrite to nitrate within a 24 hr. period. Samples kept at 4°C with no acid preservation showed better stability, while samples that were base preserved showed excellent stability. Base preservation appears to eliminate nitrite conversion caused by bacterial action.

Base preservation seems to be the method of choice to obtain accurate determination of both nitrite and nitrate while still having a holding time of more than 28 days.

NITRITE/NITRATE STABILITY STUDY

Surface Water Unpreserved

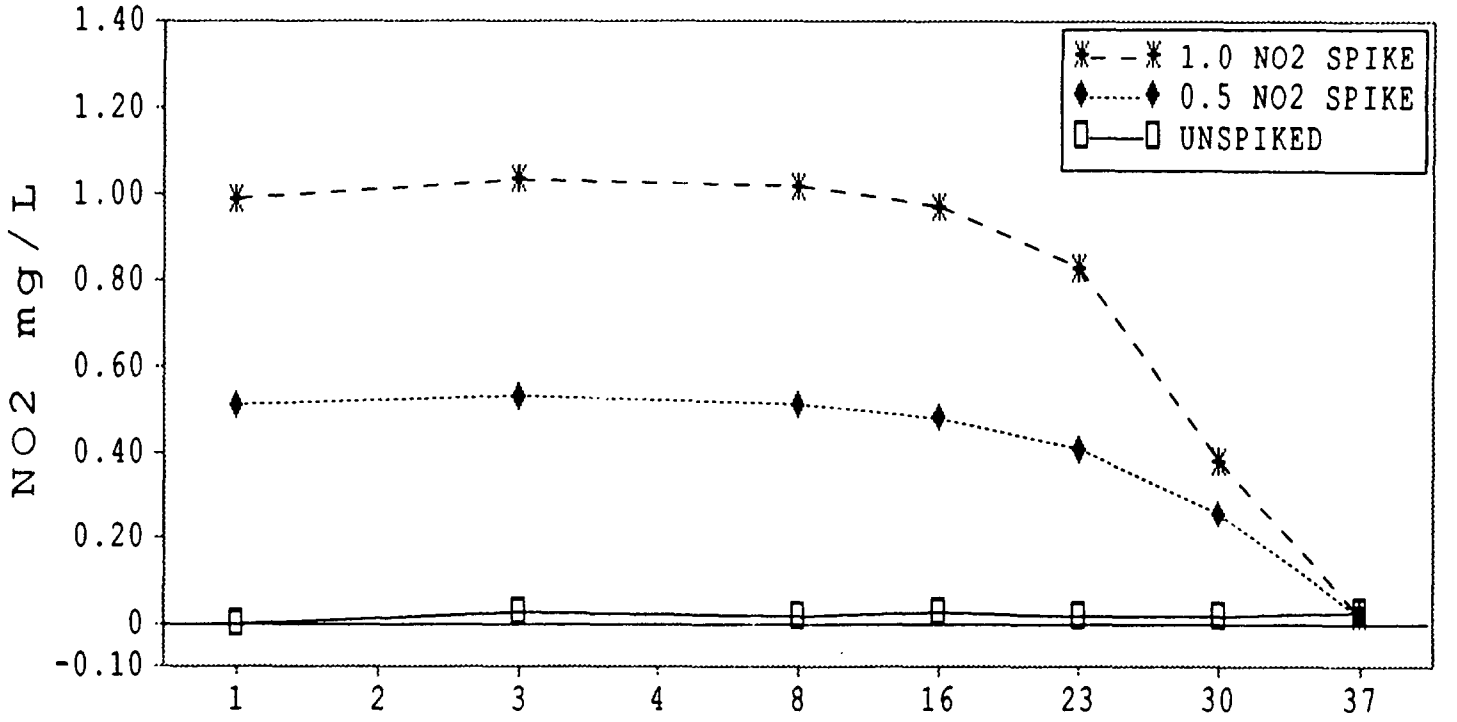


FIG. 1

NIRTITE/NITRITE STABILITY STUDY

Surface Water Unpreserved

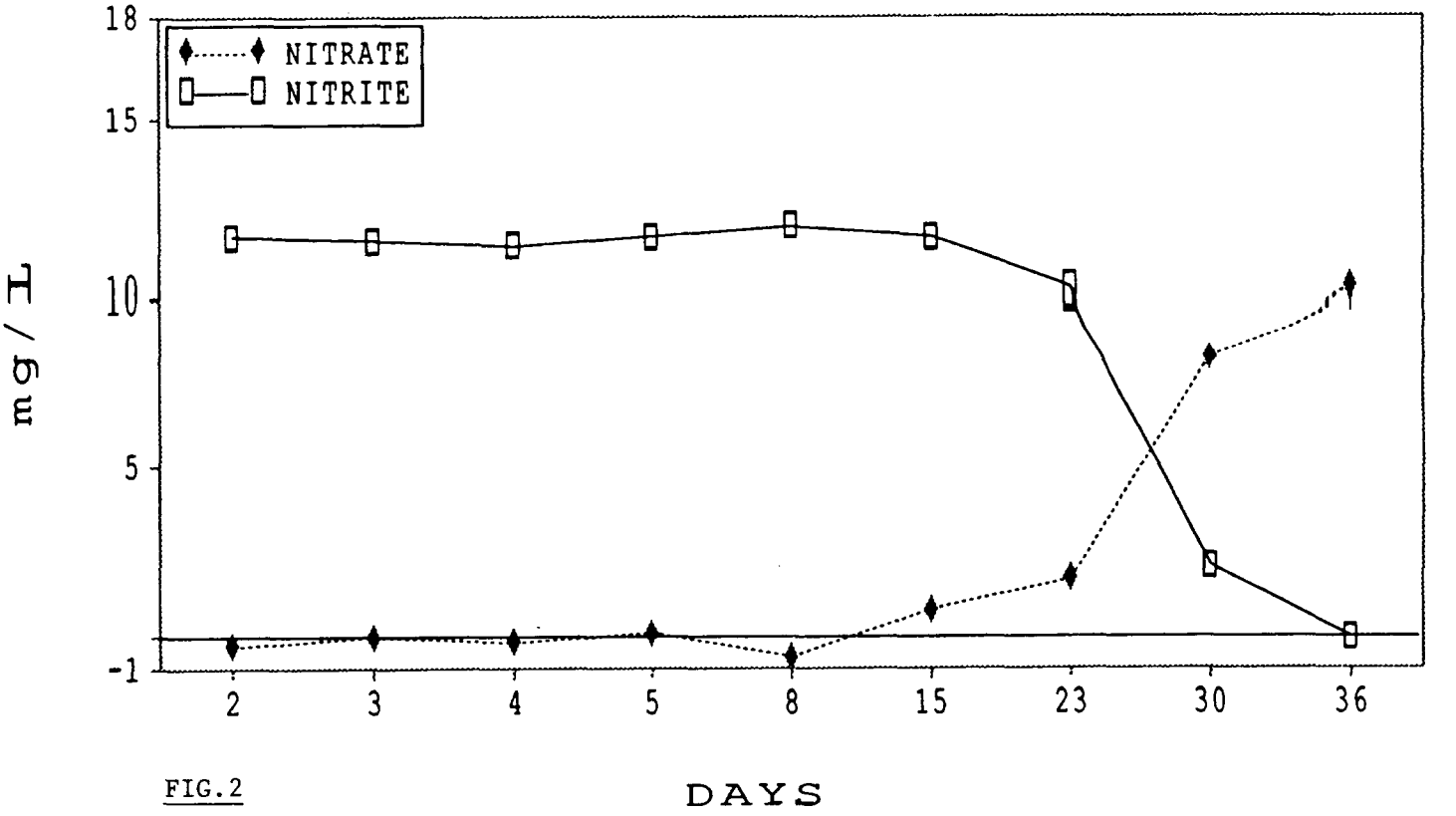


FIG.2

NITRITE/NITRATE STABILITY STUDY

Ground Water Unpreserved

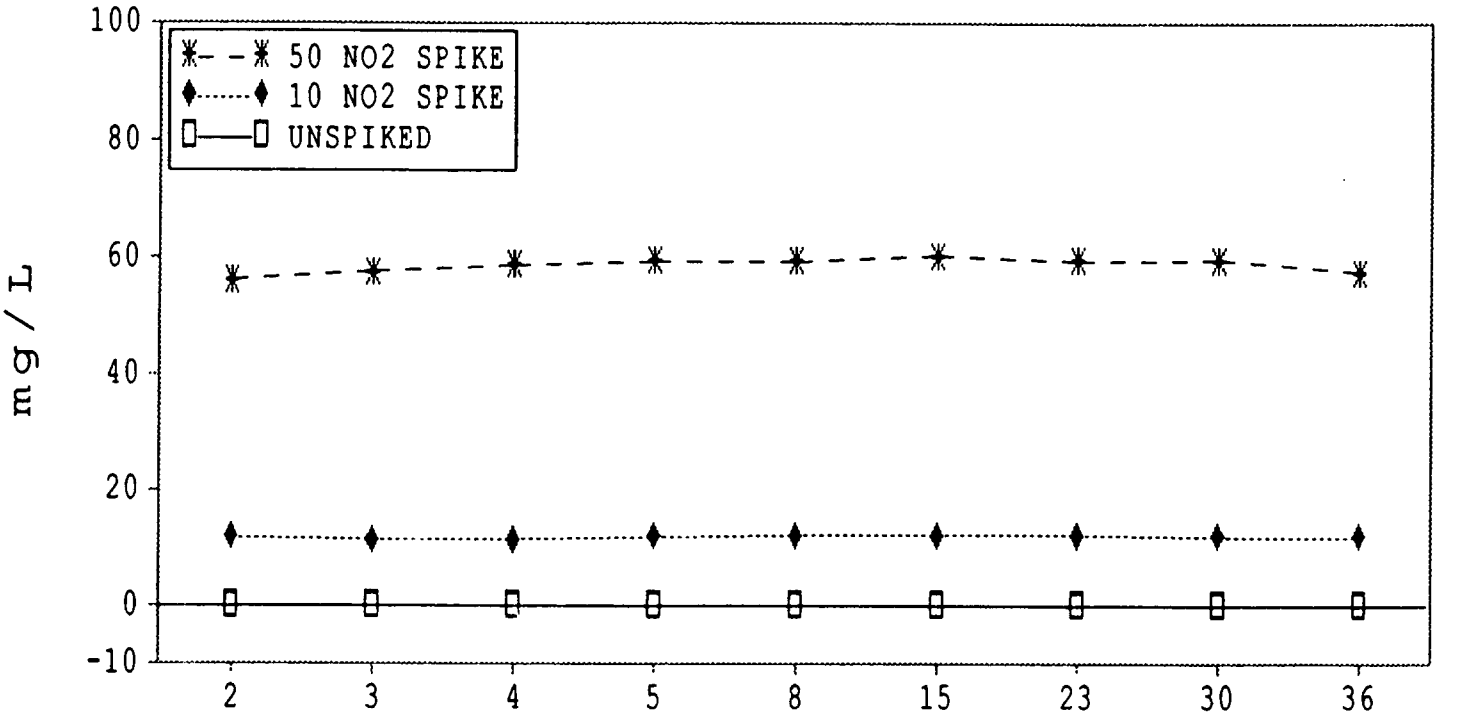


FIG. 3

NITRITE\NITRATE STABILITY STUDY

Leachate Water Unpreserved

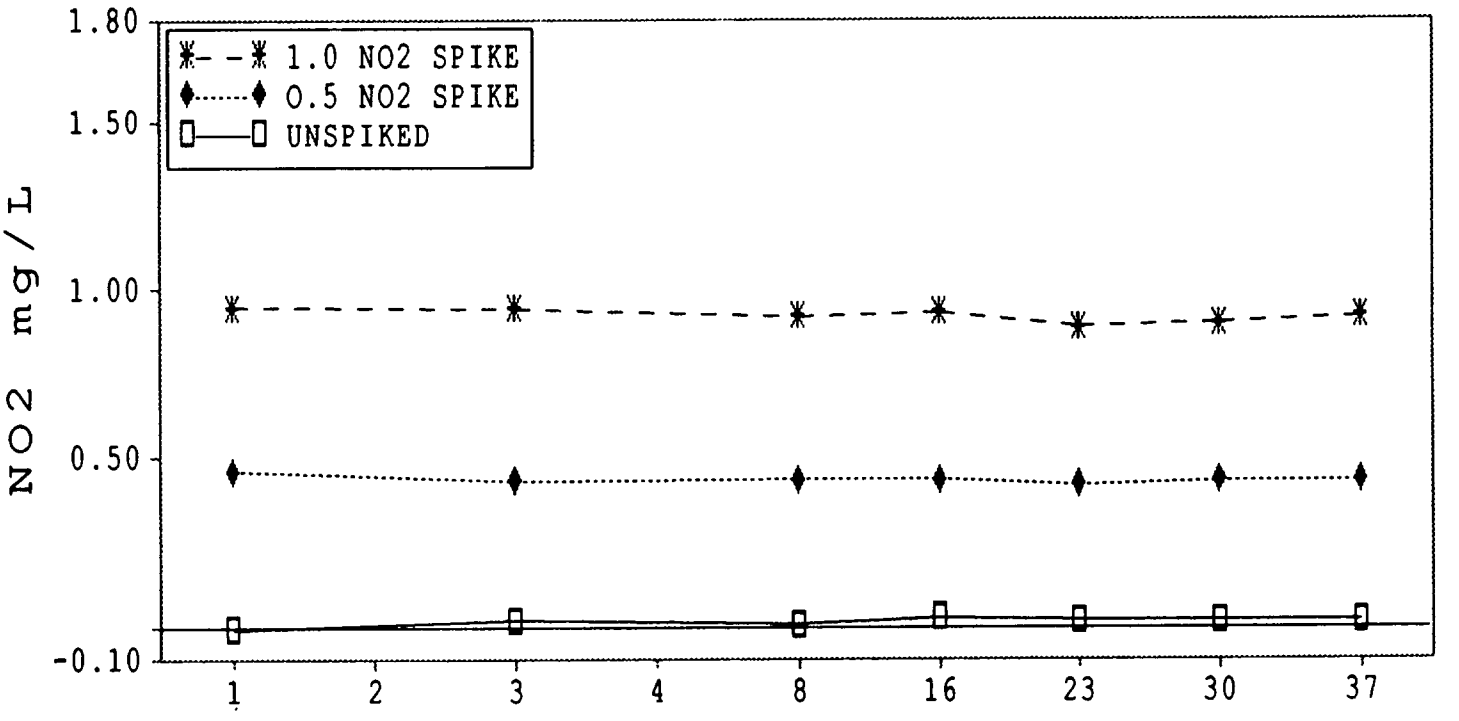


FIG. 4

NITRITE/NITRATE STABILITY STUDY

NITRITE SPIKED WATER ACIDIFIED pH=2

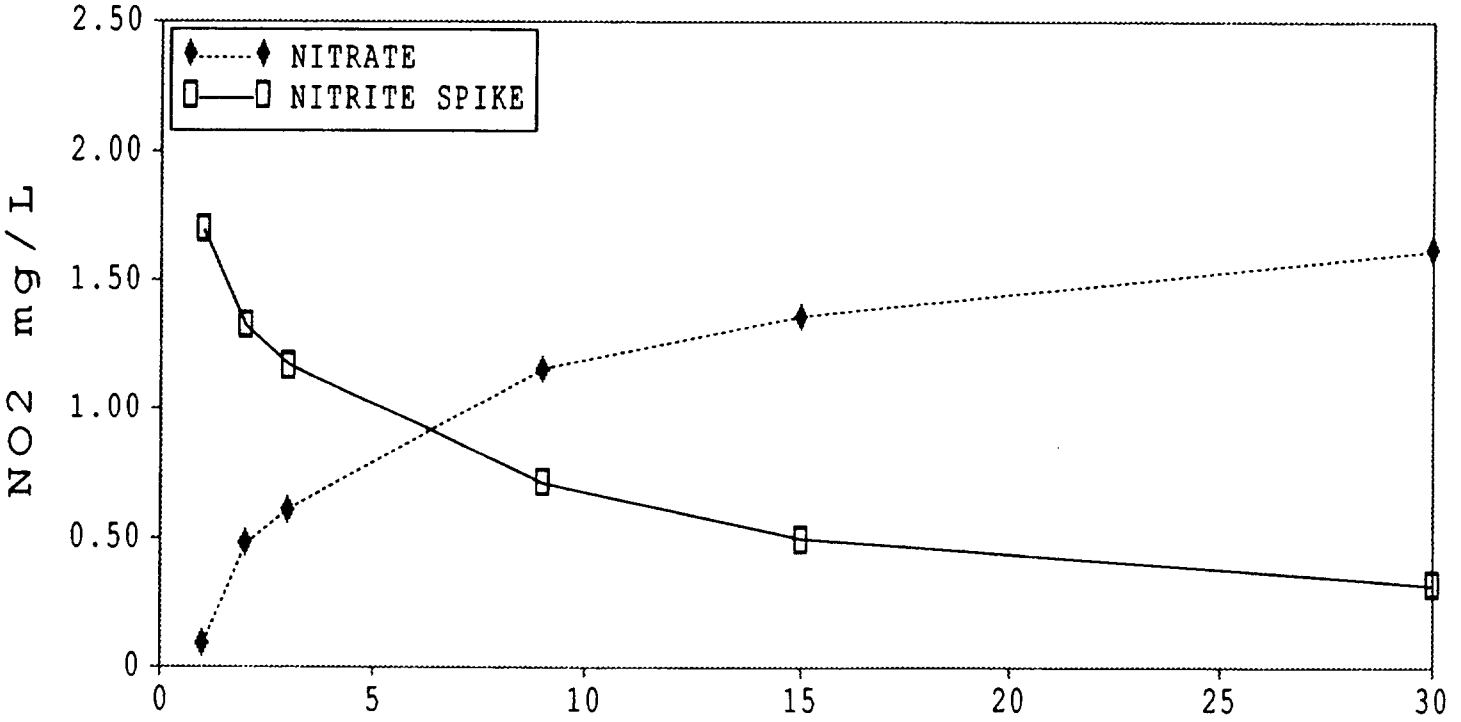


FIG. 5

NITRITE/NITRATE STABILITY STUDY

Nitrite Spiked Water Acidifed pH<2

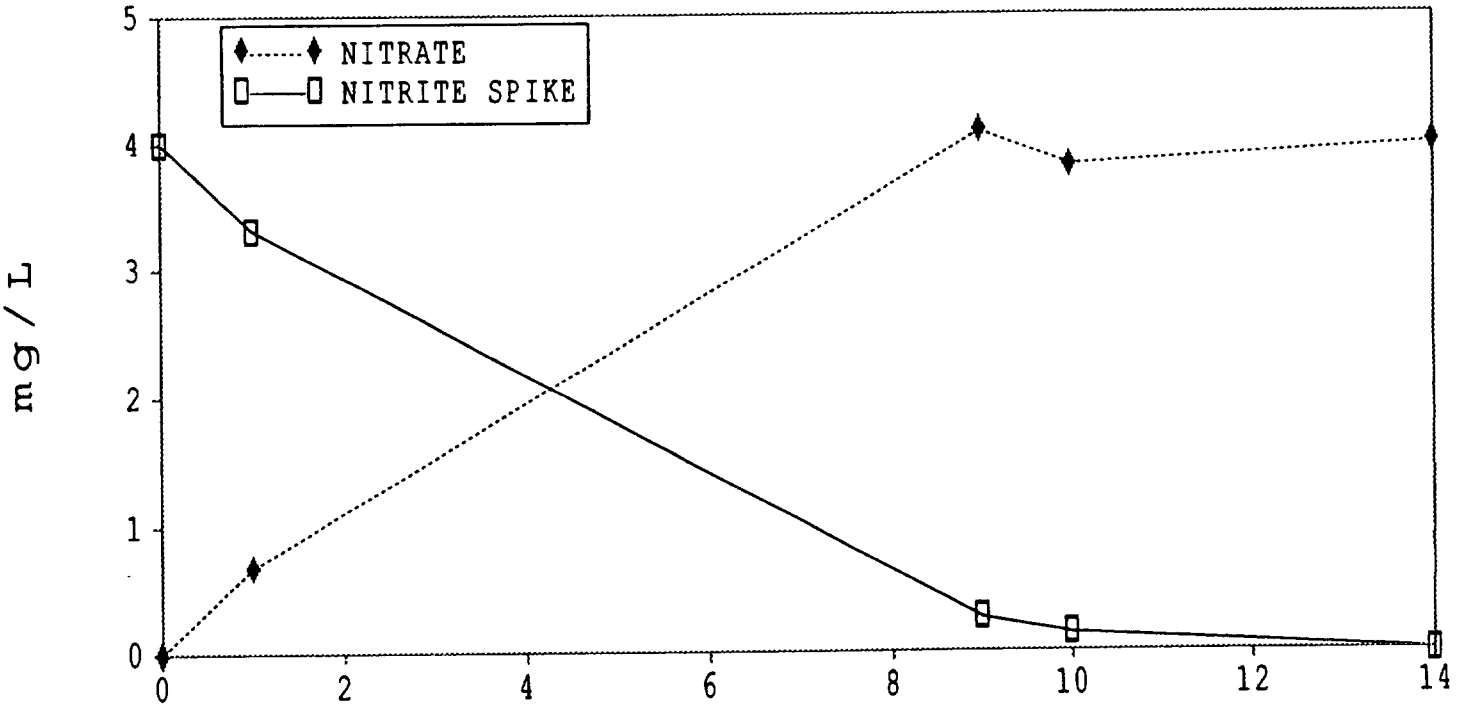


FIG. 6

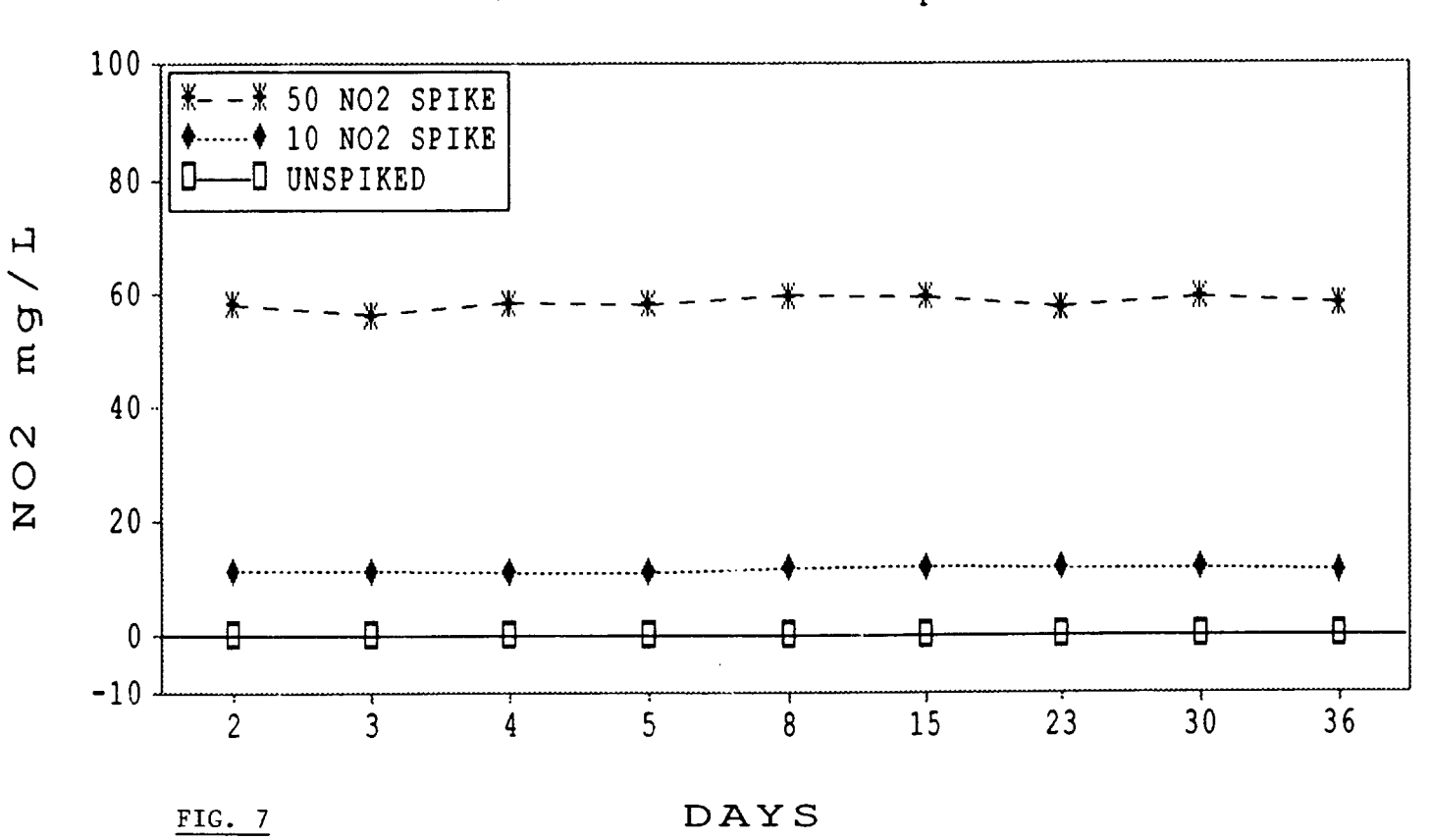
NITRITE/NITRATE STABILITY STUDY
Surface Water Preserved pH=12
50 NO2 SPIKE
10 NO2 SPIKE
UNSPIKED
NO2 mg/L
100
80
60
40
20
0
-10
2
3
4
5
8
15
23
30
36
DAYS

FIG. 7

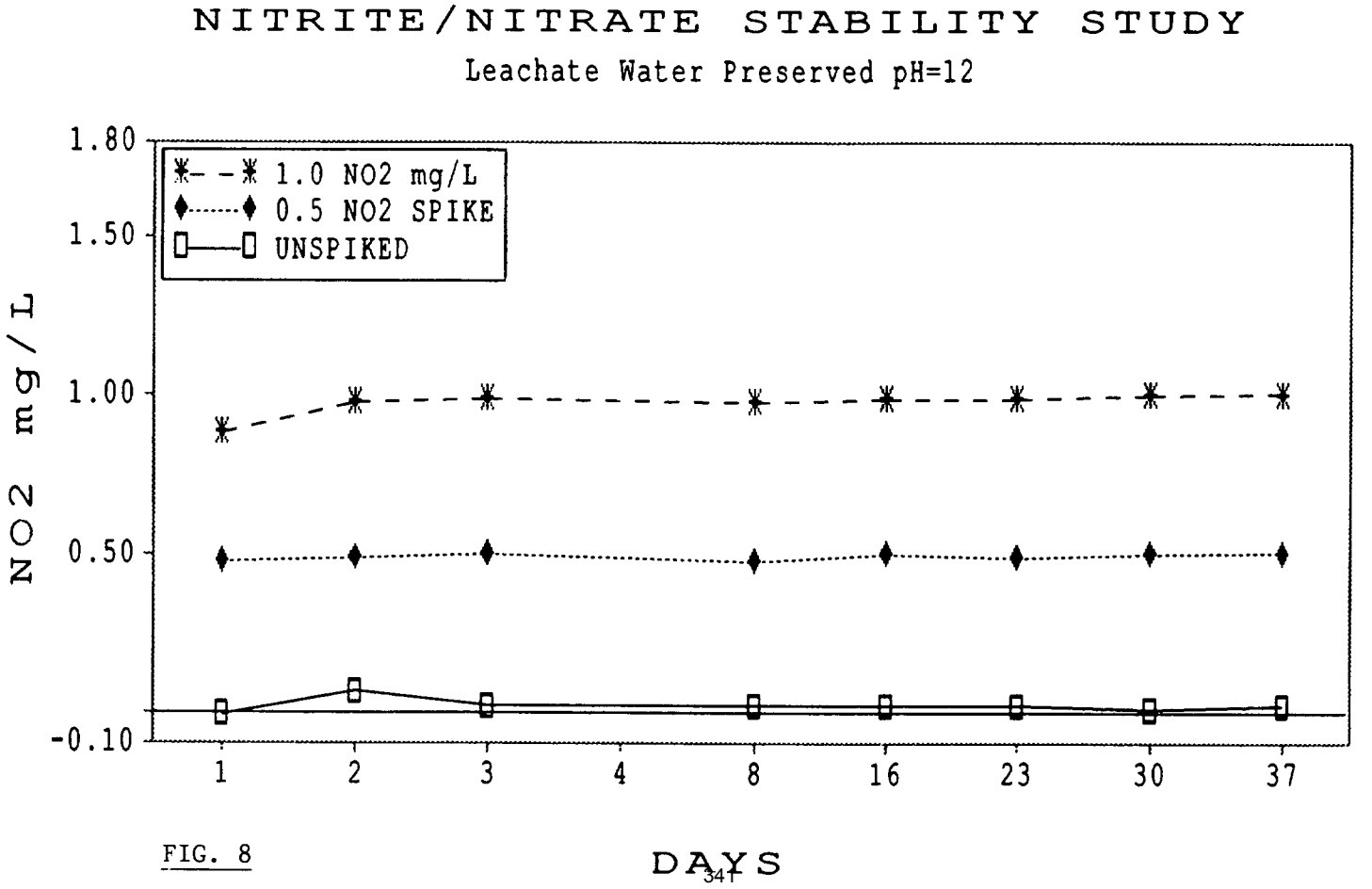
NITRITE/NITRATE STABILITY STUDY
Leachate Water Preserved pH=12
1.0 NO2 mg/L
0.5 NO2 SPIKE
UNSPIKED
NO2 mg/L
1.80
1.50
1.00
0.50
-0.10
1
2
3
4
8
16
23
30
37
DAYS

FIG. 8

# NITRITE/NITRATE STABILITY STUDY

## Ground Water Preserved pH=12

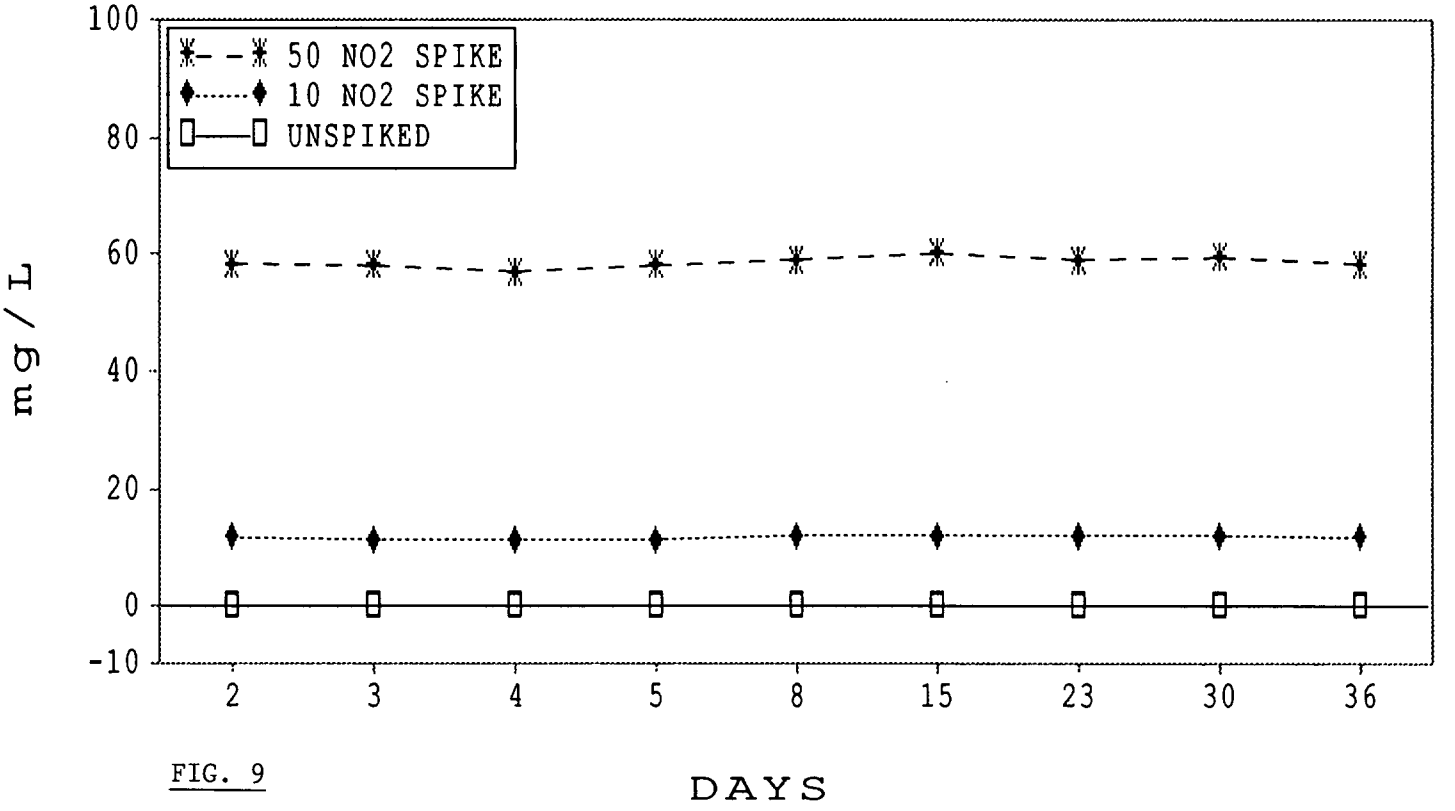


FIG. 9

95

# A STUDY OF THE EFFECTIVENESS OF SW 846 METHOD 9010 FOR THE DETERMINATION OF TOTAL AND AMENABLE CYANIDE IN HAZARDOUS WASTE MATRICES

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## ABSTRACT

Recently imposed regulations on the hazardous waste industry include specific levels for Total and Amenable Cyanide. Precise measurements of these parameters at these regulatory levels are critical. The accepted method for the determination of these analytes is EPA SW 846 Method 9010. Cyanide amenable to chlorination is the result of the difference between two total cyanide measurements; the first on the sample "as is" and the second on the same sample that has been treated with hypochlorite. Since chlorination is intended to break down cyanide, the second total cyanide level should always be less than the first result (before pretreatment).

The applicability of this method for hazardous waste matrices is evaluated in this paper by: 1) investigating the factors that influence the performance of this method; 2) examining cyanide amenable to chlorination results that are negative; and 3) proposing potential solutions to the problems encountered.

## INTRODUCTION

The recently mandated Land Disposal Restrictions as found in 40CFR Part 268, impose regulatory levels on total and amenable cyanide concentrations for land disposal. Some of the waste codes have regulatory levels associated with them that are quite low which will make accurate and precise measurements of these components critical. The accepted method for the measurement of total and amenable cyanide is SW-846 Method 9010 2nd Ed. Although this method may perform well in water and related matrices, its performance in hazardous waste matrices is in question. The purpose of this paper will be to evaluate applicability of this method when used to determine total and amenable cyanide concentration in hazardous waste matrices, and to be able to better understand the information provided by the results of Method 9010.

## CYANIDE AMENABLE TO CHLORINATION

A major part of Method 9010 is devoted to determining cyanide amenable to chlorination. Cyanide amenable to chlorination is actually the difference between two total cyanide analyses. A sample is split into two equal test portions: the first is used to determine total cyanide concentration, and the second test portion is subjected to an alkaline chlorination procedure and then analyzed under the identical conditions as the first test portion

to determine the total remaining cyanide concentration. It is the difference between these two "total" cyanide analyses that is defined as the cyanide amenable to chlorination. It is the intention of the alkaline chlorination to destroy the cyanide present in the waste material. As a result of this, the cyanide remaining after chlorination should always be lower than before the chlorination step. We have observed that when working with hazardous waste matrices, this is frequently not the case. It is a very common occurrence for the cyanide amenable to chlorination to have a negative result due to the fact there is a higher concentration of cyanide remaining following chlorination than was present in the test portion that was not chlorinated.

This situation presents a dilemma to those disposing of cyanide-bearing hazardous wastes. It is entirely possible that the total cyanide concentration will be below the appropriate regulatory level for a particular waste (when analyzed by Method 9010), but when it is subjected to alkaline chlorination the resultant cyanide concentration is above the regulatory level. In this case, the result for cyanide amenable to chlorination is negative. Although in this scenario, the waste would be acceptable from a legal standpoint, the chemistry that supports the evaluation of this waste does not always work. In fact, the guidance from the EPA in reference to this scenario is that a negative result for cyanide amenable to chlorination is to be considered "zero," which will be below the regulatory level, thus, making the material acceptable for disposal. Obviously, there was more cyanide present than was originally detected by the total cyanide analysis, but because the higher result of the cyanide analysis following chlorination is only used for calculating purposes, the information that this result provides is ignored.

One might propose many ideas as to why more cyanide is detected following chlorination than before. A discussion of some of these theories follows. It must, however, be understood that the exact cause of this phenomena is not yet known or understood and that the following discussion explores only possibilities that may influence this occurrence.

One idea is that when hypochlorite is added to the sample to break down the cyanide it introduces an interference into the distillate. The assumption is that upon completion of the chlorination step some of the chloride remained in solution and distilled over with the HCN gas. In order to investigate this possibility, several distillate samples were analyzed for chloride. It was determined that all of the distillates that were analyzed contained less than 10 ppm chloride, and it was decided that this possibility of interference could be disregarded.

One theory as to the cause of higher results for total cyanide after chlorination than before is due to the complexation of cyanide with various metals. Although in some cases these compounds are easily dissociable and quantitated; some are not--such as $Fe[CN]_x$ complexes. This theory assumes that the cyanide complexes that are dissociable will be broken down in the acid reflux distillation while the nondissociable

cyanide complexes will not. Upon the addition of hypochlorite into these materials which contain nondissociable cyanide complexes to oxidize the cyanide, some of the metals are also oxidized thus weakening the complex. When these treated materials are now subjected to the acid reflux distillation the cyanide associated with these complexes will also be released, producing HCN gas.

To investigate the relationship between metal content and cyanide amenable to chlorination results, the metal content for samples which had both higher and lower cyanide concentrations following chlorination were reviewed. Review of the data did not seem to provide any definite answers to the problem of higher cyanide concentrations following treatment with hypochlorite. However, this information does propose some interesting suggestions. In looking at the matrices presented in both cases, it was noted that there are similar matrices in both situations. This suggests that this problem is not matrix specific unless all hazardous wastes are to be considered one matrix. Also, there does not seem to be any definite trend corresponding to one metal affecting a recovery as there seem to be high levels of the same metals in both cases.

In considering the vast array of matrices that qualify as hazardous waste, Figures 1 - 6 show the concentration of cyanide before and after chlorination in several different matrices.

It can be concluded from the these graphs that in each matrix studied, with the exception of aqueous and cyanide by-product matrices, that the problem with recoveries before and after chlorination is not matrix specific. Another conclusion that can be drawn about these negative cyanide amenable results is that all of the data presented here indicate that much more study needs to be done so that this problem can be thoroughly understood.

## TOTAL CYANIDE

In order to better understand the problems associated with the cyanide amenable to chlorination results, a greater knowledge of all of the contributing factors used to determine cyanide concentration by Method 9010 must be achieved. There are several variables inside of the method that will drastically affect the performance of this method. They are: distillation time, test portion size, particle size, effectiveness of the sulfuric acid, and the efficiency of the quantitation procedure used. Once the effects of all of the variables have been taken into account, perhaps it will be easier to evaluate the information provided by the results of this method.

## DISTILLATION TIME

The section of Method 9010 which contains the instructions that pertain to the actual distillation step is Section 7.3.4 which gives the following instructions:

> "Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for 1 hour. Turn off the heat and continue the airflow for at least 15 min."

This step incorporates many variables which are not entertained in the evaluation of the data that this method produces. The actual length of time that the sample is heated is directly proportional to the recovery of cyanide in the absorber tube. This is illustrated in Figures 7 - 9. These figures present the results of 3 actual hazardous waste samples of varying cyanide concentration where all parameters of the distillation were held constant except for the length of time they were distilled.

Figure 7 illustrates the results of an incinerator ash sample of low cyanide concentration (<40 ppm), where a 10g sample size was used. The length of distillation time was varied by one-half hour intervals. As can be seen from this graph, the recovery of cyanide tends to increase as distillation time increases.

Figure 8 illustrates the results of a sample of moderate cyanide concentration (500 - 4000 ppm), where a 10g sample size was used. The length of the distillation time was varied by one-half hour intervals. As can be seen from this graph, the recovery of cyanide increases as distillation time increases.

Figure 9 illustrates the results of a copper cyanide waste sample of high cyanide concentration (2-5%), where a 1g sample size was used. As can be seen from this graph, the recovery of cyanide increased initially but then leveled off as the distillation time increased.

Several conclusions can be drawn about the dependency of the recovered cyanide on the length of the distillation procedure. It seems that when working with materials with a cyanide concentration less than 1%, the amount of cyanide which is recovered is directly proportional to the length of the distillation process. This particular study only covered a five-hour time span, but it is believed that this relationship would continue. It would be difficult to determine when all of the cyanide would be distilled because these tests were performed on actual hazardous waste whose exact total cyanide concentrations are unknown.

In Figure 9, when a material with a high concentration of cyanide was distilled, the recovered cyanide seemed to level off after just one hour, which may indicate that only a certain portion of cyanide will be distilled regardless of how long the distillation period. Another possible source of error could be that the sodium hydroxide in the scrubber will only trap a certain amount of cyanide which this sample might have exceeded. Both of these possibilities will require further investigation.

In looking at the data, one will also notice points that seem to be out of line with that particular graph's trend. It is believed that this may have been due to inconsistency in the heating mantles, which may point out another potential source of error in this procedure. Perhaps the temperature at which the samples reflux will also effect the recovery. This point would be especially significant at the beginning of the distillation process when the procedure calls for heating to boiling, prior to the reflux period. A quicker heating period may have a differing result possibly lower than a slower and consequently longer heating period. The increased distillation time, in turn, would increase the amount of cyanide recovered as shown by the graphs in the above section.

## SAMPLE SIZE

The only guidance in the method regarding the size of a test portion states that a sample aliquot of 500 ml or a sample volume diluted to 500 ml should be used. This seems to imply that only liquids can be analyzed by this method. Since this is the same method being used on hazardous wastes, most of which is of a solid or semi-solid type matrix, there really is no clear guidance as to what is a suitable test portion size. When duplicate analyses were run on some samples, it was noticed that the amount of cyanide that was recovered differed significantly. Upon investigation, it was observed that the only variable that was different was the size of the test portion used for each distillation. This indicated that the recovery of the cyanide was dependent upon the size of the test portion that was analyzed. The relationship between sample size (with all other variables held constant) and cyanide recovery is illustrated in Figures 10 - 13.

Figure 10 illustrates the effect of varying the test portion from 1g to 100g on a material of relatively low cyanide concentration (25 - 200 ppm). As can be seen from this graph, the amount of cyanide recovered decreases as the test portion increases.

Figure 11 illustrates the effect of varying the test portion from 1g to 100 g on a material of a relatively moderate cyanide concentration (500 - 5000 ppm). As can be seen from this graph, the amount of cyanide recovered decreases as test portion increases.

Figure 12 illustrates the effect of varying the test portion from 0.25g to 50g on a sample of relatively high cyanide concentration (2500 ppm - 20%). The reason that the test portion range is lower in this graph is due to the high level of cyanide present in the material. Again, the amount of cyanide recovered decreases as the test portion increases.

Figure 13 illustrates the effect of varying the test portion from 0.25g to 10g on a sample of approximately twice the cyanide concentration as Figure 6. Again, the reason for the lowered test portion range is due to the high level of cyanide present in the material. Once again, the same relationship, although not as dramatic, seems to be present with the

amount of cyanide recovered decreasing as the test portion is increased.

The obvious conclusion that can be drawn from these data is that the sample size is inversely proportional to the amount of cyanide that is recovered from the distillation. This relationship, however, did seem to decline in proportion when working with high level cyanide containing samples (concentrations >2%).

## EFFECTIVENESS OF THE SULFURIC ACID

The most basic assumption of Method 9010 is that when sulfuric acid is added to a sample it will liberate HCN gas. The gas is then bubbled through sodium hydroxide to convert the HCN to NaCN, and it is the NaCN which is subsequently quantitated. The first comment when discussing the performance of this method always seems to be that since many of the matrices subjected to this analysis are of a caustic nature that the amount of acid is not sufficient to lower the pH so as to provide the proper conditions for HCN to be formed. Figures 14 - 16 present the information gathered when investigating this potential problem.

Figure 14 illustrates the pH in the distillation flask following the addition of 50 mL of 50% sulfuric acid. The pH is compared to the percentage of sodium hydroxide present in a 10g test portion. It can be seen from this graph that even with a sample of 100% sodium hydroxide, if a 10g test portion is used, the pH is <0.4 which provides the proper conditions for the generation of HCN gas.

Figure 15 illustrates the change in pH in the distilling flask following the addition of the sulfuric acid using a 10g test portion with an increasing percentage of sodium hydroxide in the test portion.

Figure 16 illustrates the neutralization capacity of the sulfuric acid in the distilling flask as it corresponds to number of grams of sodium hydroxide present in the flask. It can be seen from this graph that even if the material being analyzed for cyanide is as caustic as sodium hydroxide, a test portion of up to 25g can be used and a sufficiently low pH will still be achieved.

The conclusion that can be drawn from the above information is that as long as the test portion used is 25g or less, the amount of acid required to be added to the distillation flask should be sufficient to create the conditions for the generation of HCN gas.

## PARTICLE SIZE

A common difficulty in all analytical chemistry techniques is the ability to ensure that a complete reaction takes place to enable the proper quantitation of the desired analyte. Obviously, if the reagents are not allowed to fully react with the material being tested, an inaccurate result will be reached. One factor that may inhibit a complete reaction

with reagents is particle size. The effect of particle size on the amount of cyanide recovered was examined below in an F006 waste. The material was run through a series of sieves of the following pore sizes: 9mm, 4.5mm, 2mm and subsequently analyzed with the results being presented in Figure 17.

This graph illustrates the relationship between particle size and the amount of cyanide recovered. Test portions, distillation times, and aliquot sizes were all kept constant.

In this particular waste it seems particle size did not affect the amount of cyanide recovered. This may have been due to the fact that the material used in this study, regardless of the particle size, completely solubilized during the distillation procedures. It is also interesting to note that the test portions taken from the material that was >9mm in size had the most consistent recoveries. It is possible that when this material was broken into smaller pieces, the accurate representation of the material was lost. In any event, this graph is an excellent example of the variability of Method 9010.

## CONCENTRATION AS RELATED TO CYANIDE RECOVERY

In order to assess the effectiveness of the acid reflux distillation for the recovery of cyanide, several concentrations of cyanide ranging from 120 ppm to 10,000 ppm were prepared from commercially available NaCN. Approximately 10g of each NaCN solution was distilled in accordance with Method 9010 with a reflux/distillation period of 2 hours. The results of this study are summarized in Figure 18.

This graph illustrates that the percentage of cyanide recovered is independent of the initial cyanide concentration. On the average, approximately 90% of the cyanide was recovered regardless of the initial cyanide concentration.

These results suggest that the acid distillation method does not allow for complete cyanide recovery from aqueous solutions of simple alkali metal cyanides after a two-hour period. Since the 2-hour reflux/distillation period resulted in an incomplete cyanide recovery, the aqueous NaCN solutions were further distilled for periods of 4.75 and 5.75 hours. The results of this study are summarized graphically in Figure 19.

This graph illustrates the increase in the amount of cyanide recovered as the distillation time increases for a sample of aqueous NaCN. The NaCN stock solutions containing relatively high cyanide concentrations; i.e., 4,000 ppm to 10,000 ppm, showed only a slight increase in the amount of cyanide recovered after lengthening the distillation period. Complete cyanide recovery, however, was achieved for those NaCN solutions which had a low cyanide concentration.

The results of this study on aqueous NaCN suggest that cyanide can be

quantitatively recovered for low cyanide concentrations only after a distillation period which is considerably longer than that which is prescribed by Method 9010. The correlation that can be drawn from these data to that which was gathered on actual hazardous waste is: if an incomplete cyanide recovery is achieved on a simple sample matrix of low concentration such as aqueous NaCN in a specified reflux period, a complete recovery in complex hazardous waste matrices of unknown concentrations cannot be expected.

## EFFICIENCY OF THE QUANTITATION STEP

The actual quantitation of the cyanide recovered from the material being tested is performed on the distillate collected in the scrubber system which converts the HCN gas generated to NaCN. Since this is the actual step which quantifies cyanide, the effectiveness of the titration procedure must also be evaluated. Since the complexiметric titration is the generally accepted method of determination for materials with a concentration level greater than 1 ppm and the evaluation of cyanide in hazardous waste seldom has to be performed below that level, it is the titration procedure which is investigated here.

Several stock solutions were prepared with cyanide concentrations ranging from 100 ppm to 10,000 ppm using fresh reagent grade NaCN. The silver nitrate solution utilized in the determination was standardized against standard NaCl solution using the argentometric method with $K_2CrO_4$ indicator. The titrations were carried out in accordance with the procedure in Method 9010. The results of these titrations can be seen in Figure 20.

This graph illustrates the results of titrations of NaCN which is exactly what is done in Method 9010. In each case, the amount of cyanide recovered was approximately 90%, regardless of the concentration of cyanide involved in the titration.

The obvious conclusion reached here is that the quantitation step itself is not completely effective. Taking into account that the complexiметric titration does not accurately quantify the total amount of cyanide present in standard NaCN stock solutions, it is not surprising that the cyanide recoveries after the acid reflux distillation are not quantitative. It may be possible that the 10% discrepancy in the titration may account for the incomplete cyanide recovery experienced in the acid reflux distillation. However, it is interesting to note that the amount of cyanide recovered for the 120 ppm and 400 ppm aqueous NaCN solutions approached 100% after the extended distillation period (Figure 19).

## CONCLUSION

The intent of this paper was to explore the effectiveness of SW 846 Method 9010 for hazardous waste matrices. The information presented has shown that there are many factors which can influence the results that are

obtained by using this method. This method does not produce a result which can be accurately called "Total Cyanide," since varying parameters within the method can produce drastically different results. It would, perhaps, be better to refer to the results achieved through the use of this method as "Cyanide by Method 9010." It would also have been better, if when regulatory levels were established, these variabilities would have been taken into account. These factors should have also been considered when the regulatory level was set in terms of forcing this method down to analyzing cyanide levels where even a slight variability could cause a drastic mistake.

In order to alleviate some of the inherent method discrepancies, one suggestion is that the method be made more definite by mandating the use of standardized quantities and times. This will enable any lab which analyzes a sample to arrive at the same result as another lab, not necessarily a "total" cyanide but at least there would be consistency. Another suggestion is that the way that the results are reported needs to be regulated, especially for cyanide amenable to chlorination when the results are negative because, obviously, there is more cyanide in the material than first thought.

In closing, Method 9010 either needs to be better understood by all concerned, or another way of determining cyanide concentration must be developed.

FIGURE 1
INCINERATOR ASH

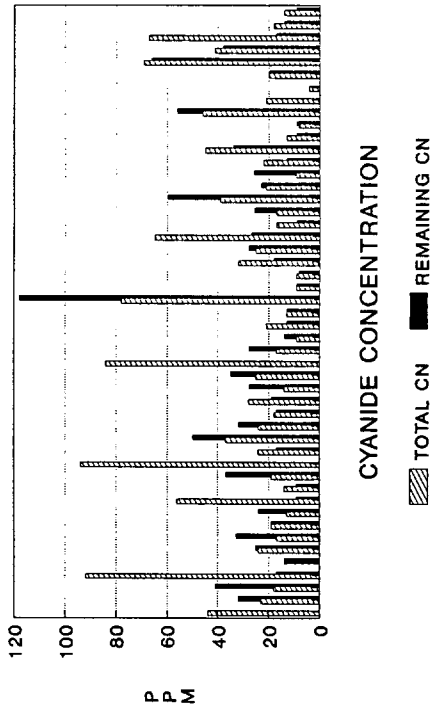



FIGURE 2
METALS DERIVATIVES

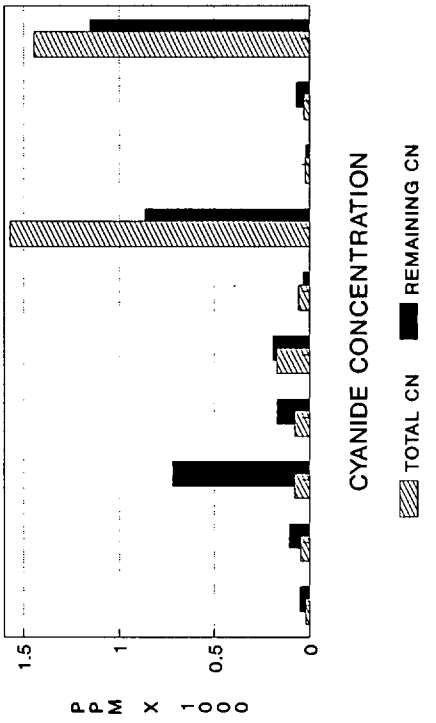



FIGURE 3
WASTE SLUDGE

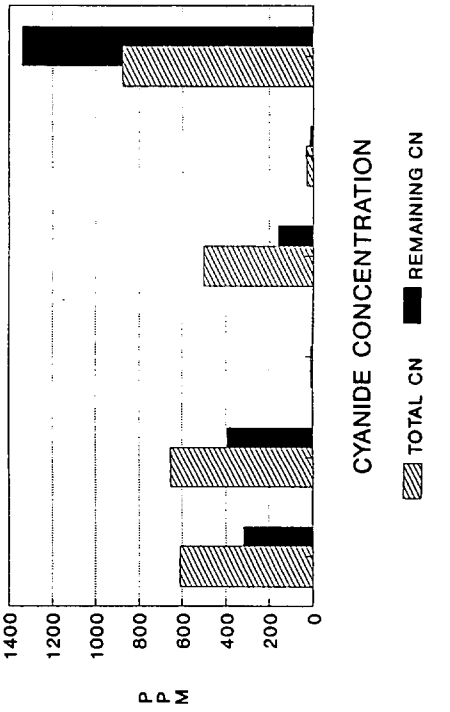



FIGURE 4
MISCELLANEOUS WATERS

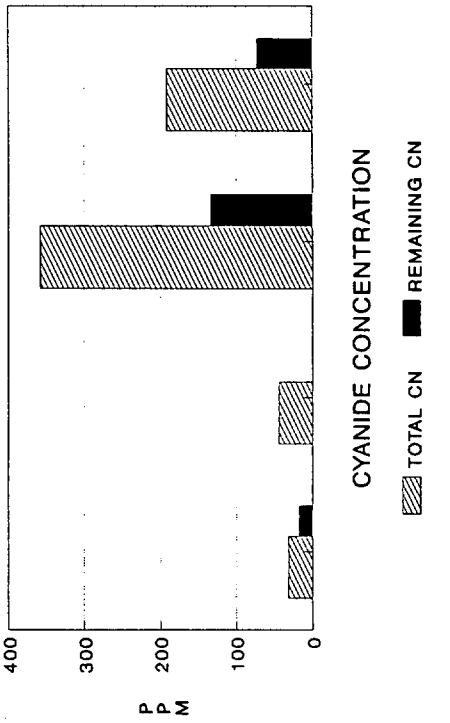


FIGURE 5
MISCELLANEOUS SOLIDS

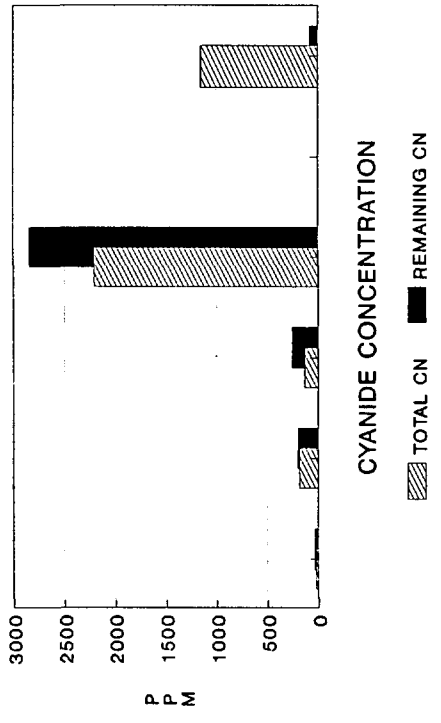



FIGURE 6
CYANIDE SOLUTIONS/COMPOUNDS

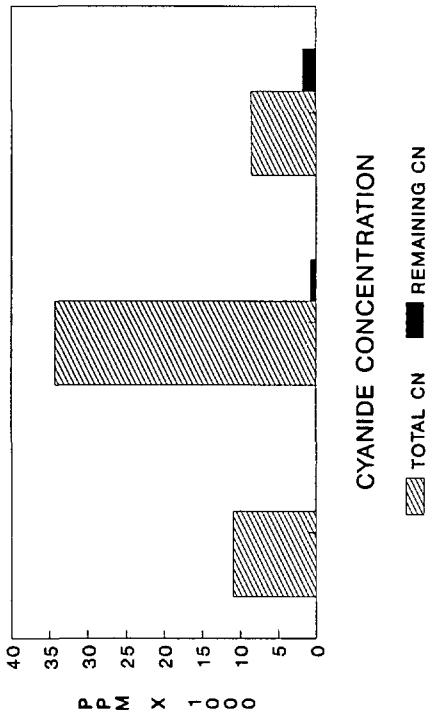



FIGURE 7

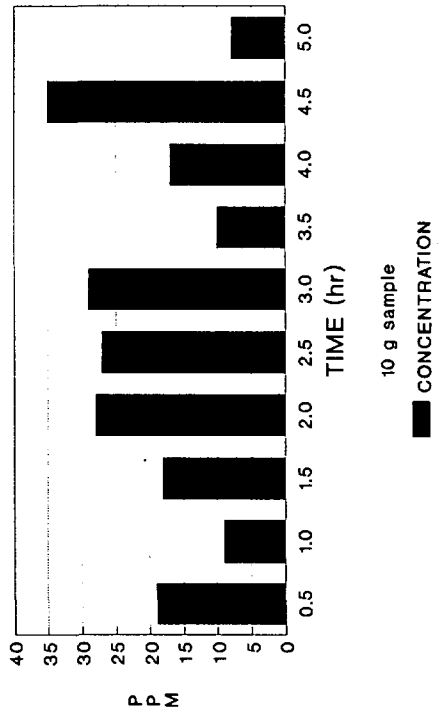



FIGURE 8

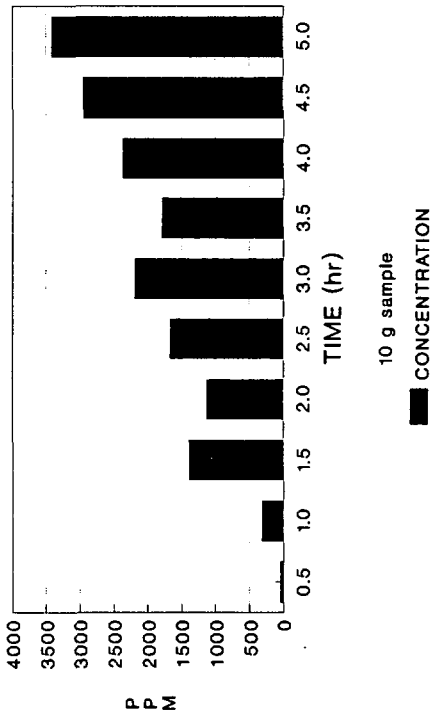


FIGURE 10

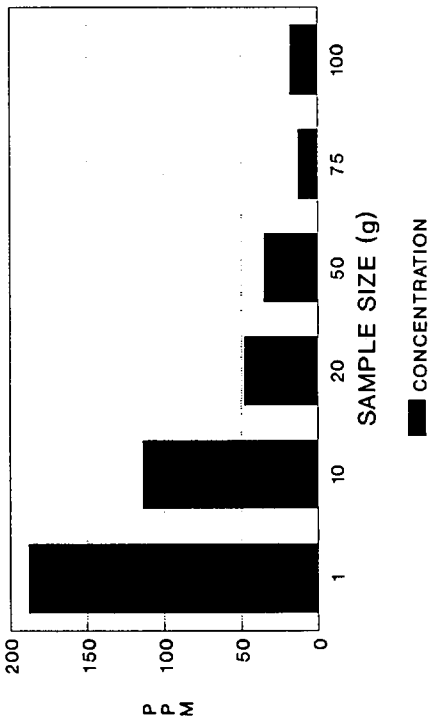



FIGURE 12

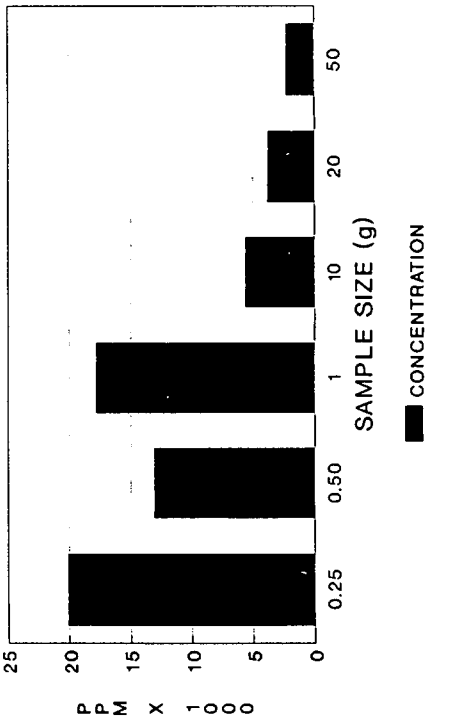



FIGURE 9

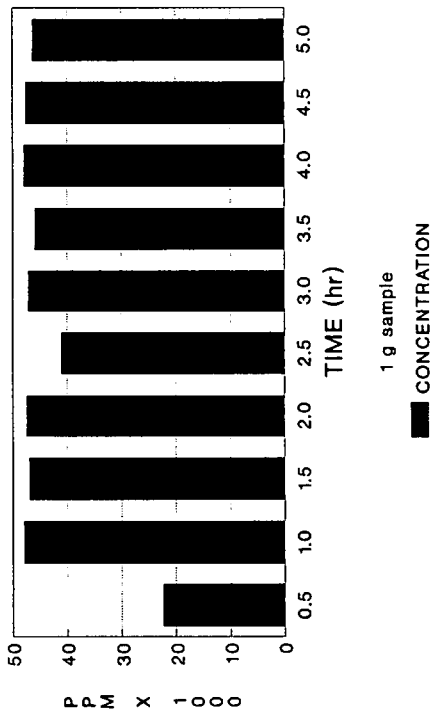



FIGURE 11

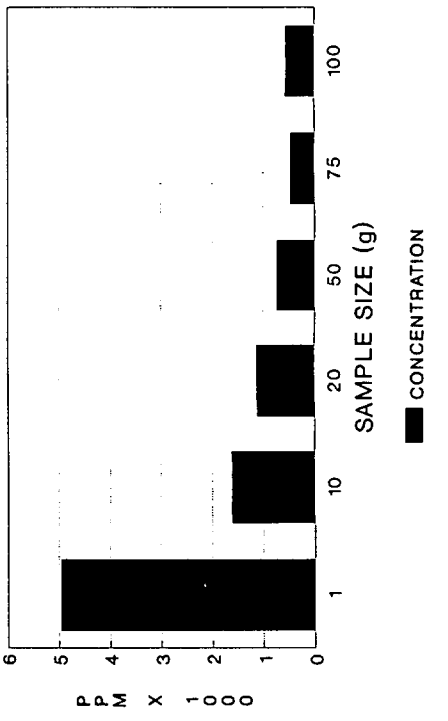


FIGURE 13

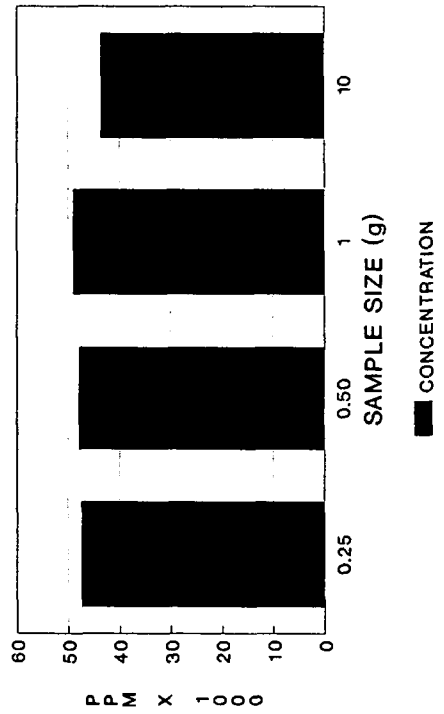



FIGURE 14

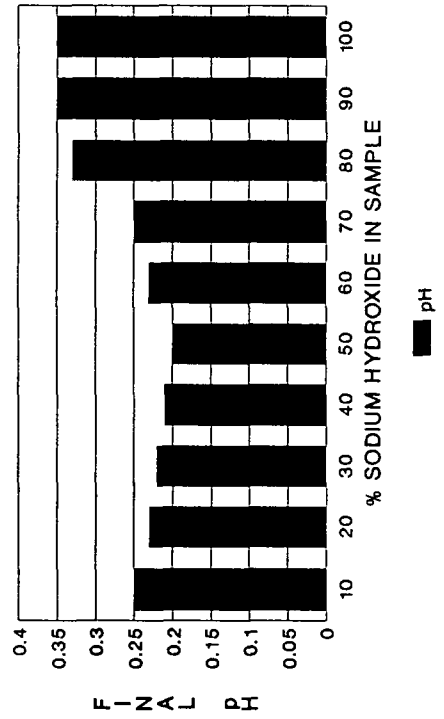



FIGURE 15

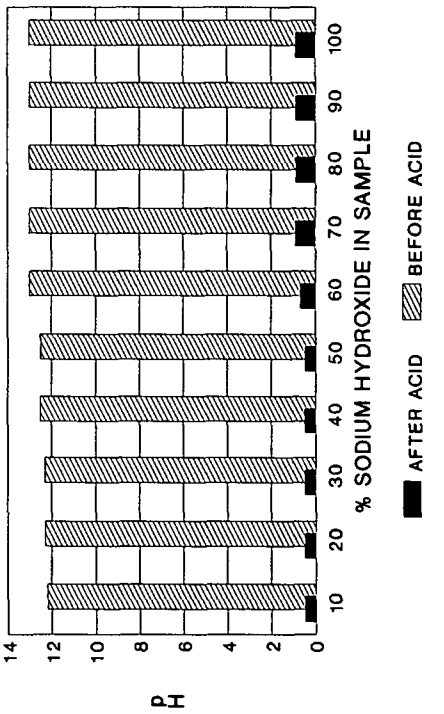



FIGURE 16

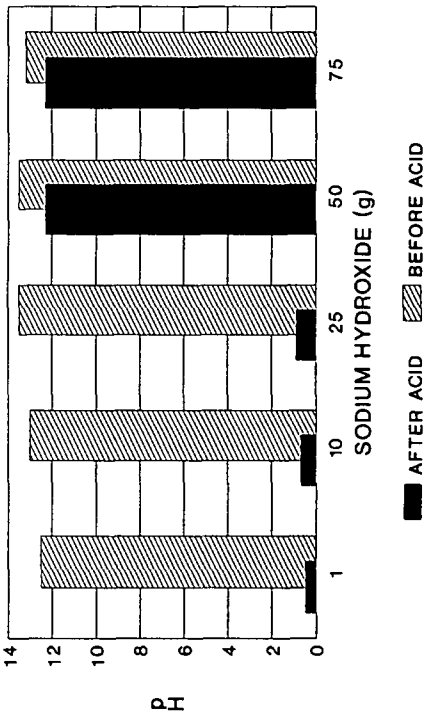


FIGURE 17

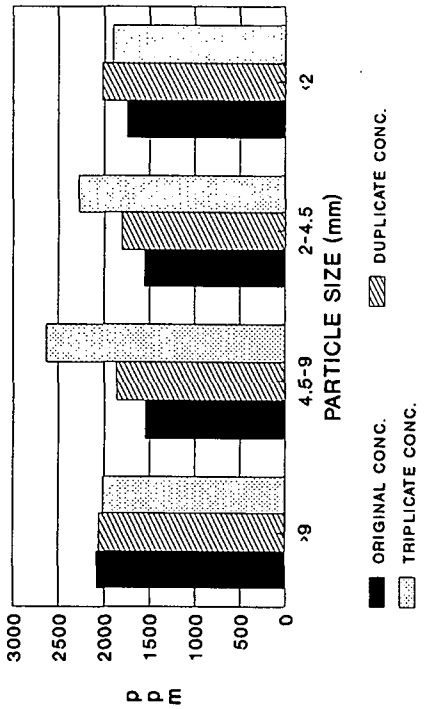



FIGURE 18

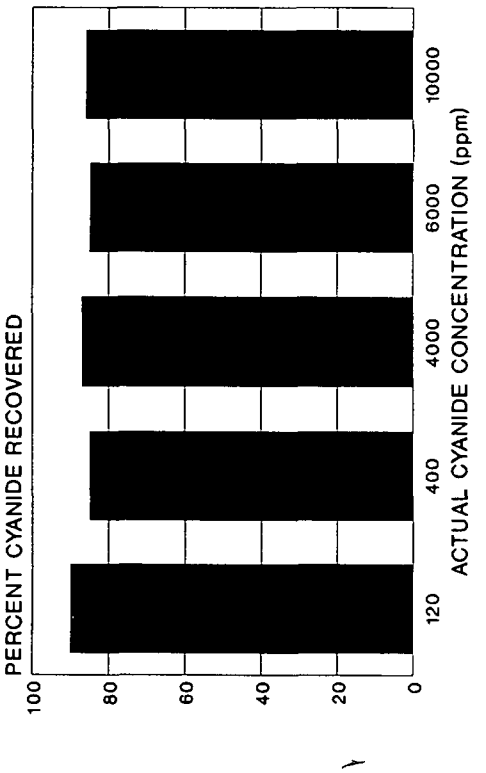



FIGURE 19

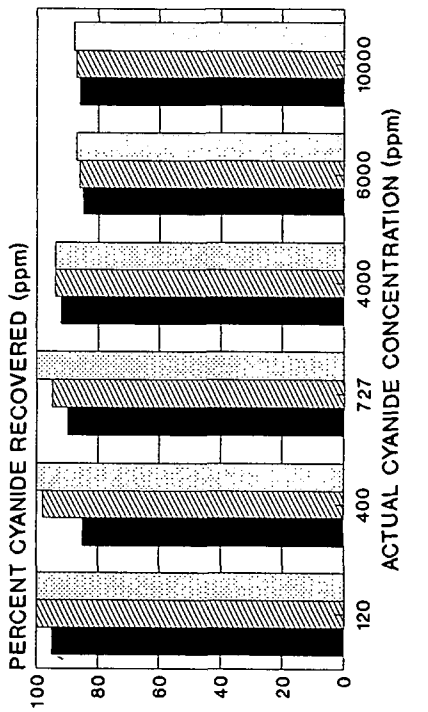
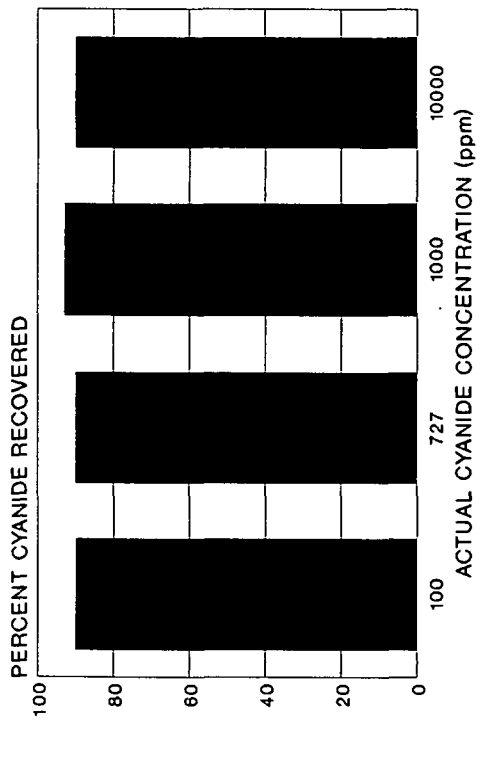



FIGURE 20



96

# MICROWAVE DIGESTION PRESSURE CONTROL AND MONITORING

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ABSTRACT

Microwave Digestion is now an EPA-CLP approved method for waters and solids digestion before analysis by GFAA and ICP. In the effort to recognize Microwave Digestion, a great deal of study was put into calibration of the oven power. If one were to establish a procedure based upon % power and time in one oven, how is the procedure going to be repeated in another oven?

In this paper we explain true pressure control; how it can be used as a much more reproducible method for establishing procedures, and how it can enhance closed vessel microwave for many types of organic samples.

Examples are offered to show how reactions in a closed vessel can be controlled by small incremental changes in pressure. Comparisons are also made between power control and pressure controlled methods.

Finally, we conclude that calibration of power introduces too many variables and that the more correct method to establish true reproducibility is by incremental control of pressure.

97

# COMPARISON OF CHROMATOGRAPHIC AND COLORIMETRIC TECHNIQUES FOR ANALYZING CHLORIDE AND SULFATE IN GROUND AND SURFACE WATERS

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## ABSTRACT

A two part study was performed which compared Suppressed Ion Chromatography, Non-suppressed Ion Chromatography, and Conventional Colorimetric instrumentation used in analyzing for chloride and sulfate in ground and surface waters. Part I is a study comparing Automated Colorimetric and Non-suppressed Ion Chromatography instrumentation. The intent of this study is to show comparability between EPA approved methodology 375.2 and 325.1 (Colorimetric) with EPA accepted methodology 300.0 (Ion Chromatography) when analyzing for secondary pollutants. Part II is a study comparing Suppressed and Non-suppressed Ion Chromatographic instrumentation. Several IC methods are recommended for analyzing inorganic anions in ground and surface waters. They are EPA Method 300.0, ASTM D4327-84, and Method 429 which is found in "Standard Methods for Water and Wastes". These methods are all written using "Suppressed" IC techniques, but each makes reference to "Equivalent" instrumentation which can be used to generate results. It is this instrumentation difference outlined in these IC methods that forms the basis for this comparison.

## INTRODUCTION

The Automated Colorimetric instrument used in this study is a TRAACS 800 autoanalyzer. The autoanalyzer is used to liberate highly colored ions that form in concentrations proportional to the anions of interest. In the case of analyzing for chloride, mercuric thiocyanate and ferric nitrate react with the sample to form ferric thiocyanate and mercuric chloride. The amount of ferric thiocyanate read at 480nm corresponds to the chloride concentration in the sample. In the case of sulfate analysis, the sample first passes through an ion-exchange column to get rid of cations in the sample. Sample then reacts with barium/methylthymol blue (MTB) in the presence of acid to form barium sulfate and MTB. This mixture then reacts with sodium hydroxide where excess barium reacts with MTB to form a blue chelate. The amount of uncomplexed MTB (gray in color) measured at 460nm is proportional to the concentration of sulfate in the sample.

For colorimetric analyses, very little sample preparation is required. If a sample is out of the linear range of the instrument, a dilution is made. This occurs in approximately 10% of samples tested. Reagent and stock solution

preparations include standards, color reagents, and numerous reacting solutions.

Tests involving Non-suppressed Ion Chromatography (Waters) allow for the simultaneous conductimetric detection of chloride and sulfate in an eluent of low background conductivity. Sample is introduced into an eluent stream of borate/gluconate and is carried to the anion exchange column. Separation of the individual anions is effected by their differing affinities to the exchange sites of the resin within the column. Competition between the analyte anions and the anions present in the eluent for these exchange sites results in the separation of the ions of interest into discrete bands which are carried by the eluent through the column. The separated ions are then introduced into a temperature controlled conductivity detector which produces an electrical signal for each of the anionic species that is proportional to the amount present. The electrical signal is documented as a peak on a recording device. The anions are qualitatively identified by the retention time of the peak and quantitation is obtained by the measurement of peak area as compared to known standards.

Analyses performed by IC include two preparation steps: 1)samples are first diluted then 2) passed through a 0.45micron filter. Few reagents are used in testing with this system. Only borate/gluconate eluent and calibration standards are frequently prepared.

In the case of Suppressed Ion Chromatography (Dionex) a suppressor "membrane" is used to exchange eluent and sample cations for hydronium ions. These reactions neutralize the eluent but do not affect the sample anions. The exchange reaction results in a reduction of eluent conductivity and an increase in the conductivity of the sample anions. As in the Non-suppressed system, anions are qualitatively identified by the retention time of the peak and quantitation is obtained by the measurement of peak area or height as compared to known standards.

## SUMMARY

Several factors were used to evaluate comparability between systems:

1. Strength of association between techniques.
2. Identify systematic bias (i.e. results from one technique generally higher than the other.)
3. Proportion of variance in common between two variables (i.e. overlap of one technique with the variance of the other).

The data set from Part I of this study covered a dynamic range in analyte concentrations. The measured concentration ranges were as follows:

.Below detection limit to 1080mg/L for chloride
.Below detection limit to 767mg/L for sulfate

Statistical evaluation of this data was provided using a linear regression model, pearson correlation coefficient, coefficient of determination, and paired t-Tests. The linear regression model described the strength of association between the two techniques; correlation coefficients identified shared variances, and the paired t-Test was used to identify systematic bias.

After performing this statistical evaluation, the two techniques show a 98.8% shared variance for chloride and 99.0% shared variance for sulfate. There is no significant bias of results at the 95% confidence level, yet, with regards to low concentrations of chloride (around 5ppm), the autoanalyzer produces consistently lower values for chloride than the IC. One explanation for this might be that in the reaction, the presence of chloride is necessary for the dissociation of mercuric thiocyanate into mercury and thiocyanate. If the chloride level is low in the solution, not all of the mercuric thiocyanate will be dissociated, therefore, the amount of measured ferric thiocyanate would be low. Since the concentration of ferric thiocyanate is proportional to the concentration of chloride in solution, the chloride value would be low. Although this difference is of statistical significance, the magnitude of the effect (i.e. bias) is less than 1/2 of a standard deviation unit which is negligible. Overall, these results indicate that the agreement between the two instruments is excellent for these analytes.

In order to determine comparability between systems in Part II of this study, a statistical evaluation similar to the one mentioned in Part I was used. The comparison showed 98.7% shared variance for sulfate and 99.3% shared variance for chloride. However, a systematic difference in chloride values was found for suppressed chromatography relative to non-suppressed technique. On average, the suppressed technique yielded 11% higher values for chloride. This finding is consistent with results obtained on four runs of a 10ppm chloride standard included in the sample batch. Chloride values for this standard averaged 10% high. It is possible that the increased chloride values may be due to differences in instrumentation calibration.

## CONCLUSION

Results obtained in Part I of this study show excellent correlation between chloride and sulfate values when analyzed by either technique. In Part II, no difference was observed when comparing sulfate values between IC systems, yet the question of the chloride discrepancy could warrant further investigation to determine comparability between techniques.

98

# METALS DIGESTION: A COMPARATIVE STUDY

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## ABSTRACT

The USEPA SW 846 Method 3050, 2nd Edition "Acid Digestions of Sludges," is a commonly applied technique to digest metals from heated samples in an open vessel using low pressure and an acid environment. Currently, closed vessel microwave digestion is receiving much attention as the new "high tech" means of metals digestion. This is indicated by the numerous microwave digestion studies being reported, as well as by the evolution of microwave digestion systems. Because many of these studies indicate important applications to our area of analytical chemistry, we propose to provide a comparative overview of the various digestion techniques available. In this study, comparisons are made of the data produced from the analysis of hazardous waste streams containing silver, chromium, lead, arsenic, and selenium digestates utilizing: 1) open vessel hot plate digestion; 2) high temperature/pressure Parr bombs; and 3) a closed vessel Teflon-lined microwave digestion vessel. Utilizing ICAP and GFAA methods of instrumental analysis, these comparisons demonstrate the precision, accuracy, efficiency of performance, and the applications of each technique as well as commentary on the results obtained.

## INTRODUCTION

The analytical division of Chemical Waste Management's Riverdale, Illinois, Technical Center is a high performance analytical laboratory which analyzes over 1,000 samples per month for various parameters. The results of these analyses are used to determine the final disposition of a customer's waste stream and support the company's R&D and Methods Development efforts. Common disposal decisions made on the data generated are incineration, landfilling, fuels blending, and resource recovery.

The Spectroscopy Group at the CWM Technical Center utilizes a modification of SW 846 Method 3050 to prepare samples for certain metals analysis by inductively coupled argon plasma emission spectroscopy (ICAP) and graphite furnace atomic absorption (GFAA) with Zeeman background correction. Ag, Cr, and Pb are analyzed by SW 846 Method 6010. As and Se are analyzed by SW 846 Methods 7060 and 7740, respectively.

The laboratory goal of twelve day sample turnaround time includes the long digestion times needed for certain samples by the traditional hot plate technique prescribed by Method 3050. To circumvent this problem, ASTM Method C (E926-88) "Bomb, Acid Digestion Method" (modified) is often employed. This method uses Parr digestion bombs to quickly digest samples by increasing the temperature/pressure. This is an adequate technique but includes many drawbacks, not least of which is the bomb's cumbersome

nature and possible contamination due to the breakdown of the bomb's metal constituents.

In order to improve costs, turnaround time, and handling techniques while maintaining QA/QC and safety performance, it was decided to investigate microwave digestion technology as it applies to hazardous waste analysis.

To accomplish this task, five sample matrices were selected. Of these five, two were of known values: 1) an aqueous multi-element standard; and 2) a NBS certified solid standard. The other three samples were "typical" of the lab's sample flow and were primarily selected because of their physical composition:

SAMPLE 3: an unknown sludge with free liquid.
SAMPLE 4: a homogenous metal dust.
SAMPLE 5: a mixed oily granulated clay.

To further enhance the "real world" nature of the study, five "problem" metals at the following wavelengths were analyzed for: Ag 328.07, Cr 267.72, Pb 220.3, As 197.3, and Se 196.

The data was generated after digesting each sample in duplicate and spike utilizing hot plate (Method 3050), Parr acid bomb, and microwave-aided methodologies.

## PROCEDURE/METHODOLOGY

General. Each sample was set up in duplicate and spiked for determination of precision and accuracy. The spike contained an aqueous 5 ppm spike for Ag, Cr, and Pb, and .1 ppm spike for As and Se.

The sample matrix was kept at 10% $HNO_3$ by volume, and all samples were filtered through Whatman 42 paper. Double deionized water was used to bring the samples to final volume. Appendix I lists the standards, reagents, and apparatus used in the study.

Method 3050 (modified). Approximately 2.000g of test portion was weighed into a 125ml Erlenmeyer flask. Five (5) mls of $HNO_3$ were then added, and the samples placed on a hot plate to near boiling. They remained there until no NOx fumes were observed. The samples were then removed from the hot plate and cooled. At this time, 3mls of $H_2O_2$ were added, and the samples were returned to the hot plate to start the peroxide reaction. This peroxide process was repeated a second time, and the digestion continued until the flask became clear; i.e., the production of NOx fumes ceased. The samples were cooled, diluted to volume in a 50ml volumetric flask, filtered, and analyzed.

Parr Bomb Digestion. Approximately 0.5g of test portion was weighed into the 125ml Teflon sample cups, and 2.5mls of $HNO_3$ and 2.5mls of $H_2O$ were added. The cups were then placed into the Parr stainless steel bomb and

the bomb assembled.

After bringing up the oven temperature to 130 degrees C, the bombs were placed inside and digested for 24 hours. The bombs were then cooled and disassembled. The samples were diluted to 25mls, filtered, and analyzed.

Microwave Digestion. Approximately 0.5g of test portions were weighed into 60ml narrow-mouth bottles. 2.5mls of $HNO_3$ were added, and the samples were left to react under the fume hood for 4-5 minutes. 2.5mls of $H_2O_2$ were added and after any effervescing ceased, the bottles were capped and tightened. The caps were then unscrewed 1/4 turn to prevent the bottles from rupture due to the rising internal pressures.

Before placing the 60ml bottles into the Teflon digestion vessels, 2mls of $HNO_3$ were added to the vessel itself in order to maintain the same vapor pressure within and outside of the 60ml bottles.

The vessels were then capped and torqued to pressure in the capping station, placed in the sample turntable, and hooked to vapor exhaust/condensate collection hoses, and the digestion was started.

The following 4-stage digestion method was developed by visually monitoring at which power setting the internal vessel pressure caused venting and condensate to form in the hoses.

MICROWAVE DIGESTION PROGRAM

| STAGE | MINUTES | %POWER |
|---|---|---|
| 1 | 10 | 10 |
| 2 | 10 | 30 |
| 3 | 40 | 50* |
| 4 | 60 | 45 |

* Slight condensate formed toward end of stage. Power reduced, and the digestion continued smoothly.

The vessels are designed to vent at 100psig, and lacking the optional pressure controller, this method proves adequate. The main intention is to slowly raise the vessel temperature/pressure to optimize digestion efficiency. When digestion was complete, the vessels were disassembled, the digestate collected, diluted to a 25ml volume, filtered, and analyzed.

RESULTS

The results of the study are contained in the chart presented in Appendix II. Each sample type is listed individually. The left side of the chart lists the methods used, and the top of the chart tells of the metal of interest, listing the values for the original (O), duplicate (D), and spike (S). Percent error (%E) and percent recovery (%R) are also shown.

Most notable when reviewing the data are the problems with Ag and Se spike recoveries in complex matrices; also, the bomb method of digestion generally yields the highest concentration.

SAMPLE 3 had precision and accuracy problems that were not acceptable. This was primarily due to sample inhomogeneity. Arsenic errors in SAMPLES 2 and 4 were due to a high aluminum content. In all samples, iron interfered at a level that even with matrix modifiers and Zeeman background correction, interferences could still not be corrected.

OBSERVATIONS/CONCLUSIONS

This study aimed to compare the analytical equivalence in terms of precision and accuracy of three methods of metal digestion by hot plate, Parr bomb, and microwave. Many observations can be made from studying the derived data. Appendix III lists general advantages and disadvantages of each method.

From those "real world" samples in complex matrices, analytical reproducibility is only as good as the test portions and methods of sample prep themselves. As instrumentation has become more accurate and sophisticated, sample prep methodologies have lagged far behind. In general, we can observe (as expected) that when sample homogeneity is assured, high temperature/pressure Parr bombs yield the best recoveries, and it is also apparent that microwave digestion is accomplished faster. The volatility of arsenic and the many spectral and chemical interferences on selenium also make firm conclusions favoring one method over another difficult.

At this time, Method 3050 in SW 846 will not give an answer that is absolute. With this in mind, the results show that for the five metals selected, all three methods have some applicability and have the same probability of variability; some have more severe problems than others that in time must be addressed as have other methods in the past.

In any case, the endpoint of digestion in two of the three prep methods is a fixed time; only the hot plate method is indefinite. As was revealed in the data, the bomb method appears to generally yield the larger results when compared to the others. Method 3050 uses a reaction indicator (NOx evolution) which compensated for matrix variation; microwave methods have a set time usually determined by standards or only a few matrices and does not cover all sample variability.

Until sample prep methods become more precise, laboratories may be at an advantage utilizing all three prep methods (depending on sample types analyzed). The validity of test portions and hence analytical integrity is a major consideration and is guaranteed by QA/QC Policy. Blind duplicates, ten percent duplicate and spike ratios, strict acceptance/sample reset criteria, instrument performance checks, and

continuing instrument calibration verification are all among the necessary ingredients to ensure the production of defensible data.

## APPENDIX I

## STANDARDS, REAGENTS, AND APPARATUS

STANDARDS. Leeman Labs Plasma Pure multi-element in 10% $HNO_3$ for ICAP calibration (Lowell, Ma.). Single element As and Se for Varian 400 GFAA in 10% $HNO_3$ from EM Science (Cherry Hill, NJ). Spike standard was multi-element in 10% $HNO_3$ from Spex Industries (Edison, NJ).

REAGENT WATER. Double deionized from a Millipore system.

HNO3. Baker Instra Analyzed 70.0%-71.0%.

H2O2. Baker Analyzed--30%.

HOT PLATE. Variable temperature control.

FILTER PAPER. Whatman 42.

FLASKS. 125ml Erlenmeyer with Tuttle caps, 50ml and 25 ml volumetrics.

PARR BOMBS. Model 4748 with 125ml Teflon sample cups.

BOMB OVEN. Thermolyne mechanical oven with temperature and timer settings.

MICROWAVE DIGESTION SYSTEM. CEM model MDS-81D 600 watt microwave oven. 120ml. Teflon sample vessels. Turntable/vessel carrier. Vent tubing and vapor collection container. Capping station.

NARROW-MOUTH BOTTLES. 60ml. FEP Fluorocarbon.

INSTRUMENTATION. Leeman Labs Plasma Spec 2.5 and Varian 400 GFAA with Zeeman correction.

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## APPENDIX II

### SAMPLE 1 QC

| | Ag | | | | | Cr | | | | | Pb | | | | | As | | | | | Se | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| METHOD | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R |
| HOT PLATE | 3.97 | 4.71 | 9.52 | 8.52 | 103.6 | 5.18 | 5.15 | 9.95 | 0.29 | 95.7 | 5.11 | 5.07 | 9.76 | 0.39 | 93.4 | .119 | .121 | .232 | 0.8 | 112 | .108 | .107 | .175 | 0.5 | 67.5 |
| BOMB | <.055 | <.034 | <.034 | 23.5 | 0.21 | 5.58 | 5.81 | 10.8 | 2.02 | 102 | 5.51 | 5.81 | 11.0 | 2.65 | 107 | .130 | .140 | .262 | 3.7 | 127 | .131 | .136 | .239 | 1.9 | 106 |
| MWD | <.034 | <.034 | <.034 | 0 | 0 | 5.17 | 5.12 | 10.4 | .486 | 105 | 5.05 | 4.99 | 10.3 | .598 | 106 | .135 | .138 | .248 | 1.1 | 112 | .122 | .122 | .219 | 0 | 97 |

### SAMPLE 2 NBS CERTIFIED SOLID STANDARD

| | Ag | | | | | Cr | | | | | Pb | | | | | As | | | | | Se | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| METHOD | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R |
| HOT PLATE | <.79 | <.79 | 12.3 | 0 | 10.6 | 93.9 | 95 | 197 | .582 | 88.5 | 122 | 122 | 222 | 0 | 86.3 | 20.2 | 18.7 | 20.8 | 3.9 | 60 | .16 | .16 | .44 | 0 | 19 |
| BOMB | <1.7 | <1.7 | <1.7 | 0 | .044 | 112 | 107 | 346 | 2.28 | 96.4 | 143 | 138 | 353 | 1.78 | 86.7 | 24.8 | 28.5 | 28.9 | 6.9 | 10.0 | <.31 | <.33 | 2.40 | 0 | 49 |
| MWD | <1.7 | <1.7 | <1.7 | 0 | 0 | 88.1 | 89.7 | 329 | 0.90 | 97.9 | 159 | 126 | 366 | 11.5 | 91.1 | 22.6 | 23.0 | 28.9 | 0.9 | 120 | .38 | <.34 | 3.14 | 100 | 64 |

### SAMPLE 3 SLUDGE/LIQUID

| | Ag | | | | | Cr | | | | | Pb | | | | | As | | | | | Se | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| METHOD | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R |
| HOT PLATE | <.80 | <.80 | 10.3 | 0 | 8.78 | 107 | 424 | 205 | 59.7 | 51.5 | 214 | 147 | 180 | 18.5 | 40.4 | 7.44 | 6.38 | 7.89 | 8.1 | 42.0 | 99.6 | 83.3 | 92.0 | 8.9 | 0 |
| BOMB | <1.6 | <1.6 | 1.80 | 0 | 0.734 | 173 | 132 | 343 | 13.4 | 77.7 | 304 | 229 | 368 | 14 | 41.4 | 9.82 | 6.79 | 12.4 | 18.2 | 72.0 | 151 | 118 | 449 | 12.3 | 314 |
| MWD | <1.5 | <1.5 | <1.5 | 0 | 0 | 290 | 83.5 | 299 | 55.2 | 49.3 | 318 | 99.5 | 486 | 523 | 121 | 1.83 | 1.81 | 5.82 | 0.5 | 85.0 | 24.6 | 16.8 | 51.8 | 18.8 | 65 |

### SAMPLE 4 METAL DUST

| | Ag | | | | | Cr | | | | | Pb | | | | | As | | | | | Se | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| METHOD | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R |
| HOT PLATE | <.84 | <.84 | 37.1 | 0 | 30.1 | 605 | 626 | 736 | 1.7 | 97.6 | 51.8 | 50.5 | 126 | 1.27 | 60.6 | 9.12 | 10.2 | 9.06 | 5.6 | 0 | <.17 | <.17 | 1.44 | 0 | 59.0 |
| BOMB | <1.6 | <1.6 | 2.89 | 0 | 1.27 | 518 | 529 | 742 | 1.05 | 96.1 | 75.2 | 79.2 | 259 | 2.59 | 80 | 10.9 | 10.8 | 23.4 | 0.5 | 223 | <.32 | <.34 | 3.36 | 0 | 74.0 |
| MWD | <1.6 | <1.6 | <1.6 | 0 | 0 | 455 | 444 | 648 | 1.22 | 81 | 71.4 | 74.9 | 247 | 2.89 | 70.9 | 9.95 | 10.2 | 18.4 | 2.3 | 172 | <.32 | <.33 | 2.84 | 0 | 58.0 |

### SAMPLE 5 OILY CLAY

| | Ag | | | | | Cr | | | | | Pb | | | | | As | | | | | Se | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| METHOD | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R | O | D | S | %E | %R |
| HOT PLATE | <.82 | <.82 | 81.2 | 0 | 68.2 | 56.4 | 56.4 | 163.0 | 0 | 89.5 | 2.75 | 2.31 | 99.5 | 8.69 | 81.4 | 0.50 | 0.69 | 0.27 | 16.0 | 0 | <.17 | <.17 | 0.52 | 0 | 22 |
| BOMB | <1.6 | <1.6 | <1.6 | 0 | 0 | 62.3 | 61.0 | 296 | 1.05 | 99.3 | 2.89 | 1.90 | 212 | 20.6 | 88.8 | 3.56 | 3.68 | 7.78 | 1.7 | 86.0 | <.32 | <.32 | 2.59 | 0 | 55 |
| MWD | <1.7 | <1.7 | <1.7 | 0 | 0 | 34.3 | 53.1 | 282 | 21.5 | 102 | 2.35 | 3.97 | 209 | 25.6 | 88.9 | 3.41 | 3.62 | 7.35 | 3.0 | 83.0 | <.30 | <.31 | 3.01 | 0 | 65 |



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## APPENDIX III

## METHOD ADVANTAGES AND DISADVANTAGES

| METHOD | ADVANTAGE | DISADVANTAGE |
|---|---|---|
| HOT PLATE | 1) Analyst acceptance.<br>2) Method currently generates defensible data. | 1) Digestion time varies 1-10 days.<br>2) Equipment in contact with acid fumes.<br>3) Constant analyst observation.<br>4) Boil-overs greater safety risk.<br>5) Applicable to certain metals only.<br>6) Sludge digestion procedure. |
| PARR BOMB | 1) Higher temp./pressure yields better recoveries.<br>2) No acid loss.<br>3) 24-hour digestion time.<br>4) No loss of samples.<br>5) Equipment not exposed to acid fumes.<br>6) Applicable to all matrices. | 1) Bombs are cumbersome.<br>2) Bombs' metal constituents may break down causing contamination problem.<br>3) Bombs costly.<br>4) Small sample size accentuates inhomogeneous samples. |
| MICROWAVE | 1) Staged program gives strict control over temp./pressure.<br>2) Approx. 2-hour digestion time.<br>3) Sample contamination minimized. | 1) Microwave digestion system is expensive.<br>2) Labor intensive.<br>3) Reduced sample size. |

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99 Using Flow Injection to Meet QA Criteria for ICPMS Method 6020

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In EPA Method 6020, Inductively Coupled Plasma-Mass Spectrometry (ICPMS) is used to determine trace metal analytes in sample digests. However it has been reported that under the current protocol of conventional sample introduction using solution nebulization difficulties are encountered in meeting QC control limits such as continuing calibration and internal standard response drift (1,2). Many of these problems can be caused by deposition of solids on the sampling and skimmer cones and detector fatigue form high analyte concentrations. In this work a protocol was sought using flow injection of the sample digests which would minimize exposure of the equipment to the sample matrix. By flow injecting a small aliquot of the digest and by limiting data aquisition times to correspond to the flow of the aliquots, one can reduce the amount of sample introduced from several milliliters to fractions of a milliliter. The results of this study on continued calibration and internal standard response drift will be presented. Additional benefits of increased sample through put and reduced memory effects will also be demonstrated.

1. Aleckson, K., et al., Fifth Annual Waste Testing and

Quality Assurance Symposium, July 24-28, 1989.

2. Hinners, T.A., et. al., Fifth Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989.

100

# COMPARISON OF THE DETERMINATION OF HEXAVALENT CHROMIUM BY ION CHROMATOGRAPHY COUPLED WITH ICP-MS OR WITH COLORIMETRY

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## ABSTRACT

A method for the determination of hexavalent chromium in aqueous samples or sample extracts using ion chromatography (IC) combined with inductively coupled plasma mass spectrometry (ICP-MS) has been developed. Its performance is compared to a method using the same ion chromatographic separation coupled with a post-column reactor and the colorimetric detection of a Cr(VI) diphenylcarbohydrazide complex. The observed detection limits and linear dynamic ranges are similar for both methods, i.e., about 1-2 ppb and 4 decades respectively. Compared to the colorimetric method, IC-ICP-MS has the advantage that it can also be employed to determine oxy-anions of other metals, such as arsenic, selenium, vanadium, molybdenum and tungsten. In addition, ICP-MS without the preceding IC separation can be used to quantitate total metals. In the case of chromium, Cr(III) can then be determined by difference.

## INTRODUCTION

The determination of hexavalent chromium in addition to total and trivalent chromium in environmental samples is important because of the large difference in toxicity between Cr(III) and Cr(VI). Most popular methods for the selective determination of hexavalent chromium are based on the reaction of Cr(VI) with diphenylcarbohydrazide (DPC) in acidic solution, resulting in the formation of a complex which has an absorption maximum at 540 nm [1-3]. Analysis of bulk samples using this methodology is possible, but suffers from potential interferences by other colored species (e.g., Fe(III) or Cu(II) complexes) or species forming colored reaction products with DPC such as vanadium, molybdenum and mercury. Low results and poor spike recoveries are observed when samples contain substances which reduce Cr(VI) in acidic solution [1,2]. Furthermore, the presence of chemical species which oxidize Cr(III) to Cr(VI), e.g., free chlorine, can give rise to erroneously high results [3].

To avoid the aforementioned interferences, methods have been developed which isolate hexavalent chromium by ion chromatography before reacting it with DPC [4,5]. The chromatographic separation of Cr(VI) from other sample constituents, and especially from other chemical species of the same element, also makes it possible to use element specific atomic spectrometry methods for its selective determination.

All of the major atomic spectrometry techniques employed in environmental analysis, namely atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) have been interfaced with liquid chromatography for chemical speciation work. Of those detection methods, ICP-MS is the most versatile and useful, because it can measure several elements simultaneously and with very high sensitivity.

One of the first published reports on interfacing ICP-MS with liquid chromatography (LC) appeared in 1986 [6], only three years after the first commercial ICP-MS instrument was introduced. Since then, a number of research groups, including our own, have explored the potential of coupling ICP-MS with LC for studies involving the speciation of metals [e.g., 7-10] as well as non-metals [10,11]. Although interest in this area has been growing steadily, progress is hampered somewhat by the fact that specialized data transfer techniques are still required to analyze LC-ICP-MS chromatograms, i.e., to perform peak detection and integration (cf. Experimental section).

In this report, a method for the determination of Cr(VI) based on the combination of IC and colorimetry is compared to a technique which uses ICP-MS for the detection of chromium in the chromatographic effluent. In addition, applications of ICP-MS to the selective detection of oxy-anions of vanadium, molybdenum, tungsten, arsenic and selenium are presented.

## EXPERIMENTAL

All ion chromatographic separations were performed with a Dionex 4000i ion chromatograph, a Dionex AS4A anion exchange column and an AG4A guard column. Typical operating conditions and the main eluent system employed in this work are summarized in Table 1. Other eluent systems and conditions were also tested; they are described in the Results and Discussion sections where appropriate. The ICP-MS instrumentation and operating parameters are listed in Table 2.

**Table 1:** IC operating conditions and eluent system

| | |
|---|---|
| Injection volume | 25 or 100 ul |
| Elution mode | isocratic |
| Eluent | 6 mM $(NH_4)_2SO_4$, $10^{-5}$ M $HClO_4$; pH adjusted to 9.0 with $NH_4OH$ |
| Flow rate | 1.0 ml/min |

For ICP-MS work, the effluent from the analytical column was passed to the ICP nebulizer through a 60 cm long Tefzel transfer line (1.5 mm OD,

0.3 mm ID). At the nebulizer end, the Tefzel tubing was stretched and cut to form a taper in order to reduce the dead volume at this juncture.

**Table 2:** ICP-MS instrumentation and operating conditions

| | |
|---|---|
| Spectrometer | Sciex ELAN 500 |
| RF power | 1.25 kW |
| Plasma gas flow | 14 l/min |
| Auxiliary gas flow | 1.4 l/min |
| Nebulizer gas flow | 1.24 l/min |
| Nebulizer type | Meinhard |
| Spray chamber | Water cooled (20 °C) |
| Interface cones | Platinum |
| Data acquisition mode | Multichannel |
| Individual dwell time | 50 ms |
| Total integration time per point | 1 or 2 s |

For the colorimetric work, the IC effluent was mixed with the DPC reagent in a T-fitting (Dionex PN 024313) and then passed to the UV detector, using either a 60 cm Tefzel (0.3 mm ID) transfer line or a Dionex packed-bead reaction coil (PN 036036), which has a length of 122 cm. The color reagent was prepared fresh daily by dissolving 50 mg of 1,5-diphenylcarbohydrazide in 10 ml methanol, adding this solution to a mixture of 80 ml deionized water and 5 ml concentrated $H_2SO_4$, and making up to a final volume of 100 ml. The DPC reagent was supplied to the mixing "T" by a Gilson Minipuls II peristaltic pump using 0.76 mm ID pump tubing. Absorbance of the effluent/reagent mixture at 540 nm was measured with a Linear UVIS 203 detector equipped with a 6mm path length cell. The detector signal was acquired, stored and analyzed using a Dynamic Solutions Maxima 820 chromatography data station and software.

In the case of ICP-MS detection, the time-dependent signals for metal ions were acquired by the ICP-MS computer with the Multiple Elements program. The data in ASCII format was transferred to the Maxima computer via serial interface and translated to data interchange format (DIF) using a Turbo Pascal program written by one of the authors (RR). The DIF files were read and analyzed with the Maxima software in the same fashion as the UV chromatograms.

## RESULTS

**Ion Chromatography.** The ion chromatographic conditions used in this study were adopted after considerable experimentation with different columns, eluent systems, and flow rate settings. Our primary requirements for the separation system were: (1) an eluent system which is compatible with the ICP-MS and colorimetric detection methods, (2) a column/eluent combination resulting in good chromatographic

separation of chromate from other chemical species, and (3) short analysis times (preferably 10 min or less).

Most of this work was performed with a Dionex AS4A anion exchange column because that column type had been employed successfully in earlier IC-ICP-MS speciation studies [10]. The utility of a Dionex OmniPac PAX-500 column was also explored briefly. However, the necessity of maintaining a low percentage of an organic solvent (e.g., 1 % methanol or acetonitrile) in the eluent resulted in excessively high background counts from $^{40}Ar^{12}C^{+}$ when $^{52}Cr$ was monitored by ICP-MS.

Eluent systems based on slightly alkaline ammonium sulfate solutions had been used successfully for Cr(VI) determinations with other anion exchange columns and colorimetric detection [4,5]. We observed some peak tailing for chromate when a pH 9 buffered ammonium sulfate eluent was tested in conjunction with an AS4A column. This peak tailing could be minimized by adding $10^{-5}$ M perchlorate to the eluent.

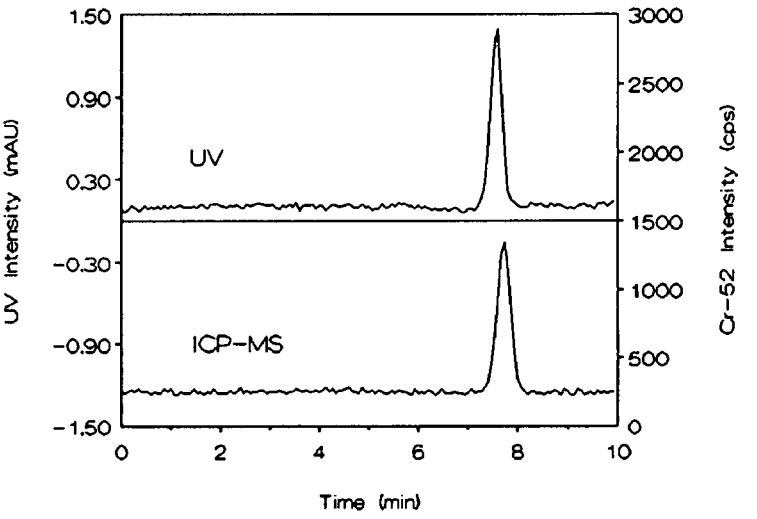


**Figure 1:** Chromatograms obtained for a 10 ug/l solution of Cr(VI) with colorimetric detection and ICP-MS detection of Cr-52

Figure 1 shows chromatograms obtained for a 10 ug/l Cr(VI) solution analyzed by IC-colorimetry and IC-ICP-MS using the conditions given in the Experimental section. As expected, the peaks obtained with ICP-MS detection were somewhat wider because of additional band broadening in the ICP spray chamber.

**Detection Limits.** Exploratory measurements had indicated that the detection limits for Cr(VI) with both detection methods and with both isotopes used in ICP-MS ($^{52}Cr$ and $^{53}Cr$) were in the range 1-3 ug/l. The actual detection limits were determined by making nine repetitive injections of a 5 ug/l Cr(VI) standard onto the IC column (cf. Fig. 2) and letting the chromatography software find peak areas and peak heights. The peak detection parameters were set using the software's automatic peak integration setup mode. Detection limits were taken to correspond to three times the standard deviations of the peak areas or heights for a given set of conditions. All of the results compiled in Table 3 were obtained using 100 ul injections and the eluent

parameters given in Table 1. It was interesting to find that significantly smaller injections (25 ul) resulted in only slightly inferior detection limit values.

**Table 3:** Chromium (VI) Detection Limits in ug/l[1]

| | Peak Area | Peak Height |
|---|---|---|
| Colorimetry with PBR[2] | 0.9 | 0.8 |
| Colorimetry without PBR | 2.2 | 1.5 |
| ICP-MS using $^{52}Cr$ | 1.3 | 1.1 |
| ICP-MS using $^{53}Cr$ | 1.9 | 1.4 |

[1] Based on three standard deviations of integrated peaks

[2] PBR = Packed-bead reactor

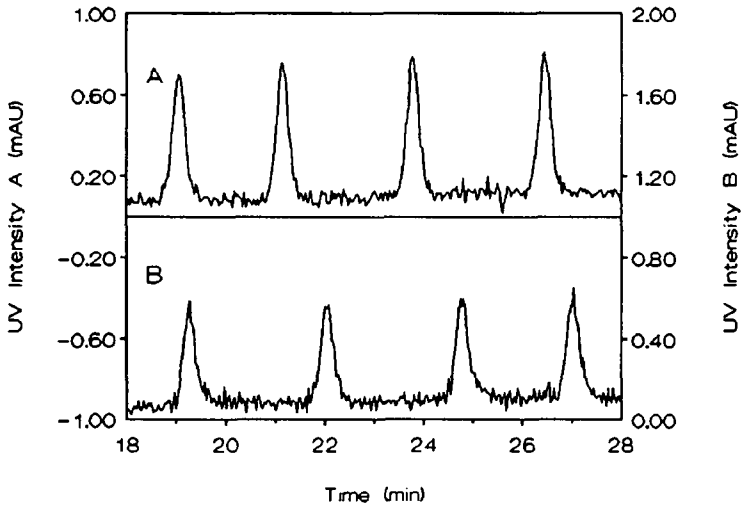


**Figure 2:** Four repetitive injections of a 5 ug/l Cr(VI) standard onto the IC column using colorimetric detection: (A) with, (B) without the packed-bead reactor

The colorimetric measurements were repeated with and without the packed-bead reactor (PBR) inserted between the mixing "T" and the UV detector. As can be seen from Fig. 2, use of the PBR resulted in somewhat larger peaks and less baseline noise, which explains the improvement of the detection limits by a factor of about 2. The chromatographic traces shown in Fig. 2 were also analyzed to estimate detection limits based on the commonly employed method of calculating three standard deviations of the baseline noise. Values of 0.4 and 0.6 ug/l were obtained for the experiments with and without the PBR respectively; they are comparable to the detection limits given in Table 3.

With ICP-MS, the signals for $^{52}Cr$ and $^{53}Cr$ were recorded simultaneously, i.e., the total acquisition time was divided between the two isotopes. The signal-to-noise ratios, and therefore the detection limits, could probably be improved by a factor of 1.4 by employing single ion monitoring. A detailed description of the advantages and disadvantages of using either one of the two chromium isotopes for ICP-MS measurements is given in the Discussion section.

**Linear Dynamic Range.** The upper concentration limit of the colorimetric method was assumed to be reached when the measured absorbance exceeded 1.0 AU. With our IC system and UV detector, this was found to occur at about 10 mg/l of Cr(VI). Analysis of a series of standards ranging up to 10 mg/l showed that there was no significant deviation from linearity between the detection limit and 10 mg/l, resulting in a linear dynamic range spanning at least four decades.

For ICP-MS detection, the dynamic range was expected to be limited by channel electron multiplier (CEM) saturation, which generally occurs when count rates exceed $10^6$ $s^{-1}$. Under the experimental conditions used in this study, CEM saturation should have been observed for $^{52}Cr$ at Cr(VI) concentrations exceeding about 30 mg/l (or 300 mg/l for $^{53}Cr$). However, peak heights as well as peak areas for both isotopes began to deviate from linearity at concentrations above 10 mg/l. Therefore, the linear dynamic range of the IC-ICP-MS combination is identical to that of the colorimetric method.

**Analysis of Field Samples.** The performance of the two ion chromatography methods with actual field samples containing low levels of Cr(VI) was evaluated by analyzing a series of filters, probe washes and impinger solutions which had been collected during recent emission tests at a cement plant burning hazardous waste as a supplemental fuel. The samples were derived from special Cr(VI) sampling trains, consisting of Teflon coated glass fiber filters and impingers filled with 0.02 M $NaHCO_3$. Sodium bicarbonate solutions of the same strength were used to rinse the sampling probes and to extract the filters. Whereas none of the impinger solutions had detectable concentrations of hexavalent chromium, two probe washes and filter extracts were found to contain Cr(VI) at low ug/l levels. The results obtained with the two detection methods are compared in Table 4. Considering that the measured concentrations are very close to the detection limits of both methods, the results are in excellent agreement.

**Table 4:** Chromium (VI) concentrations in five field samples as determined by IC-colorimetry and ICP-MS using $^{52}Cr$. The units are ug/l.

| Sample | IC-Colorimetry | IC-ICP-MS |
|---|---|---|
| Probe Wash 1 | 4.3 | 4.0 |
| Probe Wash 2 | 2.0 | 1.9 |
| Filter Extract 1 | 2.0 | 1.6 |
| Filter Extract 2 | 5.3 | 4.7 |
| Soil Extract | 284 | 264 |

It may be noted that when the same samples were re-analyzed three months after collection, essentially identical results were obtained. This indicates that 0.02 M $NaHCO_3$ solution is a suitable storage medium for hexavalent chromium.

The performance of IC-colorimetry and IC-ICP-MS with a complex matrix containing higher levels of Cr(VI) was tested by analyzing an alkaline extract of a soil sample from the Stringfellow hazardous waste site in Riverside Co., California. This sample contains a significant amount of humic material and high levels of chloride and sulfate, in addition to a large number of other constituents. Neither method had any problems with this matrix and the results for hexavalent chromium are in good agreement (Table 4).

## DISCUSSION

This section addresses several issues which are relevant to the application of ICP-MS as a detection method for chromium in general and to the combination of ICP-MS with ion chromatography for the specific determination of Cr(VI) in particular. It also discusses some applications of IC-ICP-MS to the speciation of other elements.

**Detection of Chromium Isotopes by ICP-MS.** Chromium has four stable isotopes: $^{50}Cr$ (4.31 % relative abundance), $^{52}Cr$ (83.8 %), $^{53}Cr$ (9.6 %) and $^{54}Cr$ (2.38 %). However, only the isotopes with masses of 52 and 53 are of analytical utility in ICP-MS, because measurements of the $^{50}Cr$ and $^{54}Cr$ isotopes generally suffer from high background counts due to $^{36}Ar^{14}N^+$ and $^{38}Ar^{16}O^+$ respectively.

When clean water or dilute nitric acid are analyzed by ICP-MS, the background at mass 52 is mostly due to $^{36}Ar^{16}O^+$ and is significantly higher than that at mass 53 ($^{36}Ar^{17}O^+$, $^{36}Ar^{16}O^1H^+$). This largely offsets the abundance advantage of the $^{52}Cr$ isotope for the determination of chromium, as illustrated by the detection limit results given in Table 3. Additional interferences for $^{52}Cr$ can arise when samples contain high concentrations of carbon (e.g., TCLP extracts) or sulfur; the primary interferant species in those cases are $^{40}Ar^{12}C^+$ and $^{36}S^{16}O^+$. The measurement of the $^{53}Cr$ isotope can suffer significant interference from $^{37}Cl^{16}O^+$ when high concentrations of chlorine are present.

Although the list of possible interferences in the determination of chromium by ICP-MS may appear intimidating at first, it must be emphasized that those interferences do not seriously affect the IC-ICP-MS method for Cr(VI) presented in this report, because ion chromatography effectively separates chromate from potentially interfering anionic species which may occur at high concentrations in environmental samples (e.g., carbonate, sulfate and chloride). The level of sulfate in the IC eluent used in this work (6 mM) increased the background for $^{52}Cr$ only to a small extent. It should be noted that an eluent containing 250 mM $(NH_4)_2SO_4$, such as is used with the Dionex AS7 column [5], would probably preclude the use of $^{52}Cr$ for IC-ICP-MS determinations of Cr(VI).

The aforementioned interferences must be considered when total chromium is determined by ICP-MS without a preceding IC separation. In this case, the presence of potentially interfering concentrations of carbon, sulfur or chlorine can be detected by simultaneously monitoring for $^{13}C^+$, $^{34}S^+$ and $^{35}Cl^+$. The best isotope for the quantification of chromium can then be selected based on the results of those additional measurements. The extent to which molecular ion species, such as $ArC^+$ or $ClO^+$, affect ICP-MS measurements can also be reduced by mixing a small amount of nitrogen into the argon supplying the ICP [Roehl and Alforque, unpublished work].

**Application of IC-ICP-MS to Other Oxy-Anions.** Earlier work performed in this laboratory had indicated that vanadate, molybdate, tungstate and chromate could be separated with an AS4A column using a 2 mM $Na_2CO_3$ eluent [10]. However, even at a flow rate of 2 ml/min, the retention time for chromate was rather long (20 min; capacity factor k' = 31). Oxy-anions of the different oxidation states of arsenic (III and V) and selenium (IV and VI) were separated very well by this chromatographic system, with retention times ranging from 0.9 to 13.8 min (k'= 0.16 - 17). It should be noted that those earlier experiments were performed with an older AS4A column than the one used for the work presented here.

Switching to a new column and changing from a 2 mM $Na_2CO_3$ eluent at a flow rate of 2 ml/min to a 6 mM $(NH_4)_2SO_4$ eluent at 1 ml/min resulted in a significantly shorter retention time for chromate (about 7.5 min); the capacity factor for Cr(VI) was reduced from 31 to 3.8. Therefore, it was of interest to also explore the behavior of other oxy-anions under the new IC conditions.

Figure 3 shows a set of chromatograms obtained when a mixed standard of vanadate, tungstate, molybdate and chromate was analyzed by ICP-MS. The concentration of each metal was 10 ug/l. Vanadate exhibited pronounced peak tailing, which made peak area determinations difficult. Tungstate, molybdate and chromate, on the other hand, produced sharp, well resolved peaks. Compared to our earlier experiments with the sodium carbonate system, all four oxy-anions eluted more rapidly.

Similar results were obtained for the inorganic arsenic and selenium species. Arsenite eluted at 1.8 min, i.e., just after the void volume, closely followed by selenite and arsenate (both at 2.7 min). Eluting after 4.0 min, selenate was the most strongly retained species in this set of four analytes. With the carbonate system, the elution order had been arsenite < selenite < selenate < arsenate.

When an alkaline extract of a soil sample from the Stringfellow site (cf. Results section) was analyzed for oxy-anions, no arsenic or selenium was detected. However, vanadate, tungstate and molybdate were present in addition to chromate (Fig. 4). Based on peak height analysis, their concentrations were estimated to be 49 ug/l (vanadate), 3.6 ug/l (tungstate) and 45 ug/l (molybdate) respectively. The Cr(VI) concentration (264 ug/l) was already given in Table 4.

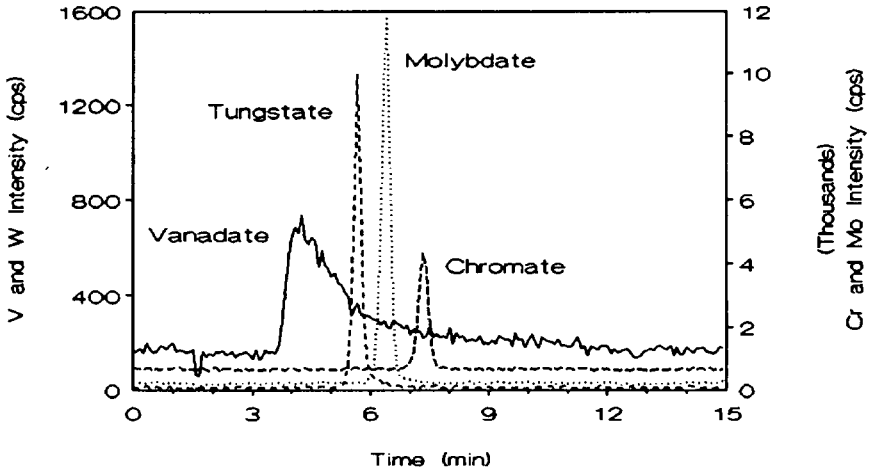


**Figure 3:** Chromatograms of a standard containing 10 ug/l each of V, W, Mo and Cr in the form of their oxy-anions. V-51, W-182, Mo-98 and Cr-52 were detected simultaneously by ICP-MS

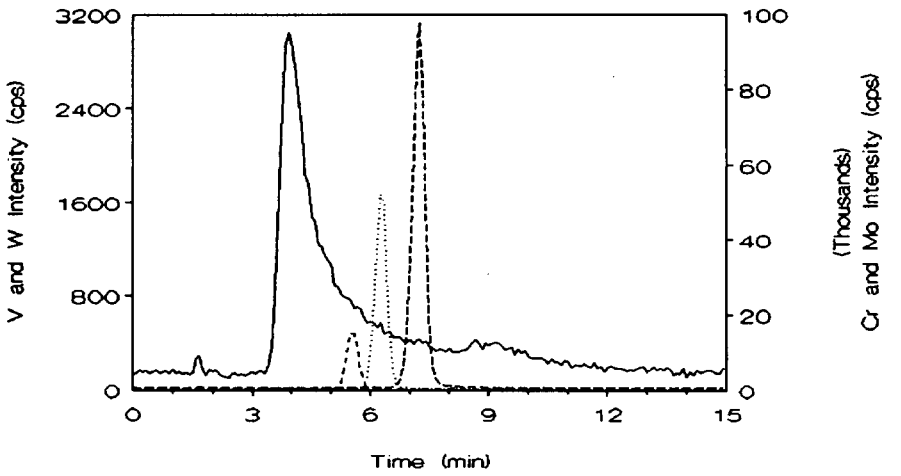


**Figure 4:** Chromatograms of an alkaline soil extract from the Stringfellow site showing the presence of vanadate, tungstate, molybdate and chromate. See Fig. 3 for peak identification

## SUMMARY

The method comparison in this report has shown that IC-ICP-MS is a viable alternative to the more classical technique of IC-colorimetry for the determination of hexavalent chromium in aqueous samples. The detection limits and dynamic ranges of both methods are similar. Compared to colorimetry, ICP-MS is a much more expensive technology to implement in a laboratory, but if the instrumentation is already available, IC-ICP-MS has the advantage that it can be used to speciate other elements as well.

## ACKNOWLEDGEMENTS

The authors thank John Riviello and Robert Joyce of Dionex Corporation for suggesting the addition of perchlorate to the IC eluent and for several very helpful discussions.

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# MOBILITY

# A Proposed Waste Component Mobility Scale

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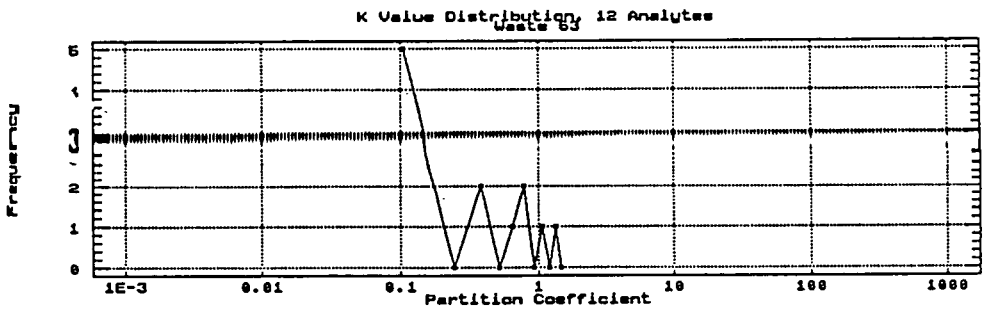
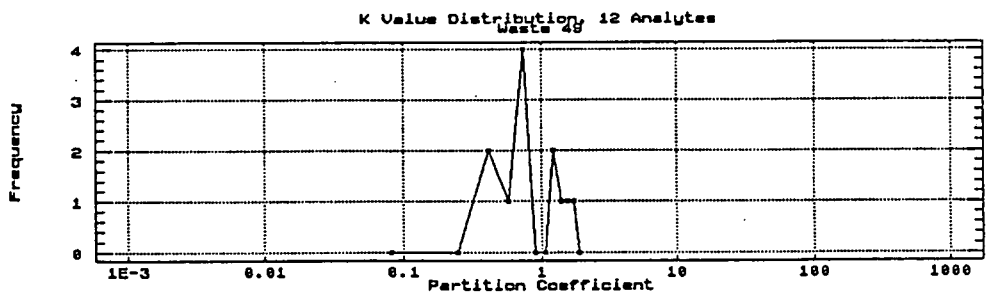
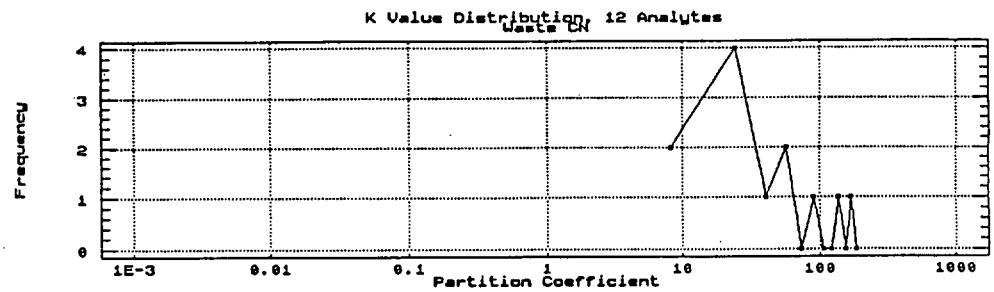
A universal scalling system would be of use in studies where waste component mobility in solid/liquid systems is of interest. A technically accurate scaling system would be useful to, for example, compare waste component ( organic, inorganic and other species ) mobility between treated and untreated wastes to demonstrate the effect of waste fixation technologies. Alternatively, such a scale or meteric could be useful in comparing mobility of waste components between various waste to assess one aspect of a wastes potential to contaminate ground water. Also, such a scale would have utility in comparing waste component mobility under varying analysis conditions including: extraction time; liquid phase properties and solid phase characteristics. In this paper, we assert that where biphasic systems are accurate representations of the system under study or where solid/liquid partitioning information is of import in describing, comparing or assessing waste component mobility (as it virtually always is) that elementary physical chemistry and statistics has already given us the tools to propose such a scale. In this paper we propose a mobility scale based on partition coefficients for organic compounds.

To visualize this approach, we show below a comparison of partition coefficients for 12 volatile organic compounds for three wastes. It is clear that for these waste and analytes that K values differ by about 3 orders of magnitude from the top to the bottom graph. In our paper, we discuss our mobility K Scale(s) applied to organic wastes, inorganic species and we consider statistical and graphical interpretation of our results. We propose that a such a scale be adopted for the classification of waste component mobility in solid/liquid systems. Extension to gas/solid/liquid systems is also discussed.



102

# CONTAMINATED SOILS LEACHING PART I MOBILITY OF SOLUBLE SPECIES

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## Introduction

The development of laboratory tests that may be used to predict whether a waste is hazardous has been and continues to be of paramount importance to EPA and the regulated community. The development of these tests is a two step process. The first step is used to establish what will happen to waste when it is disposed in a given environment. That is, what components from the waste will migrate and what will their concentrations be in the migrating media (usually water). The second step is to devise a laboratory test that will model the migration potential of the waste. The laboratory test is then used by EPA and the regulated community to determine the risk posed by the waste.

Contaminated soils have become a significant environmental medium over the past few years. The EPA regional labs, as well as superfund remediation contractors, need methods to establish whether soil that has been contaminated as the result of a spill is hazardous; and, if they remove to treat contaminated soil, what post-treated toxicant concentration would be considered protective. The question being asked is "What test can be used to best determine whether a site is safe?" This research was undertaken to address this question.

## Experimental

Four soils were collected that represented a range of soil types and characteristics. Two soils were clay type, designated alfisol and ultisol, one soil was a very dark organic rich soil, designated Mollisol, and one soil was a sandy carbonaceous soil, designated aridisol. The soils were tested for alkalinity, cation exchange capacity, pH, and Total organic carbon.

The soils were then spiked with inorganic and organic contaminants at concentrations that would cause them to be judged hazardous using the toxicity characteristic leaching procedure if only 2% of the spiked amount leached from the soil. Soils were spiked in two groups. One group was spiked with metals and semivolatile organic compounds. The other set was spiked with volatile organic compounds and cyanide. Water soluble chloride salts were used for spiking for all metals except lead, which was spiked as the nitrate. Semivolatile compound were spiked in methylene chloride and benzene solutions. Cyanide was spike in water as sodium cyanide. After spiking the soils were allowed to dry in the hood to remove the solvent. Volatile compound were spike directly onto prechilled soil.

Metals that were spiked included Cadmium, Chromium, Copper, Lead, and Mercury. Semivolatiles included phenol, paracresol, nitrobenzene, pentachlorophenol, and hexachlorobenzene. Volatiles included chlorobenzene, 1,2-dichloroethane, Methylethyl ketone, tetrachloroethylene, and toluene. Cyanide was also spiked. After spiking each soil was analyzed in triplicate to establish the spiking levels that were actually found in the soil.

The soils were packed into laboratory scale lysimeters constructed from pyrex glass to a depth of 2 feet. The soil compaction was adjusted to give the same compaction that would be expected for undisturbed soil. Two lysimeters of each spiked soil were prepared for each soil batch to provide an estimate of lysimeter variability. One unspiked soil lysimeter was also prepared to serve as a control and to provide samples for laboratory recovery experiments. Thus for each soil batch there were 12 lysimeters (i.e. 4 soils x 2 spiked and 4 controls). A total of 24 lysimeters were prepared in all. The lysimeters were 3 inches internal diameter and 5 feet long. Each lysimeter was filled with a leaching fluid to a height of 2 feet above the top of the soil in the lysimeter. Simulated acid rain leaching fluid (unbuffered deionized water adjusted to pH 4.2 with 60:40 $H_2SO_4$:$HNO_3$) was used for the metal and semivolatile soil batch and deionized water was used for the volatile and cyanide soil batch.

The pore volume of each lysimeter was calculated by measuring the distance the leaching fluid level fell until liquid exited the bottom of the lysimeter. Samples were then collected every pore volume until the concentration of at least 5 consecutive pore volumes did not change.

Spiked soils were also tested using the EP Toxicity test (Method 1310), the Toxicity Characteristic Leaching Procedure (Method 1311), and the simulated acid raid test (Method 1312).

## Results and Discussion

The results of the lysimeter studies provided the leaching profiles of each contaminant spiked onto the soil and their leaching rates. With lead being the only exception the leaching curves all represented a exponential decay. The leaching of components was complete within the first ten pore volumes, again with lead the exception.

All of the leaching curves derived from this lysimeter study can be described as gaussian curves. The curves all follow the general formula for a bell shaped curve:

$$Y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\left(\frac{x-\mu}{\sigma}\right)^2} \quad \textbf{(1)}$$

where:

$\sigma$ = standard deviation of the curve and
x = displacement from the top of the peak, i.e. the mean
u = mean.

That is, all of the curves follow this equation even though the top of the peaks may be shifted due to a strong interaction with the soil. Thus, some curves seem to follow a simple exponential decay while others show, what appears to be, a chromatographic profile. The $\sigma$ value reflects how broad the curve is. If a curve peaks at u, then u-x describes the shape of the curve in the positive and negative directions.

$$C_t = \frac{C_{max}}{\sigma\sqrt{2\pi}} e^{-\left(\frac{t-t_r}{\sigma}\right)^2} \quad \textbf{(2)}$$

where:

$C_t$ = analyte concentration at t
$C_{max}$ = analyte concentration at $t_r$
$\sigma$ = peak standard deviation
t = time displacement from peak maxima
$t_r$ = peak maxima.

Equation 2 is the gaussian analog for compounds eluting under chromatographic conditions. Here, however, the mean and displacement are replaced with time variables.

Under a chromatographic system, a mobile phase percolates over the stationary phase. In the case of the lysimeters, the homologs are the leaching media and the soil, respectively. An analyte introduced into the mobile phase will eventually exit the column, with the time of elution dependent on any interactions (and therefore retardation) with the stationary phase. Thus, a strong interaction (physical or chemical) between the analyte and the stationary phase (soil) will produce a long retention time $t_r$.

The leaching curves show that all significant leaching (from the elution peak shape) takes place within the first 10 lysimeter pore volumes. This was much faster than anyone had expected. The general view is that the soils would interact with the contaminants to a greater degree and retain them. Furthermore, almost all of the curves show maximum leaching in the first pore volume. Thus, the mechanism of the leaching, particularly for the metals, probably depends on solubility and adsorption.

The summary results of the lysimeter experiments for the metals are provided in Table 1 along with the results of the leaching tests.

Table 1
Percent Recovery of Metals from Lysimeters
and Batch Leaching Tests

| Soil | Column 1 | Column 2 | EP | TCLP | Acid Rain |
|---|---|---|---|---|---|
| Cadmium | | | | | |
| Alfisol | 65.4 | 96.2 | 96.4 | 89.2 | 94.2 |
| Aridisol | 33.2 | 38.8 | 73.7 | 80.1 | 47.7 |
| Mollisol | 61.5 | 68.8 | 73.8 | 80.7 | 82.1 |
| Ultisol | 64.8 | 87.8 | 84.2 | 82.3 | 95 |
| Copper | | | | | |
| Alfisol | 74.5 | 110.8 | 114 | 85.6 | 101 |
| Aridisol | 0.6 | 0.3 | 13.3 | 28.7 | <1.6 |
| Mollisol | 8.9 | 10.1 | 16.1 | 16 | 13.6 |
| Ultisol | 81.7 | 104.4 | 92.7 | 70.3 | 110 |
| Mercury | | | | | |
| Alfisol | 96.4 | 118.6 | 90.2 | 81.6 | 89 |
| Aridisol | 89.4 | 58 | 94.4 | 73.7 | 76.4 |
| Mollisol | 44.2 | 53 | 42.5 | 66.5 | 67.8 |
| Ultisol | 88.8 | 109 | 100 | 92.4 | 99.1 |
| Chromium | | | | | |
| Alfisol | 49.4 | 70.7 | 52.6 | 57.1 | 47.1 |
| Aridisol | 0.0 | 0.0 | <0.9 | 5.4 | 0.9 |
| Mollisol | 0.1 | 0.2 | <1.1 | 2.4 | 1.1 |
| Ultisol | 57.9 | 82.7 | 61.5 | 59.8 | 62.9 |
| Lead | | | | | |
| Alfisol | 58.2 | 64.7 | 97 | 80.9 | 97.9 |
| Aridisol | 3.8 | 2.4 | 22.2 | 37.5 | 0.8 |
| Mollisol | 13.0 | 10.7 | 24.8 | 44.8 | 24.8 |
| Ultisol | 88.8 | 78.4 | 95.4 | 82.1 | 100.0 |

Experimental results for the organic compounds show that the higher the water solubility of the compound, the faster it eluted from the lysimeters. For the semivolatile compounds, phenol is the most soluble and it eluted the most rapidly, followed by p-cresol, and nitrobenzene. Hexachlorobenzene and pentachlorophenol did not elute from the lysimeters. Similar to the metals, the elution of the semivolatile compounds ended within the first 10 pore volumes.

Detectable amounts of all of the volatile compounds eluted from the lysimeters. Recoveries of the volatile compounds from the lysimeters were generally very low. This may be due to evaporative losses or interaction with the soil. Volatile data was only obtained for aridisol. The other soils interacted so strongly with the volatile constituents that leaching fluid would not pass through the lysimeters.

Data for the organic compounds are contained in Tables 2 and 3.

Table 2
Recovery of Semivolatile Organics from Lysimeters
and Batch Leaching Tests

| Soil | Column 1 | Column 2 | EP | TCLP | Acid Rain |
|---|---|---|---|---|---|
| Phenol | | | | | |
| Alfisol | 39.5 | 49.5 | | 10.0 | 10.7 |
| Aridisol | 29.6 | 58.6 | 27.1 | 27.8 | 34.2 |
| Mollisol | 71.8 | 65.7 | 40.3 | 23.5 | 24.3 |
| Ultisol | 71.1 | 70.7 | 13.7 | 13.7 | 16.1 |
| Cresol | | | | | |
| Alfisol | 5.5 | 10.8 | | 2.3 | ND |
| Aridisol | 7.1 | 43.3 | 1.2 | 1.7 | 1.7 |
| Mollisol | 36.4 | 31.9 | 14.2 | 0.7 | 6.3 |
| Ultisol | 50.2 | 32.7 | 1.3 | 1.3 | 0.8 |
| Nitrobenzene | | | | | |
| Alfisol | 3.7 | 7.0 | | 3.4 | 2.3 |
| Aridisol | 3.9 | 6.0 | 22.3 | 16.4 | 11.0 |
| Mollisol | 6.0 | 10.0 | 23.4 | 35.0 | ND |
| Ultisol | 20.3 | 9.6 | 5.5 | 0.4 | ND |

Table 3
Recovery of Volatile Organics from Lysimeters
and Batch Leaching Tests

| Soil/Analyte | Column 1 | Column 2 | EP |
|---|---|---|---|
| Aridisol | | | |
| DCE | 27.0 | 32.8 | 20.8 |
| MEK | 7.5 | 3.5 | 12.3 |
| TCE | 0.3 | 0.2 | 11.1 |
| Toluene | 34.3 | 30.7 | 83.0 |
| CL-Benzene | 12.6 | 11.6 | 43.2 |

The soils were leached using batch extraction methods 1310, 1311, and 1312 to determine which, if any, of these tests best simulate the column data. Tables 1, 2, and 3 provide the recoveries for the inorganic and organic contaminants leached respectively by these methods. All three extraction methods proved to be similar in terms of percent analyte extracted, with few variances observed.

All inorganic analytes extract well, dependent upon their solubilities. Organic analytes similarly follow this solubility trend.

In general, the batch leaching of the metal analytes with synthetic acid rain showed good agreement with that of the acid rain lysimeters. In addition, the batch leaching data using the EP procedure resembled that of the acid rain data. The extraction data for the organics seems to be less comparable with that of the columns.

Again, both analyte leaching in the lysimeter and the extraction vessel seem wholly dependent on the solubility of a chemical species. Anomalies to this behavior are copper, chromium, and lead on aridisol and mollisol, showing depressed extraction levels under both methods.

Low level leaching of chromium, copper, and lead in aridisol could be due to formation of metal carbonates or hydroxides. The high alkalinity of aridisol supports this conclusion.

One can also note a higher or equivalent extraction efficiency for the batch method than for the lysimeter for most of the analytes. This is to be expected as the batch method uses a 20 to 1 liquid to solid ratio whereas the lysimeters end up with a final liquid to solid ratio between 0.1 and 0.2 at 10 pore volumes. The constant agitation coupled to the high liquid volume of the batch method favors a high level of extraction, especially with the solubility dependence of the contaminants involved.

In summary, the column lysimeters and the batch extractions produced approximately the same results with regards to percent toxicant recovered. The contaminants were leached to a similar extent due to their solubility behavior in the media. The different liquid media slightly affected the leaching efficiency, and of the three batch tests, the acid rain procedure gave similar results to the lysimeter, as expected. The EP method, however, also produced analogous data.

103

# CONTAMINATED SOILS LEACHING PART II
# MOBILITY OF LEAD FROM CONTAMINATED SOILS

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## Introduction

Recently, EPA Region I and several states have expressed concern regarding the disposition of lead contaminated soils. Their concern is founded on the fear that a significant percentage of soil in urban areas may fail the Toxicity Characteristic Leaching Procedure (TCLP) for lead. Specifically, they are concerned that lead contaminated soils may be classified as a hazardous waste if it is moved during excavation or landscaping. Such a situation, if it could be enforced, would require that homeowners and building contractors comply with the hazardous waste regulations.

Because of these concerns, EPA conducted two interlaboratory studies designed to compare the aggressiveness of several leaching media toward lead contaminated soils. In one study, six different leaching media were used on five soils taken from Region I. The leaching media varied in acid strength from simulated acid rain to the acetic acid buffer used in the TCLP. A microwave digestion method was also evaluated for determining the concentration of lead in the soils during this study. The second interlaboratory study compared the leachability of lead from five soils taken around Baltimore, Maryland. This second study utilized the EP, TCLP, and simulated acid rain as leaching media.

The questions we attempted to answer involved whether there was a significant difference between the EP and TCLP, the soil concentration required to exceed 5 mg/L in the leachate, the affect of diluted acetic buffers, and whether there was a significant difference between standard digestion methods and the microwave method.

## Experimental

Five soil samples were collected by EPA Region I personnel from an area surrounding a house in Boston, MA believed to contaminated with lead from leaded paint. These samples were used in the first interlaboratory study. Five soil samples were collected by personnel from the State of Maryland Department of the Environment.

Each soil was sieved to remove debris (i.e. rocks and plant material) and tumbled to achieve a homogeneous sample. The soils were then aliquoted and sent to the participating laboratories.

Samples were characterized by analyzing pH (Method 9045), alkalinity, total metals (Methods 3050, 3051, and 6010). The boston soils were leached using methods 1310 (EP), 1311 (TCLP), 1312 (Synthetic acid rain), 1311 @ 10% buffer, 1311 @ 25%, and 1311 @ 50% buffer. The baltimore soils were leached via methods 1310, 1311, and 1312.

## Results and Discussion

The pH of the boston soils ranged from 5.7 to 6.5 with alkalinity from 150 to 300 mg/kg. The pH of the baltimore soils ranged from 6.6 to 7.9 with alkalinity going from non detectable to 200 mg/kg.

Boston Soil Interlaboratory Study

Table 1 shows a comparison of the microwave digestion method and method 3050 for lead. The lead concentrations determined with the microwave digestion were similar to those determined using method 3050. The precision for these measurements were also about the same. Generally, the microwave digestion gave equal or higher concentrations and equal or better precision than the conventional digestion for all metals tested.

Table 1
Comparison of Digestion Methods for Lead ± % RSD

| Soil Sample | Method 3050 | Method 3051 (Microwave) |
|---|---|---|
| 1 | 3700 ± 29 | 4299 ± 27 |
| 3 | 2214 ± 24 | 1510 ± 3 |
| 4 | 2750 ± 4 | 5690 ± 13 |
| 5 | 874 ± 6 | 798 ± 4 |

The apparent discrepancies in total lead values can be attributed to small paint chips in the soil. Although, the chips were not visible, upon addition of acid small paint chips would float to the surface and effervesce. This observation agrees with the assumption that the soil was contaminated by lead from paint chips since lead carbonate was the primary pigment used in white house paint prior to 1950. Thus, the differences in total lead shown by both methods may be due to different amounts of paint chips in each sample aliquot taken rather than to the methods themselves.

Table 2 shows the results form the interlaboratory leaching study of the soils. The results show that Method 1311 leached the highest concentration of lead of any of the leaching media. Furthermore, the concentration of lead leached is proportional to the amount of acid present in the leaching media.

Table 2
Results of the Interlaboratory Study
Average Lead Concentration in the Leachate (mg/L)

| Soil Number | 1311 | 1311 50% | 1311 25% | 1311 10% | 1312 | 1310 |
|---|---|---|---|---|---|---|
| 5 | 0.8 | 0.36 | 0.17 | 0.125 | 0.21 | 0.05 |
| 4 | 10.5 | 6.1 | 2.8 | 0.78 | 0.91 | 0.5 |
| 3 | 2.1 | 0.86 | 0.41 | 0.23 | 0.35 | 0.07 |
| 1 | 4.75 | 2.7 | 1.12 | 0.375 | 0.63 | 0.17 |

The results of the interlaboratory study of the Baltimore soils were similar to the Boston soils. Method 1311 was clearly more aggressive than either method 1310 or 1312. The results of the Baltimore soil interlaboratory study are summarized in Table 3.

Table 3
Results of the Interlaboratory Study
Average Lead Concentration
Total and Leachate (mg/kg and mg/L)

| Soil Number | Total | Methods 1311 | 1312 | 1310 |
|---|---|---|---|---|
| 1 | 8253 | 29.0 | 0.56 | 0.79 |
| 2 | 1533 | 1.3 | 0.38 | 0.09 |
| 3 | 19900 | 50.8 | 2.70 | 3.03 |
| 4 | 1633 | 3.0 | 0.12 | 0.61 |
| 5 | 1046 | 1.6 | 0.10 | 0.07 |

Conclusions

This study showed that soils containing lead at concentrations greater than about 2000 mg/kg would likely leach lead in excess of 5 mg/L when using method 1311. When using methods 1310 or 1312, however, lead concentration in excess of 10,000 mg/kg are required to produce leachates greater than 5 mg/L. The leaching power of each solution was proportional to the acid (buffer) content.

By using this approach, one could estimate the effect of the TCLP on the disposition of urban soils, assuming one knew the distribution of lead in the soils. Soils adjacent to buildings that were painted with leaded paints will have a higher likelihood of being judged hazardous. Since this type of paint was in wide use prior to 1950, property with older structures would be more likely to have elevated soil lead concentrations.

104

# MOBILITY OF CONTAMINANTS FROM MUNICIPAL WASTE COMBUSTION ASH

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## Introduction

The health and environmental hazards posed by the disposal of municipal waste combustion (MWC) ash are largely unknown. Several legislative proposals have been introduced in both houses of Congress dealing with regulating the disposal of MWC ash. EPA has conducted several studies over the past few years to determine whether MWC ash is a RCRA hazardous waste and whether the ash would require special management standards for safe disposal. While these studies have contributed a great deal to our understanding about the placement of MWC ash in the environment, very little is known about the basic mechanism of release of hazardous materials from the ash over time.

The Office of Solid waste has conducted a study to establish the leaching behavior of MWC ash over time and to compare these results with laboratory batch leaching tests. The time dependent leaching behavior of MWC ash is important since it influences not only disposal design standards, but also our basic understanding regarding the hazardousness of MWC ash.

## Experimental

Three municipal waste incinerators, representing the three basic types of combustors (i.e., mass burn, modular, and refuse derived fuel), were sampled. Samples were taken of mixed ash (combined fly and bottom ash) over a four hour period and composited to provide the ash sample for testing. During sampling, large particles were removed or broken to provide a reasonably homogenous (i.e. particle size of 1/2 in diameter, or less) ash sample. A total of about 300 lb of ash was collected at each incinerator.

The ash was shipped to the laboratory and placed in a series of lysimeters. The lysimeters were constructed of pyrex glass and were 4 inches in diameter and 5 feet long. Ash was placed in each lysimeter to a height of 3 feet. The lysimeters were tapped lightly to allow the ash to settle. Each column typically contained between 15 and 20 lbs of ash.

There were a total of 6 lysimeters for each ash or 18 lysimeters in all. For each ash two lysimeters were leached with distilled water, two with simulated acid rain (60:40 $H_2SO_4$:$HNO_3$), and two with simulated landfill leachate. The lysimeters were maintained under a head pressure of approximately 2 ft of leachate during the leaching experiments. The effluent from the lysimeters were collected every 1/2 lysimeter pore volume. The pore volumes were established by measuring the amount of leaching fluid needed to filling the lysimeters just to the top of the ash.

Samples were analyzed for total dissolved solids, specific conductivity, pH, chloride, sulfate, and metals (As, Ba, Cd, Cr, Cu, Ni, Pb, and Zn). Ash samples were also subjected

to the EP Extraction Procedure (Method 1310), the Toxicity Characteristic Leaching Procedure (TCLP - Method 1311), and the Simulated Acid Rain Leaching Test (Method 1312).

## Results and Discussion

The leaching curves were established for each lysimeter for each analyte. Generally, water soluble species (e.g. chloride and sulfate) leached from the lysimeters very rapidly. These species were essentially washed from the lysimeters within the first 10 pore volumes (See Table 1). All of these curves exhibited an exponential decay. Several of the metals also followed this pattern. Figures 1 and 2 demonstrate the leaching of barium and lead from two of the ashes using simulated acid rain. Barium and lead were the most mobile metals from the lysimeters regardless of the leaching medium.

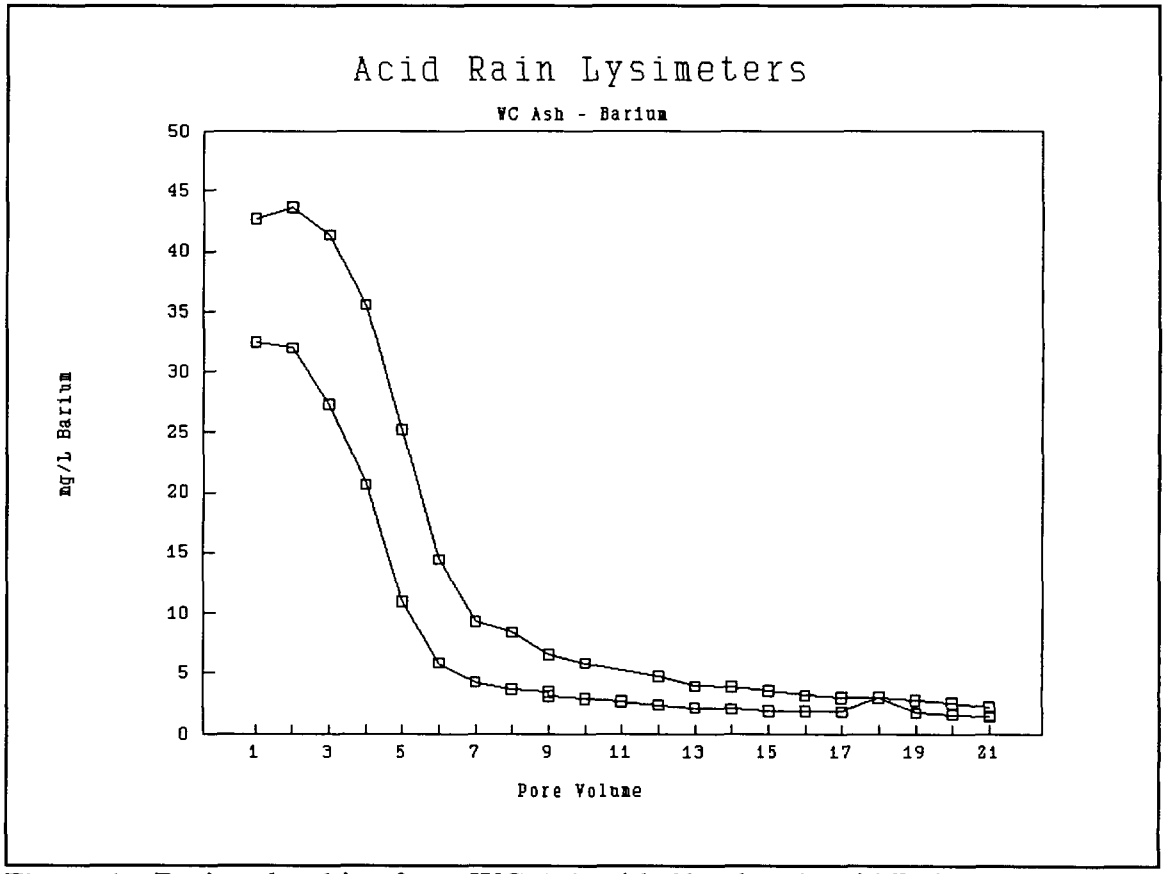


**Figure 1** - Barium leaching from WC Ash with Simulated Acid Rain

It was somewhat unexpected that barium and lead would be so mobile. This may be due to the pH. The pH of the leachates from the lysimeters were quite high due to lime addition to the fly ash. The fly and bottom ash are mixed to produce the ash that was sampled.

In this case the pH ranged from about 11.5 to 12.5. It is possible that these metal species are fairly soluble in this pH range and thus are washed from the lysimeters.

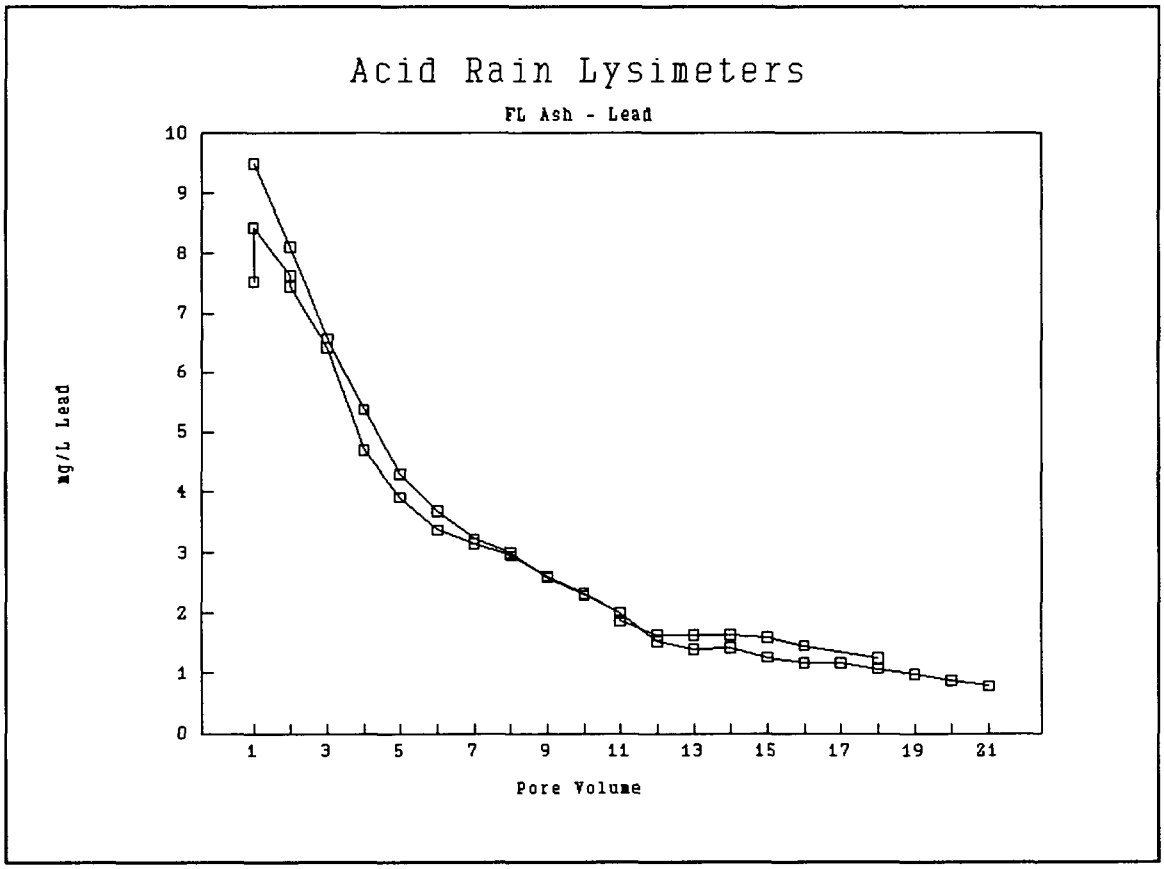


**Figure 2** - Leaching of Lead from FL Ash with Simulated Acid Rain

Appreciable leaching was observed for lead, barium, zinc, and copper for the three ashes. As with anions, most of the leaching for the metals occurred within the first 10 pore volumes.

Batch leaching was performed for each ash type using the EP, TCLP, and Deionized Water (DI). There was reasonably good agreement between the leaching tests and the column results when pH of the leaching media is taken into account. For example, when using the EP or TCLP the final pH of the leaching solution was around 6. At this pH little or no barium and lead leached from the ash, however, zinc leaching is increased dramatically.

Table 1 - Chloride mg/L

| Pore Number | DI Water | Acid Rain | Synthetic Leachate |
|---|---|---|---|
| 0.5 | 7000 | 7900 | 6280 |
| 1.0 | 4950 | 6000 | 4560 |
| 1.5 | 3040 | 4500 | 2870 |
| 2.0 | 2010 | 2720 | 1970 |
| 2.5 | 1030 | 1880 | 2080 |
| 3.0 | 530 | 1200 | 1610 |
| 3.5 | 390 | 700 | 1160 |
| 4.0 | 270 | 460 | 870 |
| 4.5 | 200 | 450 | 650 |
| 5.0 | 180 | 350 | 660 |
| 5.5 | 160 | 200 | 380 |

105

# THE WASTE INTERFACE LEACHING TEST: A LONG-TERM STATIC LEACHING METHOD FOR SOLIDIFIED/STABILIZED WASTE

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## ABSTRACT

The purpose of a solidification/stabilization process is to reduce the leachability of hazardous constituents in treated wastes to a level required to protect groundwater resources if the solidified waste is placed in a landfill. Many stabilization processes include the addition of cement or other pozzolanic materials to the wastes to produce a product which can be molded into monolithic shapes. The Waste Interface Leaching Test (WILT) was developed to assess the leachability of monolithic waste forms exposed to an aqueous environment.

Features of the WILT include; (1) large monolithic samples up to 11 Kg in mass, (2) a low leachant to unit surface area ratio of less than 1.5:1, and (3) a sequential leaching period of up to 6 months. The WILT was used to evaluate solidified waste produced by the Soliditech process as part of a U.S.EPA SITE demonstration project. Solidified masses were placed in plastic tanks with sand packing and were sequentially with distilled water on a biweekly basis. A diffusion coefficient and leachability index for several inorganic constituents were determined at the end of the 6-month leaching period. Results from the WILT corroborated results from other leaching tests in demonstrating the effectiveness of the solidification process.

The WILT was shown to be a leaching method that can provide long-term data on large monolithic forms to evaluate the efficacy of solidification/stabilization processes.

106

# ALTERNATIVE METHODS FOR ESTIMATING LEACHING OF INORGANIC CONSTITUENTS FROM COAL-COMBUSTION RESIDUES

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## ABSTRACT

In this paper, we compare data on leachates obtained by the extraction procedure (EP), by the toxicity characteristic leaching procedure (TCLP), in field leachate samples, and in pore waters for five coal-combustion disposal sites. The results for the EP and the TCLP extracts and the concentrations in the other leachates are also compared with predictions made using the reaction-based FOWL™ computer code. With the exception of Ba, whose concentration is typically higher in the EP and TCLP extracts than that observed in disposal site pore waters or drainage leachate, leachate concentrations obtained by the EP and TCLP methods are about a factor of 10 lower than those observed in the disposal site leachates. The EP and TCLP methods appear to dilute the effect of highly soluble salts because of the 20:1 solution-to-solid ratio used and to solubilize large amounts of Ca from calcareous samples because of the low pH of the extracts. Concentrations for Ca, Ba, Sr, and $SO_4$ predicted by the FOWL™ code were closer to the concentrations in the pore waters than were the concentrations in the EP and TCLP extracts, in several cases to within a factor of 2. These comparisons and other experiments have provided the additional information needed to improve the geochemistry incorporated in the FOWL™ code. The results presented show that planned modifications to the FOWL™ code will improve its accuracy for predicting concentrations of several of the elements discussed in this paper and of several elements that are described only empirically in the current version of FOWL™.

## INTRODUCTION

Coal-combustion residues include fly ash, bottom ash, and scrubber sludge. These solid wastes are disposed of on land in ponds and landfills. The 1980 Bevill Amendment to the Resource Conservation and Recovery Act (RCRA) exempted these high-volume solid wastes from the hazardous-waste provisions of the law. Therefore, the use of the U.S. Environmental Protection Agency's (EPA's) extraction procedure (EP) or toxicity characteristic leaching procedure (TCLP) is not required for determining whether or not these wastes are to be considered hazardous wastes. Nonetheless, a number of samples of fly ash, bottom ash, and scrubber sludge have been analyzed for leachate composition using the EP, the TCLP, and a water-extraction procedure, and by field sampling of disposal

facilities. In addition, the Electric Power Research Institute (EPRI) has developed a reaction-based computer code, FOWL™, for predicting compositions and quantities of leachates generated at disposal sites. The current discussions on RCRA reauthorization are likely to result in the development and adoption of new methods and approaches to determine the leaching characteristics of nonhazardous wastes. This paper is our contribution to the scientific debate.

The Electric Power Research Institute has sponsored a variety of research projects to develop the scientific understanding necessary for predicting leaching characteristics of coal-combustion wastes disposed of in landfills and ponds. Both laboratory and field studies have been carried out to define the leaching chemistry of inorganic constituents contained in fly ashes, bottom ashes, and scrubber sludges (Ainsworth and Rai 1987; Rai et al. 1987, 1989; Fruchter et al. 1988; Mattigod et al. 1990; Eary et al. 1990). Extensive laboratory and field studies of numerous samples have resulted in identification of fundamental chemical reactions responsible for leaching of several elements in the coal-combustion wastes. As a result, the reaction-based model FOWL™ was developed and released for general use in 1988 (Hostetler et al. 1988). Additional research, including sampling and analysis of waste and leachates from a variety of sites where coal-combustion wastes have been disposed of, has resulted in improvements to the FOWL™ code. The enhanced FOWL™ (Version 2.0) will be released in late 1990.

In this paper, we focus on leachate studies conducted with five waste samples from actual waste-disposal sites. The aqueous concentrations observed in 1) pore waters extracted from the moist field samples by immiscible displacement (Kinniburgh and Miles 1983), 2) leachates collected from the field disposal sites, 3) extracts obtained by the EP and TCLP tests, and 4) calculations made with the FOWL™ code were compared. It was found that the FOWL™-calculated concentrations for several elements were closer to those observed in the pore waters than were either the leachates or the EP or TCLP extracts.

## MATERIALS AND METHODS

### MATERIALS

Five samples of combustion wastes were collected from disposal areas at five power plants in Pennsylvania. The wastes consisted of fly ash, bottom ash, and scrubber sludge removed from active disposal areas that ranged in age from 6 months to 4 years. The materials were typically collected by mixing several samples taken from depths of 3 to 7 feet from two areas in each landfill. A brief description of the samples is presented in Table 1.

## METHODS

The pH of each material after 1 hour was determined from a 1:2 solid-to-solution (mass/vol) paste using deionized water. The total chemical composition of the dried samples was determined by proton-induced X-ray emission spectroscopy (PIXE).

The leachates for chemical analyses were generated by several methods (the EP and TCLP; extraction of pore water from the moist field samples by immiscible displacement with heavy liquid; and collection of leachates in the field). The methods to obtain EP and TCLP extracts have been described elsewhere (EPA 1982 and 1986, respectively). Pore water from the moist samples was extracted under a $N_2$ atmosphere by displacement with Freon®(1) (Kinniburgh and Miles 1983). The field leachates were collected and analyzed by participating utilities. It should be noted that, unfortunately, the pathways of some of the field leachates (corresponding to samples 703 and 705) intercepted springs and other offsite water and that, therefore, these leachates do not accurately represent what would be leached from coal-combustion wastes alone.

The composition of the extracts was determined by inductively coupled plasma (ICP) spectroscopy, and anions were analyzed by ion chromatography or ion-specific electrode.

### Geochemical Interpretations and Predictions

To determine the aqueous speciation and types of solid phases that may control the aqueous concentrations of selected elements, the compositions of pore-water extracts were modeled using the geochemical code MINTEQ (Felmy et al. 1984). In addition, the chemical compositions of the solid samples, along with pore-water pH values, were used as the input for calculating the leachate compositions with the FOWL™ code (Hostetler et al. 1988).

## RESULTS AND DISCUSSION

Several methods (EP, TCLP, FOWL™ calculations) can be used to estimate aqueous concentrations of different elements. These estimates in turn can be used to estimate the potential impacts of disposing of coal-combustion wastes on land surfaces. To check the validity of these methods for estimating leachate composition, their results must be compared with leachates collected from actual disposal sites. We obtained actual field leachates by two methods: 1) extracting pore water from samples collected at disposal sites and 2) collecting the drainage leachate from the same disposal sites. If the sampling site is chemically relatively homogeneous, as most coal-combustion disposal sites are, then the field leachates and pore waters should have similar concentrations. However, a comparison of the pH, which generally influences the leachate

composition through its effect on both precipitation and adsorption reactions for most elements, showed that for two of the samples (samples 703 and 705), the pH values were considerably different (Table 1). Such a difference indicates that these field leachates may not truly represent the leachates that would be generated solely from the wastes that were sampled. Correspondingly, the chemical analysis of field leachates for sample 705, for example, showed concentrations of Al, Fe, and Zn of 123, 756, and 3.28 mg/L, respectively, and a pH of 3.31, in contrast to the concentrations of these elements in pore waters (0.29, <0.01, and >0.05 mg/L) and the pH of 6.70. Therefore, the comparisons in this paper will be based on the pore-water compositions.

In the EP and TCLP, the pH of the waste/water suspensions generally ends up at about 5, and these methods use 1:20 solid-to-solution ratios. Under such conditions, 1) those elements that are present in the wastes as very soluble salts will be extracted and proportionately diluted, 2) those elements that are present in fairly insoluble solids and whose solubilities are pH-dependent will occur in concentrations that are different from those that would be found in equilibrium with field leachates with different pH, 3) anions whose concentrations are controlled by adsorption will occur in reduced concentrations because of the acidic pH of the extractants, and 4) those elements that are solubility controlled but have one ion that is affected by dilution will show enhanced concentrations for the other ion. In addition, the pH values of the EP and TCLP are artificially low and do not represent field conditions associated with disposal of coal-combustion wastes. Although acidic fly ash is sometimes produced, recent research would indicate that the pH increases to pH 7 (for example, see Roy et al. 1984). In addition, the pH of scrubber sludge and calcareous fly ashes would be expected to be closer to 8.3, as dictated by $CaCO_3$ equilibrium with $CO_2$ in the air. In view of these conditions, therefore, the EP and TCLP results may not reflect the concentrations actually to be expected at a given site. As a matter of fact, the Ca concentrations observed in the EP and TCLP extracts of scrubber sludge samples (sample 703, Table 2) are higher than those in the pore waters by about a factor of 3, because of $CaCO_3$ dissolution as a result of the low pH levels reached in these extracts. An additional problem with these extraction tests is that the results cannot be used to predict changing leachate concentrations with time. When EP and TCLP results are compared for other selected elements that are present in measurable concentrations and important in coal-combustion wastes, the concentrations are about a factor of 10 lower than those observed in pore waters (except for Ba, whose concentrations are about a factor of 10 higher). For many of the other trace elements, such as Pb, Cr, and Cd, no valid comparisons could be made, because these elements were present in the EP, TCLP, and pore waters at or near the detection limits.

A fundamental approach that relates the aqueous concentrations of elements to specific chemical reactions that may occur in different wastes and disposal environments is currently being developed. Under this approach, information regarding the precipitation/dissolution and adsorption/desorption reactions that may occur in the wastes is needed. If it can be shown for a given element that the concentrations are limited by precipitation/dissolution reactions and if the identity of the solubility-limiting solid is known, then the concentrations of the element are predictable from the thermochemical data for the appropriate solid and aqueous species. Therefore, as a first approximation in developing a fundamental approach, emphasis has been placed on the precipitation/dissolution reactions. Based on initial studies using a large number of coal-combustion residues, it appeared that the concentrations of several elements, such as Al, Ba, Ca, Sr, $SO_4$, and Mo, in laboratory studies involving samples obtained from dry collection systems and a dry fly ash disposal site were controlled by their respective solid phases [$AlOHSO_4$, $Al(OH)_3$, sulfate solids of Ca, Ba, and Sr, and $CaMoO_4$]. This solubility information, along with empirical observations of leachate quality for several other elements (i.e., As, Cd, Cu, Mg, K, Na, Ni, Se, and Zn), was used to develop the FOWL™ code (Hostetler et al. 1988) for predicting aqueous concentrations based on pH and the total chemical composition of the wastes. When the analytical concentrations in pore waters are modeled using an equilibrium model (MINTEQ; Felmy et al. 1984) and the resulting activities of Ca, Ba, and Sr are plotted as a function of $SO_4$ activity (Figure 1), the Ca, Sr, and Ba concentrations in the extracts appear to be controlled by their respective sulfate solids. (In the case of Ba, it is controlled by a solid that is slightly more soluble than barite, as observed in many other samples in studies we have conducted.) Given that the FOWL™ code uses the same solids as the basis of its calculations, the FOWL™-calculated results would be expected to be similar to those obtained in the pore waters.

The FOWL™-predicted leachate concentrations of several elements associated with the wastes are given in Table 2. The FOWL™-predicted concentrations of As shown in Table 2 are typical of those of several other trace elements (e.g., Cd, Cr, Cu, Fe, Pb, and Zn) determined empirically. That is, the pore-water concentrations of these elements are below their respective detection limits, and the FOWL™-predicted values also fall below the detection limits of the analytical techniques used.

Although the FOWL™-predicted concentrations for most elements that are above detection limits are within a factor of 3, the model overpredicts Ba and underpredicts $SO_4$, Ca, Mg, Mo, Na, Ni, and Sr. Therefore, further improvements are being carried out. These improvements include 1) use of an equilibrium geochemical code, instead of looking values up in tables, 2) better estimation of $SO_4$ concentrations by incorporating electrical conductance and its relationship to sulfate, which would in turn improve predictions of Ca, Ba, and Sr, 3) more reliable and verified

thermochemical data, 4) incorporation of thermochemical data for additional elements (e.g., Cu, Zn, and Cr) that have been found to be limited by solubility since the development of FOWL™, and 5) incorporation of mechanistically determined masses of particular solid phases instead of empirically estimated leachable fractions. Several of these improvements have already been incorporated into FOWL™ Version 2.0, resulting in significantly better predictive capabilities. The concentrations of Ca, $SO_4$, and Sr predicted by FOWL™ Version 2.0 (Table 2) differ in most cases from concentrations in actual pore waters by significantly less than a factor of 2. Barium predictions have also been improved significantly, although they are so far still unsatisfactory.

## CONCLUSIONS

The EP and TCLP extracts of coal-combustion wastes do not, in most cases, reflect the leachate composition found at disposal sites. Often this is a result of either dilution or adjustment of pH to artificially low levels. Typically, the EP and TCLP extracts underestimate concentrations by as much as an order of magnitude. In contrast, concentrations of selected elements predicted by the computer code FOWL™ (Version 2.0) differ from concentrations observed in pore waters from coal-combustion waste disposal sites by less than a factor of 2. Further improvements to FOWL™ based on thermochemical data collected from sound laboratory experimentation and tested using data collected in the field will provide an even better predictive capability, for an even larger suite of elements associated with coal-combustion waste leachate.

TABLE 1. Waste-Material Location, Type, Age, and pH

| Sample Number | Material[a] | Age (yr) | pH | |
|---|---|---|---|---|
| | | | Pore Water | Field Leachate |
| 701 | FA | 4 | 7.3 | 7.2 |
| 702 | FA/BA | 2 | 6.8 | 7.2 |
| 703 | SS/FA | 0.5 | 10.1 | 7.4 |
| 704 | FA/BA | 0.5 | 6.5 | 7.0 |
| 705 | FA | 1.5 - 2 | 6.7 | 3.3 |

(a) FA = fly ash; BA = bottom ash; SS = scrubber sludge.

TABLE 2. Concentrations of Selected Elements Extracted from Coal-Combustion Wastes by EP and TCLP and in Pore Waters and Field Leachates Associated with Actual Disposal Sites, and Values Predicted by FOWL™

| Method | Concentrations (mg/L) in Different Samples | | | | |
|---|---|---|---|---|---|
| | 701 | 702 | 703 | 704 | 705 |
| As | | | | | |
| EP | 0.085 | 0.011 | 0.032 | 0.24 | 0.071 |
| TCLP | 0.20 | 0.047 | 0.038 | 0.26 | 0.20 |
| Pore Water | <0.16 | <0.16 | <0.16 | <0.16 | <0.16 |
| Field Leachate | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| FOWL™ | 0.1 | 0.01 | 0.01 | 0.1 | 0.1 |
| B | | | | | |
| EP | 0.45 | 0.29 | 10.7 | 1.11 | 0.45 |
| TCLP | 1.7 | 1.7 | 7.1 | <0.6 | <0.6 |
| Pore Water | 10.4 | 3.45 | 0.19 | 77.7 | 23.3 |
| Field Leachate | 21.6 | 3.3 | 1.3 | 38.1 | 1.6 |
| FOWL™ | --- | --- | --- | --- | --- |
| Ba | | | | | |
| EP | 0.64 | 0.64 | 0.73 | 0.68 | 0.17 |
| TCLP | 0.58 | 0.44 | 0.53 | 0.33 | 0.22 |
| Pore Water | 0.06 | 0.06 | 0.06 | 0.08 | 0.07 |
| Field Leachate | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| FOWL™ | 0.25 | 0.25 | 0.27 | 0.25 | 0.25 |
| FOWL™ (Version 2.0) | 0.012 | 0.012 | 0.012 | 0.010 | 0.011 |
| Ca | | | | | |
| EP | 69 | 80 | 1,880 | 70 | 97 |
| TCLP | 77 | 83 | 1,630 | 139 | 97 |
| Pore Water | 587 | 597 | 642 | 458 | 473 |
| Field Leachate | 410 | 339 | 452 | 467 | 323 |
| FOWL™ | 394 | 394 | 408 | 394 | 394 |
| FOWL™ (Version 2.0) | 611 | 611 | 611 | 444 | 468 |

(a) FOWL™ (Version 2.0) is currently under development and will be available in late 1990. FOWL™ (Version 2.0) will differ from Version 1.0 in that it will contain 1) a code for calculating geochemical equilibrium instead of looking it up in tables, 2) an improved thermochemical database, 3) an improved database for empirical elements that is based on field and laboratory experiments, and 4) an improved ability for application to sluiced sites.

(contd)

| Method | Concentrations (mg/L) in Different Samples | | | | |
|---|---|---|---|---|---|
| | 701 | 702 | 703 | 704 | 705 |
| Sr | | | | | |
| EP | 1.10 | 2.04 | 3.96 | 1.22 | 1.19 |
| TCLP | 1.02 | 2.67 | 3.89 | 1.48 | 1.54 |
| Pore Water | 12.40 | 16.80 | 4.25 | 10.50 | 7.40 |
| Field Leachate | 4.97 | 4.10 | 3.67 | 8.73 | 6.63 |
| FOWL™ | 1.62 | 1.62 | 1.72 | 1.62 | 1.62 |
| FOWL™ (Version 2.0) | 12.2 | 12.2 | 12.2 | 8.9 | 9.4 |
| $SO_4^{2-}$ | | | | | |
| EP | 160 | 190 | 2,400 | 190 | 260 |
| TCLP | 170 | 190 | 1,800 | 210 | 250 |
| Pore Water | 1,850 | 1,748 | 1,284 | 4,488 | 4,333 |
| Field Leachate | 1,800 | 2,140 | 1,230 | 3,940 | 4,260 |
| FOWL™ | 945 | 945 | 945 | 945 | 945 |
| FOWL™ (Version 2.0) | 1,478 | 1,478 | 1,478 | 3,793 | 2,914 |

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FOOTNOTES

(1) Freon® is a trademark of E. I. Dupont de Nemours & Co., Wilmington, Delaware 19898.

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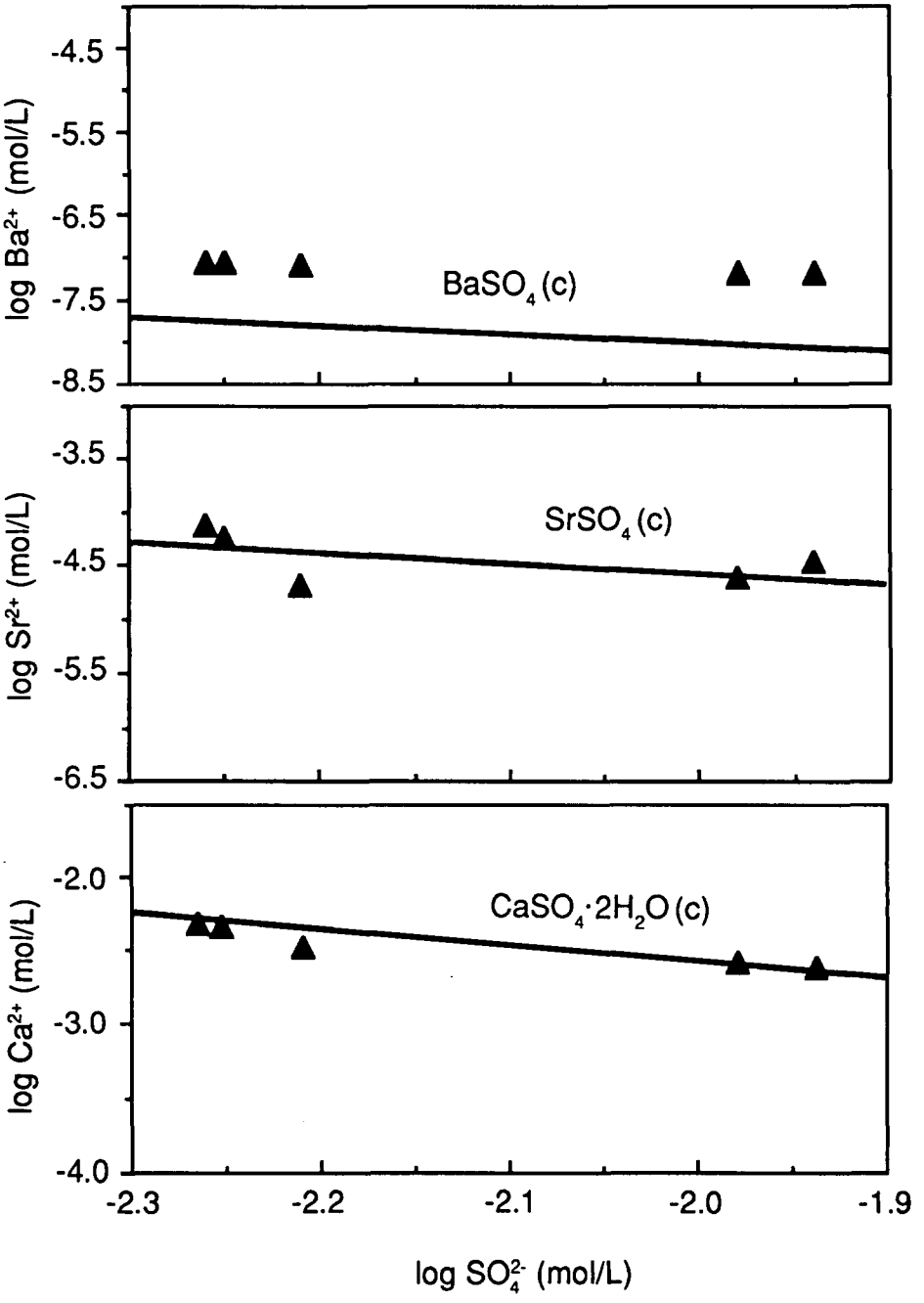
FIGURE 1. Activities of Ca, Sr, and Ba in Pore Waters as a Function of Sulfate in Different Samples. Solid lines represent ion activities calculated to be in equilibrium with the solids identified in the figure.


log $Ba^{2+}$ (mol/L)
-4.5
-5.5
-6.5
-7.5
-8.5
$BaSO_4$ (c)
log $Sr^{2+}$ (mol/L)
-3.5
-4.5
-5.5
-6.5
$SrSO_4$ (c)
log $Ca^{2+}$ (mol/L)
-2.0
-3.0
-4.0
$CaSO_4 \cdot 2H_2O$ (c)
-2.3
-2.2
-2.1
-2.0
-1.9
log $SO_4^{2-}$ (mol/L)

# AIR/GROUNDWATER

# 107 DETERMINATION OF TARGET ORGANICS IN AIR USING ION TRAP MASS SPECTROMETRY

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As a result of their simplicity, versatility, sensitivity, and ease of operation, ion trap mass spectrometers are emerging as a potentially important new technology for environmental monitoring applications. In particular, the tolerance of these mass spectrometers toward relatively high operating pressures places fewer restraints on the interfacing of these devices with a variety of sample introduction systems. For example, we have previously demonstrated the ability to rapidly detect and quantify trace volatile organics in water, soil slurries, oil, and other matrices by purging a sample directly into an ion trap through an open/split capillary interface. Detection limits of 1 ppb or less are possible with no sample preconcentration and with splitting 90% or more of the sample to a vent. As an extension of this work, we have been investigating the use of ion traps for the determination of trace organics in ambient air.

The equipment used for this research consists of a Finnigan ITMS ion trap mass spectrometer which is equipped with a specially designed thermal desorption device as well as a direct air sampling probe. The ITMS is equipped with the hardware and software required for chemical ionization, selective ion storage, and collision induced dissociation (CID) tandem mass spectrometry (MS/MS). Volatile organics in air can be detected in real time at levels of 10-100 ppb using the direct sampling probe. Trace analysis is performed by preconcentration on resin traps followed by rapid thermal desorption into the ITMS through an open/split interface. Using preconcentration and thermal desorption, low pptr levels of semivolatile compounds have been successfully determined. Methods have been developed and evaluated for the determination of nicotine in environmental tobacco smoke, organophosphonate compounds in ambient air, and certain chemical warfare agents using direct thermal desorption into the ITMS. The turn around time between samples is typically 2-3 minutes (not counting the collection of a sample on a resin trap). For real-time measurements, the direct air sampling probe is being tested for its applicability to monitoring constituents in environmental tobacco smoke, process streams, and headspace of various wastes.

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*Research sponsored jointly by the U.S. Army Toxic and Hazardous Materials Agency, Interagency Agreement 1769-A073-A1, and the National Cancer Institute, Interagency Agreement 0485-0485-A1, under Martin Marietta Energy Systems, Inc., contract DE-AC05-84OR21400 with the U.S. Department of Energy.

108

# Ion Chromatography for the Detection of Formic Acid in Incinerator Emissions and Ash from the Use of Formic Acid as a POHC

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Formic acid has many advantages as a Principle Hazardous Organic Constituent (POHC) for hazardous waste incinerator trial burns. The compound is water soluble, available in bulk, inexpensive, and is high on the incinerability list. One of the major drawbacks in the use of formic acid has been the lack of analytical methodologies suitable for determining formic acid at levels sufficient to verify destruction efficiency.

Ion chromatography has been previously applied to the detection of the formate ion in impinger solutions generated by incineration trial burns. However, limited success was obtained with limits of detection too high for verification of destruction efficiency. We have modified and expanded the ion chromatographic method for formate analysis in impingers as well as in ash extracts from incinerator trial burns. Method limits of detection are 30ppb for

impinger solutions and 1000ppb for ash samples. A caustic extraction of the ash produced recoveries of better than 90% from spiked ash samples. Preliminary studies of the M5 train indicate that no carryover of the formic acid (formate) is experienced between the first and second caustic impinger if 0.1N hydroxide is used as the scrubber solution. Over 75% of the fromic acid (formate) is found in the condensate impingers in the trial burn in which formic acid was an aqueous and solid feed POHC. Data will be presented on this revised method as well as a discussion of the application of the analytical methodology under a variety of scenarios.

109

# Ambient Air Monitoring for Benzene and Ethylene Oxide at Texaco Conroe Chemical Plant, Conroe, Texas

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## ABSTRACT

During the month of April 1989, Texaco Conroe Chemical Plant, Conroe, Texas, collected approximately three hundred samples of benzene and ethylene oxide in adsorption tubes at the upwind fenceline, the downwind fenceline, the benzene processing unit, the ethylene oxide processing unit, and outside the fenceline in a near-by commercial area. All of the samples in this study were duplicated and analyzed at the Southwest Research Institute Laboratories, San Antonio, Texas. Analytical results show that the highest measured benzene and ethylene oxide concentrations were found at the process unit. These measured values of 246.6 and 429.4 micrograms per cubic meter for benzene and ethylene oxide are well below the OSHA 8-hour occupational Threshold Limit Value (TLV) of 3,187 and 1,798 micrograms per cubic meter, respectively.

## INTRODUCTION

Toxic chemicals released from chemical plants in the United States have become an issue of national concern. These concerns include both health effects and the threat of continued degradation of environmental quality[1]. The Superfund Amendments and Reauthorization Act (SARA) was signed into law by President Ronald Reagan on October 17, 1986. Section 313 of the SARA Title III requires all facilities that store, manufacture, or process hazardous chemicals to report the type and quantity of toxic chemicals their operations release to the air, land, and water. Title III is also known as the Emergency Planning and Community Right-to Know Act of 1986. It is a free-standing statute to provide the public with information about release of toxic chemicals that results from the

operations of facilities in their community. The results of ambient air monitoring for benzene and ethylene oxide from the Texaco Conroe Chemical Plant can be used to address public exposure issues that may be raised by Section 313 reporting under SARA Title III regulations.

## MATERIAL AND METHODS

During the month of April 1989, Texaco Conroe Chemical Plant, Conroe, Texas, collected approximately three hundred samples of benzene and ethylene oxide in adsorption tubes at the upwind fenceline, the downwind fenceline, the benzene processing unit, the ethylene oxide processing unit, and the outside fenceline (Conservatex Company). During collection of the samples, the following meteorological measurements were recorded:

(1) Wind speed
(2) Wind direction
(3) Relative humidity
(4) Temperatures at 3 foot and 75 foot elevations above grade

Figures 1 and 2 show the ambient air monitoring sites for benzene and ethylene oxide, respectively. Figures 1 and 2 show that on days 1 and 2, points A, C, E, F, and FS-20 represented the monitoring sites at the downwind fenceline, the upwind fenceline, the outside fenceline, at pump number 8, and at the process unit, respectively. Figures 1 and 2 also show that on days 3, 4, 5, 6, 7, and 8, points B, D, E, F, and FS-20 represented the monitoring sites at the upwind fenceline, the downwind fenceline, the outside fenceline, at pump number 8, and at the process unit, respectively.

In this study, the Occupational Safety and Health Administration (OSHA) Method 50[2] and Method 7[3] were used to sample and analyze for ethylene oxide and benzene, respectively. All of the on-site samples in this study were duplicated and analyzed at the Southwest Research Institute Laboratories, San Antonio, Texas. The quality control protocol outlined in OSHA Method 50 and Method 7 were used to determine the average desorption efficiency for the samples.

## RESULTS AND DISCUSSIONS

Table I shows the benzene concentrations measured during the eight day ambient air monitoring program for five sites. The five sites are: (1) downwind at fenceline, (2) upwind at fenceline, (3) process unit, (4) outside fenceline (Conservatex Company), and (5) pump number 8. Pump number 8 is located between the process unit and the downwind fenceline.

Table II shows the maximum and minimum concentrations of benzene measured for each of the five sites during the eight day monitoring program. Table II also shows that the highest measured value of benzene concentration was found at the process unit. This measured value of 246.6 micrograms per cubic meter for benzene is below the OSHA 8-hour occupational Threshold Limit Value (TLV) of 3,187 micrograms per cubic meter. The OSHA 8-hour occupational TLV is a time weighted average concentration limit, based on eight hour workday and 40 hours per week, to which workers can be repeatedly exposed without adverse effect. Furthermore, Table II also shows that the maximum concentration values of benzene at the downwind fenceline, the upwind fenceline, the outside fenceline, and pump number 8 are 45.64, 60.75, 51.66, and 53.18 micrograms per cubic meter, respectively. The measured values of benzene concentrations for these sites are below the OSHA 8-hour occupational TLV of 3,187 micrograms per cubic meter. In this study, the Texas Air Control Board (TACB) Effects Screening Level (ESCL) and the monitored concentrations are not directly comparable due to differences between the concentration averaging times used in the TACB ESCLs (30-minute and annual) and the sample collection period (3.0-11.5 hours).

Table III shows the ethylene oxide concentrations measured during the eight day ambient air monitoring program for the the same five sites as described above. Table IV shows the maximum concentrations of ethylene oxide measured for each of the five sites during the eight day monitoring program. The highest measured value of ethylene oxide concentration was found at the process unit. This measured value of 429.4 micrograms per cubic meter for ethylene oxide is below the OSHA 8-hour occupational TLV of 1,798 micrograms per cubic meter. Furthermore, Table IV also shows that the maximum concentration values of ethylene oxide at the downwind fenceline, the upwind fenceline, the

outside fenceline, and pump number 8 are 45.67, <26.0, <26.00, and 77.6 micrograms per cubic meter, respectively. The measured values of ethylene oxide concentrations for these sites are below the OSHA 8-hour occupational TLV of 1,798 micrograms per cubic meter.

In this study, all of the desorption efficiency samples were analyzed at the Southwest Research Institute Laboratories, San Antonio, Texas. Table V shows the average percent desorption efficiency values of benzene and ethylene oxide are 75% and 76%, respectively.

## CONCLUSIONS

The results of benzene and ethylene oxide concentrations at the upwind fenceline, the downwind fenceline, the processing unit, the outside fenceline, and pump number 8 are below the OSHA 8-hour occupational TLV of 3,187 and 1,798 micrograms per cubic meter, respectively. The advantages of conducting ambient air monitoring in this study are listed as follows: (1) measured ambient air quality directly, (2) was more accurate than air dispersion modeling, (3) used the results to address public exposure limits, and (4) reduced community concern of toxic air emissions.

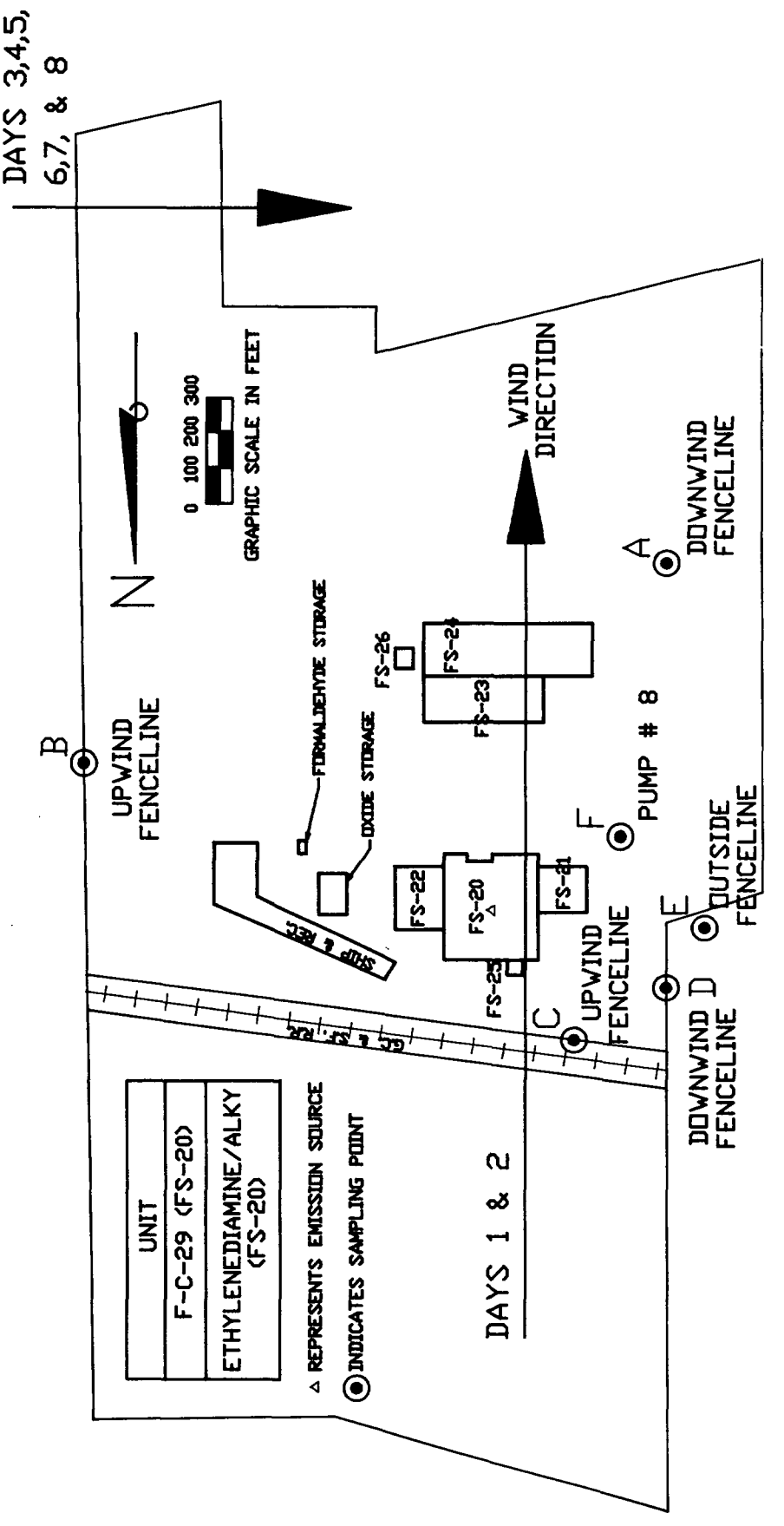
## REFERENCES

1. C. B. Doty and C. C. Travis, "The Superfund Remedial Action Decision Prosess: A Review of Fifty Records Decision," JAPCA 39:1535(1989).

2. K. J. Cummins, "OSHA Method No. 50, Ethylene Oxide," January, 1985, OSHA Analytical Laboratory, Salt Lake City, Utah 84115.

3. M. Shulsky, "OSHA Method No. 07, Benzene," March, 1985, OSHA Analytical Laboratory, Salt Lake City, Utah 84115.

# FIGURE 1
# TEXACO CONROE CHEMICAL PLANT
# AMBIENT AIR MONITORING FOR BENZENE



# FIGURE 2
# TEXACO CONROE CHEMICAL PLANT
# AMBIENT AIR MONITORING FOR ETHYLENE OXIDE

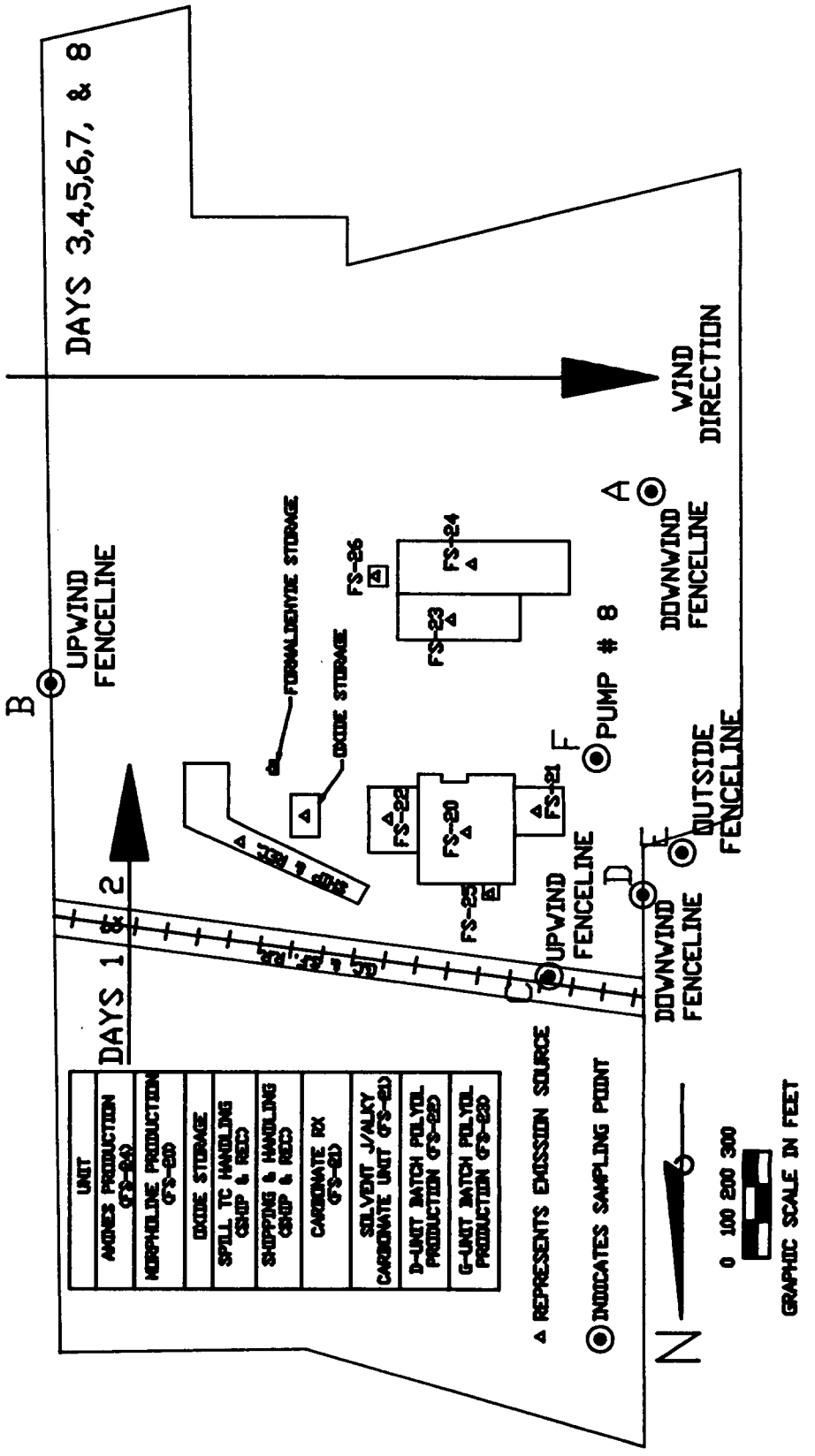


TABLE I
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 1 DATE 4-10-89 TO 4-11-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 1 | 4 | PROCESS UNIT | FS-20 | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 12:00AM-4:20PM (4.33) | 0.0995 | 2.050 | 20.61 |
| DAY 1 | 5 | PROCESS UNIT | FS-20 | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 9:14AM-4:28PM (7.23) | 0.0381 | 0.054 | 1.416 |
| DAY 1 | 6 | PROCESS UNIT | FS-20 | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 9:14AM-4:28PM (7.23) | 0.0381 | 2.228 | 58.47 |
| DAY 1 | 8 | DOWN WIND | A | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 9:24AM-5:02PM (7.63) | 0.0391 | 0.082 | 2.097 |
| DAY 1 | 10 | DOWN WIND | A | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 9:24AM-5:05PM (7.64) | 0.1015 | 0.067 | 0.660 |
| DAY 1 | 12 | UP WIND | C | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 9:48AM-5:05PM (7.64) | 0.0353 | 0.128 | 3.626 |
| DAY 1 | 14 | UP WIND | C | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 9:14AM-4:50PM (7.60) | 0.0339 | 0.058 | 1.711 |
| DAY 1 | 16 | CONSER-VATEX | E | 12.0 | 6.3 | 60.2 | N.D. | N.D. | 9:45AM-5:28PM (7.72) | 0.0382 | 0.062 | 1.623 |
| DAY 1 | 20 | PROCESS UNIT | FS-20 | 6.5 | 332 | 65.3 | N.D. | N.D. | 4:36PM-11:38PM (7.03) | 0.1115 | 2.36 | 21.17 |
| DAY 1 | 21 | PROCESS UNIT | FS-20 | 6.5 | 332 | 65.3 | N.D. | N.D. | 4:40PM-11:38PM (7.04) | 0.0528 | 3.61 | 68.37 |
| DAY 1 | 24 | DOWN WIND | A | 6.5 | 332 | 65.3 | N.D. | N.D. | 5:13PM-11:51PM (6.63) | 0.1127 | 0.16 | 1.42 |
| DAY 1 | 26 | DOWN WIND | A | 6.5 | 332 | 65.3 | N.D. | N.D. | 5:13PM-11:51PM (6.63) | 0.0434 | 0.073 | 1.682 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 1 DATE 4-10-89 TO 4-11-89 | SAMPLE | | | AVERAGE WIND | | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) | | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NUMBER | LOCATION | POINT | SPEED (MPH) | DIR. | | AT 3 FT. | AT 70 FT. | | | | |
| DAY 1 | 28 | DOWN WIND | A | 6.5 | 332 | 65.3 | N.D. | N.D. | 5.13PM-11:55PM (6.64) | 0.0462 | 0.150 | 3.247 |
| DAY 1 | 29 | UP WIND | C | 6.5 | 332 | 65.3 | N.D. | N.D. | 5:00PM-11:45PM (6.75) | 0.0514 | 0.084 | 1.634 |
| DAY 1 | 31 | CONSER-VATEX | E | 6.5 | 332 | 65.3 | N.D. | N.D. | 5:30PM-11.11PM (5.80) | 0.0490 | 0.084 | 2.054 |
| DAY 1 | 35 | PROCESS UNIT | FS-20 | 5.0 | 152 | 85.3 | 44.6 | N.D. | 11:39PM-8:35AM (8.93) | 0.0446 | 10.50 | 235.4 |
| DAY 1 | 36 | PROCESS UNIT | FS-20 | 5.0 | 152 | 85.3 | 44.6 | N.D. | 11:39PM-8:35AM (8.93) | 0.0446 | 11.00 | 246.6 |
| DAY 1 | 38 | PROCESS UNIT | FS-20 | 5.0 | 152 | 85.3 | 44.6 | N.D. | 11:45PM-8:40AM (8.92) | 0.0411 | 0.087 | 2.117 |
| DAY 1 | 39 | DOWN WIND | A | 5.0 | 152 | 85.3 | 44.6 | N.D. | 11:53PM-9:03PM (9.17) | 0.0446 | 0.096 | 2.152 |
| DAY 1 | 40 | DOWN WIND | A | 5.0 | 152 | 85.3 | 44.6 | N.D. | 11:53PM-9:03AM (9.17) | 0.0446 | 0.096 | 2.085 |
| DAY 1 | 46 | CONSER-VATEX | E | 5.0 | 152 | 85.3 | 44.6 | N.D. | 11:20PM-9:12AM (9.87) | 0.0407 | 0.098 | 2.408 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C, July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 2 DATE 4-11-89 TO 4-12-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 2 | 49 | PROCESS UNIT | FS-20 | 5.9 | 75.6 | 59.8 | 61.3 | N.D. | 8:40AM-3:35PM (6.92) | 0.0519 | 0.110 | 2.119 |
| DAY 2 | 50 | PROCESS UNIT | FS-20 | 5.9 | 75.6 | 59.8 | 61.3 | N.D. | 8:40AM-3:35PM (6.92) | 0.0519 | 0.110 | 2.119 |
| DAY 2 | 52 | UP WIND | C | 5.9 | 75.6 | 59.8 | 61.3 | N.D. | 8:42AM-3:40PM (6.97) | 0.0530 | 0.130 | 2.453 |
| DAY 2 | 54 | DOWN WIND | A | 5.9 | 75.6 | 59.8 | 61.3 | N.D. | 8:23AM-3:27PM (7.07) | 0.0463 | 0.140 | 3.024 |
| DAY 2 | 57 | DOWN WIND | A | 5.9 | 75.6 | 59.8 | 61.3 | N.D. | 9:15AM-3:48PM (6.55) | 0.0462 | 0.150 | 3.247 |
| DAY 2 | 58 | DOWN WIND | A | 5.9 | 75.6 | 59.8 | 61.3 | N.D. | 9:15AM-3:48PM (6.55) | 0.0462 | 0.140 | 3.030 |
| DAY 2 | 60 | CONSER-VATEX | E | 5.9 | 75.6 | 59.8 | 61.3 | N.D. | 9:17AM-3:18PM (6.00) | 0.0247 | 0.240 | 9.717 |
| DAY 2 | 63 | PROCESS UNIT | FS-20 | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3:36AM-10:13PM (6.60) | 0.0465 | 1.600 | 34.40 |
| DAY 2 | 64 | PROCESS UNIT | FS-20 | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3:36PM-10:13PM (6.60) | 0.0465 | 1.578 | 33.93 |
| DAY 2 | 66 | PUMP #8 | F | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3:38PM-9:43PM (6.08) | 0.0398 | 0.150 | 3.769 |
| DAY 2 | 69 | DOWN WIND | A | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3:40PM-10:04PM (6.40) | 0.0309 | 0.210 | 6.800 |
| DAY 2 | 70 | DOWN WIND | A | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3:40PM-10:04PM (6.40) | 0.0309 | 0.220 | 7.120 |
| DAY 2 | 72 | UP WIND | C | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3.50PM-9:55PM (6.08) | 0.0280 | 0.200 | 7.143 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 2 DATE 4-11-89 TO 4-12-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 2 | 74 | CONSER-VATEX | E | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3:20PM-9:48PM (6.47) | 0.0301 | 0.240 | 7.973 |
| DAY 2 | 77 | PROCESS UNIT | FS-20 | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 10:14PM-8:38AM (10.40) | 0.0780 | 2.67 | 34.23 |
| DAY 2 | 78 | PROCESS UNIT | FS-20 | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 10:14PM-8:38AM (10.40) | 0.0780 | 2.84 | 36.41 |
| DAY 2 | 80 | UP WIND | C | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 9:58PM-8:24AM (10.43) | 0.0794 | 0.250 | 3.149 |
| DAY 2 | 83 | DOWN WIND | A | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 10:05PM-8:28AM (10.38) | 0.0722 | 0.290 | 4.017 |
| DAY 2 | 84 | DOWN WIND | A | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 10:05PM-8:28AM (10.38) | 0.0722 | 0.280 | 3.878 |
| DAY 2 | 86 | PUMP #8 | F | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 9:45PM-8:45AM (11.00) | 0.0721 | 0.210 | 2.913 |
| DAY 2 | 88 | CONSER-VATEX | E | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 9:50PM-8:19AM (10.48) | 0.0432 | 0.370 | 6.944 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 3 DATE 4-12-89 TO 4-13-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 3 | 91 | PROCESS UNIT | FS-20 | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:40AM-3:18PM (6.63) | 0.0467 | 2.970 | 63.60 |
| DAY 3 | 92 | PROCESS UNIT | FS-20 | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:40AM-3:18PM (6.63) | 0.0467 | 3.090 | 66.17 |
| DAY 3 | 94 | PUMP #8 | F | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:50AM-2:00PM (5.17) | 0.0339 | 0.250 | 7.375 |
| DAY 3 | 97 | DOWN WIND | D | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:30AM-3:07PM (5.62) | 0.0271 | 0.190 | 7.011 |
| DAY 3 | 98 | DOWN WIND | D | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:30AM-3:07PM (5.62) | 0.0271 | 0.170 | 6.273 |
| DAY 3 | 100 | UP WIND | B | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:25AM-2:58PM (6.55) | 0.0301 | 0.044 | 1.462 |
| DAY 3 | 102 | CONSER--VATEX | E | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:20AM-2:50PM (6.54) | 0.0323 | 0.082 | 2.539 |
| DAY 3 | 105 | PROCESS UNIT | FS-20 | 7.0 | 66.4 | 69.7 | 62.5 | 58.1 | 3:18PM-8:00PM (4.73) | 0.0291 | 2.470 | 84.88 |
| DAY 3 | 108 | PROCESS UNIT | FS-20 | 7.0 | 66.4 | 69.7 | 62.5 | 58.1 | 2:57PM-7:58PM (5.02) | 0.0289 | 0.055 | 1.903 |
| DAY 3 | 111 | DOWN WIND | D | 7.0 | 66.4 | 69.7 | 62.5 | 58.1 | 3:10PM-8:00PM (4.83) | 0.0347 | 0.410 | 11.81 |
| DAY 3 | 112 | DOWN WIND | D | 7.0 | 66.4 | 69.7 | 62.5 | 58.1 | 3:10PM-8:00PM (4.83) | 0.0347 | 0.440 | 12.68 |
| DAY 3 | 114 | UP WIND | B | 7.0 | 66.4 | 69.7 | 62.5 | 58.1 | 2:56PM-8:00PM (5.07) | 0.0357 | 0.059 | 1.653 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 4 DATE | SAMPLE | | | AVERAGE WIND | | AVERAGE RELATIVE | AVERAGE TEMP. (F) | | TIME SAMPLE (HOUR) | SAMPLE VOLUME | SAMPLE MASS | SAMPLE CONC. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4-12-89 TO 4-13-89 | NUMBER | LOCATION | POINT | SPEED (MPH) | DIR. | HUMIDITY (%) | AT 3 FT. | AT 70 FT. | | (M3) | (UG) | (UG/M3) |
| DAY 3 | 116 | PUMP #8 | F | 7.0 | 66.4 | 69.7 | 62.5 | 58.1 | 3:35PM-8:00PM (4.42) | 0.0213 | 0.440 | 20.66 |
| DAY 3 | 119 | PROCESS UNIT | FS-20 | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 9:05PM-7:49AM (10.73) | 0.0662 | 6.190 | 93.50 |
| DAY 3 | 120 | PROCESS UNIT | FS-20 | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 9:05PM-7:49AM (10.73) | 0.0662 | 5.930 | 89.58 |
| DAY 3 | 122 | PUMP #8 | F | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 8:55PM-7:50AM (10.93) | 0.0731 | 0.890 | 12.18 |
| DAY 3 | 125 | DOWN WIND | D | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 8:52PM-7:47AM (10.93) | 0.0671 | 0.460 | 6.86 |
| DAY 3 | 126 | DOWN WIND | D | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 8:52PM-7:47AM (10.93) | 0.0671 | 0.210 | 3.129 |
| DAY 3 | 128 | CONSER-VATEX | E | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 9:12PM-7:43AM (10.52) | 0.0725 | 0.210 | 2.897 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 4 DATE 4-13-89 TO 4-14-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 4 | 131 | PROCESS UNIT | FS-20 | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 00:58AM-8:02PM (7.13) | 0.0344 | 3.110 | 90.41 |
| DAY 4 | 132 | PROCESS UNIT | FS-20 | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 0:58AM-8:02PM (7.23) | 0.0344 | 3.180 | 92.44 |
| DAY 4 | 134 | PUMP #8 | F | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 0:50AM-7:55PM (7.08) | 0.0498 | 0.930 | 18.67 |
| DAY 4 | 137 | DOWN WIND | D | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 0:55AM-7:59PM (7.05) | 0.0407 | 0.033 | 0.811 |
| DAY 4 | 138 | DOWN WIND | D | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 0:55AM-7:59PM (7.05) | 0.0407 | 0.140 | 3.440 |
| DAY 4 | 138 | DOWN WIND | D | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 0:55AM-7:59PM (7.05) | 0.0407 | 0.140 | 3.440 |
| DAY 4 | 140 | UP WIND | B | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 0:41AM-7:48PM (7.12) | 0.0463 | 0.150 | 3.240 |
| DAY 4 | 142 | CONSER-VATEX | E | 8.0 | 47.3 | 88.3 | 63.1 | 60.2 | 0:46AM-7:44PM (7.12) | 0.0496 | 0.290 | 5.847 |
| DAY 4 | 145 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:40PM-7:41AM (11.0) | 0.0675 | 1.280 | 18.96 |
| DAY 4 | 146 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:40PM-7:41AM (11.0) | 0.0675 | 3.150 | 46.66 |
| DAY 4 | 148 | PUMP #8 | F | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:30PM-7:38AM (11.13) | 0.0694 | 1.050 | 15.13 |
| DAY 4 | 151 | DOWN WIND | D | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:33PM-7:35AM (11.05) | 0.0768 | 0.690 | 8.98 |
| DAY 4 | 152 | DOWN WIND | D | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:33PM-7:35AM (11.05) | 0.0768 | 0.980 | 12.76 |
| DAY 4 | 154 | CONSER-VATEX | E | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:26PM-7:28AM (11.02) | 0.0678 | 0.580 | 8.55 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3
N.D. = NO DATA

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 5 DATE 4-15-89 TO 4-16-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 5 | 157 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 54.3 | 52.1 | 10:30PM-8:41AM (10.18) | 0.0491 | 1.680 | 34.22 |
| DAY 5 | 158 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 54.3 | 52.1 | 10:30PM-8:41AM (10.18) | 0.0491 | 1.740 | 35.44 |
| DAY 5 | 164 | CONSER-VATEX | E | N.D. | N.D. | N.D. | 54.3 | 52.1 | 10:45PM-8:35AM (10.83) | 0.0625 | 0.440 | 7.040 |
| DAY 5 | 166 | UP WIND | B | N.D | N.D. | N.D. | 54.3 | 52.1 | 11:02PM-8:33AM (9.51) | 0.0674 | 0.447 | 6.63 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 6 DATE 4-15-89 TO 4-16-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 6 | 169 | PROCESS UNIT | FS-20 | 5.1 | 293 | 73.3 | 68.2 | 67.4 | 8:40AM-3:45PM (7.08) | 0.0456 | 0.520 | 11.40 |
| DAY 6 | 170 | PROCESS UNIT | FS-20 | 5.1 | 293 | 73.3 | 68.2 | 67.4 | 8:40AM-3:45PM (7.08) | 0.0456 | 3.680 | 80.70 |
| DAY 6 | 172 | PUMP #8 | F | 5.1 | 293 | 73.3 | 68.2 | 67.4 | 9:21AM-3:40PM (6.32) | 0.0414 | 0.010 | 0.245 |
| DAY 6 | 175 | DOWN WIND | D | 5.1 | 293 | 73.3 | 68.2 | 67.4 | 9:21AM-3:34PM (6.34) | 0.0432 | 0.029 | 0.671 |
| DAY 6 | 178 | CONSER-VATEX | E | 5.1 | 293 | 73.3 | 68.2 | 67.4 | 9:35AM-3:31PM (5.93) | 0.0306 | 0.031 | 1.013 |
| DAY 6 | 180 | UP WIND | B | 5.1 | 293 | 73.3 | 68.2 | 67.4 | 9:28AM-3:26PM (5.97) | 0.0348 | 0.056 | 1.609 |
| DAY 6 | 183 | PROCESS UNIT | FS-20 | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:20AM-10:29PM (6.15) | 0.0432 | 0.400 | 9.259 |
| DAY 6 | 184 | PROCESS UNIT | FS-20 | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:20AM-10:29PM (6.15) | 0.0432 | 0.780 | 18.06 |
| DAY 6 | 186 | PUMP #8 | F | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:15PM-10:36PM (6.35) | 0.0413 | 0.690 | 16.71 |
| DAY 6 | 189 | DOWN WIND | D | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:11PM-10:56PM (6.76) | 0.0437 | 0.010 | 0.229 |
| DAY 6 | 190 | DOWN WIND | D | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:11PM-10:56PM (6.76) | 0.0437 | 0.310 | 7.094 |
| DAY 6 | 192 | CONSER-VATEX | E | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:28PM-10:56PM (6.50) | 0.0420 | 0.200 | 4.762 |
| DAY 6 | 194 | UP WIND | B | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:04PM-10:49PM (6.75) | 0.0418 | 0.230 | 5.502 |
| DAY 6 | 197 | PROCESS UNIT | FS-20 | 2.0 | 206 | 92.4 | N.D. | N.D. | 10:28PM-8:58AM (10.38) | 0.0627 | 0.710 | 11.32 |
| DAY 6 | 198 | PROCESS UNIT | FS-20 | 2.0 | 206 | 92.4 | N.D. | N.D. | 10:28PM-8:58AM (10.38) | 0.0627 | 2.510 | 40.03 |
| DAY 6 | 200 | PUMP #8 | F | 2.0 | 206 | 92.4 | 44.6 | N.D. | 10:38PM-8:50AM (10.20) | 0.0656 | 0.010 | 0.152 |
| DAY 6 | 203 | DOWN WIND | D | 2.0 | 206 | 92.4 | 44.6 | N.D. | 10:50PM-8:52AM (10.03) | 0.0658 | 0.470 | 7.143 |
| DAY 6 | 206 | CONSER-VATEX | E | 2.0 | 206 | 92.4 | 44.6 | N.D. | 11:03PM-8:45AM (9.70) | 0.0565 | 0.430 | 7.611 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 7 DATE 4-17-89 TO 4-18-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 7 | 211 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 69.0 | 66.2 | 9:48AM-1:32PM (3.75) | 0.0239 | 1.58 | 66.11 |
| DAY 7 | 212 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 69.0 | 66.2 | 9:48AM-1:32PM (3.75) | 0.0239 | 0.53 | 22.18 |
| DAY 7 | 214 | PUMP #8 | F | N.D. | N.D. | N.D. | 69.0 | 66.2 | 9:40AM-1:25PM (3.75) | 0.0233 | 0.74 | 31.76 |
| DAY 7 | 217 | DOWN WIND | D | N.D. | N.D. | N.D. | 69.0 | 66.2 | 9:39AM-0:37PM (3.01) | 0.0195 | 0.83 | 42.54 |
| DAY 7 | 220 | CONSER-VATEX | E | N.D. | N.D. | N.D. | 69.0 | 66.2 | 9:58AM-0:40PM (2.70) | 0.0190 | 0.83 | 43.68 |
| DAY 7 | 222 | UP WIND | B | N.D. | N.D. | N.D. | 69.0 | 66.2 | 10:02AM-1:35PM (2.55) | 0.0158 | 0.96 | 60.75 |
| DAY 7 | 225 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 85.7 | 79.1 | 1:25PM-5:00PM (3.58) | 0.0185 | 1.11 | 60.00 |
| DAY 7 | 226 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 85.7 | 79.1 | 1:25PM-5:00PM (3.58) | 0.0185 | 2.00 | 108.1 |
| DAY 7 | 228 | PUMP #8 | F | N.D. | N.D. | N.D. | 85.7 | 79.1 | 1:28PM-5:00PM (3.55) | 0.0173 | 0.92 | 53.18 |
| DAY 7 | 231 | DOWN WIND | D | N.D. | N.D. | N.D. | 85.7 | 79.1 | 1:15PM-5:00PM (3.75) | 0.0241 | 1.03 | 42.74 |
| DAY 7 | 232 | DOWN WIND | D | N.D. | N.D. | N.D. | 85.7 | 79.1 | 1:15PM-5:00PM (3.75) | 0.0241 | 1.10 | 45.64 |
| DAY 7 | 234 | CONSER-VATEX | E | N.D. | N.D. | N.D. | 85.7 | 79.1 | 1:30PM-5:00PM (3.50) | 0.0211 | 1.09 | 51.66 |
| DAY 7 | 236 | UP WIND | B | N.D. | N.D. | N.D. | 85.7 | 79.1 | 0:55PM-5:00PM (4.08) | 0.0238 | 1.06 | 44.53 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE I (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR BENZENE

| DAY 8 DATE 4-18-89 TO 4-19-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 8 | 239 | PROCESS UNIT | FS-20 | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:20PM-7:35PM (5.29) | 0.0329 | 0.010 | 0.304 |
| DAY 8 | 240 | PROCESS UNIT | FS-20 | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:20PM-7:35PM (5.29) | 0.0329 | 2.140 | 65.04 |
| DAY 8 | 241 | PUMP #8 | F | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:10PM-7:30PM (5.33) | 0.0375 | 0.010 | 0.267 |
| DAY 8 | 245 | DOWN WIND | D | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:15PM-7:26PM (5.22) | 0.0333 | 0.033 | 1.00 |
| DAY 8 | 248 | CONSER-VATEX | E | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:30PM-7:22PM (4.87) | 0.0361 | 0.050 | 1.385 |
| DAY 8 | 250 | UP WIND | B | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:25PM-7:40PM (5.25) | 0.0325 | 0.066 | 2.031 |
| DAY 8 | 293 | DOWN WIND | D | N.D. | N.D. | N.D. | N.D. | N.D. | 7:52PM-7:48AM (11.93) | 0.0812 | 0.520 | 6.404 |
| DAY 8 | 295 | CONSER-VATEX | E | N.D. | N.D. | N.D. | N.D. | N.D. | 8:43PM-6:30AM (8.78) | 0.0576 | 0.620 | 10.76 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE II
TEXACO CONROE CHEMICAL PLANT
MAXIMUM AND MINIMUM BENZENE CONCENTRATIONS
FROM AMBIENT AIR MONITORING

| MONITORING SITE | CONCENTRATION (UG/M3) | |
|---|---|---|
| | MINIMUM | MAXIMUM |
| DOWNWIND AT FENCELINE | 0.229 | 45.64 |
| UPWIND AT FENCELINE | 1.462 | 60.75 |
| PROCESS UNIT | 0.304 | 246.6 |
| OUTSIDE FENCELINE (CONSERVATEX CO) | 1.013 | 51.66 |
| PUMP NUMBER 8 | 0.150 | 53.18 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF BENZENE = 3,187 UG/M3

TABLE III
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR ETHYLENE OXIDE

| DAY 1 DATE 4-10-89 TO 4-11-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 1 | 17 | PROCESS UNIT | FS-20 | 6.5 | 332 | 65.3 | N.D. | N.D. | 4:24PM-11:32PM (7.15) | 0.1136 | 9.60 | 84.51 |

| DAY 2 DATE 4-11-89 TO 4-12-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 2 | 61 | PROCESS UNIT | FS-20 | 5.7 | 119 | 51.6 | 65.7 | 62.1 | 3:33PM-10:09PM (6.60) | 0.0341 | 6.51 | 190.9 |
| DAY 2 | 75 | PROCESS UNIT | FS-20 | 4.4 | 87.6 | 71.3 | 56.5 | 52.5 | 10:10PM-8:34AM (10.4) | 0.0708 | 2.82 | 39.83 |

| DAY 3 DATE 4-12-89 TO 4-13-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 3 | 90 | PROCESS UNIT | FS-20 | 7.0 | 80.5 | 69.0 | 59.1 | 55.5 | 8:35AM-3:14PM (6.65) | 0.0344 | 2.90 | 84.30 |
| DAY 3 | 117 | PROCESS UNIT | FS-20 | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 8:52PM-7:48AM (10.93) | 0.0681 | 3.00 | 44.05 |
| DAY 3 | 118 | PUMP #8 | F | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 8:52PM-7:48AM (10.93) | 0.0681 | 1.86 | 27.31 |
| DAY 3 | 121 | PUMP #8 | F | 4.6 | 101 | 88.8 | 54.3 | 52.1 | 8:55PM-7:50AM (10.93) | 0.0731 | 2.83 | 38.71 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF ETHYLENE OXIDE = 1,798 UG/M3
N.D. = NO DATA

TABLE III (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR ETHYLENE OXIDE

| DAY 4 DATE 4-14-89 TO 4-15-89 | SAMPLE | | | AVERAGE WIND | | AVERAGE RELATIVE | AVERAGE TEMP. (F) | | TIME SAMPLE (HOUR) | SAMPLE VOLUME | SAMPLE MASS | SAMPLE CONC. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NUMBER | LOCATION | POINT | SPEED (MPH) | DIR. | HUMIDITY (%) | AT 3 FT. | AT 70 FT. | | (M3) | (UG) | (UG/M3) |
| DAY 4 | 143 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:36PM-7:40AM (11.07) | 0.0672 | 1.24 | 18.45 |
| DAY 4 | 144 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:36PM-7:40AM (11.07) | 0.0672 | 3.15 | 46.88 |
| DAY 4 | 147 | PUMP #8 | F | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:30PM-7:38AM (11.13) | 0.0694 | 2.28 | 32.85 |
| DAY 4 | 149 | DOWN WIND | D | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:32PM-7:35AM (11.05) | 0.0738 | 1.49 | 20.19 |
| DAY 4 | 150 | DOWN WIND | D | N.D. | N.D. | N.D. | 63.1 | 60.2 | 8:32PM-7:35AM (11.05) | 0.0738 | 0.98 | 13.28 |

| DAY 5 DATE 4-15-89 TO 4-16-89 | SAMPLE | | | AVERAGE WIND | | AVERAGE RELATIVE | AVERAGE TEMP. (F) | | TIME SAMPLE (HOUR) | SAMPLE VOLUME | SAMPLE MASS | SAMPLE CONC. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NUMBER | LOCATION | POINT | SPEED (MPH) | DIR. | HUMIDITY (%) | AT 3 FT. | AT 70 FT. | | (M3) | (UG) | (UG/M3) |
| DAY 5 | 159 | PUMP #8 | F | N.D. | N.D. | N.D. | 54.3 | 52.1 | 10:25PM-8:38AM (10.22) | 0.0719 | 2.06 | 28.65 |
| DAY 5 | 162 | DOWN WIND | D | N.D. | N.D. | N.D. | 54.3 | 52.1 | 10:32PM-8:40AM (10.13) | 0.0624 | 2.85 | 45.67 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF ETHYLENE OXIDE = 1,798 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE III (CONTINUED)
TEXACO CONROE CHEMICAL PLANT
RESULTS OF AMBIENT AIR MONITORING FOR ETHYLENE OXIDE

| DAY 6 DATE 4-16-89 TO 4-17-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 6 | 182 | PROCESS UNIT | FS-20 | 2.8 | 238 | 66.7 | 70.4 | 70.0 | 4:15PM-10:30PM (6.25) | 0.0463 | 1.220 | 26.35 |

| DAY 7 DATE 4-17-89 TO 4-18-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 7 | 223 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | 69.0 | 66.2 | 1:25PM-5:00PM (3.58) | 0.0235 | 1.55 | 65.96 |

| DAY 8 DATE 4-18-89 TO 4-19-89 | SAMPLE NUMBER | SAMPLE LOCATION | SAMPLE POINT | AVERAGE WIND SPEED (MPH) | AVERAGE WIND DIR. | AVERAGE RELATIVE HUMIDITY (%) | AVERAGE TEMP. (F) AT 3 FT. | AVERAGE TEMP. (F) AT 70 FT. | TIME SAMPLE (HOUR) | SAMPLE VOLUME (M3) | SAMPLE MASS (UG) | SAMPLE CONC. (UG/M3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DAY 8 | 237 | PROCESS UNIT | FS-20 | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:18PM-7:36PM (5.30) | 0.0345 | 9.100 | 263.8 |
| DAY 8 | 241 | PUMP #8 | F | 6.0 | 218 | 59.2 | 85.4 | 82.3 | 2:10PM-7:30PM (5.33) | 0.0375 | 2.910 | 77.6 |
| DAY 8 | 284 | PROCESS UNIT | FS-20 | N.D. | N.D. | N.D. | N.D. | N.D. | 9:14AM-4:28PM (11.8) | 0.0687 | 29.5 | 429.4 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF ETHYLENE OXIDE = 1,798 UG/M3

N.D. = NO DATA



Sixth Annual Waste Testing and Quality Assurance Symposium Vol. II, Washington D.C. July 16 – 20, 1990

TABLE IV
TEXACO CONROE CHEMICAL PLANT
MAXIMUM ETHYLENE OXIDE CONCENTRATIONS
FROM AMBIENT AIR MONITORING

| MONITORING SITE | MAXIMUM CONCENTRATION (UG/M3) |
|---|---|
| DOWNWIND AT FENCELINE | 45.67 |
| UPWIND AT FENCELINE | <26.00 |
| PROCESS UNIT | 429.4 |
| OUTSIDE FENCELINE (CONSERVATEX CO) | <26.00 |
| PUMP NUMBER 8 | 77.6 |

OSHA 8-HOUR OCCUPATIONAL THRESHOLD LIMIT VALUE OF ETHYLENE OXIDE= 1,798 UG/M3

TABLE V
TEXACO CONROE CHEMICAL PLANT
RESULTS OF DESORPTION EFFICIENCY STUDIES
FOR BENZENE AND ETHYLENE OXIDE

| | BENZENE | |
|---|---|---|
| AMOUNT SPIKE PER (MICROGRAMS) | AMOUNT RECOVERED (MICROGRAMS) | RECOVERED (%) |
| 440 | 376 | 85 |
| 220 | 211 | 96 |
| 44 | 39.7 | 90 |
| 8.8 | 6.9 | 78 |
| 1.76 | 0.43 | 25 |
| AVERAGE % RECOVERED FOR BENZENE | | 75 |

| | ETHYLENE OXIDE | |
|---|---|---|
| AMOUNT SPIKE PER (MICROGRAMS) | AMOUNT RECOVERED (MICROGRAMS) | RECOVERED (%) |
| 18 | 14.6 | 81 |
| 35.9 | 25.6 | 71 |
| AVERAGE % RECOVERED FOR ETHYLENE OXIDE | | 76 |

110

# USEPA PROPOSED METHOD 25D FOR DETERMINING THE VOLATILE ORGANIC CONTENT OF WASTES: EVALUATION ON REAL-WORLD WASTE SAMPLES

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## ABSTRACT

USEPA is developing regulations to control secondary emissions from hazardous waste TSDFs and industrial wastewater systems. Supporting this effort, they have developed proposed Method 25D to determine the aggregate volatile organic compound (VOC) content of hazardous wastes and wastewaters. The Chemical Manufacturers Association (CMA) has conducted a study using four real-world wastes to compare the proposed method to routinely used methods and to evaluate its reproducibility.

Based on this CMA study, proposed Method 25D appears to give a "ballpark", but somewhat high, estimate of the total volatiles; it apparently picks up a significant amount (10 to 30 percent) of the semi-volatiles. It does, therefore, show potential as a screening tool. Although there was some heterogeneity of the waste samples, the magnitude of the lab to lab variation, and the sometimes large, variable RSDs, suggest that the reproducibility of the current proposed method is lacking. Recommendations are made to study/improve the accuracy and precision and to then set the conditions to simulate, more accurately, actual expected secondary emissions of volatile organic compounds from real waste facilities.

## INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is developing regulations to control secondary emissions from hazardous waste treatment, storage and disposal facilities (TSDFs) and industrial wastewater systems. Supporting this effort, the Agency's Office of Air Quality Planning and Standards (OAQPS) at Research Triangle Park, NC, has developed a proposed method to determine the aggregate volatile organic compound (VOC) content of hazardous wastes and wastewaters. EPA has conducted a multi-lab study of the proposed method which focused on synthetic wastes, but they also plan to evaluate it further on real wastes. In cooperation with EPA, CMA has conducted a separate study using four actual chemical industry wastes to compare proposed Method 25D to

routinely used methods, i.e., SW-846 Methods 8240 and 8270. The major objectives of this study were to determine whether proposed Method 25D gives a reasonable estimate for the VOC content and to evaluate its reproducibility.

## EPA PROPOSED METHOD 25D

As proposed Method 25D, Determination of the Volatile Organic Content of Waste Samples, has been published by EPA, the details of the proposed method will not be repeated here.

According to the proposed Method 25D protocol, the samples of waste/wastewater are dissolved/dispersed in polyethylene glycol (PEG). The solutions/dispersions are heated to 75°C, stirred in a chamber and purged with nitrogen for thirty minutes at a rate of six liters per minute. The effluent gas is split into two streams; one is analyzed for carbon content with a flame ionization detector (FID), and the other is analyzed for chlorine content (as chloride) with a Hall electrolytic conductivity detector (HECD).

The detectors are calibrated with gas(es), in the form of propane and dichloroethane, containing known amounts of carbon (C) as methane and chlorine (Cl) per liter. Curves are determined for each detector to establish detector response and linearity. Sample quantitation is accomplished through the use of average response factors from the multipoint calibration curves and, if required according to the method, the end of day calibration checks. The VOC by proposed Method 25D is the sum of the carbon (as methane) and chlorine contents of the sample.

## COMPARISON METHODS

Two of the samples were also analyzed by GC/MS for volatiles and semi-volatiles as a means of comparing the results obtained by proposed Method 25D to existing, routinely used methodology. Samples CMA-3 and CMA-4 were analyzed by Radian (Austin, TX) by Methods 8240DI (Direct Injection), 8240 (purgeable volatiles), and 8270 (semi-volatiles). The GC/MS analytical methodology followed EPA SW-846 (Third Edition) protocol.

## THE REAL-WORLD WASTE SAMPLES

The four chemical industry wastes were purposely selected to be very different in nature and to challenge the proposed method across a wide range of waste types and concentrations. Since the purpose of the study was to test the proposed Method 25D, i.e., not to determine the actual contents of the wastes, two of the wastes were modified to broaden the scope of the test; one is a mixture of high-salt and high-organic content waste streams and one was diluted to broaden the concentration range of the organics in the waste samples. The identities of the waste samples tested are listed in Table I, as follows:

TABLE I

IDENTITIES OF REAL WASTE SAMPLES

| SAMPLE ID | SOURCE | DESCRIPTION |
|---|---|---|
| CMA-1 | Partially-stripped styrene tar | Highly-viscous tar |
| CMA-2 | Mixture of high-salt and high-organic content wastewater streams | Wastewater with slight sheen |
| CMA-3 | Wastewater treatment plant | Primary sludge |
| CMA-4 | Wastewater treatment plant skimming tank | Diluted two-phase supernatant from top of clarifier |

## SAMPLING TECHNIQUES

Single samples were collected in clean bottles from each source, and some were combined and/or diluted to give the final samples. CMA-2 was prepared by mixing the two wastewater stream samples in a separate, single bottle; the final sample mixture had a slight sheen. CMA-4 was prepared by mixing samples of organic and aqueous layers from the skimmer, and then diluting the mixture further with distilled, deionized water; the final mixture had two distinct phases. CMA-3 was not mixed with any other material or diluted; it was the most homogeneous.

Radian provided cleaned, labeled and weighed sample bottles containing polyethylene glycol (PEG) with approximately 10 to 15 ml of headspace available for sample collection. The four final CMA samples were shaken or stirred in their single sample bottles to improve homogeneity just before they were added to the vials; care was taken to not spill the waste on the outside of the bottles. Samples were shipped to Radian under ice and received at approximately ice temperatures (4°C). The sample bottles received at Radian were then reweighed to obtain, by difference, the weight of the sample collected.

Five replicate proposed Method 25D samples were collected from each of the four final sample bottles. Three of the samples from each waste stream were analyzed to provide an estimate of laboratory precision. Two samples were kept in reserve in case of breakage or equipment failure. Five additional samples were collected from each of the same four final sample bottles and sent to an EPA contracted laboratory for analysis.

Samples of CMA-3 and CMA-4 were also collected for analysis by Methods 8240, 8240 Direct Injection, and 8270. Samples for Method 8240 were collected in PEG in the same manner as the proposed Method 25D samples. PEG was used as the collection media because it does not purge and it inhibits sample volatility prior to analysis. The 8240 samples were collected (diluted) in PEG due to the expected high concentrations of volatiles. Samples collected for the 8240 Direct Injection and 8270 analyses were not collected in the PEG. All of these samples came from the same final sample bottles that were used to fill the proposed Method 25D vials.

## RESULTS AND DISCUSSION

### Proposed Method 25D Analysis of CMA Waste Samples

The analytical results from the proposed Method 25D analyses of the CMA waste samples are presented in Table II. Each sample, with the exception of CMA-4 at Radian, was analyzed in triplicate. Triplicate analyses of the CMA-4 samples at Radian were not possible because the flame on the FID was extinguished during analysis of three of the replicate samples and a data system failed on one of the two remaining samples. The reason for the extinguished flame on the FID has not been determined.

The concentrations of volatile organic compounds in the four waste samples, as measured with proposed Method 25D, ranged from about 350 ppm to about 20,000 ppm. Three of the samples contained 1-3 ppm chlorine and the other about 300 to 600 ppm chlorine. Broad ranges of chlorine, carbon as methane, and volatile organic content, as measured by proposed Method 25D, were, therefore, covered by these four real-world wastes.

The averages, the percent relative standard deviations, and the percent differences between the averages from the two laboratories are presented in Table III. In some cases the percent relative standard deviations were fairly large; this is possibly due in part to some heterogeneity of the samples, but the variabilities in the percent RSDs suggest that measures need to be taken to improve the reproducibility of the method. The lab to lab variation is even more severe, with differences of 14 to 71 percent for carbon (as methane) and of the order of 100 percent for chlorine. Statistical analysis of the data showed significant differences in intra-laboratory precision, and significant differences in the results from the two laboratories.

### GC/MS Analysis of CMA Waste Samples

Compounds (volatiles) detected in samples CMA-3 and CMA-4 by Methods 8240 and 8240DI are listed in Tables IV and VI, respectively. Compounds (semi-volatiles) detected in samples CMA-3 and CMA-4 by Method 8270 are listed in Tables V and VII, respectively. Several different types of volatile and semi-volatile compounds were present in both of these real wastes.

Each of the Tentatively Identified Compounds (TICs) and the unknown compounds have been quantitated using the response factor from the nearest internal standard as they are not target analytes for the particular method and response factors have not been determined. Since the actual response factor is not known, the concentrations for the TICs can be very close to the true concentration or vary widely. Therefore, the values of the TICs are estimated concentrations.

The carbon and chlorine contents which were calculated from the empirical formulas of the compounds are also shown in Tables IV - VII. For the unknowns, 75 percent carbon and zero percent chlorine were used, i.e., the same percentages as for methane.

## Comparison of Results from Proposed Method 25D to Results from Methods 8240, 8240DI and 8270

Table VIII provides comparisons of the results from proposed Method 25D to the results from Methods 8240 and 8240 DI (volatiles) for both CMA-3 and CMA-4. Note that the comparison here is for the results as reported for the two methods, i.e., observed for the 8000 methods and the sum of carbon (as methane) plus chlorine for 25D. There are wide variations in the results from the different labs and the two samples, but on the average it appears that proposed Method 25D overpredicts the total volatiles content of real-world wastes, i.e., that proposed Method 25D picks up a significant amount (10 to 30 percent) of the semi-volatiles. In two out of three cases, the proposed Method 25D data were statistically significantly higher than those from Method 8240/8240DI. Perhaps the proposed Method 25D test conditions are too vigorous causing excessive amounts of semi-volatiles to also be driven off the wastes.

The numbers in parentheses are an attempt to make the comparisions on a more uniform basis, i.e., carbon as carbon plus chlorine for both methods. The differences are not great, but it does illustrate that the method of presenting the results does influence the reported contents as well as the comparisons.

Table IX provides comparisons of the results from proposed Method 25D to the sum of the results from 8240/8240DI and 8270, i.e., the sum of the volatiles plus semi-volatiles. Again, the variations are large.

## CONCLUSIONS

Based on triplicate analyses by proposed Method 25D at two separate laboratories of four real-world chemical industry wastes, and comparisons of the proposed Method 25D results with SW-846 Methods 8240 and 8270 analyses of two of the real wastes, it appears that:

Proposed Method 25D gives a "ballpark", but somewhat high, estimate of the total volatiles contents of the two real-world wastes. In two out of three cases, the proposed Method 25D data were statistically significantly higher than those from Method 8240/8240DI. It also picks up a significant amount (10 to 30 percent) of the semi-volatiles. It does, therefore, show potential as a screening tool. It is expected that the extent to which it will overpredict the volatiles content will be a function of the actual composition of the waste.

In some cases, the percent relative standard deviations were fairly large. This is possibly due in part to observed heterogeneity of the samples, but there were significant variabilities in the percent RSDs. The lab to lab variations are even more severe, with observed differences of 14 and 71 percent carbon (as methane) and of the order of 100 percent for chlorine. Statistical analysis of the data showed significant differences in the intra-laboratory precision, and significant differences in the results from the two laboratories. The magnitude of the lab to lab variation, and the sometimes large, variable percent RSDs, suggest that the reproducibility of the proposed method is lacking.

## RECOMMENDATIONS

### Accuracy

It is recommended that the comparison of proposed Method 25D to Methods 8240, 8240DI and 8270 be pursued further. Artificial waste samples should be prepared containing known concentrations of specific compounds, such as those identified in the CMA wastes, and analyzed by proposed Method 25D and Methods 8240, 8240DI and 8270 using actual standards for the compounds of interest. Audit sample results for Methods 8240 and 8270 should be reviewed for accuracy and precision to ensure proper identifications and quantitation. Direct comparison could then be made between the known concentrations, the alternate method results, and proposed Method 25D results.

Should the results of proposed Method 25D not agree with the alternate methods, it is also strongly suggested that a Quality Control Check Sample be prepared for proposed Method 25D using known concentrations of specific compounds to determine if the problem originates with proposed Method 25D. This check sample would then be used to validate the gas based calibration curve. A check sample would allow evaluation of the entire apparatus in a mode equivalent to that used in sample analysis. Verification of the check sample concentration by Method 8240 or 8240DI would also provide a measure of the accuracy of proposed Method 25D.

The calibration gas is not introduced through the entire purge apparatus when calibrating proposed Method 25D. It is, therefore, recommended that this feature be altered to introduce the standard through the entire apparatus. It is currently being introduced through the

coalescing filter and not through the purge chamber. The gaseous standards should also be compared to liquid standards (calibration check standards) on a routine basis to insure the validity of a gaseous calibration.

Once the accuracy of the proposed method is established, the specified purge conditions should be set to simulate more accurately actual expected secondary emissions of volatile organic compounds from actual waste facilities.

## Precision

The precision of the proposed method needs to be improved. The stability/reproducibility of the detectors and the effects of gas flow rates need to be investigated further. Improvements in calibration and quality control procedures may be required. Since many real-world wastes are nonhomogeneous, homogeneity must be addressed from the sampling viewpoint. Addition of the static mixer, as described in the proposed method, to streams which contain multiple phases should help to obtain more homogeneous samples of liquid wastes. This sampling apparatus should be evaluated using real-world wastes.

## Detection Limit

A detection limit study using artificial samples of known concentration should be initiated to determine the lower working range of the proposed method. Seven replicate samples at a concentration considered to be within a factor of 10 of the method detection limit would be analyzed. The detection limit would be defined as 3.14 times the standard deviation from the seven replicates. The detection limit will, of course, vary depending on the compounds present, even in water, and also vary further in different matrices.

## ACKNOWLEDGEMENTS

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TABLE II

RESULTS
PROPOSED METHOD 25D ANALYSIS OF CMA WASTE SAMPLES
BY CMA (RADIAN, AUSTIN, TX) AND EPA CONTRACT LABORATORIES
CONCENTRATIONS IN PARTS PER MILLION BY WEIGHT

| SAMPLE ID CMA- | CARBON (AS $CH_4$) | | CHLORINE | | TOTAL VO CONTENT | |
|---|---|---|---|---|---|---|
| | RADIAN | EPA | RADIAN | EPA | RADIAN | EPA |
| 1 | 11300 | 14300 | ND | 1.75 | 11300 | 14300 |
| | 18600 | 15100 | ND | 1.47 | 18600 | 15100 |
| | 29800 | 14700 | ND | 1.34 | 29800 | 14700 |
| 2 | 13000 | 6930 | 1.20 | 1.71 | 13000 | 6930 |
| | 7910 | 6600 | 0.42 | 1.84 | 7910 | 6600 |
| | 4120 | 8150 | ND | 1.97 | 4120 | 8150 |
| 3 | 3050 | 3680 | 301 | 601 | 3350 | 4280 |
| | 3000 | 3800 | 232 | 606 | 3230 | 4410 |
| | 3500 | 3860 | 334 | 645 | 3830 | 4500 |
| 4 | 163 | 296 | ND | 4.24 | 163 | 300 |
| | --- | 320 | --- | 2.35 | --- | 322 |
| | --- | 415 | --- | 1.64 | --- | 417 |

TABLE III

PRECISION
PROPOSED METHOD 25D ANALYSIS OF CMA WASTE SAMPLES
BY CMA (RADIAN, AUSTIN, TX) AND EPA CONTRACT LABORATORIES
PERCENT RELATIVE STANDARD DEVIATION AND LAB TO LAB VARIATION
CONCENTRATIONS IN PARTS PER MILLION BY WEIGHT

| | CARBON (AS $CH_4$) | | PERCENT | CHLORINE | | PERCENT |
|---|---|---|---|---|---|---|
| | RADIAN | EPA | DIFFERENCE | RADIAN | EPA | DIFFERENCE |
| CMA-1 | | | | | | |
| Average | 19900 | 14700 | 30 | ND | 1.52 | --- |
| RSD (%) | 47 | 2.7 | | --- | 14.0 | |
| CMA-2 | | | | | | |
| Average | 8340 | 7230 | 14 | 0.54(1) | 1.84 | 109 |
| RSD (%) | 55 | 11.2 | | 113 | 7.2 | |
| CMA-3 | | | | | | |
| Average | 3180 | 3780 | 17 | 289 | 617 | 72 |
| RSD (%) | 8.7 | 2.4 | | 18 | 3.9 | |
| CMA-4 | | | | | | |
| Average | 163(2) | 344 | 71 | ND(2) | 2.74 | --- |
| RSD (%) | --- | 18.3 | | --- | 49 | |

(1) One ND averaged in as zero.
(2) Value for analysis of a single sample only.

TABLE IV

VOLATILES IN SAMPLE CMA-3
COMPOUNDS DETECTED BY METHODS 8240 AND 8240DI

| COMPOUNDS | CONCENTRATION (mg/L) OBSERVED | CARBON | CHLORINE |
|---|---|---|---|
| Toluene | 1220 | 1114 | --- |
| 2-Propylfuran(1) | 97(580)(2) | 443 | --- |
| Ethanedioic Acid, Dibutyl Ester(1) | 58 | 35 | --- |
| Chlorotoluene isomer(1) | 1120 | 747 | 313 |
| Chlorotoluene isomer(1) | 500 | 334 | 140 |
| Unknown(3) | (54)(2) | 41 | --- |
| Total Volatiles | 3532 | 2714 | 453 |

(1) Tentatively Identified Compound, quantitated using an assumed relative response factor of one.

(2) Identified in direct injection sample. Values used in the concentration totals/calculations. All others by Method 8240.

(3) Quantitated using an assumed relative response factor of one. The carbon content was assumed to be 75 percent and the chlorine content to be zero percent.

TABLE V

SEMI-VOLATILES IN SAMPLE CMA-3
COMPOUNDS DETECTED BY METHOD 8270

| COMPOUND | CONCENTRATION (mg/L) OBSERVED | CARBON | CHLORINE |
|---|---|---|---|
| Benzyl Alcohol | 190 | 148 | --- |
| Butylbenzylphthalate | 2900 | 2120 | --- |
| Di-n-octylphthalate | 160 | 118 | --- |
| Phenol | 260 | 199 | --- |
| Benzaldehyde(1) | 2.4 | 1.9 | --- |
| Tributylphosphate | 12 | 6.5 | --- |
| Unknown(2) | 39 | 29 | --- |
| Unknown(2) | 1.9 | 1.4 | --- |
| Unknown(2) | 0.42 | 0.32 | --- |
| Unknown(2) | 1.5 | 1.1 | --- |
| Unknown(2) | 13 | 9.8 | --- |
| Unknown(2) | 5.2 | 3.9 | --- |
| Total Semi-Volatiles | 3585 | 2639 | --- |

(1) Tentatively Identified Compounds, quantitated using an assumed relative response factor of one.

(2) Quantitated using an assumed relative response factor of one. The carbon content was assumed to be 75 percent and the chlorine content to be zero percent.

TABLE VI

VOLATILES IN SAMPLE CMA-4
COMPOUNDS DETECTED BY METHODS 8240 AND 8240DI

| | CONCENTRATION (mg/L) | | |
|---|---|---|---|
| COMPOUNDS | OBSERVED | CARBON | CHLORINE |
| Benzene | 1.24 | 1.14 | --- |
| Styrene | 1.84 | 1.71 | --- |
| Toluene | 2.92 | 2.67 | --- |
| Xylenes | 2.99 | 2.71 | --- |
| $C_6$-Alkene(1) | 4.68 | 4.01 | --- |
| Diisopropyl Ether(1) | 7.80(14)(2) | 9.88 | --- |
| $C_7$-Alkane(1) | 1.58 | 1.33 | --- |
| $C_7$-Alkane(1) | 1.04 | 0.87 | --- |
| Propanoic Acid, Methylpropyl Ester(1) | 6.60(8.8)(2) | 5.78 | --- |
| Chlorotoluene(1) | 0.78 | 0.52 | 0.22 |
| Ethyl Acetate(2) | 7.9 | 4.31 | --- |
| Unknown(3) | 42 | 31.5 | --- |
| 2-Propyl Furan(2) | 70 | 53.5 | --- |
| Propanoic Acid, Ethoxyethyl Ester(2) | 36 | 20.7 | |
| Total Volatiles | 196 | 141 | 0.22 |

(1) Tentatively Identified Compound, quantitated using an assumed relative response factor of one.

(2) TIC from the 8240DI analysis. Used in the concentration totals/calculations. All others by Method 8240.

(3) Identified in the 8240DI analysis and used in the concentration totals/calculations. Quantitated using an assumed relative response factor of one. The carbon content was assumed to be 75 percent and the chlorine content to be zero percent.

TABLE VII

SEMI-VOLATILES IN SAMPLE CMA-4
COMPOUNDS DETECTED BY METHOD 8270

| COMPOUND | CONCENTRATION (mg/L) OBSERVED | CARBON | CHLORINE |
|---|---|---|---|
| Acenaphthene | 0.67 | 0.63 | --- |
| Acenaphthylene | 0.73 | 0.69 | --- |
| Anthracene | 0.20 | 0.19 | --- |
| Butylbenzylphthalate | 0.60 | 0.44 | --- |
| Fluorene | 1.20 | 1.13 | --- |
| 2-Methylnaphthalene | 18 | 16.7 | --- |
| Naphthalene | 27 | 25.3 | --- |
| Phenanthrene | 1.40 | 1.32 | --- |
| Pyrene | 0.24 | 0.23 | --- |
| Unknown(1) | 30 | 22.5 | --- |
| $C_6$-Hydrocarbon(2) | 13 | 10.9 | --- |
| $C_6$-Hydrocarbon(2) | 7.9 | 6.61 | --- |
| 1,2,3,4-Tetrahydronaphthalene(2) | 35 | 31.8 | --- |
| 1-Methylnaphthalene(2) | 13 | 12.1 | --- |
| Unknown(1) | 8.1 | 6.08 | --- |
| $C_{14}$-Alkane(2) | 9.1 | 7.72 | --- |
| $C_{15}$-Alkane(2) | 7.2 | 6.11 | --- |
| $C_{17}$-Alkane(2) | 7.1 | 6.03 | --- |
| Unknown(1) | 13 | 9.75 | --- |
| Total Semi-Volatiles | 193 | 166 | 0 |

(1) Quantitated using an assumed relative response factor of one. Carbon content was assumed to be 75 percent and chlorine content to be zero percent.

(2) Tentatively Identified Compound, quantitated using an assumed relative response factor of one.

TABLE VIII

COMPARISON OF PROPOSED METHOD 25D TO METHODS 8240, 8240DI (VOLATILES)
PROPOSED METHOD 25D (METHANE PLUS CHLORINE) VERSUS 8240, 8240DI (OBSERVED)
CONCENTRATIONS IN PARTS PER MILLION BY WEIGHT

| | PROPOSED METHOD 25D (METHANE + CHLORINE) | 8240, 8240DI (OBSERVED) | 25D AS PERCENT OF 8240, 8240DI METHODS (C + Cl) | |
|---|---|---|---|---|
| CMA-3 | | | | |
| Radian | 3470 | 3530 | 98 | (84) |
| EPA Contract Lab | 4400 | (3530)(1) | 125 | (110) |
| Average | 3940 | (3530)(1) | 112 | (98) |
| CMA-4 | | | | |
| Radian | 163(2) | 196 | 83 | (87) |
| EPA Contract Lab | 347 | (196)(1) | 177 | (185) |
| Average | 255 | (196)(1) | 130 | (136) |

(1) Measured at Radian (Austin, TX) only.
(2) Single analysis. All others are averages of three analyses.

TABLE IX

COMPARISON OF PROPOSED METHOD 25D TO METHODS 8240, 8240DI AND 8270 (VOLATILES PLUS SEMI-VOLATILES) PROPOSED METHOD 25D (METHANE PLUS CHLORINE) VERSUS 8240, 8240DI AND 8270 (OBSERVED) CONCENTRATIONS IN PARTS PER MILLION BY WEIGHT

| | PROPOSED METHOD 25D (METHANE + CHLORINE) | 8240 8240DI, 8270 (OBSERVED) | 25D AS PERCENT OF 8240, 8240DI, 8270 METHODS | (C + Cl) |
|---|---|---|---|---|
| CMA-3 | | | | |
| Radian | 3470 | 7117 | 49 | (46) |
| EPA Contract Lab | 4400 | (7117)(1) | 62 | (59) |
| Average | 3940 | (7117)(1) | 55 | (52) |
| CMA-4 | | | | |
| Radian | 163(2) | 389 | 42 | (40) |
| EPA Contract Lab | 347 | (389)(1) | 89 | (85) |
| Average | 255 | (389)(1) | 66 | (63) |

(1) Measured at Radian (Austin, TX) only.
(2) Single analysis. All others are averages of three analyses.

111

# GROUND WATER SAMPLING PROCEDURES NECESSARY TO OBTAIN DEFENSIBLE ANALYTICAL DATA

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ABSTRACT

Various types of sampling equipment and procedures necessary to obtain representative samples of ground water will be discussed with emphasis placed on how to:

- Prevent contamination of the well and well waters
- Prevent cross contamination of well and well waters
- Prevent contamination of samples during collection, containerization and storage.
- Obtain and record well and field data
- Initiate, maintain and document groundwater sampling quality control (QC) procedures
- Prepare sample labels and sample seals
- Initiate, maintain and document sample Chain of Custody
- Provide adequate instructions to the analytical laboratory

Utilizing the equipment and following the procedures discussed in the paper should result in pertinent, defensible analytical data from a quality environmental laboratory. Laboratory Chain of Custody and QA/QC will not be discussed.

## INTRODUCTION

The purpose of a good groundwater sampling is to:

- Obtain representative samples of ground water.
- Prevent contamination of well and well waters.
- Prevent cross contamination of wells and well waters.
- Prevent contamination of samples during collection, containerization and storage.
- Obtain and record proper well data.
- Prepare proper sample labels.
- Maintain Chain-Of-Custody.
- Provide adequate instructions to laboratory.

Resulting in:

- Obtaining meaningful and defensible groundwater data from a qualified laboratory.

## I. CONTAINER PREPARATION

1) The laboratory performing the groundwater analyses should supply all necessary coolers, pre-cleaned containers, trip blanks, field water supply, chemical preservatives, packaged refrigerant, labels, custody seals, chain of custody and shipping forms. The field sampling log and sample analysis request forms should be provided by the individuals or firm collecting the samples. It is highly recommended that the sample collection team be employed by or employees of the laboratory responsible for the analytical data. One firm, preferably the laboratory, should be totally responsible for all of the data concerning any sampling event.

2) The container needs to be constructed of a material compatible and non-reactive with the material it is to contain. Consult Attachment 1, Recommended Containerization and Preservation of Samples, to determine the number, type and volume of containers needed. The containers designated may be purchased thru local container distributors with the exception of the septum vial and the Teflon lined caps needed for the various analyses which are available thru laboratory supply companies. Metal lids should not be utilized. Plastic lids with polyethylene liners are acceptable in many cases. However, Teflon lined lids are to be used for samples requiring organic analyses.

2.a) Individual containers are not necessarily required for each determination or test. If two or more tests require the same container and preservation, and a container of sufficient size is available, the samples may be combined.

2.b) The cleanliness of the containers, evacuating and sampling equipment is most important. It is recommended that bottles and lids to contain samples for metals or conventional analyses be hand washed with a non-phosphate detergent, rinsed in hot tap water, rinsed with chemically pure or reagent grade nitric acid, rinsed with distilled or deionized water and let to air dry. Glass bottles used to collect samples for the determination of organic compounds by GC, GC/MS, or HPLC analysis should be washed with a non-phosphate detergent, rinsed with hot tap water, rinsed with pesticide grade hexane and methanol, rinsed with copious amounts of D.I. water (at least six rinses), and kiln baked at 300°C. Caps and Teflon liners should be prepared in the same manner, except without the kiln bake. When the bottles are cool, the caps and liners completely dry, cap the bottles and store them in a clean and dry environment. Additionally, all equipment used to bail or sample a well must be cleaned in the same manner prescribed for cleaning the caps and liners above, and stored in a

clean and dry environment. It is suggested that clean bailers be wrapped in foil or Kraft paper for storage.

3) If the sample locations and tests are known prior to field collection, it may be desirable to label the containers and add the chemical preservatives (where applicable) before sampling.

II. BLANKS

1) One complete set of trip, field, and equipment blanks should be prepared for each sampling event, or for a minimum of one in ten monitor well and/or field samples. The trip blank samples are to be prepared in the laboratory by filling the appropriate clean sample bottles with laboratory grade carbon free deionized water with a specific conductance of 1.0 umhos/cm or less that has been passed through activated carbon, and adding the appropriate chemical preservatives (if any) as indicated in Attachment 1 for each type of sample. These bottles are then to be labeled "trip blank", the analyses to be performed indicated on each, and placed in the appropriate sample shuttle cooler(s) to be utilized for sample transport to the field and back to the Laboratory. This procedure accounts for any contamination that may occur as a result of the containers, the sample coolers, the cleaning operations, or the chemical preservatives.

1.a) The field blank samples are to be prepared in the field or site at which the sampling event is taking place. Field blanks are to be prepared when dedicated or non-dedicated sampling equipment is used in the sampling project. The field blank samples are prepared in the field by filling the appropriate sample bottles from the field supply of laboratory grade carbon free deionized water. This procedure accounts for any contamination that may occur as a result of site ambient air conditions, and serves as an additional check for contamination in the containers, the sample coolers, the cleaning operations, or the chemical preservatives.

1.b) Equipment (rinsate) blank samples are to be prepared in the field immediately following any decontamination cleaning procedures and before non-dedicated equipment is used for evacuation, sampling, or sample preparation. Bailers, funnels, filters, and vacuum filter pump vessels may be considered possible sources of cross contamination. Following decontamination, laboratory grade carbon free deionized water from the field supply source is passed through the non-dedicated equipment in the same manner as the sample itself, contacting the equipment in question. This procedure serves to validate any decontamination procedures carried out on non-dedicated equipment utilized in the field or cleaned in the laboratory prior to field use.

III. WELL EVACUATION

1) An Organic Vapor Analyzer (OVA) or portable gas chromatograph (GC) should be used to determine the presence of total organic volatile compound emissions prior to the evacuation of the monitor wells. The measurements are taken immediately after the well cap has been removed. Historically dry wells should also be tested in the same manner. All necessary calibrations and maintenance procedures found in the manufacture's operation manual are to be followed. Calibrations and readings are to be recorded on the applicable field sampling log (see Attachment 2) for each well tested.

1.a) If organic vapors are determined to be present at the well head, a water-hydrocarbon interface probe is to be employed to determine if an immiscible layer is present in the well waters. Depth to any light or dense immiscible layer(s), and thickness of each layer should be measured from a marked measurement reference point (see note below) at the top of the well casing to the immiscible layer(s) and through the immiscible layer(s). If immiscible layers are present, measurements are to be recorded on the well's field sampling log.

Note: Each well should have a reference point from which its water level is taken. The reference point should be established by a licensed surveyor and is typically located at the top of the well casing with the locking cap off. The reference point should be established in relation to mean sea level and the survey must also note the well location coordinates. The device which is used to detect the water level surface must be sufficiently sensitive so that a measurement to $\pm$ 0.01 foot can be obtained reliably.

1.b) Sampling of any immiscible layer(s) present will precede well evacuation procedures. A bottom filling Teflon bailer is lowered to the levels at which the light or dense phase immiscibles are found and a sample taken. Care must be taken to gently lower the bailer to avoid, as much as possible, disturbing the interface between the hydrocarbon and water layers.

2) Prepare equipment blanks by passing laboratory grade carbon free deionized water through the purging equipment, if possible, then into the appropriate pre-labeled container for transport to the Laboratory. This blank is to be prepared in the field, utilizing any clean

purging equipment, prior to evacuating the wells. These containers are to be labeled "evacuation equipment blank", and placed in the coolers utilized to ship the samples to the Laboratory.

3) All equipment, except that dedicated to the well, is to be washed before evacuating each well. It should be detergent washed, rinsed with tap water, deionized water, and chemically pure hexane/methanol, and allowed to air dry. See Section I.2.b.

4) Prior to sampling a monitor well, it should be flushed or evacuated no more than 24 hours in advance of sampling. A maximum of one day's time is suggested to allow the well to properly recharge prior to sampling, and yet prevent the accumulation of stagnant or "spoiled" water. For rapidly recovering wells, the time between well flushing and sampling could be considerably less. At the time of sampling, there should be a net flow of formation water into the well, increasing the probability that the samples consist of fresh formation water only. The requirements for flushing a well are as follows:

- For a low yield or slow recovering well, evacuate to dryness. If time permits, additional evacuation is suggested. Sample immediately upon recovery.
- Four well volumes should be removed from a rapidly recovering well. If the well cannot be evacuated to dryness, it is recommended that pH and specific conductance be monitored to stabilization during evacuation to assure that a representative sample of ground water is collected. Sample as the well is recovering.

4.a) In order to prevent well contamination, either of the following well flushing procedures are recommended for wells less than 25 feet deep:

- Bailers constructed of the same material as the well casing, PVC, Teflon or stainless steel are recommended purging equipment. The bailers should be attached to a a down-rigger reel with a polyethylene (PE) coated steel cable, single strand stainless steel wire, or a PE monofilament line. The reel should be mounted on a tripod with the cable pulley set directly above the well opening. The bailer and cable should be the only sampling equipment to contact the internal well casing and its contents. As the last bailer-full is pulled, the cable is to be wiped with a reagent grade methanol/D.I. water saturated cloth. If monofilament line is used, it may be practical and a good practice to simply provide clean, fresh line at each well.
- Evacuation may also be accomplished by means of a dedicated non-collapsible 1/2 inch discharge tube or pipe, preferably of Teflon or high density polyethylene, placed inside the

well, and a portable vacuum, peristaltic or centrifugal pump operating at the well collar. In an effort to collect all the stagnant water during draw-down, the inlet of the tube or pipe must be moved down as the well draws down, maintaining it just below the surface of the water.

4.b) For wells deeper than 25 feet, one of the following flushing methods is recommended:

- A dedicated bailer constructed of the same material as the well casing, of Teflon, stainless steel or PVC, attached to a down-rigger reel with a polyethylene coated steel cable, single strand stainless steel wire, or a monofilament line may be used. The reel should be mounted as noted above in Section 3.a.
- A less time consuming method is the electrically powered Teflon/stainless steel submersible pump, or a gas operated positive displacement (bladder or piston) Teflon/stainless steel pump. A dedicated submersible pump, or at least dedicated discharge tubing, is preferred. The discharge tube and fittings should be of Teflon or high density polyethylene. A dedicated submersible electrical pump should be retained about a foot above the bottom of the screened area to prevent burn-out upon total evacuation, and should not be operated dry. If a pump does not evacuate the well to dryness, the inlet of the pump should be placed just below the surface of the water column, and lowered as the well draws down.

IV. FIELD RECORDS - EVACUATION

1) A bound field book containing numbered pages or a separate field log for each well should be maintained by the collector to record all pertinent information regarding the evacuation and sampling of monitor wells. See Attachment 2. This recorded information is necessary to maintain well sampling data and should become part of the analytical report. The sample collector should sign and date each page of the field book or the log. The following data should be determined as follows and recorded upon the evacuation of each well:

a) Collector's name, date, and time that evacuation was initiated and completed.
b) Site and Location - Name of the facility, city and state
c) Well Identification - i.e., monitor well number, code or name.
d) Well Depth - Measure from the reference point at the top of the well casing to the bottom of the well to the nearest 0.01 foot wit a weighted measuring tape or a calibrated water level indicator prior to purging. The water level indicator should be calibrated and any correction factors noted on the meter and in the manufacture's instruction book which accompanies the meter. See note in Section III.1.a.

e) Water Level Depth - Measure from the reference point at top of the well casing to the water surface to the nearest 0.01 foot with a pre-cleaned calibrated water level indicator. As the probe and line are pulled from the wells, the lines should be wiped with a fresh reagent grade methanol/D.I. water saturated cloth. The probe should be washed with a non-phosphate detergent and rinsed twice with laboratory grade deionized water.
f) Depth to any light or dense immiscible layer(s), and thickness of each layer - Measure from the reference point at the top of the well casing to the immiscible layer(s) and through the immiscible layer(s) utilizing a water-hydrocarbon interface probe. If immiscible layers are present, document the method of collection and identification of samples. See Section III.1.
g) Well casing inside diameter to the nearest 0.01 inch.
h) The well volume - Calculate the amount of water in gallons occupying the well prior to bailing.

Volume (gallons) = (3.14) $r^2h/231$.
r = inside well casing radius in inches.
h = height of water in well in inches (well depth minus the water level depth).

i) Total gallons evacuated - Well yield.
j) Water level following evacuation, ft.
k) If organic vapors are to be measured in the well head, utilize a OVA or a portable gas chromatograph and record measurements. Field calibration must be conducted and recorded.
l) Method of Evacuation - type of bailer, pump, etc. including description.
m) Comments - Information pertaining to the condition of the well, such as no cap, broken casing, grout deterioration, etc.

V. SAMPLING

1) The wells should have been properly flushed or evacuated, the containers and samplers prepared and the initial log data entered upon evacuation.

1.a) Determine the water level depth to the nearest 0.01 of a foot - Record on the field log.

1.b) All non-dedicated equipment used to sample the well (e.g., bailer, funnel, etc.) must be cleaned and stored as per the cleaning procedures outlined in Section I.

1.c) Prepare equipment blanks by passing laboratory grade deionized water through the sampling equipment, if possible, (and filtering device, if applicable), then into the appropriate pre-labeled container for transport to the Laboratory. This blank is to be prepared in the field, utilizing the pre-cleaned sampling equipment, but prior to the collection of samples. These containers are to be labeled "sampling equipment blank"), and placed in the coolers utilized to ship the samples to the Laboratory.

1.d) A dedicated positive displacement Teflon/stainless steel pump may be utilized to sample the well. When collecting samples for the analyses of volatile constituents, such as volatile organics, total organic carbon (TOC) or total organic halide (TOX), pumping rates should be minimized, if possible. No headspace shall exist in the sample containers for these parameters. A dedicated discharge/peristaltic pump system may also be utilized to sample groundwater monitoring wells, but is only recommended when sampling for non-volatile components.

1.e) Samples may also be withdrawn from a well utilizing a pre-cleaned or dedicated bailer constructed from the same material as the well casing, Teflon, PVC, or stainless steel attached to a clean polyethylene coated steel cable, single strand stainless steel wire, or a monofilament line. The cable is raised and lowered by means of a down-rigger reel mounted on a tripod and set directly above the well opening. The first bailer-full, if adequate sample exists, should be used to rinse the bailer and discarded. Subsequent samples should be slowly transferred from the bailer to the container and preserved immediately according to the specific test requirements (see Attachment 1). Upon withdrawing the last bailer-full, wipe the cable with a clean cloth saturated with laboratory grade deionized water and reagent grade methanol. If monofilament line is utilized, discarding the used portion of the line may be more appropriate.

1.f) Samples withdrawn from the well should be collected in the following order if there is sufficient volume:

field pH, Specific Conductance, Temperature
Volatile organics
Total organic halogen
Total organic carbon
Extractable organics

Total recoverable metals
Dissolved metals
Wet chemistry parameters

2) All samples collected for transport to the Laboratory should be chemically preserved (if applicable) and immediately placed on wet ice. See Attachment 1 for specific requirements. Samples collected for dissolved metal analyses should be immediately filtered through a 0.45 micron glass fiber or membrane filter prior to transfer to the sample container and preservation. All containers, especially those containing samples to be analyzed for volatile constituents, should be filled to the top to maintain anaerobic conditions and to prevent volatilization.

3) The following determinations should be made in the field at the time of sampling and recorded on the field logs:

- pH* - Specific Conductance* - Temperature - Calibration checks

(* in quadruplicate)

Field monitoring equipment or test probes should be calibrated in the field prior to each sample collection according to the manufacturers specifications and in compliance with EPA recommended methods. Calibration checks utilizing standards for pH and specific conductance should be performed and documented at the time of sampling.

4) Sample Shipment - Samples are to be shipped in sealed insulated shipping containers, ice chests or coolers supplied by the analytical laboratory conducting the analyses. Shipment and receipt of samples must be coordinated with the laboratory to minimize time in transit. All samples for organic analysis (and many other parameters) should arrive at the laboratory within one day after sampling and be maintained at zero to 4°C with wet ice or packaged refrigerant ("blue ice"). Wet ice should be replaced with frozen packaged refrigerant just prior to shipment. To insure arrival at the laboratory in good condition, the samples should be sent in sturdy insulated ice chests (coolers) equipped with bottle dividers. An air courier or equivalent over-night courier service is recommended.

VI. FIELD RECORDS - SAMPLING

1). It is most important to maintain an accurate and thorough field log in case one is required to recall particular information concerning the evacuation and sampling of a monitor well. In addition to the information to be logged covered in Section III and IV, the following information is also to be recorded at the time of sampling. See Attachment 2.

a) Collector's name, date and time of sampling.
b) Water Level Depth - Measure from the reference point at the top of casing to the water surface to the nearest 0.01 foot with a calibrated water level indicator.
c) Sample identification number.
d) Sample pH and specific conductance in quadruplicate, and temperature. See Section V.3.
e) Method of sample collection - type of bailer, pump, etc. Include a description of the pump - brand name, model, etc.
f) Sample characteristics - color, turbidity, odor, sediment, surface oil, etc.
g) Sample volume, containers, preservatives.
h) Test to be performed on each sample (if known).
i) Weather conditions at the time of sampling.
j) Sample sequence number - Order in which well was sampled with respect to other wells on site.
k) Any additional field observations, comments or recommendations - e.g., split sampling (with whom), re-sampling, equipment failures, condition of the well, etc.
l) Sample Custody Statement - If the samples are transferred to the receiving laboratory by the collector or an over-night common courier, a statement to this effect should be noted on the field log.

2) Prepare a sample label for each sample container employing a waterproof pen and adhesive label. The following is to be indicated on the label -

a) Collector's name, date and time of sampling.
b) Sample source.
c) Sample Identification number.
d) Sample preservatives.
e) Test(s) to be performed on the sample, if known.

3) The samples must be sealed to protect their worth. The collector is to date, sign and identify each sample on a seal and attach it to each sample container and lid. A waterproof adhesive seal and pen must be used. The sample shuttle kit (cooler) is sealed with a tamper proof uniquely numbered seal, and this number is recorded on the chain of custody record. See Attachment 3.

VII. CHAIN-OF-CUSTODY

1). Proper Chain-of-Custody records are necessary to insure the integrity of the sampling event and the analyses.

1.a) A Chain-of-Custody record (see Attachment 3) shall be completed for all monitor well samples collected by the sample collector.

1.b) The sample collector, or the initiator, is to forward the original with the sample to the laboratory performing the analyses.

1.c) Upon receipt of the samples at the laboratory, the sample coordinator or his/her representative is to complete the record, make a copy for his files, and return the original with the analytical data to the appropriate party.

VIII. INSTRUCTIONS TO THE LABORATORY

1). Written instructions to the analytical laboratory must accompany the sample to avert communication difficulties. The instructions will be recorded on a form such as the Sample Analysis Request Form, Attachment 4, or equivalent. The instructions should specifically note the sample identification, date of sampling, and analyses to be performed. The samples must be delivered to the laboratory as soon as possible. If the samples cannot be delivered immediately, they should be secured and where necessary, maintained at 4 C. At no time should the samples be delivered to the laboratory for analysis after the permitted holding times have expired.

2). As soon as field personnel are ready to transport samples from the field to the laboratory, they shall notify the laboratory by telephone. If the samples are shipped by common carrier, the laboratory should be telephoned as soon as the shipping containers are cosigned to the shipper, and provided with shipping document numbers . In addition to the estimated time of arrival, the field personnel should provide the following minimum information to the laboratory:

- Date of Shipment
- Time of Shipment
- Number of Containers Shipped
- Mode of Shipment
- Sample Type
- Source of Samples

3). Some recommended specific laboratory requirements are as follows -

- Maintain preservation of the samples - refrigerate.
- Log-in samples - record pertinent information, note the condition of samples, the sample shuttle and sample seals.
- Maintain Chain-of-Custody - External, and in-house or intra-lab Chain-of-Custody.
- Analyses - perform analyses within prescribed holding time limits - record date and time of analysis.
    - o Identify methods of analyses.
    - o Use only methods acceptable to the involved regulatory agency.
- Employ good analytical practices and techniques, such as:
    - o Clean glassware and analytical tools, e..g., pipettes, syringes, etc. Use sulfuric-dichromate cleaning solution when applicable.
    - o Analytical reagent grade reagents and certified standards.
    - o Distilled and/or deionized water with a conductivity of 1.0 umhos/cm or less, "organic free" where necessary.
    - o Adequately trained, experienced personnel, with special emphasis on laboratory safety.
    - o Adequate physical facilities and equipment.
    - o Frequent documented servicing and calibration of instruments.
- Maintain a quality assurance/quality control program. The quality assurance/quality control program must include the following minimum components:
    - o Calibration of laboratory instruments to within acceptable EPA and manufacturer's limits.
    - o Inspection, maintenance, and servicing of all laboratory instruments and equipment.
    - o Use of reference standards and quality control samples (blanks, spikes, duplicates, etc.).
    - o Use of thorough, documented QC procedures to monitor accuracy and precision of data.
    - o Regular participation in external laboratory evaluations (i.e. EPA Performance Audit Program).
    - o Continuous in-house training program. New analysts must become thoroughly familiarized with all laboratory safety procedures and equipment.
    - o Maintenance of laboratory notebooks for each analytical method and copies of all

analytical reports. All raw data produced must be checked for validity before reported and permanently stored.

IX. DATA REPORTING

1) All analytical reports will be complete with analytical data, sample ID, sample source, date sampled, date received, parameters tested, results, percent recovery, date extracted (if applicable) and analyzed, analyst, referenced methodologies, QA/QC data, field logs, analysis request forms, and chain-of-custody forms.

2) The report should be tamper proof bound,and include the following information:
- Title Page - The title page should include the site/project name, date of report, date(s) the samples were received, the laboratory's name and address, and the laboratory supervisor's name and signature.
- Analytical Methodologies - A table should be prepared listing all the analytical test method employed in the analyses of the samples with a reference for each made to the method manual and test method.
- Field Logs and Sample Analysis Request Forms - These forms list pertinent field information and all requested analyses.
- Chain-of-Custody - Both field and laboratory chain-of-custody records should be included in the final report package. This should include a summary of sample movement through the laboratory with date(s) of receipt, date(s) of analysis, and date(s) of sample storage/disposal.
- Analytical Data - including sample source, date sampled, date received, parameters tested, results with the appropriate units of measurement, data extracted (if applicable) and analyzed, and the analyst's initials or name.
- All applicable QC Data not mentioned above - for example, laboratory blank data, internal standard and surrogate recoveries, chromatograms, and tuning data.

ATTACHMENT 1
RECOMMENDED CONTAINERIZATION AND PRESERVATION OF SAMPLES

| Measurement | Volume Required mL | Container[a] | Preservative | Holding Times | Reference |
|---|---|---|---|---|---|
| **Physical Properties** | | | | | |
| Color | 50 | P, G | Cool, 4°C | 48 Hrs | 1 |
| Conductance | 100 | P, G | Cool, 4°C | 28 Days | 1 |
| Hardness | 100 | P, G | Cool, 4°C $HNO_3$ to pH <2 | 6 Mos | 1 |
| Odor | 200 | G only | Cool, 4°C | 24 Hrs | 1 |
| pH (Per Replicate) | 50 | P, G | None | Det. on Site | 1 |
| Residue | | | | | |
| Filterable | 200 | P, G | Cool, 4°C | 7 Days | 1 |
| Non-Filterable | 200 | P, G | Cool, 4°C | 7 Days | 1 |
| Total | 200 | P, G | Cool, 4°C | 7 Days | 1 |
| Volatile | 200 | P, G | Cool, 4°C | 7 Days | 1 |
| Settleable Matter | 1000 | P, G | Cool, 4°C | 48 Hrs | 1 |
| Temperature | 1000 | P, G | None | Det. on Site | 1 |
| Turbidity | 100 | P, G | Cool, 4°C | 48 Hrs | 1 |
| **Metals (except mercury)** | | | | | |
| Dissolved | 500 | P, G | Filter on Site $HNO_3$ to pH <2 | 6 Mos | 1, 2 |
| Suspended | 500 | P, G | Filter on Site | 6 Mos | 1, 2 |
| Total | 500 | P, G | $HNO_3$ to pH <2 | 6 Mos | 1, 2 |
| Total Recoverable | 500 | P, G | $HNO_3$ to pH <2 | 6 Mos | 1, 2 |
| Mercury-Dissolved | 300 | P, G | Filter on Site $HNO_3$ to pH <2 | 28 Days | 1, 2 |
| -Total | 300 | P, G | $HNO_3$ to pH <2 | 28 Days | 1, 2 |
| Chromium (Hexavalent) | 200 | P, G | Cool, 4°C | 24 Hrs | 1, 2 |
| **Inorganics, Non-Metallics** | | | | | |
| Acidity | 200 | P, G | Cool, 4°C | 14 Days | 1, 2 |
| Alkalinity | 200 | P, G | Cool, 4°C | 14 Days | 1, 2 |
| Boron | 100 | P only | Cool, 4°C | 28 Days | 1 |
| Bromide | 200 | P, G | None | 28 Days | 1, 2 |
| Chloride | 200 | P, G | None | 28 Days | 1, 2 |
| Chlorine | 200 | P, G | None | Det. on Site | 1, 2 |
| Cyanides | 500 | P, G | Cool, 4°C NaOH to pH >12 | 14 Days | 1, 2 |
| Fluoride | 50 | P | None | 28 Days | 1, 2 |
| Iodide | 100 | P, G | Cool, 4°C | 24 Hrs | 1 |
| Nitrogen Ammonia | 400 | P, G | Cool, 4°C $H_2SO_4$ to pH <2 | 28 Days | 1, 2 |
| Kjeldahl, Total | 500 | P, G | Cool, 4°C $H_2SO_4$ to pH <2 | 28 Days | 1, 2 |
| Nitrate plus Nitrite | 200 | P, G | Cool, 4°C $H_2SO_4$ to pH <2 | 28 Days | 1, 2 |
| Nitrate | 100 | P, G | Cool, 4°C | 48 Hrs | 1, 2 |
| Nitrite | 50 | P, G | Cool, 4°C | 48 Hrs | 1, 2 |
| Dissolved Oxygen | | | | | |
| Probe | 300 | G only | None | Det. on Site | 1, 2 |
| Winkler | 300 | G only | Fix on Site | 8 Hrs | 1, 2 |
| Phosphorus | | | | | |
| Ortho-phosphate, Dissolved | 100 | P, G | Filter on Site Cool, 4°C | 48 Hrs | 1, 2 |
| Hydrolyzable | 100 | P, G | Cool, 4°C $H_2SO_4$ to pH <2 | 28 Days | 1, 2 |
| Total | 100 | P, G | Cool, 4°C $H_2SO_4$ to pH <2 | 28 Days | 1, 2 |
| Total, Dissolved | 100 | P, G | Filter on Site Cool, 4°C | 24 Hrs | 1, 2 |
| Silica | 50 | P only | Cool, 4°C | 28 Days | 1, 2 |
| Sulfate | 100 | P, G | Cool, 4°C | 28 Days | 1, 2 |
| Sulfide | 250 | P, G | Cool, 4°C 2mL zinc acetate plus NaOH to pH >9 | 7 Days | 1, 2 |
| Sulfite | 100 | P, G | None | Det. on Site | 1 |

| Measurement | Volume Required mL | Container[a] | Preservative | Holding Times | Reference |
|---|---|---|---|---|---|
| Coliform, Total and Fecal | 100 | Sterile P, G | Cool, 4°C | 6 Hours | 3 |
| Gross Alpha, Gross Beta, Radium | 4000 | P, G | $HNO_3$ to pH <2 | 6 Mos. | 3 |
| BOD | 1000 | P, G | Cool, 4°C | 48 Hrs | 1, 2 |
| COD | 50 | P, G | $H_2SO_4$ to pH <2 | 28 Days | 1, 2 |
| Oil & Grease (One Replicate) | 1000 | G only | Cool, 4°C $H_2SO_4$ or HCl to pH <2 | 28 Days | 1, 2 |
| Organic Carbon | 100 | G only Teflon lined cap | Cool, 4°C $H_2SO_4$ or HCl to pH <2 | 28 Days | 1, 2 |
| Phenolics | 1000 | G only | Cool, 4°C $H_2SO_4$ to pH <2 | 28 Days | 1, 2 |
| MBAS (Surfactants) | 1000 | P, G | Cool, 4°C | 48 Hrs | 1, 2 |
| TOX (2 Rep) | 500 | G only | Cool, 4°C | 7 Days | 1, 2 |
| (4 Rep) | 1000 | Teflon lined cap | $H_2SO_4$ to pH <2 | | |
| Organics | | | | | |
| Volatile Organics by GC (2 vials @ 40mL) | 100 | G, Teflon septum cap | Cool, 4°C | 7 Days | 2, 3 |
| | | | Cool, 4°C, HCl to pH <2 | 14 Days | |
| Volatile Organics by GC/MS (2 vials @ 40mL) | 100 | G, Teflon septum cap | Cool, 4°C | 7 Days | 3 |
| | | | Cool, 4°C, HCl to pH <2 | 14 Days | 2 |
| Phenols by GC | 1000 | G, Teflon cap liner | Cool, 4°C | 7 Days[b] | 2, 3 |
| | | | | 30 Days[d] | 2 |
| | | | | 40 Days[c] | 3 |
| Benzidines by GC | 1000 | Amber G, Teflon cap liner | Cool, 4°C | 7 Days[b] | 3 |
| | | zero head-space | prepare oxidant free | 7 Days[c] | 3 |
| Phthalate Ester by GC | 1000 | G, Teflon cap liner | Cool, 4°C | 7 Days[b] | 2, 3 |
| | | zero headspace | | 30 Days[d] | 2 |
| | | | | 40 Days[c] | 3 |
| Nitrosamines by GC | 1000 | Amber G, Teflon cap liner | Cool, 4°C | 7 Days[b] | 3 |
| | | zero head-space | prepare oxidant free | 40 Days[c] | 3 |
| Organochlorine Pesticides/PCBs by GC | 1000 | G, Teflon cap liner | Cool, 4°C | 7 Days[b] | 2, 3 |
| | | | | 30 Days[d] | 2 |
| | | | | 40 Days[c] | 3 |
| Nitroaromatics and Isophorone by GC | 1000 | G, Teflon cap liners | Cool, 4°C | 7 Days[b] | 2, 3 |
| | | | | 30 Days[d] | 2 |
| | | | | 40 Days[c] | 3 |
| Polynuclear Aromatic Hydrocarbons by GC | 1000 | Amber G, teflon cap liners | Cool, 4°C | 7 Days[b] | 2, 3 |
| | | | | 30 Days[d] | 2 |
| | | | | 40 Days[c] | 3 |
| Organophosphorus Pesticides by GC | 1000 | G, Teflon cap liners | Cool, 4°C | 14 Days[b] | 2 |
| | | | | 30 Days[d] | 2 |
| Haloethers by GC | 1000 | G, Teflon cap liners | Cool, 4°C | 7 Days[b] | 3 |
| | | | | 40 Days[c] | 3 |
| Chlorinated Hydrocarbons by GC | 1000 | G, Teflon cap liners | Cool, 4°C | 7 Days[b] | 2, 3 |
| | | | | 30 Days[d] | 2 |
| | | | | 40 Days[c] | 3 |
| Organics | | | | | |
| Chlorinated Herbicides by GC | 1000 | G, Teflon cap liner | Cool, 4°C | 7 Days[b] | 2 |
| | | | | 30 Days[d] | 2 |
| Semi-Volatiles by GC/MS | 2000 | G, Teflon cap liner | Cool, 4°C | 7 Days[b] | 3 |
| | | | | 40 Days[c] | 3 |
| | | | | 14 Days[b] | 2 |
| | | | | 40 Days[d] | 2 |

NOTES:

a - Plastic (P) or Glass (G). For metals, polyethylene with an all polypropylene cap is preferred.
b - Maximum holding time from sampling to extraction.
c - Maximum holding time from extraction to analysis.
d - Maximum holding time from sampling to analysis.

REFERENCES:

1 - Methods for Chemical Analysis of Water and Wastes, March 1983, USEPA, 600/4-79-020 and additions thereto.
2 - Test Methods for Evaluating Solid Waste, Physical/Chemical Method, November, 1986, Third Edition, USEPA, SW-846 and additions thereto.
3 - "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act", Environmental Protection Agency, Code of Federal Regulations (CFR), Title 40, Part 136.

Rev: 2/89

ATTACHMENT 2
FIELD LOG

Facility _____ Location _____

Collector/Operator _____ BFI Lab No._____ Shuttle No._____

Sample Point ID _____ Method of evac. _____

EVACUATION: Date/Time _____ Well Depth, Ft _____

Water Level Depth, Ft. _____ Well Volume, gal _____

Casing Diameter, in. _____ Total gallons evac. _____

Well level after evac., ft._____ Completed-Date/Time _____

IMMISCIBLE LAYER: Detected ( ) Yes ( ) No ( ) N/A Depth to top of layer(s), Ft. _____:_____

Sample Collected ( ) Yes ( ) No ( ) N/A Depth to bottom of layer(s), Ft. _____:_____

ORGANIC VAPORS: Detected ( ) Yes ( ) No ( ) N/A Method of Detection _____
Concentration measured, ppm _____ as _____ Conc. of Calib. Standard, ppm ._____ Amt of Calib. Stdn found, ppm _____

SAMPLING: Collector _____ Sample Sequence _____
Initiated Date/Time _____ Well Stick-up, Ft._____ Water Level Depth, ft _____
Completed Date/Time _____ Method of Sample Collection _____
PARAMETERS: ( ) annual ( ) semi-annual ( ) quarterly ( ) monthly ( ) other

REPLICATE SAMPLE DATA: pH and Conductance are automatically temperature compensated at time of measurement

Temp. Deg C _____ pH @ 25 _____ Cond. @ 25, umhos/cm:_____

Temp. Deg C _____ pH @ 25 _____ Cond. @ 25, umhos/cm_____

Temp. Deg C _____ pH @ 25 _____ Cond. @ 25, umhos/cm_____

Temp. Deg C _____ pH @ 25 _____ Cond. @ 25, umhos/cm_____

Instrument Calibration Check Data.

pH 4 stdn: _____ 100 umhos Cond. stdn @ 25:_____
pH 7 stdn: _____ 1000 unhos Cond. stdn @ 25:_____
pH 10 stdn: _____ 10000 umhos Cond. stdn @ 25: _____

GENERAL INFORMATION:
Weather Conditions at time of sampling: _____

Sample Characteristics: _____

Sample Containers, Volumes, Preservatives and Tests to be Performed:_____

_____

_____

_____

_____

Comments and Observations: _____

_____

Recommendations: _____

_____

Certification:

_____ _____ _____
Signed Date

rev 03/90

ATTACHMENT 3

CHAIN-OF-CUSTODY

Shuttle Number: _____ Seal No. _____ Prepared/ Sealed By: _____ (print name)

Laboratory: _____ _____ (signature)

SHIP TO
Company: _____ Attn: _____

Address: _____ Phone: _____

SAMPLE IDENTIFICATION
Facility/Site: _____

SHUTTLE CONTENTS

| LAB I.D. | Site Sample Source I.D. | # of Bottles | Size | P* G* | Preser-vative | Parameter(s) |
|---|---|---|---|---|---|---|
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Container type: P* = Plastic, G* = Glass

| | | | |
|---|---|---|---|
| (1) Shuttle opened by: _____ (print name) | Date | Time | Seal Intact Yes No No._____ _____ (signature) |
| (2) Shuttle prepared for shipment by: _____ (print name) | Date | Time | New Seal Installed Yes No No._____ _____ (signature) |
| (3) Shuttle received at Lab by: _____ (print name) | Date | Time | Seal Intact Yes No No._____ Lab's Name: _____ _____ (signature) |

DP/dp
Rev: 12/89

ATTACHMENT 4

SAMPLE ANALYSIS REQUEST / CHAIN OF CUSTODY

Assigned to Laboratory: _____ BFI Shuttle Kit ID: _____

Location: _____ BFI LAB Project ID: _____

Lab Phone: _____ Laboratory Contact: _____

| BFI No(s): | Sample Point | Matrix code | Date Sampled | volume/ container | preser-vative | Analysis (Codes) Requested |
|---|---|---|---|---|---|---|
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Matrix Codes: GW = groundwater; SF = surface water; SO = soil; MP = multi-phase; OR = organic/oil; SW = solid waste; WW = wastewater; L = Leachate. Other Codes: MT = tot. metal; MD = dissol. metal; MR = tot. recoverable metal

P.O. No: _____ Quote Per: _____ $_____ Date _____

Remarks: _____

Safety Precautions: _____ Normal Laboratory Hygiene, _____ Avoid skin/eye contact, _____ Avoid breathing vapors/dust,

Sample Custody Statement: _____ All samples properly preserved, iced and hand delivered to _____

Special Handling/ Storage: _____ Receiving Lab's Comments:(Headspace, etc.) _____

**Sample(s) submitted by:**
Custody Seal Intact: yes / no

Name _____ Title _____

Company _____ Date/Time _____

**Sample(s) received by:**
Custody Seal Intact: yes / no

Name _____ Title _____

Company _____ Date/Time _____

**REPORT RESULTS TO:**
**PROJECT MANAGER,** _____
**Browning-Ferris Industries**
**5630 Guhn Rd.**
**Houston, Texas 77040**

**SEND INVOICE(S) TO:**
**ACCOUNTING MANAGER**
**Browning-Ferris Industries**
**5630 Guhn Rd.**
**Houston, Texas 77040**

**Return a copy of this signed form after receiving samples and indicate lab project IDs.**

**Project IDs:** _____

Rev: 11/89

112

# TECHNIQUES & QUALITY CONTROL IN GROUNDWATER SAMPLING

Frank Perugini, Manager-Sample Management and
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WMI-Environmental Monitoring Laboratories, Inc.,
2100 Cleanwater Drive, Geneva, Illinois 60134

## INTRODUCTION

The basic objective of a groundwater monitoring program at a land disposal facility is to determine whether or not the facility has impacted the groundwater. Federal, state and local regulatory agencies have established criteria that must be met at each facility. These criteria involve standards that the groundwater samples must meet with respect to chemical concentrations. In order to comply with these criteria, an effective and comprehensive monitoring program must be established for the facility.

The quality of the data collected at these land disposal facilities is dependent upon the following six major activities:

1. Define the Geology and Hydrogeology.
2. Groundwater Monitoring System.
3. Define the Analyte Requirements.
4. Select Dedicated Monitoring Equipment.
5. Establish Proper Sampling Procedures.
6. Establish Chain-of-Custody Record and Field Information Documentation.

Each of these activities are of equal importance adherence to the six items listed above will lead to a successful groundwater monitoring program with quality assurance at the time of sample collection.

## 1. DEFINE GEOLOGY AND HYDROGEOLOGY

Hydrogeological investigation is an attempt to identify geological structures and characterize the movement of groundwater within a specific area. The first step is to describe the regional and site topographic conditions. Topographical maps are available from a number of sources and in a variety of scales. The U.S.G.S. is widely used and provides maps covering a quadrangle range bounded by lines of latitude and longitude. The U.S.G.S. quadrangle maps indicate ground surface contours, surface water bodies, building sites, cemeteries, and private well locations. Other information may be obtained from local town offices which will identify surrounding land uses such as residential, commercial, agricultural or recreational.

Defining the hydrogeology at the facility will provide a clearer understanding of the potential migration pathways to the groundwater. Therefore, development of a conceptual model can be accomplished in two phases - an initial reconnaissance and a field investigation. When the hydrogeology of a project area is relatively uncomplicated and well documented in the literature, the initial reconnaissance may provide sufficient information to identify flow paths and the target monitoring zones. However, where little background data is available or the geology is complicated, a field investigation is necessary. The field investigation routinely involves performing numerous soil borings, soil samples and installation of piezometers followed by monitoring wells in the target monitoring zones.

## 2. GROUNDWATER MONITORING SYSTEM

Before samples can be collected, an overall summary of the monitoring wells should be identified. Table 1 is a typical chart identifying the wells used in the groundwater monitoring program and summarizes construction and monitoring information. Geological boring logs and well construction logs for each monitoring well would also be attached to Table 1.

## 3. DEFINE THE ANALYTE REQUIREMENTS

One important component of any groundwater monitoring program is defining the analyte requirements. The primary source for this information is the facility permit. Facility permits usually contain details concerning the frequency of sampling required, a list of analytes to be tested, the reporting requirements, the reporting limits or detection limits required and in some cases the test methods that must be used. The following list should be used in defining the analyte requirements for a groundwater monitoring program.

- Determine the list of analytes required.
- Identify holding times, preservative and sample volume requirements.
- Define any additional QA/QC requirements and report due date.

Determining the List of Analytes - There is a wide variation in the way facilities permits specify the analytes to be tested. Some permits will provide tables that contain the

GROUNDWATER MONITORING SYSTEM SUMMARY

SITE: Example ( 000 ) DATE: _____

SAMPLE POINT TYPE, LOCATION, AND SAMPLING EQUIPMENT

| | | | Type | | | | | Location | | | | Sampling Equipment | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WMI Well ID No. | Former Well ID (if different from WMI) | Agency Well ID (if different from WMI) | Active/ Inactive/ Decomm. (A/I/D) | Source Code | Program Type | Sampling Frequency | On-Site Off-Site | [redacted] | N/S Coord. E/W Coord. | Formation at Screen | Gradient | Purge and Sample Equipment | Filtering Equipment | Sample Tubing Material |
| PW19 | PW-19 | 19 | SEE | W | S | Q | Off | SE | 808110N 214600E | Outwash | SEE | NA/GR | NA | NA |
| B07D | B-7D | 7D | WELL | W | P, S | S, Q | On | NW | 808000N 2147000E | Outwash | WELL | W/WP1100 | IN | PP |
| B18 | B-18 | 18 | ID | W | S | NA | On | SE | 808215N 2147500E | Till | ID | NA | NA | NA |
| S01 | S-1 | S1 | CHART[1] | R | S | S | Off | SE | 808100N 2146500E | NA | CHART[2] | NA/GR | NA | NA |
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GROUNDWATER MONITORING SYSTEM SUMMARY (continued)

SITE: Example ( 000 )

DATE: .a,

WELL CONSTRUCTION INFORMATION

| WMI Well ID No. | Well Depth (ft) | Bottom of Well Elev. (ft MSL) | Ground Elev. (ft MSL) | Internal Casing Material | Internal Casing ID (in.) | Top of Internal Casing or Well Wizard Cap (ft MSL) | Bottom of Internal Casing (ft MSL) | Internal Casing Length (ft) | Internal Casing Stick up (ft) | Top of Screen Elev. (ft MSL) | Bottom of Screen Elev. (ft MSL) | Screened Length (ft) | Screen Material | External Casing Material | External Casing ID (in.) | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PW19 | SEE | UK | UK | S | 8.0 | SEE | UK | UK | UK | UK | UK | UK | UK | NA | NA | |
| B07D | WELL | 650.23 | 705.23 | PVC | 2.0 | WELL | 645.33 | 53 | 3.0 | 645.53 | 650.33 | 5.0 | PVC | A | 4.0 | |
| B18 | ID | 690.63 | 712.63 | PVC | 2.0 | ID | 685.63 | 20.0 | 3.0 | 685.53 | 690.63 | 5.0 | PVC | S | 4.0 | |
| S01 | CHART[3] | NA | NA | NA | NA | CHART[4] | NA | NA | NA | NA | NA | NA | NA | NA | NA | |

TABLE 1.3

GROUNDWATER MONITORING SYSTEM SUMMARY (continued)

SITE: Example ( 000 ) DATE: _____

WELL CONSTRUCTION INFORMATION (continued)

| WMI Well ID No. | Top of External Casing (ft MSL) | Bottom of External Casing (ft MSL) | External Casing Stick up (ft) | Cons. to WMI Spec. (Y/N) | Cons. Date | Drilling Firm | Drilling Method | Devel. Method | Packing Material | Packing Length | Length of Filter Sand Above Packing (ft) | Length of Bentonite Seal (ft) | Length of Filter Sand Above Seal (in.) | Type of Grout | Grout Length | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PW19 | UK | UK | UK | N | UK | UK | UK | UK | UK | UK | UK | UK | UK | UK | UK | |
| B07D | 708.73 | 704.73 | 3.5 | Y | 5-24-85 | OK Drillers | HSA | AS&A | S | 10.0 | 2.0 | 3.0 | 6.0 | Volclay | 41.5 | |
| B18 | 716.10 | UK | 3.5 | N | 6-23-83 | NG Drillers | WRM | UK | S | 5.0 | 2.0 | NA | NA | 0 | 17 | |
| S01 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | |
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TABLE 1.4

GROUNDWATER MONITORING SYSTEM SUMMARY (continued)

SITE: Example ( 000 ) DATE: _____

WELL ID CHART

| WMI Well ID No. | 1 Active/ Inactive/ Decomm. (A/I/D) | 2 Gradient | 3 Depth of Well (feet) | 4 Elevation at Top of Casing (msl) | Normal Range: Purge Volume (gallons) | Depth to Water (feet) | Recharge Time (hrs) | Temp. (°C) | pH (Std.) | Specific Conduct. (µmhos) at 25°C | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PW19 | A | D | 60 | UK | NA | UK | NA | 15° | 7.0-7.3 | 340-345 | Private well; sample taken at outside faucet |
| B07D | A | U | 58 | 708.24 | 8.15 | 5.0 | 3.0 | 10° | 6.8-7.3 | 850-960 | |
| B18 | D | D | 25 | 715.63 | NA | NA | NA | NA | NA | NA | Well grouted 8/84 |
| S01 | A | D | NA | NA | NA | NA | NA | 2-25° | 7.3-7.5 | 1000-1500 | |
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specific analytes, reporting limits or detection limits to be achieved and in some cases the analytical methods to be used. Other permits simply indicate the analytes or classes of analytes and allow the permittee discretion on methods to be used and what reporting limits are acceptable.

If specific methods are not specified, it is advised that 40CFR Part 136 and the tables contained in this regulation be used in determining the most appropriate method to be followed. Tables are included for biological, inorganic, organic and radiological analytes. The methods specified are widely used and understood by the analytical community.

Reporting limit requirements vary widely from state to state. In the absence of specific requirements in the permit, the Contract Required Detection Limits (CRDLs) specified in the USEPA Contract Lab Program (CLP) or Practical Quantitation Limits (PQLs) are recommended. One should consult the laboratory to be used for guidance. If the laboratory personnel are not familiar with these concepts a different laboratory should be considered.

Identify Holding Times, Preservative and Sample Volume Requirements - Many permits will not specify these requirements. In setting up a groundwater monitoring program, these three factors should be determined and discussed with the laboratory personnel to insure that there are no misunderstandings after the event.

Table II of 40CFR Part 136 specifies precise holding times and preservation requirements for most common analytes. The most important part of this table are the notes that follow it. Particular attention must be paid to differences between certain analytes that may or may not be analyzed together depending on the preservation and holding times used. For example, purgeable halocarbons, purgeable aromatic hydrocarbons, acrolein and acrylonitrile can only be analyzed together from the same bottle, if no preservative other than cooling to 4°C is used and the analysis is completed within 3 days after sampling. If acid preservation is used to extend the holding time, then these compounds must be analyzed in three separate analytical tests and three separate containers must be used.

Additional Special Requirement - Examples of the types of data that may be included as QA/QC data are results from specific samples included in the batch of samples run during one shift or on one analytical instrument. These may include calibration standards, lab blanks, matrix spikes and matrix spike duplicates and blank spikes. Each of these samples provides information that is useful in determining if the analysis met the requirements of accuracy and precision

usually published with the method. Additional information that may be required by a facility's permit include the date of analysis, the name of the analyst, chronicles showing which samples were rerun because of matrix interferences or dilutions.

Some permits require additional QA/QC data be submitted along with the analytical results and/or be available for inspection at the facility. The laboratory should know what additional QA/QC is required prior to analysis and what is to be reported to the client with the sample results. NO ANALYTICAL PROCEDURES SHOULD BE CONDUCTED IN THE ABSENCE OF QA/QC.

The laboratory should be aware of the regulatory agency report due dates. This generally is expressed in days after the sampling event or in some cases after completion of analysis. In either case, the laboratory must be held to a specific due date to insure that ample time is available to review the results prior to submission to the regulatory agency. Penalties for failing to meet the agreed upon "turnaround times" should be agreed to in advance with the laboratory.

## 4. SELECT DEDICATED MONITORING EQUIPMENT

Proper selection of monitoring equipment is an important factor in controlling sampling quality and sampling costs. Dedicated groundwater sampling systems are an example of cost effective monitoring equipment which provides high quality samples, while drastically reducing labor costs.

Groundwater monitoring focuses on very low levels of contaminant concentration and slight changes in physical and chemical properties. As contaminant measuring techniques advance and detection levels of part per billion become common, consistent sampling procedures and reliable equipment are needed to provide useful, accurate and high quality data. Sampling procedures which allow exposure to air, airborne particulate matter, temperature changes and contact with contaminated surfaces can significantly alter the physical and chemical properties of a sample.

The extended length of monitoring required at modern facilities also place a heavy burden on the monitoring program, from the standpoint of both sampling and quality. Over many years of monitoring, changes in personnel and sampling procedures may combine to introduce erroneous results to the data base, thereby jeopardizing the integrity of the facility's data base. The sampling methods and equipment should be selected with the objective of limiting the potential for variability over the monitoring period.

Based on the needs of the groundwater monitoring program, the equipment selected for use should provide for: 1. accurate sampling, 2. ease of use, 3. ease of set up and calibration, 4. rugged to withstand continued use and 5. INDEPENDENT OF OPERATOR TECHNIQUES.

Dedicated bladder pumps provide an advantage by eliminating air/water contact, no loss of volatile organics due to air stripping and no change in sample temperature. The bladder pump is permanently dedicated in the well, at a fixed position within the well screen. Water enters the bladder via the bottom check valve assembly. When the bladder is full, compressed air is delivered via an air line to the space between the body and the bladder, which squeezes the bladder. This action closes the bottom check valve and forces the water contained inside the bladder through the upper check valve and into the attached water discharge tube. After the bladder is fully evacuated, the pressure inside the pump is released back through the air line to the surface. This action causes the upper check valve to seat (close) and the bottom check valve to open, refilling the bladder. Continuous operation of this pump relies upon alternating the compression/release cycle.

## 5. ESTABLISH PROPER SAMPLING PROCEDURES

The objective of a groundwater sampling procedure is to obtain a representative sample. The techniques for collecting a representative sample should include the following:

- o Establish purge volume.
- o Consistent sampling procedures.
- o Filtration procedures.
- o Sample preservation and shipment.

Establish Purge Volume - The purpose of purging is to obtain fresh, representative, formation water. In this instance, "representative" means characteristic of geochemical conditions in undisturbed parts of the formation (1). The equivalent of three to five standing water volumes is generally agreed upon in permeable formation as the standard purging volume. This procedure should insure that samples are drawn from the aquifer, not from stagnant water left in the well between sampling events.

Consistent Sampling Procedures - A combination of proper sampling procedures and sampling equipment is necessary to maintain consistency during the sampling event. The dedicated equipment should be used for both purging and sampling and information such as purge volume, purge rate, groundwater elevation and material of the equipment must be documented each time samples are collected. The flow rate of

the pump must be adjustable in order to collect volatile organic samples and other sensitive parameters without aeration. Whenever possible, groundwater samples should be collected immediately after purging is completed ensuring a representative sample from the formation water is collected.

Specific conductance, pH and groundwater temperature measurements are taken after the well is purged. The field meters should be calibrated daily and checked every 4 hours during the sampling event. All calibration techniques should be in accordance with manufacturers specifications. All results are recorded on the Field Information Form.

Field and trip blanks are used as external QA/QC samples to detect contamination that may be introduced in the field or during transportation to and from the site. The blanks will also reflect any contamination that may occur during bottle preparation and storage within the laboratory. Upon return to the laboratory, field and trip blanks are logged-in and analyzed as if they were another sample.

Trip blanks are samples of organic free water in 40 ml VOA vials which are prepared at the same time sample bottles are prepared for shipment. They remain with the sample bottles under Chain-Of-Custody while in transit to the site, during sampling and during the return trip to the laboratory. At no time during these procedures are the vials opened.

Field blanks are samples of deonized water used by the sampling teams (at a specific sample point) to clean field equipment (meters, depth to water probe and non-dedicated filtration equipment). The deonized water is exposed to the air and transferred into empty sample bottles, and returned to the laboratory.

Filtration Procedures - Filtering is necessary in order to analyze ions and compounds that are dissolved in the groundwater. Detection monitoring wells are not constructed like drinking water wells and often contain suspended materials like silt and clay. Any suspended sediment contained in the sample can react with the sample and change the concentration of some of the dissolved constituents, yielding a sample that is not representative of true groundwater quality (2). The sample must be free of particulates and must not be exposed to air (3). Positive pressure filtering should be performed at the same time samples are collected-thereby, minimizing change in sample temperature and preventing the de-gassing of $CO_2$. An in-line 0.45 $\mu$m filter is recommended. The filter is connected to the discharge tubing of dedicated bladder pumps and filtered samples are collected directly in the sample bottle. The in-line filter is disposed of after each sample point is collected, minimizing cross-contamination between sample points.

**WMI** Environmental Monitoring Laboratories, Inc.

AquaPak™ PREP
AquaPak™ # _____
Date Sealed | | | | | | | YY / MM / DD
Seal # _____
By: _____

# FIELD CHAIN-OF-CUSTODY RECORD

SITE/FACILITY # | | | | | SITE NAME: _____

Sample Point: | | | | | | | | | Source Code

SAMPLE DATE: - | | | | | | | YY / MM / DD

SAMPLE TIME: | | : | | | (2400 HR.)  MATRIX CODE: _____

Water . . . . . (W)  Leachate . . . . . (C)
Soil . . . . . (S)  Other . . . . . (X)

Source Codes:

Well . . . . . (W)
Dewatering/Pressure Relief . . . . (D)
Surface Water Impoundment . . . (I)
Leachate System . . (C)
Gas Condensate . . . (M)
Air . . . . . (A)
Pretreatment Facility . . . (P)
Influent . . . . . (U)
Effluent . . . . . (T)
River/Stream/Brook . . (R)
Lake or Ocean . . . . . (L)
Outfall . . . . . (O)
Soil . . . . . (S)
Bottom Sediment . . . (B)
Noise . . . . . (N)
Generation Pt. . . . . (G)
Other . . . . . (X)
Specify _____

ENS #

## AquaPak™ CONTENT

| SAMPLE I.D. | # OF BOTTLES | BOTTLE TYPE | PRESERVATIVE TYPE | ANALYTES/LAB GROUPS | FILTER Y — N | FIELD COMMENTS | E.M.L. COMMENTS |
|---|---|---|---|---|---|---|---|
| | | | | | Y N | | |
| | | | | | Y N | | |
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## CHAIN OF CUSTODY CHRONICLE

1. AquaPak™ Opened By: (print) _____ Date: / / Time: : 2400 HR.
   Signature: _____ Seal #: _____ Intact: _____

I have received these materials in good condition from the above person.

2. Name: _____ Signature: _____
   Date: / / Time: : 2400 HR. Remarks: _____

I have received these materials in good condition from the above person.

3. Name: _____ Signature: _____
   Date: / / Time: : 2400 HR. Remarks: _____

4. AquaPak™ Seaded By: (print) _____ Date: / / Time: : 2400 HR.
   Signature: _____ Seal #: _____ Intact: _____

**LAB USE ONLY**
Opened By: (Signature) _____ Date: / / Time: : 2400 HR.
AquaPak™ # _____ TEMP: °C _____ SEAL # _____ INTACT. _____

EML FF-1A 4/90

documented on the C-O-C form. The C-O-C must be signed each time the samples are transferred to the responsibility of another person. The C-O-C form must be signed and enclosed with the samples when the cooler is sealed for transported back to the lab. A tamper proof seal is placed on the cooler and the seal number is recorded on the C-O-C form.

In addition to documenting custody, the C-O-C form is also used to identify field sample point, source code, date and time sampled. It also documents which sample ID's were field filtered. The C-O-C form lists all sample ID's, number of sample bottles and type, analyte groups and preservatives contained in the cooler. There's also additional room for comments specific to each sample ID. Refer to Figure 1.

Field Information Form - This form documents the sampling event. The form contains information regarding site and well conditions, sampling and purging procedures used, field measurements and field comments. The FI form must be filled out for each sample point. Refer to Figure 2.

Purging Information - This documents the date and time purging began, the elapsed time of purging (hrs), the volume of water calculated in one well casing and the volume actually purged.

Purging and Sampling Equipment - This refers to the types of dedicated equipment, materials and tubing used during the sampling event.

Field Measurements - During any sampling event the groundwater elevation (depth to water adjusted to MSL), specific conductance at 25°C, pH and temperature must be recorded. Additional parameters may also be required based on site specific conditions.

Field Comments - The section on field comments should include sample appearance (if applicable, odor, color, turbidity), weather conditions (wind speed, direction and precipitation) and other comments such as condition of the well, dedicated equipment, field meter calibration and general field observations.

Sampling Certification - The person signing the sampling certification must be present during the entire sampling event.

**WMI** Environmental Monitoring Laboratories, Inc.

Site # ____

Bottle Set: ____

# FIELD INFORMATION FORM

Sample Point: ____ (Source Code)

## PURGING INFORMATION

| PURGE DATE (YY MM DD) | START PURGE (2400 Hr Clock) | ELAPSED HRS | WATER VOL. IN CASING (Gallons) | ACTUAL VOLUME PURGED (Gallons) |
|---|---|---|---|---|
| | | | | |

## PURGING AND SAMPLING EQUIPMENT

Purging Equipment ..... Dedicated | Y | | N | (circle one)

Sampling Equipment ..... Dedicated | Y | | N | (circle one)

| | | | | | |
|---|---|---|---|---|---|
| Purging Device | ___ | A-Submersible Pump | D-Gas Lift Pump | G-Bailer | X-____ PURGING OTHER (SPECIFY) |
| Sampling Device | ___ | B-Peristaltic Pump | E-Venturi Pump | H-Scoop/Shovel | X-____ SAMPLING OTHER (SPECIFY) |
| | | C-Bladder Pump | F-Dipper/Bottle | I-Piston Pump | |
| Purging Material | ___ | A-Teflon | C-Polypropylene | E-Polyethylene | X-____ PURGING OTHER (SPECIFY) |
| Sampling Material | ___ | B-Stainless Steel | D-PVC | | X-____ SAMPLING OTHER (SPECIFY) |
| Tubing-Purging | ___ | A-Teflon | D-Polypropylene | F-Silicon | X-____ PURGING OTHER (SPECIFY) |
| Tubing-Sampling | ___ | B-Tygon | E-Polyethylene | G-Combination teflon/ Polypropylene | X-____ SAMPLING OTHER (SPECIFY) |
| | | C-Rope X-____ (SPECIFY) | | | |
| Filtering Devices 0.45 μ: | ___ | A-In-line Disposable | B-Pressure | C-Vacuum | |

## FIELD MEASUREMENTS

| | | | |
|---|---|---|---|
| Well Elevation | (ft/msl) | Land Surface Elevation | (ft/msl) |
| Depth to water From top of well casing | (ft) | Depth to water From land surface | (ft) |
| Groundwater Elevation | (ft/msl) | Groundwater Elevation | (ft/msl) |
| Well Depth | (ft) | Stickup | (ft) |

| | ph | spec. cond. | |
|---|---|---|---|
| 1st | (STD) | μm/cm at 25° C | Sample Temp. (° C) |
| 2nd | (STD) | μm/cm at 25° C | (other parameter) value units |
| 3rd | (STD) | μm/cm at 25° C | (other parameter) value units |
| 4th | (STD) | μm/cm at 25° C | (other parameter) value units |

## FIELD COMMENTS

Sample Appearance: ____ (if applicable) Odor: ____ Color: ____ Turbidity: ____

Weather Conditions: Wind Speed ____ Perspiration Y/N Outlook ____

Specific Comments: ____

I certify that sampling procedures were in accordance with applicable EPA, State and WMI protocols.

____ (Date) ____ (Signature) Employer: ____

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# 113 ADAPTATION OF A SIMPLE COLORIMETRIC METHOD FOR FORMALDEHYDE FOR USE WITH GROUNDWATER MATRICES

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ABSTRACT. The NIOSH Method 3500 for formaldehyde in air has been adapted by the authors for use with groundwater samples. This simple colorimetric method provides sensitive analysis with detection limits of < 100 ppb. It also provides good precision and accuracy, with recoveries generally between 90 and 110%. The authors present data from detection limit studies, precision and accuracy studies, and ruggedness testing. A discussion of the background of this method, and its application to real-world samples with formaldehyde contamination is provided. A modification of this method may also be useful for soil and sludge analysis. This method provides many advantages over traditional methods for soil and water analysis which have utilized HPLC analytical techniques.

114

# A dual bio-monitoring system for the genotoxicity of air and water at the site of hazardous waste mixtures

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## Abstract

Chromosomes of the meiotic pollen mother cells of Tradescantia (spiderwort) are the clastogenic targets in the Tradescantia-micronucleus (Trad-MCN) bioassay, while the genes (blue/pink alleles) of the stamen hair cells of Tradescantia are the genetic end points of the Tradescantia-Stamen-Hair mutation (Trad-SHM) bioassay. Tradescantia clone #4430 or 03 can be used concurrently for both of these two well established bioassays as a dual bio-monitoring system to detect the clastogenicity and mutagenicity of the gaseous or liquid mixtures at the hazardous waste site or conduct laboratory tests on the water or soil samples collected at the sites. Both Trad-MCN and Trad-SHM have the extensive database accumulated in the past 10 - 15 years. This paper presents a review of the on site monitoring and laboratory testing results in the earlier publications and current studies, and suggests that this dual system is suitable for monitoring waste sites for their potential hazards, and follow up monitoring of the sites after clean-up operation for quality assurance.

Plant cuttings (15 - 20 per group) of Tradescantia clone #4430 or 03 (a blue/pink heterozygote) were maintained in Hoagland solution for on site exposure or laboratory tests on water sample or the solution washed off from the soil samples collected at the waste sites. For Trad-MCN assay, the inflorescence (series of flower buds) were fixed in aceto-alcohol (1:3 ratio) after a 24 hr recovery time for preparation slides of tetrads (the 4-cell stage of meiosis) of pollen mother cells. Micronuclei in the tetrads derived from chromosome breakage were used as the indicators of clastogenicity of the pollutants. For Trad-SHM assay, an 11 - 14 day recovery time was needed to reveal the peak rate of pink mutation events in the stamen hairs. The pink cells as the results of somatic mutation in the predominantly blue cells in the stamen hair were scored immediately after the recovery time.

Positive results of on site air monitoring were obtained from parking garages, truck stops and bus depot, industrial districts of various cities in the US, People's Republic of China and Mexico, and from college dormitories and other indoor conditions. On site monitoring of radiation effects from nuclear power plants, radon-contaminated houses were obtained. External and internal radiation effects of X-rays, Gamma rays, beta and neutron particles were detected at very low levels. Positive test results were obtained from the wastewater and drinking water samples collected from Mexico, and People's Republic of China, and the US. Recently, on site monitoring results were obtained from the Lake Superior, Canada, as well as the results of laboratory tests on 7 chemicals selected from the US EPA Superfund Priority 1 list and the mixtures of some of these chemicals were also included..

## Introduction

Chromosome is the carrier of the DNA templates which determine the genetic traits, metabolic, developmental and all the vital processes of life. It is the most fragile structure in the cell during its interphase stage while replication takes place through the synthesis of the new halves from the dissociated double helix without the protection of its nucleoproteins. The physical or chemical agents in the environment may excise the diester bonds, or peptide bonds and/or interfere with the proper fusion of these bonds which maintain the continuity of the double helix, thus results in chromosome breaks in the dividing cells. The deletion, duplication and/or alteration of the DNA bases caused by the foreign agents in the cell may lead to the changes of genetic codes and result in gene mutation. Chromosomes in the young inflorescences of Tradescantia have the easy access to the gaseous or liquid agents by diffusion through the porous tissues, or by absorption through the efficient transporting vascular systems. Based upon the fragility of the chromosomes of the meiotic pollen mother cells and the easy accessibility to the foreign agents, the Tradescantia-Micronucleus (Trad-MCN) bioassay was developed [17, 22]. By taking the advantage of the high mutability of the blue/pink gene locus in the dividing cells of the stamen hair, the Tradescantia-Stamen-Hair-Mutation (Trad-SHM) bioassays was established [34, 35, 49]. A dual bio-monitoring system was developed by applying both Trad-MCN and Trad-SHM bioassays concurrently to the same group of Tradescantia plant cuttings (clone 4430, or 03) which were subjected to the same treatment or exposed at the same site. Both of these bioassays were able to detect gaseous, liquid or radioactive pollutants [21,26], and already had a broad database which includes in situ and in laboratory studies and the test results of 7 chemicals from the US EPA Superfund Priority 1 List of the hazardous waste sites [33,39]. This paper presents a review of the publications of earlier studies and some of the current investigations [9,31,33,36] and suggests that this dual bio-monitoring system may be utilized for monitoring industrial waste sites for the potenital hazards and follow up monitoring of the waste sites after clean-up operation for the quality assurance.

## Materials and Methods

For in situ monitoring of clastogenicity and mutagenicity of hazardous chemical mixtures, this dual system is one of the most efficient bioassays. There are two major approaches to conduct the test. One approach is to bring the plant cuttings of Tradescantia clone #4430, or #03 (both are small in size and having long blooming season) to the hazardous waste sites for a short exposure (24 hr or less). This is referred to as in situ monitoring. The other approach is to grow these special clones of plants on or near the site. This is referred to as the sentinel approach. When this system is used as an in situ monitor for air pollutants, 15 plant cuttings bearing young inflorescences are held in a screen cage and left at the selected sites for an appropriate duration of exposure, and brought back to allowed a 24 hr recovery time under the control conditions before the inflorescences are fixed in an aceto-alcohol (1:3 ratio) solution. For water pollutants, the sample plant cuttings are carried on a floating device called "Aquatoon" for a continuous exposure of 30 hr without recovery time, and fixed in aceto-alcohol. The detailed procedure for tetrad selection, staining, slide preparation and micronucleus scoring are described

in the earlier publications [17,22]. An image analysis system [50] specially designed for scoring Tradescantia micronuclei was developed for Trad-MCN. Thus the scoring and data analysis can be carried out automatically to increase the efficiency. If the stamen hair pink mutation is used as the end point, a 9-14 day recovery time after treatment is needed to capture the peak mutation rate. Scoring of pink mutation events from the predominantly blue cells in the staman hair should be done immediately after the recovery time. When this system is used as a sentinel, young plantlets are transplanted to the appropriate locations of the hazardous waste sites where the minimum survival requirements for these plants are met. The pink mutation scoring procedure and the data analysis were described in earlier publications [34,35,49] The micronuclei frequency in the tetrads of the meiotic pollen mother cells, or the pink mutation rates of the flower samples from the mature plants grown on the site are the indicator of the clastogenicity and mutagenicity of the total environmental condition. A comparable lot in the field which is relatively free of pollutants of all kinds should be used for growing the control group for sentinel monitoring. In both of these two approaches of in situ monitoring, climatic conditions of the site several days before, and during the days of test should be recorded for better interpretation of the data obtained.

## Database and Discussion

The current literature survey covers the studies of in situ monitoring of the gaseous mixtures at the outdoor and indoor sites, the in situ monitoring of liquid mixtures. The studies on the pure gases in the controlled chambers, and the wastewater or drinking water and the solution extracted from the soil samples collected from the polluted sites are also reviewed. Recent bioassay on seven chemicals selected from the Superfund Priotority 1 list and earlier studies on the effects of internal and external radiation, especially the in situ monitoring at the nuclear power plants are included In order to corroborate the efficiency and suitability of this dual system. The location of the sites monitored, the sources of the samples collected for laboratory testes and the references for each of these studies are listed in Table 1.

Table 1. Literatures pertaining to the studies on the in situ monitoring of pollutants and laboratory testing of samples collected at the site of pollution, as well as the chemicals commonly found at the hazardous waste site.

| Type of pollutants | Type of assays | Site location or chemical classes | Reference cited |
|---|---|---|---|
| Gas mixtures | | | |
| Outdoor | in situ | Bus depot, PRC, US | [19,21,26] |
| | monitor | parking garage, US | [19,21,26] |
| | Trad-MCN | Petro Company, US | [21,26] |
| | Trad-SHM | Truck stops | [19,21,26] |
| | | Industrial district, US | [15,26,40,41,42,43] |
| | | PRC | [6,21,26] |
| | | Mexico | [31] |
| Indoor | in situ | College Residential hall | [31] |
| | Trad-SHM | Smoking rooms | [21,26,29,31] |
| | Trad-MCN | Radon contaminated house | [9] |
| | | Trailers | [29] |
| | | Household cleaning agents | [31] |
| In Chamber | Lab test | Ethylene dibromide, EMS | [16,37, 45] |
| | Trad-MCN | Pesticides Malathion. DDV | [6,17,23,26] |
| | Trad-SHM | Formaldehyde | [36] |
| | | Air fresheners | [9,29] |
| | | Sulfur dioxide, Ozone, $NO_2$ | [21,45] |
| | | Diesel exhaust fumes | [20,21,24] |
| Liquid mixture | | | |
| wastewater | in situ | Lake superior, Canada | [8] |
| | Trad-MCN | Sea water, PRC | [3,5,7] |
| | Trad-SHM | Sludge, Chicago, US | [11] |
| Wastewater | Lab test | Arena canal, Mexico | [38] |
| | | Fujian, PRC | [51] |
| Tapwater | Lab test | Spring Lake,US; Sichuan,PRC | [14,25] |
| | | Shallow well, Lewistown, US | [30] |
| Priority list chemicals | Lab test | Lead tetra acetate | [33,39] |
| | Trad-MCN | Tetrachlorethylene,Aldrin | [33,39] |
| | | Dieldrin, Arsenic trioxide | [33,39] |
| | | Heptachlor,Benz(a)anthracene | [33,39] |
| | Trad-SHM | other mutagens, Japan | [48] |
| Radiation | | | |
| | In situ | | |
| | Trad-SHM | Nuclear power plant, Japan | [12] |
| Internal | Trad-MCN | P-32, H-3, I-131 | [1,26,46,47] |
| External | Trad-SHM | X-rays, | [17,18,19,37,44] |
| | Trad-MCN | Gamma rays, Neutrons | [2,37,44] |
| | Trad-SHM | Soil, Bikini, Island | [13] |

Based upon the test results of the common environmental pollutants, both Trad-MCN and Trad-SHM bioassays can detect very low concentration of chemicals at uM level, and low dose of radiation at the pCi and mR levels. This dual bio-monitoring system could be claimed to be the most sensitive and easy to operate as well as cost effective (28) one among the well known in situ bio-monitors [27, 32]. This system can be operated under the common climatic conditions and there are more than 20 species distributed through the U. S. which could be used as sentinels around the hazardous waste sites if the clones #4430 and #03 are not suitable in certain geographic areas. There are more than 10 clones of Tradescantia plants with heterozygous blue-pink locus which are suitable for Trad-SHM tests. The plant cuttings can survive in the in vitro conditions for indefinite length of time and function as the intact live plants. Thus the plant cuttings used for testing are the portable in vitro test materials but at the same time they can provide effectively the results comparable to the data obtained from the in vivo tests.

The results of this dual system can elucidate the relationship between the chromosome damage and gene mutation. The damage on the meiotic chromosomes in the gametes of the Trad-MCN system can also serve as the indicator of the genetic effects which may be passed on to the future generations. This dual bio-monitoring system is specially suitable for monitoring hazardous industrial waste sites where fumes, contaminated water and soil can be monitored in the form of mixtures. This bio-monitoring process accompanied with chemical analysis would also be able to isolate the prime hazardous agents from the mixtures. Application of this kind of bio-monitors to the industrial waste site prior to the costly chemical analysis would be able to rank the relative degree of hazardous conditions of many waste sites, and set the priority for the abatement operations. This would make the waste site removal operation more effective and economical.

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# ENFORCEMENT

115

# USE OF WASTE STREAM AUDITS TO DETERMINE THE REGULATORY STATUS OF SURFACE IMPOUNDMENTS

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## ABSTRACT

The Resource Conservation and Recovery Act (RCRA) regulations list many hazardous wastes by describing a waste stream generated by a particular industrial process. Frequently, enforcement personnel discover a waste management unit or spill area which has high levels of hazardous constituents. In the absence of a thorough understanding of the industrial process, it is difficult for the inspector to legally identify the unit as a "regulated hazardous waste management unit" and thus to require corrective action using regulations applicable to regulated units.

This paper will discuss the corrective action required for RCRA regulated units as well as non-regulated units and will provide procedures for performing a waste stream audit to aid enforcement personnel in determining which units should be regulated. Waste stream audits involve a detailed evaluation of the chemical and/or manufacturing processes which are involved in the synthesis of chemical compounds and/or products. The audit includes raw materials information, chemical reaction and process details, and waste stream generation and disposal procedures. The key to the successful waste stream audit is the combination of RCRA personnel who are familiar with hazardous waste listings and regulations and field investigative personnel who are experienced in the chemical process industry and subsequent wastewater treatment and solid waste management.

A case study is presented in which both a field sampling investigation and a waste stream audit were performed at a chemical manufacturing facility. The sampling investigation identified hazardous constituents in surface impoundments which were used as a basis for investigating processes during the waste stream audit. The audit concentrated on identifying "F" and "U" coded wastes which could have been discharged into the impoundment with process wastewater. The procedures used in performing the audit are presented. The results of the audit are summarized and a corrective action outline is developed based on the results of the entire study.

## INTRODUCTION

In 1976, Congress passed the Resource Conservation and Recovery Act (RCRA) which required EPA to develop "cradle to grave" tracking and regulation of

hazardous wastes. The RCRA regulations were written so that generators could easily identify which of their wastes were hazardous without extensive laboratory analyses. The generator could then follow the requirements for storage, treatment, or disposal of the waste.

To facilitate easy identification of hazardous wastes, RCRA lists waste streams by industrial process. Waste chemicals are identified by how they are used in a manufacturing process. RCRA also identifies four characteristics that would make a waste legally defined as a hazardous waste. These are Ignitability, Corrosivity, Reactivity, and Extraction Procedure (EP) Toxicity. Each of these characteristics has a definitive laboratory test procedure which will provide conclusive evidence of whether a waste falls within the criteria of a characteristic hazardous waste. The EP toxicity test is in the process of being replaced by the Toxicity Characteristic Leachate Procedure (TCLP) test. EPA estimates that the new rule will nearly triple the amount of waste that is considered hazardous under RCRA.

The intent of the regulations to facilitate easy identification of listed wastes by identifying the industrial process has made it difficult for RCRA permitting and enforcement personnel to identify hazardous waste management units. When an inspector discovers an unknown unit or spill area, the inspector must rely on facility personnel to identify the process which generated the waste. When the inspector is not familiar with a wide variety of chemical manufacturing processes, the facility's identification goes unchecked.

By conducting an audit of the wastes generated at a facility, the inspector can become familiar with the processes at a particular plant and will gain knowledge which will enable him to determine the regulatory status of a waste management unit in question.

## WHY IDENTIFICATION OF REGULATED UNITS IS IMPORTANT

Any land based unit which received hazardous waste after July 26, 1982, is termed a "regulated unit" under RCRA. The corrective action requirements for regulated units are given in Title 40 of the Code of Federal Regulations (40 CFR), Sections 264.90 through 264.100. These 11 sections of the regulations specify such requirements as a ground-water protection standard, monitoring programs, concentration limits, a point of compliance, and a compliance period. These programs are implemented by issuing either an operating permit or a post-closure permit to the facility.

Hazardous waste management units which have not received hazardous waste and thus cannot be classified as a "regulated unit" are termed solid waste management units (SWMUs). Corrective action for SWMUs is addressed in 40 CFR Section 264.101. This single section in the regulations does not explicitly state the clean-up requirements for SWMUs. Corrective action for SWMUs is implemented by issuing a permit to the facility known as the "HSWA permit" (Hazardous and Solid Waste Amendments Permit), or by issuing a corrective

action enforcement order known as a Section 3008(h) Order. The HSWA permit or the 3008(h) order directs the facility to perform an investigation to determine the extent of contamination as well as to propose a method to rectify and clean-up the contamination.

Although the corrective action process under a HSWA permit should parallel the corrective action process for a regulated unit, there are several significant differences. Corrective action under a RCRA operating or post-closure permit theoretically happens more expeditiously. This is because the investigation under HSWA can be delayed and stretched out over several years before any corrective action begins. Once a SWMU is cleaned-up, the facility is under no obligation to continuously monitor groundwater unless the permit writer or the 3008(h) order can adequately justify the necessity to do so. For regulated units, the post-closure period is required to be 30 years. This ensures long term monitoring of groundwater and early detection of continuing releases.

More significantly, Section 264.94 requires contaminated groundwater under a regulated unit to be remedied to background levels present in upgradient wells. The HSWA process allows the facility to propose clean-up levels based on the facility's investigation and current health based levels. A complete understanding of the migration of contamination is difficult to obtain. If the investigation is not extremely thorough, then non-conservative clean-up levels could be established based on erroneous conclusions of the investigation.

Finally, under current EPA policy, once contaminated groundwater is detected under a newly discovered regulated unit (one that does not have interim status or an operation permit), the unit must be closed as a landfill. Closure as a landfill requires a cap which precludes the facility from continuing to use the unit to dispose of waste, either hazardous or non-hazardous. This enforcement hammer is especially useful to the regulatory agency when a facility has a waste water treatment system in surface impoundments and the system is suspected of receiving routine spills of hazardous waste.

## WASTE STREAM AUDIT PROCEDURES AND OBJECTIVES

The specific objectives of the waste stream audit are to (1) secure accurate production information, i.e. identify chemicals and products made at the facility, (2) acquire a workable understanding of the basic chemical, thermodynamic, and kinetic principles of the individual unit processes at the plant, (3) develop an inventory of raw chemicals, intermediate products, and catalysts used in the reactions and/or manufacturing, (4) identify waste streams and characterize their chemical contents through materials balance, and (5) determine the fate of the chemicals identified in the waste streams.

The procedures used by EPA in conducting a waste stream audit are outlined as follows: (1) the appropriate company officials are notified and informed of the intent to perform an audit. This allows the company to assign the

proper personnel to assist with the audit, to prepare the needed information, and to schedule those who may be required to provide technical assistance, (2) an initial conference is conducted which includes the opening remarks and clarifications of the audit objectives, (3) the audit is performed by guiding the company officials through the objectives. This phase is technically specific to the unit processes and includes a detailed discussion of each process and each and every waste stream associated with the reactions, (4) when the waste streams have been identified, and the investigators are comfortable with the facility nomenclature and process units, a visual inspection of those units is made, and (5) a final exit interview is made to finalize the audit and to give the company an opportunity to make any final comments.

CASE STUDY

A Region IV chemical manufacturing facility was known to treat large volumes of wastewater in unlined surface impoundments. The facility was suspected of having routine spills of listed hazardous wastes in process areas which would drain into the chemical sewer and into the surface impoundments. EPA was not familiar with all of the processes at the plant, but it seemed likely that listed waste would be associated with some of the many processes that occurred at the facility. An investigation was initiated to determine the regulatory status of the surface impoundments.

Much of the success of a waste stream audit depends upon the information generated prior to the actual conduct of the audit. EPA investigators first conducted a RCRA case development inspection/evaluation (CDIE) which provided the auditors with an opportunity to familiarize themselves with the plant layout. During the CDIE, a thorough investigation was conducted of identified SWMUs. The wastewater treatment lagoon system, storm water runoff migration routes, and an old landfill with ancillary waste piles were the primary areas of concern. Also a series of ground water monitoring wells was sampled to determine if contaminants were reaching the shallow aquifer. All of the analytical data were used to develop a chemical profile of the wastes distributed throughout the wastewater treatment system water and sludge, landfill soil, waste pile soil, runoff ditch sediments and ground water. Both water and sludge samples were obtained from several of the impoundments which were expected to have the highest concentration of hazardous constituents. Figure 1 shows the approximate location of each sample. Table 1 shows the highest concentrations of contaminants found in selected samples. All samples were collected using EPA Region IV Standard Operating Procedures and analyses were conducted according to SW-846 methods.

The high concentrations of Benzene (5300 ug/l), Xylene (110,000 ug/l), Toluene (5000 ug/l) and Phenol (24,000 ug/l), gave evidence that spills of these chemicals could be entering the wastewater treatment system. The waste stream audit was scheduled to tie the detected chemicals to hazardous waste listings.

## PERFORMING THE AUDIT

The waste stream audit was begun by discussing the findings of the CDIE with the company officials who were given an opportunity to explain the presence of specific RCRA listed compounds in their waste treatment system. Armed with chemical evidence of specific chemicals that routinely appeared in the samples collected during the CDIE, the auditor's goal was to determine their source.

This particular audit was technically compounded because the plant produces more than 200 chemical products, most by batch reactions. Before the audit was initiated, company literature, advertisements and the 1988 Directory of United States Chemical Producers was used to develop a potential list of the major chemical products manufactured in volume. The company was asked to verify the list generated by the auditors and to add any other products not on the list. Since the products made at the plant are closely related, and since it would have been impossible to analyze every process, 14 representative processes from the various production areas were selected for a detailed process review.

Company and corporate engineers were asked to explain the selected unit processes. Detailed process flow sheets outlined the chemical reactions by showing the sequence of raw materials added, the catalysts used, and the reactions, refluxes, decanting, centrifugation, filtration, and distillation operations. Solvent additions and recovery steps, washing operations and any source of a waste stream, either liquid or solid was verified. Materials balances of raw materials, intermediate products, and finished products were roughly calculated for each process audited. The amount of waste being generated for disposal must be inventoried under RCRA regulations. The information prepared for manifests and regulatory annual reports should agree with the waste streams detailed in the process flow sheets, and can be helpful in substantiating the previously cataloged chemicals found during the field investigation.

After a meticulous indoctrination in the various unit processes under review, the auditors then walked through the various units to verify critical information covered in the flow sheets. Sources of waste streams were identified, and the containment or treatment of these materials was noted. Also the route for any spills or intentional dumps within the unit area was identified. At this facility, most of the units were surrounded by chemical sewers which eventually drained into the waste water treatment system. Some process buildings had stained floors which gave evidence that spills were migrating to the chemical sewer system.

After the visual inspection, the auditors and company officials conducted a closing interview. Any final questions were settled and a brief explanation of the outcome of the audit was made to the company officials. Confidentiality was maintained on all process information not commonly listed in chemical engineering textbooks and chemical literature.

The final responsibility for the investigative scientist or engineer was to consolidate the audit findings into a final report which supplemented and expanded the initial CDIE report.

## CONCLUSIONS OF THE AUDIT

The nature of the operations at the facility made it difficult to associate listed waste codes with the process waste streams. Many "U" constituents were found in the impoundments, but these chemicals were used as raw materials in the process and thus did not meet the listing requirements of being a waste when they were introduced into the process. The F listings were not met either because in the 14 processes reviewed, benzene, xylene, and toluene entered into the chemical reaction and were not used solely as solvents as is required by the listings. The evidence of spills migrating to the chemical sewer, coupled with the knowledge of the use of xylene, toluene, and benzene in the process gave the most likely source of these chemicals in the impoundments. But because these chemicals did enter into every reaction investigated during the audit, the hazardous waste listings were not met and the surface impoundments could not be identified as regulated hazardous waste management units.

There were two processes where xylene was used as a wash solvent for the reaction vessels after the reaction had occurred. This xylene would meet the F003 listing, but the spent xylene was sent to an on-site distillation column for reclamation. There is no waste associated with the distillation column that is discharged to the impoundments.

In this case study, EPA was not able to identify listed wastes that were discharged into the impoundments. Therefore, EPA did not issue a post closure permit to require corrective action. Although the study did not show that the impoundments were regulated, the information obtained was indeed very valuable in developing the HSWA permit. By knowing the concentration of hazardous constituents in the impoundment and the construction and operational details of the impoundments, EPA was able to write specific and detailed investigative requirements in the HSWA permit. The facility is now able to delineate the plume of groundwater contamination by using the constituents found during the audit as a basis for the investigation.

This investigation was performed before the RCRA regulations were amended to include the TCLP test. EPA has added 25 organic constituents to the 14 EP toxicity characteristic constituents resulting in a new characteristic test which covers 39 constituents. The level for Benzene proposed in the March 29, 1990, Federal Register is 0.5 mg/l. Since the available data shows that the level of Benzene in the impoundment is in the range of 5 mg/l, then the impoundment would be considered a regulated unit having the new characteristic of TC toxicity. If the investigation shows that groundwater is contaminated, the facility will need to close and cap the unit, or retrofit the impoundment to meet minimum technological requirements and remediate contaminated groundwater.

SUMMARY

The regulatory procedures for implementing corrective action are more specific for RCRA regulated units than for SWMUs. Waste stream audits are an invaluable tool to use in determining the status of questionable or newly discovered land based waste management units. Although a waste stream audit is time consuming, the information obtained undoubtedly proves to be valuable in developing corrective action scenarios. Whether or not the audit shows that the unit is regulated, a superior HSWA permit can be written based upon information obtained from the study.

Table 1

| Sample Number | Constituent | Concentration | Waste Code |
|---|---|---|---|
| W-1 | Phenol | 24,000 ug/l | U002 |
| | Xylene (m&p) | 110,000 ug/l | F003 |
| | Benzene | 5,300 ug/l | F005 |
| | Toluene | 5,000 ug/l | F005 |
| W-2 | Acetone | 7,100 ug/l | U188 |
| | Tetrahydrofuran | 80 ug/l | U213 |
| S-1 | Xylene (m&p) | 25,000 mg/kg | F003 |
| | Trichloroethene | 10,000 mg/kg | U228 |
| | Toluene | 1,600 mg/kg | F003 |
| | Benzene | 410 mg/kg | F005 |
| | Chlorobenzene | 650 mg/kg | F003 |

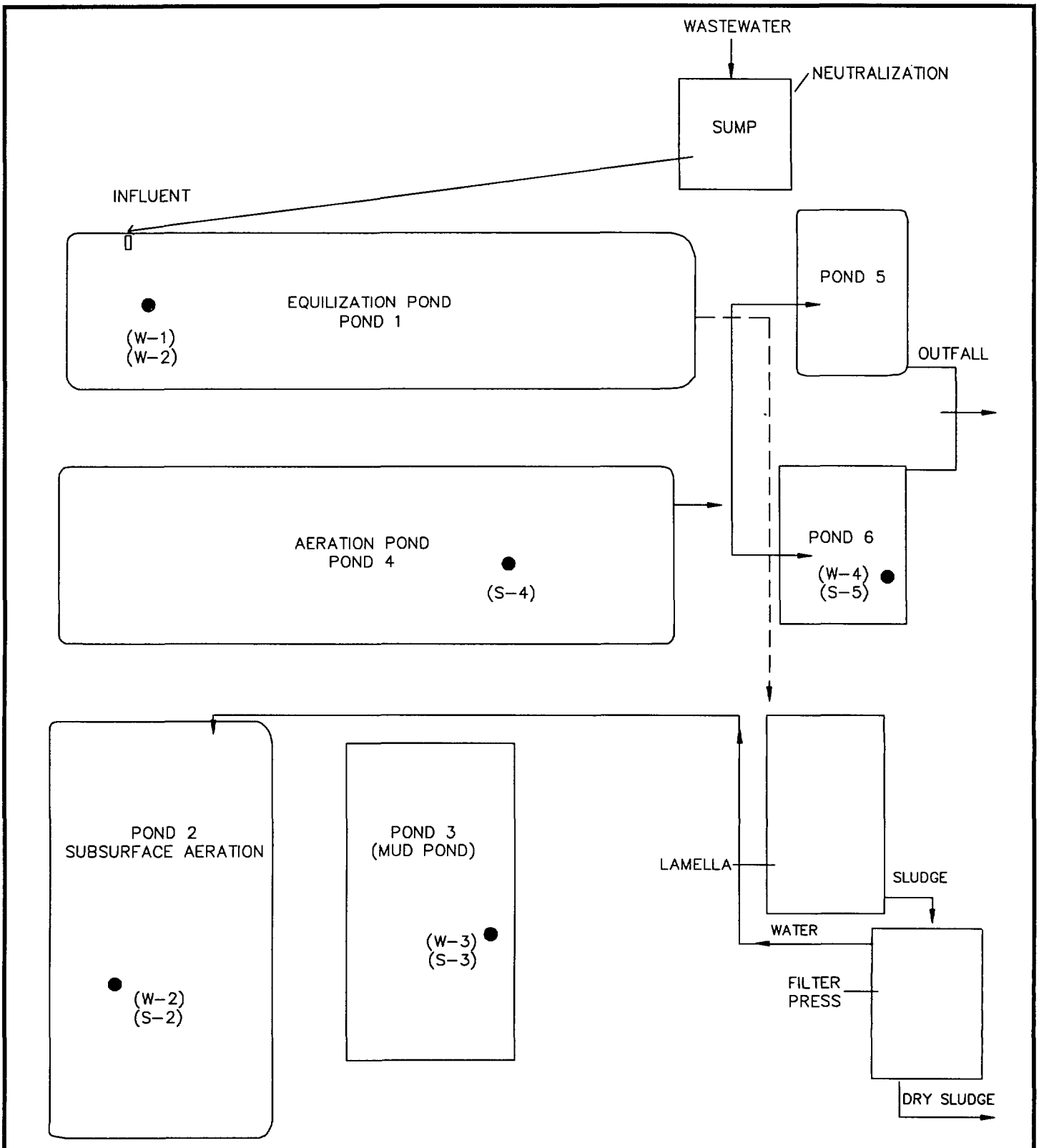


FIGURE 1
WASTEWATER TREATMENT PLANT

KEY:
W = WATER SAMPLE
S = SLUDGE SAMPLE

RD9014F3

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116

# DESIGNING A LIMS TO MEET ENFORCEMENT REQUIREMENTS

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## ABSTRACT

Many laboratory information management systems (LIMS) do not include considerations for the following activities related to enforcement requirements:

- o Verification of the condition of the sample at receipt
- o Documentation of computer-resident data
- o Accountability of computer-generated bench sheets and analysis records
- o Quality assurance of software
- o Security of LIMS
- o Custody and tracking of physical samples
- o Verification of correct data entry
- o Documentation of direct electronic data transfer
- o Standard Operating Procedures for LIMS

The author will review the highlights of two of the current commercial LIMS that are in use in many laboratories. The author will also provide detailed requirements that each laboratory should consider in designing a LIMS or purchasing a commercial LIMS. This paper will provide suggestions for systematic approaches to sample and document management with a LIMS and will include examples of user-friendly entry screens. Examples of computer-generated bench sheets that are subject to easy modification to meet the needs of an individual laboratory will also be provided.

A LIMS needs to be flexible to enable the laboratory to modify the software to meet unforeseen future sample tracking and technical considerations. A well designed LIMS is a powerful management and quality assurance tool. Adding functions to meet enforcement requirements will benefit laboratories and their clients.

# 117 The Use of Confirmed, "Tentatively Identified Compounds" to Build a Case Against the Primary Responsible Party at a Superfund Site

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During most GC/MS semi-volatile analyses, an attempt is made to identify the unknown compounds detected by using searches against the standard mass spectral analyses. Unfortunately, because of the large number of samples that must be processed by the typical CLP laboratory, the identification efforts rarely proceed further than this "tentative" identification step. This past summer, the Region II Removal program requested the ERT's assistance in identifying the unknown compounds that were found throughout one of their site at levels approaching per cent concentrations. Because these compounds were listed as only "tentatively identified", there presence could not be used by the Agency for Toxic Substances and Disease Registry (ATSDR) in their health assessment nor by the Region in their enforcement case. By acquiring standards for several of the tentatively identified compounds and other suspected compounds prior to starting the analyses, our laboratory was able to confirm the presence of several of these compounds using both GC retention times and spectral matches on the same instrument. Based upon the recommendations of the GC/MS operator, additional standards were obtained and more unknowns were confirmed.

When the newly identified compounds were compared against compound classes listed in responses to the EPA requests for information under 42 U.S.C. Section 9604 and 42 U.S.C Section 6927, one company became a readily apparent suspect. At the ERT's request the Regional Enforcement staff proceeded to request additional information on the commercial products listed in the response. Based upon a comparison of the supplied information with the compounds and spectra found in the site samples, samples were then requested of four of the commercial products. These products, two of which were mixtures of five or more distinct but related compounds, were then analyzed on the GC/MS. When the acquired spectra and relative GC retention times were compared against the data from the site samples, three of the products, one of which was a five component mixture, were confirmed to be present and in several cases were the primary wastes found. Based upon searches performed by the Analytical Operations Branch against the CARDs database, the compounds from two of the products were not commonly found at other sites by themselves and had been found together at only one other site in Superfund. Since these were all specialty chemicals, their presence at the site strongly implicated the PRP.

# EVIDENCE AUDITS: A CASE STUDY AND OVERVIEW OF AUDIT FINDINGS

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## ABSTRACT

Evidence auditors inspect the following activities to determine if complete documentation is provided by field and laboratory personnel to ensure that the chain of custody of the sample is maintained:

- Sample collection
- Sample preparation in field staging areas
- On-site field measurements
- Sample transfers
- Sample receipt at laboratory (or other location)
- Sample tracking
- Sample preparation and analysis
- Sample storage, archive, and disposal
- Site file development

The authors will present a case study of a series of field and laboratory audits related to a specific site. This case study will include a description of the audit planning process and a review of the findings of this specific series of audits.

The authors will also present a summary of the problems that are typically found during both field and laboratory evidence audits. Suggestions and a plan for the successful implementation of corrective action for evidence-related findings will be provided. Thoughtful planning and follow-up review of these issues will enable the quality assurance officer for each site to ensure that enforcement-related activities are dealt with in a efficient manner.

# 119 EPA Oversight of Federal Facility Cleanup of Radiologically Contaminated Mixed Waste Sites under the Superfund and RCRA Programs

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The Department of Energy (DOE) consists of 17 Defense Production Facilities. Many of these facilities have sites that are contaminated with both radioactive and hazardous contaminants. EPA is using its Superfund and Resource Conservation and Recovery Act (RCRA) enforcement authorities to oversee cleanup at many of these facilities. DOE implements the Atomic Energy Act (AEA) through DOE orders for the radionuclides. This paper will summarize the integration and use of all the RCRA and Superfund authorities for cleanup of the sites. State involvement in the agreement and oversight process will be discussed. A brief discussion of the EPA enforcement status of the cleanup progress at DOE's weapons complex facilities will be given.

120 **HAZARDOUS WASTE INCINERATION ENFORCEMENT PROGRAM**

ABSTRACT

The Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) required the EPA to either issue or deny permits for hazardous waste incinerator (HWI) facilities before November 8, 1989. Since most of the operating incinerators are permitted recently, the EPA is strengthening its enforcement program in inspecting these facilities.

This paper describes the current HWI universe, the status of applicable regulations, the efforts put forth by the Office of Waste Program Enforcement to support the EPA regional and state HWI enforcement programs, and the past and current enforcement actions.

121

# Evaluation of the Draft High Concentration, Multi-media Protocol Versus An Historical Database

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The U.S. Environmental Protection Agency (U.S. EPA) has developed a draft protocol for the evaluation of high concentration wastes. These wastes are generated from hazardous waste disposal sites with the analyses conducted at Contract Laboratory Program (CLP) facilities in the majority of cases. Analytical services under this protocol include pneumatic nebulization and hydride generation inductively coupled plasma emission (ICP) spectrometric analyses. The pneumatic nebulization technique for ICP involves preparation of the samples using a potassium hydroxide (KOH) fusion process. An historical database for 738 high concentration samples and the quality control associated with measurement of those samples was developed at the U.S. EPA National Enforcement Investigations Center (NEIC) during the development of the KOH fusion preparation technique. It will be demonstrated that two elements, titanium and molybdenum, should be included in the list of target analytes as both elements are found in a significantly large number of high concentration samples at levels above 1000 mg/kg. Data will be presented to show that barium and calcium may not meet the Contract Required Quantitation Limits specified by the protocol. The possible need to adjust the accuracy control limits to allow KOH fusions to be employed on soil and oil matrices will be discussed. Silver may not meet acceptable matrix spike recoveries with the spike levels suggested by the protocol. The interference check sample called for in the high concentration protocol will be evaluated.

**Notice:** Although the research described in this article has been supported by the Environmental Protection Agency under contract 68-03-3249 with Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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# Index