INORGANIC (continued)

EPA'S ENVIRONMENTAL MONITORING RESEARCH PROGRAM SESSION

References
1. BioNebraska - BiMelyze® Soil Extraction and Mercury Assay Product Literature
2. US EPA SW-846 Method 4500 (proposed Update IVA)
3. DOE Method MB 100 Rev 1 (draft)
4. California EPA Evaluation Report Certificate No. 95-01-014

UTILIZATION OF A FIELD METHOD FOR THE SEMIQUANTITATIVE DETECTION OF SILVER IN ENVIRONMENTAL SAMPLES IN THE 0 - 50 ppb RANGE

Dan Kroll
Hach, 100 Dayton Road, Ames, Iowa 50010

Abstract
Silver is commonly used in industry, and its bactericidal properties have also lead to its use for water disinfection purposes. Excess concentrations of silver may damage human health and be toxic to aquatic life. Current methods of silver analysis, in the ppb range, require expensive equipment and careful technique. There is a need for a quick, easy screening method for silver at these levels. The procedure described employs the bromopyrogallol red/1,10-phenanthroline method, described by Dagnall and West (1964), combined with a novel concentration/detection method. At a pH of 7, a ternary complex is formed with two 1,10-phenanthroline molecules binding to each silver ion, and then two of these complexes bind to a bromopyrogallol red molecule. This results in a blue precipitate. The colored precipitate is caught on a 13 µm pore size filter, and the filter is compared to a precalibrated (0, 5, 10, 25, and 50 ppb) printed color chart for quantification. All the reagents are combined in a single powder that contains both dyes, a buffer, and a masking reagent. The system is easy to use, fast, portable, and all reagents are stable for at least one year making the system ideal for field testing. This method has been evaluated on a variety of tap water, pool & spa water, river water, and sewage effluent samples that have been spiked with known amounts of silver. Some of the river water samples and the sewage effluent required a sulfuric acid digestion, but all samples resulted in good recovery of the spikes and correlated well with numbers generated using AA techniques. Various soil samples that were spiked with 25 ppb Ag resulted in good recoveries that corresponded to the appropriate color spot on the chart. Use of this method as a screening process may help to save time and money by cutting down on the need to do more accurate analysis of all samples.

Introduction
Silver is a common contaminant of industrial process and wastewater. In private industry, silver is used in applications such as jewelry, coins, dentalware, silverware, solder, electroplating, photography, and battery production. In low concentrations, silver's antibiotic properties make it desirable for use as a fungicide and for drinking water disinfection purposes, and it has been gaining in popularity as a pool and spa biocide. However, according to the World Health Organization (WHO), continuous exposure to silver in drinking water (0.4 mg or more) in humans causes arygaria, an irreversible condition which produces a bluish-gray discoloration of the skin, hair, nails and eyes.[4] Long term continuous exposure to silver has also been implicated in liver damage and enzyme inactivation in humans.[4]

Unpolluted surface water levels of silver usually range between 0.1 - 4 µg/L. Drinking water levels range between 0 - 2 µg/L; average = 0.13 µg/L.[3] The WHO has not as yet set limits for safe silver concentrations in drinking water.[5] The USEPA has adopted the Public Health Service (PHS) standard that silver in domestic water not exceed 50 µg/L.[3] The USEPA-adopted PHS standard was set to protect aquatic life and human health. Canada has adopted a similar 50 µg/L standard while the EEC standard is 10 µg/L.[5] Silver is also on the list of seven priority pollutant metals that must be monitored in landfill leachate.[7]

There are many current methods to measure silver in the ppb ranges. These include atomic adsorption by flame or electrothermal techniques, inductively coupled plasma, or colorimetry. Each of these methods requires complicated and expensive apparatus, hazardous chemicals and/or a large investment in time and equipment. Each also has its drawbacks. AA is accurate at moderate concentrations, but displays sensitivity to ion interference. ICP techniques have higher minimum detection limits and are sensitive to refractory elements. Colorimetry loses sensitivity at these

ranges and uses hazardous chemicals.[6]

There is a need for a portable, rapid, easy, and safe screening method for low levels of silver. The method described in this article meets all of these requirements and requires less time than conventional methods. The user obtains an on-site reading that only takes minutes to obtain. The procedure features a simple visual comparison for obtaining semiquanitative measurements for silver between 0-50 µg/L. Single-reagent addition and quick results make this method ideal for field testing.

Method and Chemistry

This test makes use of the fact that under certain specified conditions, metals form brightly colored precipitates with certain dyes or mixtures of dyes. In the case of saver, the complex formation is with 1-10 Phenanthroline and Bromopyrogallol Red. This chemistry is an adaptation of a reaction described by Dagnall and West.[1] In this reaction each Ag ion first reacts with two 1-10 Phenanthroline molecules to form a colorless complex. Two molecules of this complex then react with a molecule of the Bromopyrogallol Red to form a blue precipitate. Dagnall and West made use of this system for the spectrophotometric detection of silver with a lower detection limit of 20 ppb. The system that I am currently using follows this chemistry until the method of detection. I make use of the fact that the blue complex is an insoluble precipitate in an aqueous sample.

A reagent powder is prepared that contains a Sodium Citrate - Citric Acid buffer system with a pH of 7. The powder also contains Tetrasodium EDTA as a masking reagent to remove interference from other metals. An excess of 1-10 Phenanthroline is added to make sure that there is more than enough present to complex the silver along with any iron that may be present. If excess 1-10 Phenanthroline is not added, it may all bind to contaminant iron leaving none available for the silver. Finally, the reagent powder contains the Bromopyrogallol Red. The final reagent powder is then packaged at a weight fill of 2.0 g in unit dose form. This is the amount needed to react with a 100 mL sample.

After the initial chemical reaction is carried out, 100 mL of the reacted sample is filtered by being forced with a syringe through a nitrocellulose microporous filter. (Schleicher & Schuell) The blue precipitate is trapped on the filter. The intensity and hue of the filter is dependent in a quantitative manner upon the original concentration of silver present in the sample. The colored filter is then compared to a color matching chart with different shades of blue corresponding to different concentrations of silver. By manipulation of the dye concentrations, filter size, pore size, and sample volume, the levels to which the test can be made effective can be altered. Using a 100 mL sample, 5 mm dia. filter size (a Gelman #4317 13mm plastic filter holder is modified with washers to expose a 5 nun surface area on the filter), and 12 µm pore size, visual levels of detection down to 5 ppb Ag can be achieved. The final color coding chart for silver has gradations of 0, 5, 10, 25, and 50 ppb Ag (See Fig. 1). This method has been validated on a number of different water matrices using NIST standard spikes (SRM3151) and compared to AA (Varian SPECTRAA 20-plus) for verification. This method allows visual detection of silver in ranges that are comparable to, and in some cases lower than, the levels of detection that are possible with more costly and time consuming methods, such as AA.

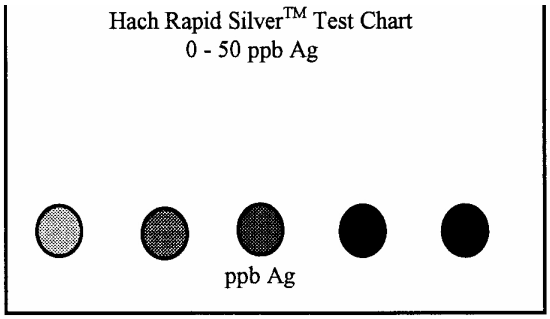


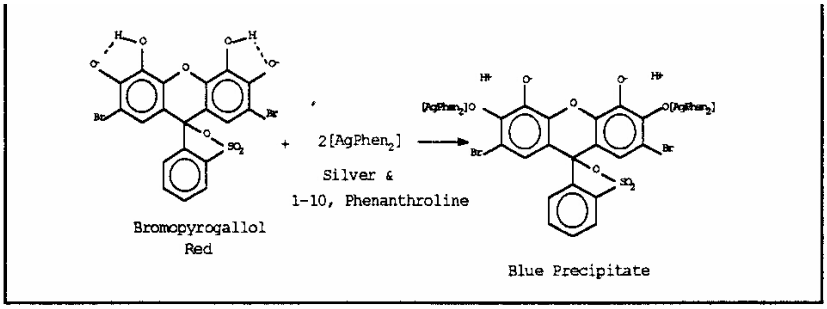
Figure 1. Color Comparator Chart

Summary of Method

Silver ions at a pH of ~7 combine with two molecules of 1,10-Phenanthroline to form a colorless water soluble complex. Two molecules of this complex then combine with a molecule of Bromopyrogallol Red to form a water insoluble blue precipitate. (See Fig. 2) This blue precipitate is then captured on a nitrocellulose filter. The filter is then compared to a color chart and matched to the appropriate spot for a semi-quantitative reading. The reagent pillow contains appropriate buffer, indicator, and EDTA as a masking reagent. A pretreatment of ascorbic acid is necessary to remove Cl_2 in excess of 2 mg/L. Digestion is needed for some samples. Other samples such as very concentrated soil digests that contain large quantities of interfering metals may require the addition of extra EDTA and or sodium citrate as chelating reagents.

Sampling and Storage

Collect samples in an acid-cleaned glass or plastic container. Adjust the pH to 2 or less with Nitric Acid (about 2 mL



per liter). Store preserved samples at room temperature for up to six months. Adjust the pH to ~7 with Ammonium Hydroxide before analysis. Do not use a pH meter as silver contamination from the electrode may occur. Phenol Red may be used as an indicator. Correct the test results for volume additions.

Figure 2. Reaction Mechanism

Interferences

Interference studies were conducted by preparing a known silver solution (approximately 0.010 mg/L) and the potential interfering ion. Positive interference was tested by running blanks of deionized water that contained the potential interfering ion. The ion was said to interfere when the resulting change threw off the color match by more than 1/2 step on the chart. The following substances, at the stated levels, show no interference on a 10 ppb Ag standard test. There should be no problem with color matching or bad blanks at these levels. These tests were run at the levels indicated, although greater concentrations may be tolerated.

Table of Interference Study Results

Cation or Anion	Level	Type of Interference	Cation or Anion	Level	Type of Interference
Aluminum Al	10 ppm	none	Manganese Mn	10 ppm	none
Antimony Sb	10 ppm	none	Mercury Hg	10 ppm	none
Bismuth Bi	10 ppm	none	Molybdenum Mo	10 ppm	none
Borate $Na_2B_4O_7$	1 g/L or 215 ppm as B	none (fades with time)	Nickel Ni	10 ppm	none
Barium Ba	10 ppm	none	Nitrate NO_3 as N	250 ppm	none > amounts appear to fade color
Chlorine Cl_2	5 ppm	Dingy but readable > OK with ascorbic acid	Nitrite NO_2 as N	100 ppm	none > amounts appear to fade color
Chloride Cl^-	400 ppm	none > amounts interfere	Ammonia NH_3^+ as N	1000 ppm	none
Chlorite HOCl	1 Ppm	none	Palladium Pd	10 ppm	none
Calcium Ca^{+2}	1000 ppm	none	Phosphate PO_4 as P	1000 ppm	none
Chromium Cr^{+3}	10 ppm	none	Potassium K	1000 ppm	none
Chromium Cr^{+6}	10 ppm	none	Platinum Pt	50 ppb	none > negative interference
Cadmium Cd^{+2}	10 ppm	none	Sulfate SO_4	1000 ppm	none
Cobalt Co	10 ppm	none	Selenium Se	10 ppm	none
Copper Cu^{+2}	10 ppm	none	Silica SiO_2	1000 ppm	none
Flouride F^-	10 ppm	none	Thallium Tl	1 ppm	none
Gold Au	10 ppb	none > negative interference	Tin Sn	10 ppm.	none
Iron Fe^{+2}	10 ppm	none	Titanium Ti	10 ppm	none
Iron Fe^{+3}	10 ppm	none (lite pink tint) >with addition extra	Phenanthroline	1 ppm	none
Lead Pb	10 ppm	none	Zinc Zn	10 ppm	none
Magnesium	1000 ppm	none			

Turbid samples should be pre-filtered through a glass fiber filter. Oils and surfactants may interfere by preventing

formation of the insoluble complex; however, appropriate digestion may eradicate some of these interferences.

Materials that were not tested, that according to the literature do interfere, are Uranium (VI), Thorium (IV), and Niobium (V). They all form blue colored complexes with Bromopyrogallol Red. They can be masked at a 10-fold excess over silver by the addition of excess fluoride for Uranium and Thorium, and of hydrogen peroxide for Niobium.[1]

Precision

In a single laboratory, using a standard solution of 0.010 mg/L silver and three representative lots of reagents, a single operator performing 50 tests per lot obtained no results that were not properly matched to the 10 ppb color dot within 1/2 step. In other words all results were within a range of 7.5 to 17.5 ppb. These results were compared to results obtained on a AA (Varian SPECTRAA 20-plus). The results for the AA on 30 repetitions using the same standard gave an average of 6 ppb with a standard deviation of 4.98 ppb. The recommended lower level of detection for the AA was 20 ppb.

Assuming the worst case scenario where the standard deviation for the visual test method is 7.5 ppb a z test was performed to compare the mean results from the two methods. This resulted in a calculated z value of 2.86. This value for the z statistic indicates that the means are not the same with over 99% confidence. In this case, where the amounts of silver to be detected are below the recommended level of detection for the AA, the visual method out performs the AA.

Performance on Environmental Samples

Samples from a hot tub utilizing bromine as a disinfectant, Ames, Iowa tap water and pool water from Carr pool, also in Ames, were spiked at a level of 10 ppb silver. Tests run in the field using the visual method resulted in 100% recovery on these spiked samples. All samples matched the 10 ppb spot.

Samples run on sewage effluent from the Ames, Iowa sewer plant and surface water from the Skunk River near Ames resulted in poor or no recovery. This is probably due to the binding of the silver ions by humic or fulvic acids present in the sample, or possibly because of reduction of the silver ions to silver metal upon addition. 100% recovery on spiked 25 ppb silver samples was found after treatment of the samples with a simple sulfuric acid - hydrogen peroxide digestion procedure (Hach Didesdahl™ Procedure)2. Strongly reducing samples, samples with high organic content, and samples which contain thiosulfate or cyanide should be digested before testing.

Summary of Results

Source of Sample	Expected Conc. Ag (ppb)	Observed Conc. Ag (ppb)
Tap Water	10	10
Pool Water	10	10
Spa Water	10	10
Sewage Efluent	25	25
River Water	25	25
Crowley Silt Loam	30-32	35
Coland Clay Loam	25	25
Clarion Loam	25	25
NIST SRM 2711	25	25

Tests were run on digested samples of a Crowley Silt Loam soil obtained from the Louisiana State University Extension Service. 0.5g of the sample was digested using the Hach Digesdahl™ procedure. The digests were then filtered through a glass fiber filter and diluted to a final volume of 1 liter. These tests resulted in no recovery. After the addition of 1.5 g of extra disodium citrate as a complexing reagent to remove interfering ions, the samples were found to give a blank of ≈8 ppb for the visual test and 4.66 with a standard deviation of 5.07 ppb on the AA. 0.5g samples of the soil were then spiked with 25 µg of silver and the procedure was repeated. All of 30 samples measured by the visual test read between the 25 and 50 ppb dots for an extrapolated average of ≈35 ppb. The same samples ran on the AA gave an average result of 36.66 ppb with a standard deviation of 4.34 ppb. Assuming the worst case scenario where the standard deviation for the visual test method is 12.5 ppb a z test was performed to compare the mean results from the two methods. This resulted in a small z statistic of -0.69. This value for the z

statistic indicates that the means for this sample using the visual and AA methods are statistically the same. The initial silver content of the soil explains the differences in the spiked and recovered amounts. Tests performed on a Coland Clay Loam and a Clarion Loam obtained in the Ames area gave similar results, but with no detectable blanks.

Finally a 0.5407 g sample of Montana soil NIST SRM 2711 was digested using the Digesdahl™ procedure. This amount of test soil results in a final solution, when diluted to 100 mL, with a reported assay value of 25 ppb silver. All of the samples tested correlated well with the reported values. All samples tested matched the 25 ppb dot using the visual method.

Stability
Reagents kept at 35ºC for 1 year still function properly.

Summary
The method described was utilized to test various soil and water samples for the presence of Ag. All of the matrices that were examined gave acceptable results. The results were comparable to those obtained with an AA, and in the case of levels of 10 ppb and below, the visual method was found to be superior to the AA. This method should be useful as a field method for determining trace amounts of silver in a variety of environmental samples.

The use of this method should save time and money without compromising the accuracy of analysis.

References
1. Dagnall, R.M, and West, T.S. 1964. A selective and sensitive colour reaction for silver. *Talanta,* 1964, vol 11. pp. 1533 - 1541.
2. *Digestion and Analysis of Wastewater, Solids, and Sludges.* 1987, Hach Company. Loveland, Colorado.
3. *Guidelines for Drinking Water Quality,* vol. 1: Recommendations, World Health Organization, 1984.
4. *Guidefines for Drinking Water Quality,* vol. 2: Health Criteria and Supporting Info, 1984.
5. *Hach Water Analysis Handbook,* 2nd edition, 1992, Hach Company. Loveland, Colorado.
6. *Standard Methods for Examination of Water and Wastewater,* 18th edition, 1992.
7. 40 CM 7-1-96 edition. Section 261.24.

DIAGNOSING ERRORS IN SPECIES ANALYSIS PROCEDURES USING SIDMS METHOD 6800

H.M. "Skip" Kingston, Dengwei Huo, Yusheng Lu
Duquesne University, Department of Chemistry and Biochemistry Pittsburgh, PA 15282-1503
412-396-5564

The determination of chemical species in environmental samples is difficult when the species are easily altered during the analysis process. A method has been developed to permit the species to undergo chemical reactions during analysis and correct for these changes. Speciated Isotope Dilution Mass Spectrometry (SIDMS) is especially suited for species that equilibrate in solution quickly and also degrade during extraction, oxidize or reduce during analysis or are difficult to separate quantitatively using conventional methods[1]. This method is a new draft EPA RCRA method (Method 6800) that utilizes isotopically enriched speciated spikes combined with isotope dilution to accurately determine and correct for species transformations that occur in sample processing. The errors in the measurement are those that are limited by the ability of the ratio measurement and the equilibrium of the species during spiking. This method was specifically developed to address the problems of accurately quantifying different species in complicated matrices that also play a role in the stability of the species during extraction, separation or manipulation. Additionally, it is a diagnostic tool for identifying both the error and bias inherent in specific method steps prior to and during sample analysis such as sampling process, storage, sample preparation, and chemical modifications prior and during measurement. The basic SIDMS method is applicable to many species of elements with multiple isotopes and extends to various oxidation states, organometallics, and molecular forms of species. The method is used as a diagnostic tool and reference method assisting with error identification in other methods permitting their development as more accurate and precise species analysis tools.

Validation data for Cr(VI) and Cr(III) demonstrate the ability of SIDMS to examine other methods in a diagnostic manner. The extraction procedure Method 3060A and analysis Method 7196A are used to demonstrate the identification of specific chemical changes that take place in these methods. These changes can be corrected by use of this very sensitive internal speciated tracer[2].

The objective of EPA Method 6800 is to provide a new reference method that is also legally defensible as a reference method for measurements that have high degrees of uncertainty and error due to highly reactive species.

1. Kingston, H.M. Skip, Dengwei Huo, Yusheng Lu, Stuart Chalk, "Accuracy in species analysis: Speciated Isotope Dilution Mass Spectrometry (SIDMS) exemplified by the evaluation of chromium species" Spectrachemica Acta B, (accepted) 1998.
2. Yusheng Lu, Dengwei Huo and H.M. Skip Kingston. "Determination of Analytical Biases and Chemical Mechanisms in the Analysis of Cr(VI) Using EPA Protocols" ES&T (submitted) 1998.

THE USE OF ^{210}Pb DATING AND DETAILED STRATIGRAPHY TO DETERMINE THE SIGNIFICANCE AND FATE OF CHROMIUM IN SEDIMENTS NEAR A HAZARDOUS WASTE SITE

Richard Rediske
The Robert B. Annis Water Resources Institute, Grand Valley State University, Allendale, MI 49401
616-895-3047
Gary Fahnenstiel
National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Lake Michigan Field Station, 1431 Beach St., Muskegon, MI 49441
Claire Schelske
Department of Fisheries and Aquatic Sciences, University of Florida, Gainesville, FL
Marc Tuchman
USEPA Great Lakes National Program Office, 77 West Jackson Blvd., Chicago, IL 60604

ABSTRACT

An innovative investigation using ^{210}Pb dating and detailed stratigraphy was conducted to determine the significance and fate of chromium in the sediments of White Lake (Michigan). Elevated sediment concentrations of chromium, arsenic, and mercury were found in the vicinity of the historical effluent discharge point of a tannery. The chromium levels found in the sediments were among the highest concentrations reported in the Great Lakes basin (20,000 mg/kg). Since the direct discharge of effluent from the tannery was discontinued in 1976, vertical depositional patterns may reflect changes in the flux of chromium into the system. Historical levels of metals may be covered by less contaminated material or resuspended by physical events. Information on sediment stability and deposition rates was critical to the development of remediation options for the site.

Traditional sampling and analytical methods would not provide information on sediment stability and accumulation patterns. Radiodating using ^{210}Pb, a technique commonly used in limnology, was employed to determine the history of sediment deposition. This technique was augmented with detailed stratigraphy analysis to provide a current and historical record of chromium deposition in the sediments. Two piston core samples were collected in the tannery discharge area and sectioned in 2 cm intervals. Total chromium was analyzed by ICP. Radiometric measurements were made using a low-background gamma counting system with a well-type intrinsic germanium detector. Total ^{210}Pb activity was obtained from the 46.5 kev photon peak, and ^{226}Ra activity was obtained from the 609.2 kev peak of ^{214}Bi. The 661.7 kev photon peak was used to measure ^{137}Cs activity. The peak in ^{137}Cs activity was measured to evaluate its usefulness as an independent time marker for the peak period of fallout from nuclear weapons testing in 1962-63.

Chromium stratigraphy in the tannery discharge area indicated that the top 15-20 cut of sediment was less contaminated (2,000-4,000 mg/kg) than sediment located at >30 cm (>5,000 mg/kg). Radionuclide results

suggested that this surface sediment layer was well mixed, however, distinct from the deeper more highly contaminated sediments. Presently this surface sediment layer (15-20 cm) does not physically mix with the deeper, more contaminated sediment. The surface layer was followed by a region (30-80 cm) that contained chromium levels in excess of 20,000 mg/kg. Since the direct discharge of tannery effluent to this area ceased in 1976, evidence of the deposition of sediment with less chromium contamination should have been apparent. The lack of a decreasing gradient of chromium concentration in the near surface zone sediments suggested that the processes of mixing and resuspension continue to be active. In addition, chromium transport to the 0-20 cm sediment zone may also have occurred by other mechanisms including surface runoff of contaminated soils and possibly groundwater advection. The lack of a significant ^{137}Cs horizon in the sediments indicated that groundwater was discharging in this region; however, the linkage with chromium mobility required further investigation.

INTRODUCTION

White Lake is a 2,571 acre, drowned-rivermouth lake located on the eastern shore of Lake Michigan in Muskegon County. The Lake is part of the White River Watershed and discharges directly to Lake Michigan through a channel located on the western end. White Lake was designated an Area of Concern (AOC) in 1985 by the International Joint Commission because of historical discharges of heavy metals and organic chemicals. Chromium, mercury, arsenic, and animal hides have been discharged into White Lake by Whitehall Leather. The tannery began operating in Whitehall near the turn of the century and used wood bark as the original tanning agent. In 1940, the tanning agent was changed to chromic sulfate, and a series of six waste treatment lagoons were constructed near an area of the shoreline called Tannery Bay. Effluent from these lagoons containing heavy metals and leather byproducts was discharged directly into the bay. In addition, dredged materials from the lagoons and other process wastes were disposed of in landfill areas adjacent to the shore. The direct discharge of wastewater effluent from the tannery ceased in 1976. Previous investigations have indicated extensive contamination of sediments in White Lake. Elevated levels of chromium, lead, arsenic, and mercury were detected in the northeastern section of the lake in 1982 (WMSRDC 1982) and in 1994 (Bolattino and Fox 1995). This area was the historical discharge point for tannery effluent from Whitehall Leather. The chromium levels found in the sediments of this area were some of the highest reported from any site in the Great Lakes. Since the direct discharge of effluent to Tannery Bay was discontinued in 1976, vertical depositional patterns may reflect changes in the flux of chromium into the system. The stability of the sediments in this region was also unknown. Without more information on sediment stability and accumulation rates, it would difficult to determine the residence time of contaminants within any specific region of the sediments. Whether historical levels of metals are being covered by less contaminated material or being resuspended by physical events are critical questions that need to be answered before evaluating remediation options.

An innovative investigation using ^{210}Pb dating and detailed stratigraphy was conducted to determine the significance and fate of chromium in the sediments of White Lake. Radiodating using ^{210}Pb provides a continuous sequence of dates from a single core utilizing the natural decay of ^{210}Pb. This technique has been widely used in limnology and has been independently verified by comparisons with other techniques (e.g., Robbins et al. 1978; Appleby et al. 1979; and Wolfe et al. 1994). ^{210}Pb is a naturally occurring radioisotope that enters lakes through wet and dry deposition following the decay of atmospheric ^{222}Rn. Once in the take, ^{210}Pb is rapidly scavenged by particles and settles to the bottom. The concentration of ^{210}Pb can then be analyzed at a series of depths in the cores from the surface to the depth where excess ^{210}Pb is no longer measurable, approximately 5-8 half-lives or 150 years. From this ^{210}Pb profile, dates and sediment accumulation rates are calculated using one of several mathematical models, such as the constant rate of supply method. Using a combination of ^{210}Pb dating and detailed metal stratigraphy, critical information related to contaminant profiles and sediment stability was obtained. The technique described can be used at hazardous waste sites where the evaluation of contaminated sediments is required for remediation.

EXPERIMENTAL

The sediment cores were collected with a VibraCore device with core lengths ranging from 6 - 8 ft. The core samples were then sectioned in three equal lengths for chemical analysis. Ponar samples were also collected at these locations to provide an assessment of the near surface zone sediments. A piston corer (Fisher et al. 1992) was used to obtain the samples for stratigraphy and radiodating since the VibraCore causes some degree of internal mixing in the core tube. VibraCore samples were collected during 1994. The ponar and piston core samples were collected during 1996. Sampling locations are shown in Figures I and 2. All samples were collected using the USEPA *R.V. Mudpuppy.*

Piston core samples were extruded and cut into 2 cm intervals. Each interval was weighed and an aliquot was

removed for metals analysis. Sample preparation and analysis methods (EPA 1994) for metals are listed below:

Arsenic	Graphite Furnace	7060/3050
Chromium	Inductively Coupled Plasma	6010/3050
Mercury	Cold vapor	7471

All metals results were reported on a dry weight basis.

The preparation for radiometric analysis consisted of freeze drying the sediment and the grinding the sample to a homogenous mixture. Sub samples were then packed and sealed with an epoxy resin in polypropylene tubes in preparation for radiometric analysis.

Radiometric measurements were made using low-background gamma counting systems with well-type intrinsic germanium detectors (Schelske et al. 1994). To prepare samples for radiometric analysis, dry sediment from each section was packed to a nominal height of 30 min in a tared polypropylene tube (84 mm high x 14.5 mm outside diameter, 12 mm. inside diameter). Sample height was recorded and tubes were weighed to obtain sample mass. Samples in the tubes were sealed with a layer of epoxy resin and polyamine hardener, capped, and stored before counting to ensure equilibrium between ^{226}Ra and ^{214}Bi. Activities for each radionuclide were calculated using empirically derived factors of variation in counting efficiency with sample mass and height (Schelske et al. 1994). Total ^{210}Pb activity was obtained from the 46.5 kev photon peak, and ^{226}Ra activity was obtained from the 609.2 kev peak of ^{214}Bi . ^{226}Ra activity was assumed to represent supported ^{210}Pb activity. Excess ^{210}Pb activity was determined from the difference between total and supported ^{210}Pb activity and then corrected for decay from the coring date. The 661.7 kev photon peak was used to measure ^{137}Cs activity. The peak in ^{137}Cs activity was measured to evaluate its usefulness as an independent time marker for the peak period of fallout from nuclear weapons testing in 1962-63.

Sediments were aged using measurements of the activity of naturally occurring radioisotopes in sediment samples. The method is based on determining the activity of total ^{210}Pb (22.3 yr half-life), a decay product of ^{226}Ra (half-life 1,622 yr) in the ^{238}U decay series. Total ^{210}Pb represents the sum of excess ^{210}Pb and supported 2 10Pb activity in sediments. The ultimate source of excess ^{210}Pb is the outgassing of chemically inert ^{222}Rn (3.83 d half-life) from continents as ^{226}Ra incorporated in soils and rocks decays. In the atmosphere, ^{222}Rn decays to ^{210}Pb, which is deposited at the earth's surface with atmospheric washout as unsupported or excess ^{210}Pb. Supported ^{210}Pb in lake sediments is produced by the decay of ^{226}Ra that is deposited as one fraction of erosional inputs. In the sediments, gaseous ^{222}Rn produced from ^{226}Ra is trapped and decays to ^{210}Pb. By definition, supported ^{210}Pb is in secular equilibrium with sedimentary ^{226}Ra and is equal to total ^{210}Pb activity at depths where excess ^{210}Pb activity is not measurable due to decay. Because the decay of excess ^{210}Pb activity in sediments provides the basis for estimating sediment ages, it is necessary to make estimates of total and supported ^{210}Pb, activities so excess ^{210}Pb activity can be deter- mined by difference. Excess ^{210}Pb activity was calculated either by subtracting ^{226}Ra activity from total ^{210}Pb activity at each depth or by subtracting an estimate of sup- ported ^{210}Pb activity based on measurements of total ^{210}Pb activity at depths where excess ^{210}Pb activity is negligible.

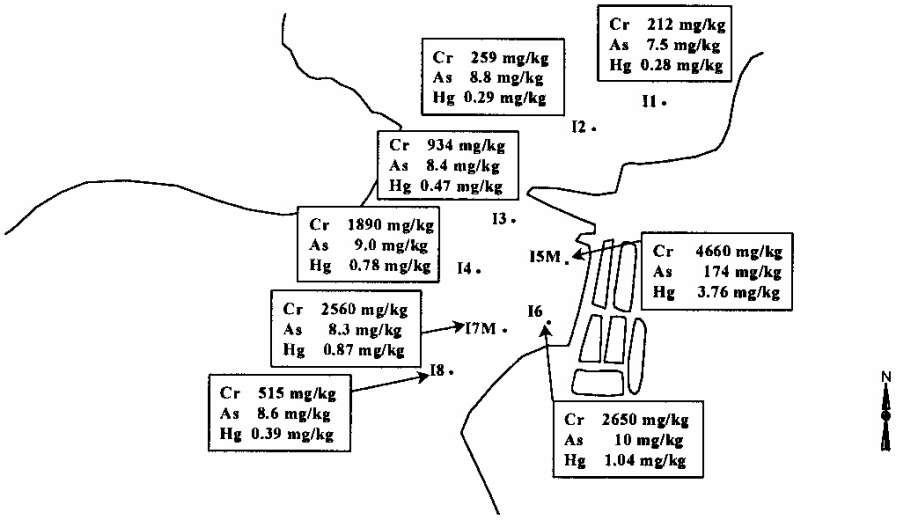


Figure 1. Conentration of chromium, arsenic, and mercury in ponar samples collected from Tannery Bay, Whitehall, Michigan (1996)

Sediment ages were calculated using a CRS model (Appleby and Oldfield 1983). This model calculates ages based on the assumption that the flux of excess ^{210}Pb, to the lake was constant and therefore that variation in ^{210}Pb activity from a pattern of exponential decrease with depth depends on variation in rate of sedimentation. Errors in age and

mass sedimentation rate were propagated using first-order approximations and calculated according to Binford (1990).

RESULTS AND DISCUSSION

The results of ponar and VibraCore samples are shown in Figures 1 and 2 respectively. Ponar samples provide an indication of the conditions present in the near surface zone of the sediments. The penetration of the ponar is variable and can range from 0-15 cm. depending on the condition of the sediment. A comparison of the results from both collection methods suggests that the highest degree of the chromium contamination is present at depths below the penetration of the ponar. In addition, the ponar results suggest that chromium continues to enter the sediments of Tannery Bay since concentrations range from 1,000 mg/kg to 4,600 mg/kg near the surface.

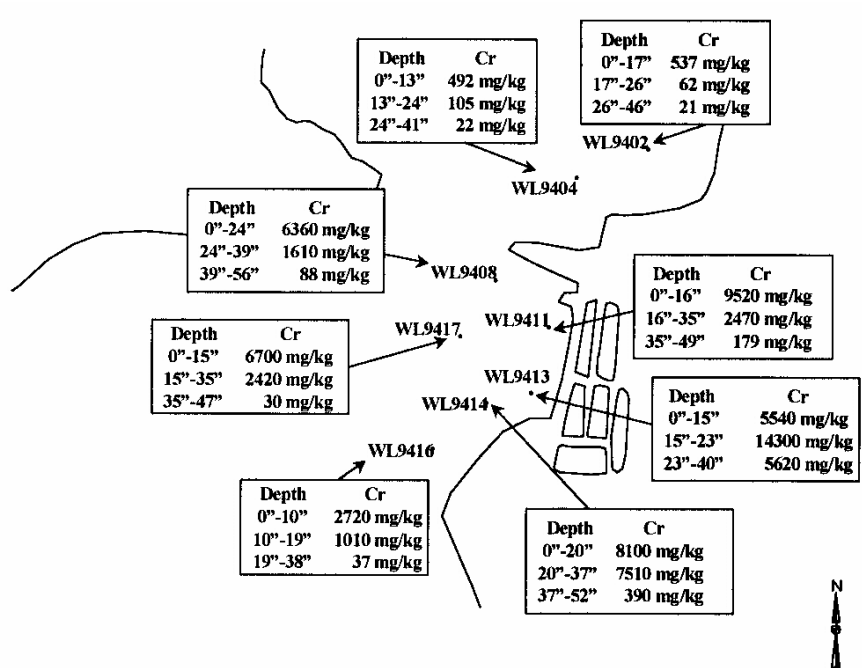


Figure 2. Concentration of chromium in core samples collected from Tannery Bay, Whitehall, Michigan (1994)

The results of the stratigraphy analyses for total chromium are given in Figures 3 and 4 for I-5M and I-7M respectively. The I-5M core shows a relatively uniform region of chromium concentrations ranging from 2,500 mg/kg to 3,600 mg/kg between 0 and 26 cm. This region is followed by more concentrated strata that vary from approximately 5,000 mg/kg to 23,000 mg/kg in the interval from 26-84 cm. Chromium in the remainder of the core decreases after 84 cm. Since this station was located in the discharge area of the waste treatment lagoons, the variations in chromium concentrations observed reflect dif-

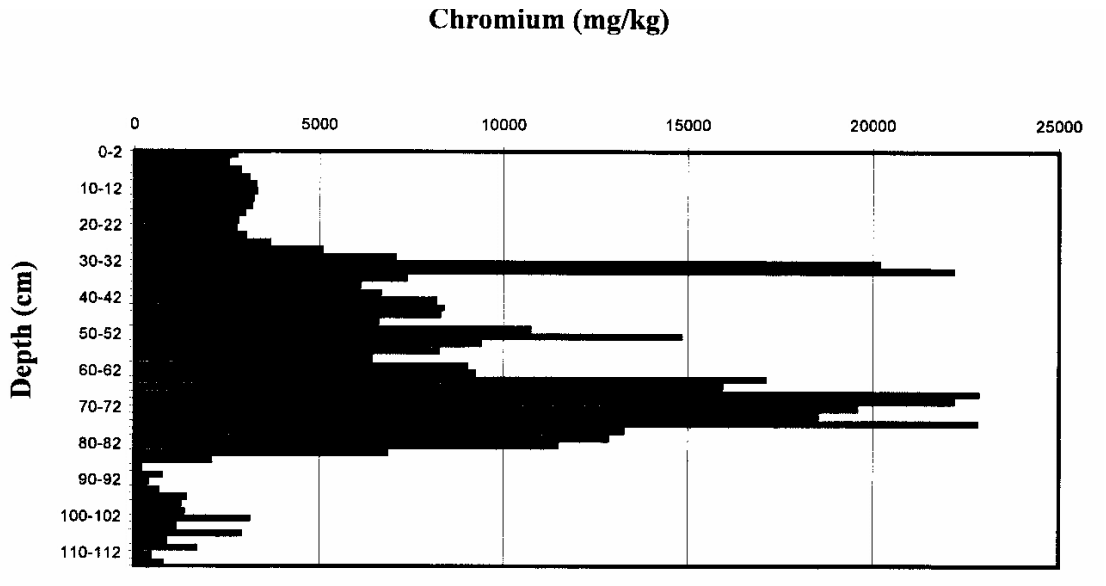


Figure 3. Results of chromium stratigraphy analysis on the core sample from I-5M

ferences in effluent composition over time. Sudden reductions in chromium levels also correspond to strata that

contain animal hair and hide fragments. The I-7M core follows a different depositional pattern. Concentrations of chromium gradually increase from approximately 2,000 mg/kg to 5,000 mg/kg over the interval from 0-36 cm. Concentrations then rapidly rise and remain elevated in the region from 38-128 cm. Chromium concentrations began to decrease after 128 cm. Higher levels of chromium were found in the I-7M core than at I-5M. The highest level found at I-5M was 22,800 mg/kg while several 2 cm strata at I-7M ranged from 34,000 mg/kg to 61,100 mg/kg.

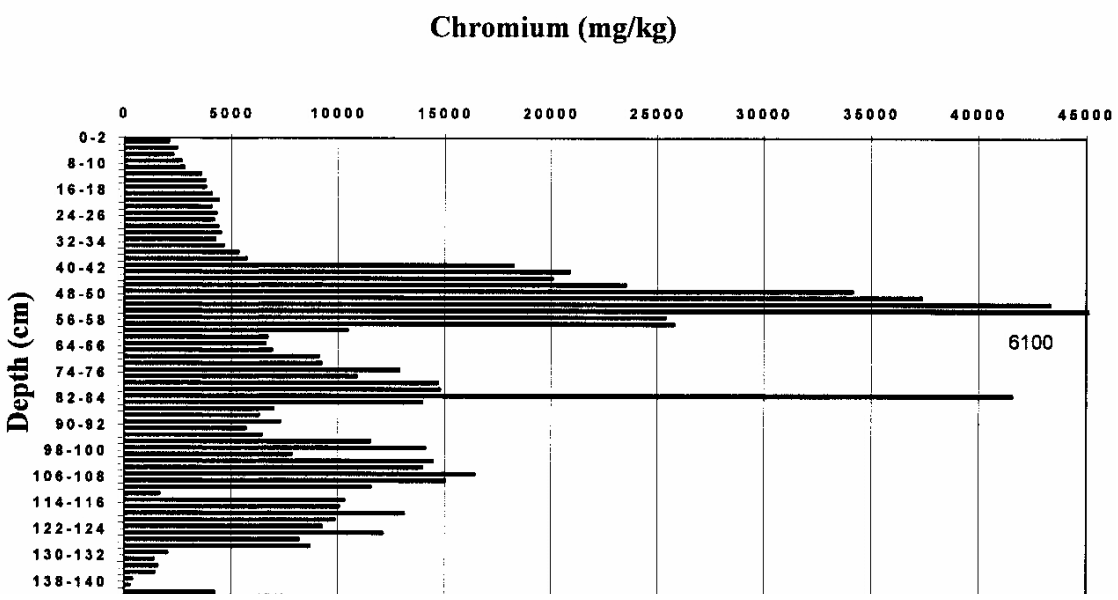


Figure 4. Results of chromium stratigraphy analysis on the core sample from I-7M

The radiochemistry data is summarized in Tables 1 and 2. The profiles of ^{210}Pb activity for Station I-5M and Station I-7M (Figure 5) provide other information about historical sedimentation at the Tannery Bay sites. First, ^{210}Pb activity generally decreases with depth. Second, several stratigraphic layers can be identified based on ^{210}Pb activity. Four layers are present in core I-5M: 0-15 cm, 15-30 cm, 30-50 cm, and 50-65 cm; and four layers can also be identified in I-7M: 0-20 cm, 20-35 cm, 35-45 cm, and 45-70 cm. The total ^{210}Pb activity in the top layer in both cores was similar, ranging from 10-12 dpm/g, and the activity in the lowest layer was also similar in both cores. Supported ^{210}Pb is by far the largest fraction in the lowest layer. Finally, because excess ^{210}Pb is generally not measurable in sediments with ages older than five or six half lives, we can conclude that the ages in sediments above the bottom layer with measurable levels of excess ^{210}Pb activity are probably not older than 110 to 130 years.

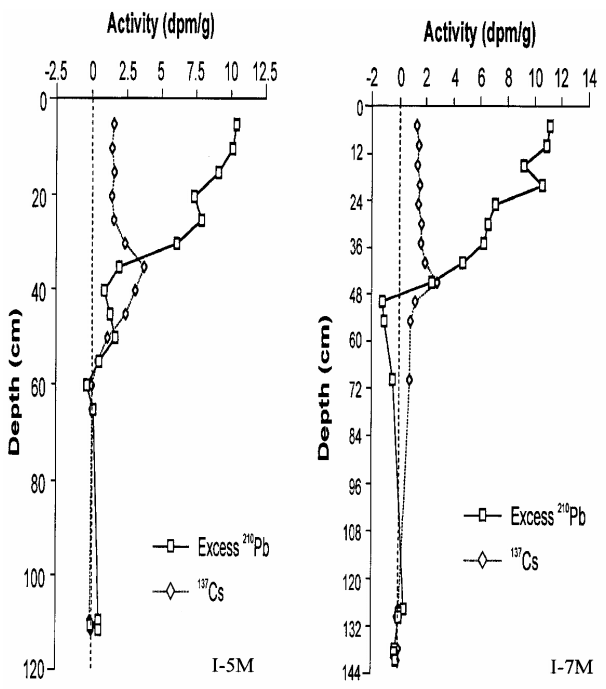
Table 1. Results of radiochemistry analysis of the core sample from I-5M.

	Total			Excess				Mass	
	Pb-210	Ra-226	Cs-137	Pb-210		Age		Sedimentation	MSR
Depth	Activity	Activity	Activity	Activity	Age	Error	Date	Rate	Error
(cm)	(dpm/g)	(dpm/g)	(dpm/g)	(dpm/g)	(years)	(1s)		(mg/cm^2/yr)	(1s)
5	11.951	1.735	1.565	10.358	3.965	1.222	1992.7	167.23	8.36
10	11.552	1.592	1.437	10.103	10.534	1.339	1986.2	145.68	7.68
15	10.70	1.73	1.614	9.1	17.992	1.490	1978.7	130.06	8.22
20	8.55	1.276	1.449	7.38	29.222	1.848	1967.5	120.21	7.18
25	8.81	1.015	1.598	7.911	46.450	2.604	1950.2	72.50	5.86
30	7.455	1.423	2.414	6.123	68.841	4.523	1927.9	50.96	5.95
35	4.931	2.967	3.769	1.996	81.028	5.603	1915.7	89.93	22.61
40	2.641	1.753	3.142	0.904	90.010	5.747	1906.7	142.5	61.92
45	2.696	1.398	2.468	1.32	104.612	6.991	1892.1	67.94	22.25
50	2.889	1.224	1.139	1.689	149.286	21.588	1847.4	22.63	9.26
55	1.243	0.703	0.437	0.549					
60	0.44	0.757	0.024	-0.322					

Combined plots of chromium stratigraphy and radiochemistry data are shown in Figure 6 for I-5M and I-7M. The four regions in each core described earlier suggest distinct layers. Sediments that are well mixed would have relatively uniform ^{210}Pb activity as illustrated from the surface to the 10-20 cm zone. These results are significant as the ^{210}Pb profile demonstrates a mixed zone near the surface that is isolated from the sediments below approximately 20 cm. Levels of chromium in excess of 20,000 mg/kg begin at 40 cm at I-7M and at 30 cm at I-5M. Based on the ^{210}Pb profile, a region of unmixed sediment lies between the heavily contaminated strata and the mixed sediment zone. The zones of greatest chromium contamination therefore appear to be isolated from the surface sediments that are subject to mixing. Sedimentation rate data for both Table 1. Results of radiochemistry analysis of the core sample from I-5M stations suggest that I-7M has a greater rate (225 mg/cm^2/yr) than I-5M (167 mg/cm^2/yr). This observation is supported by the chromium profile discussed above.

Total 2. Results of radiochemistry analysis of the core sample from I-7M.

	Total			Excess				Mass	
	Pb-210	Ra-226	Cs-137	Pb-210		Age		Sedimentation	MSR
Depth	Activity	Activity	Activity	Activity	Age	Error	Date	Rate	Error
(cm)	(dpm/g)	(dpm/g)	(dpm/g)	(dpm/g)	(years)	(1s)		(mg/cm^2/yr)	(1s)
5	12.510	1.550	1.280	11.110	2.410	1.710	1994.3	225.77	14.85
10	12.700	1.990	1.440	10.860	5.460	1.790	1991.2	212.07	16.31
15	11.090	2.030	1.350	9.190	11.620	1.940	1985.1	217.52	19.10
20	12.150	1.730	1.530	10.570	21.900	2.380	1974.8	146.84	9.77
25	8.770	1.740	1.420	7.130	31.670	2.870	1965.0	159.07	16.91
30	8.320	1.840	1.660	6.580	44.500	3.740	1952.2	121.58	15.67
35	7.980	1.800	1.640	6.270	65.110	6.130	1931.6	76.58	12.89
40	7.000	2.350	1.950	4.710	101.820	16.450	1894.9	43.32	13.97
45	5.780	3.380	2.820	2.440					
50	5.440	3.640	1.220	-1.220					
55	2.300	3.360	0.850	-1.080					



The peak input of fallout ^{137}Cs in the late 1950s and early 1960s has been used to provide a time-dependent horizon in cores. This approach was used to verify CRS dates in Lake Erie cores (Schelske and Hodell 1995). Neither a sharp peak nor a large peak in ^{137}Cs activity was found in the Tannery Bay cores. Therefore, this measurement was not useful in establishing the ^{137}Cs horizon. The low inventory of ^{137}Cs activity in both cores is in sharp contrast to the high inventory of ^{210}Pb activity. These results indicate that ^{137}CS was deposited and not retained at these sites for the following reasons:

- sediment resuspension focused the ^{137}Cs to other locations
- the ^{137}Cs was diluted by the introduction of large quantities of tannery wastes
- ionic ^{137}Cs was advected with pore waters from the core site

Figure 5. Activity versus depth of excess ^{210}Pb and ^{137}Cs at stations I-5M and I-7M

The latter mechanism is prevalent at locations where groundwater is moving through deposited sediments. It seems unlikely that resuspension or dilution was a primary mechanism because of the large inventories of ^{210}Pb activity at both sites. The most plausible explanation for the absence of the ^{137}Cs horizon is, therefore, groundwater advection.

The influence of groundwater advection on chromium may also be a factor in its fate and transport. As discussed previously, the absence of the ^{137}Cs horizon suggested that the movement of local groundwater through the sediments was responsible for advective losses. Since the local groundwater is known to discharge in the near shore area of Tannery Bay, chromium may also be mobilized from the deeper layers and transported to the surface. While the solubility of trivalent chromium is generally limited due to the precipitation of insoluble hydroxides, the formation of organic complexes has been shown to increase its solubility. Kaczynski and Kleber (1994), James and Bartlett (1983), and Hassan and Garrison (1996) noticed that the solubility of trivalent chromium was increased in the presence of organic complexing agents. The latter authors noticed an increase in solubility in the presence of cysteine under low Eh conditions. The low Eh environment present in the sediments of Tannery Bay, in addition to the organosulfur compounds produced during the decomposition of animal hides and hair, may produce conditions that promote chromium complexation. It was also noted that a large amount of humic material was released from the Tannery Bay sediments during alkaline digestion. These materials may also serve as complexing agents to increase chromium complexation. The presence of a complexed chromium fraction in the sediment pore water and its potential role in the advection of chromium needs to be evaluated as long as groundwater continues to enter Tannery Bay.

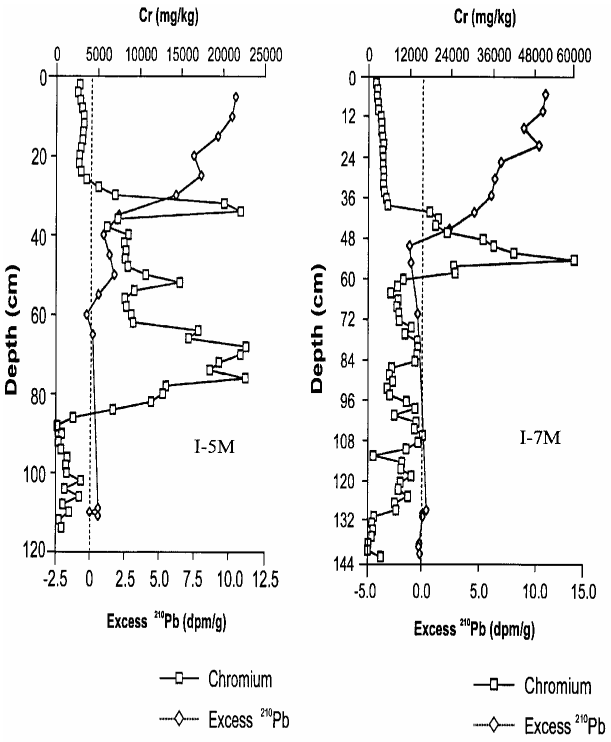


Figure 6. Chromium concentrations and excess ^{210}Pb versus depth at stations I-5M and I-7M

Since the direct discharge of tannery effluent to Tannery Bay ceased in 1976, evidence of the deposition of sediments with less chromium contamination should be evident. The lack of a decreasing gradient of chromium concentrations in the surface zone sediments (0-20 cm) may be explained by several mechanisms:

- continued surface runoff
- groundwater advection
- continual sediment mixing and resuspension in the 0-20 cm zone

Since the levels of excess ^{210}Pb in the surface zone sediments are normal and do not reflect excessive dilution with terrestrial soil, surface runoff would only be significant if small amounts of highly contaminated material were continuously eroding into Tannery Bay. As discussed previously, groundwater advection may be responsible for some migration of chromium from deeper sediment layers to the surface. It is, however, doubtful that this mechanism would be responsible for chromium levels in excess of 2,000 mg/kg. The most likely process that would produce the observed chromium levels is that of sediment mixing and resuspension. The flocculent, fine-grained sediments in Tannery Bay may be mixed to a degree that prohibits the formation of concentration gradients. The continued mixing of flocculent materials would result in unstable, resuspended sediment that could readily be exported into White Lake by currents and wave action. The prevalence of the high levels of chromium in the White Lake samples collected down gradient from Tannery Bay would support the continued export of resuspended sediments (Rediske et al. 1998)

The CRS model (Appleby and Oldfield 1983) was selected to calculate ages because of the absence of an exponential ^{210}Pb gradient (Table 1). Ages calculated from the model placed 1892 at 45 cm and 1847 at 50 cm for core I-5M, and 1895 at 40 cm for core I-7M. These ages, however, were much younger than expected based on other information available from the core. For example, the chromium concentration exceeded 10,000 mg/kg from 62-82 cm in I-5M or in sediments older than 1847 according to the calculated ^{210}Pb ages. The chromium concentration exceeded 10,000 mg/kg at depths down to 84 cm in I-7M. By contrast only the upper 40 cm of this core contained

sufficient levels of excess ^{210}Pb for dating. This lack of conformity shows that the calculated ages are not credible. Results from the CRS ^{210}Pb age model that are not credible can be a product of the point transformations that are used in the CRS model (Robbins and Herche 1993). Independent assessment of dating is therefore required for the CRS model. For the piston cores, data for chromium and tannery waste by-products provide independent time markers that are at variance with the calculated ^{210}Pb ages. Since high levels of chromium and tannery waste byproducts (hair and dye coloration) persist well below the calculated 1847 date, the dating chronology must be rejected. Large inputs of waste materials could confound the chronological record by diluting the natural sediments and by altering the physical-chemical environment.

Given the insolubility of trivalent chromium in natural water (Palmer and Puls 1994), the predominant mechanism driving the flux of this metal in White Lake appears to be sediment export. The hydrodynamics of White Lake support the progressive transport of sediments in a westerly direction following the natural water currents. Prevailing winds function to mix the near shore sediments and move the resuspended material out into the main lake. The 0-20 cm zone of sediment mixing determined by the ^{210}Pb data reflects the action of the prevailing winds and the wave induced resuspension. The well mixed nature of the top 20 cm zone also suggests that these sediments are unstable and easily exported. In addition, the differences in stratigraphy between I-5M and I-7M are consistent with wind induced wave action. Station I-5M has a greater exposure to the westerly wind and has a lower calculated sedimentation rate (167.23 mg/cm^2/yr) and a shallower interval of sediment above the highly contaminated zone. In contrast, station I-7M is more protected from wave action and exhibits a greater calculated sedimentation rate (225.77 mg/cm^2/yr) and a stratigraphy profile reflecting a greater depth of less contaminated material.

The discharge of tannery waste was located near the shore of Tannery Bay in the northeast corner. The EPA/MDEQ core samples indicate heavy sediment contamination with chromium in the near shore and middle areas of Tannery Bay. Stations near the confluence with White Lake have considerably less chromium in the sediments. This pattern reflects a discharge of insoluble chromium that was rapidly incorporated into the sediments. Based on this information, the historical and current mechanism for chromium transport in White Lake is sediment export from Tannery Bay by the prevailing circulation pattern and wave action. Chromium export from Tannery Bay into White Lake proper will continue as long as the contaminated sediments are influenced by hydrodynamic circulation patterns.

CONCLUSIONS

By using a combination of combination of traditional chemical analyses, radiometric determinations, and stratigraphy, important information concerning the nature and fate sediment contamination in the Tannery Bay area of eastern White Lake was obtained. Chromium stratigraphy in indicated that the top 15-20 cm of sediment were less contaminated (2,000-4,000 mg/kg) than sediment located at >30 cm (>5,000 mg/kg). Radionuclide results suggested that this surface sediment layer was well mixed, however, distinct from the deeper more highly contaminated sediments. Presently this sediment layer (15-20 cm) does not physically mix with the deeper, more contaminated sediment. The surface layer was followed by a region (30-80 cm) that contains chromium levels in excess of 20,000 mg/kg. Since the direct discharge of tannery effluent to this area ceased in 1976, evidence of the deposition of sediment with less chromium contamination should have been apparent. The lack of a decreasing gradient of chromium concentration in the near surface zone sediments suggests that the processes of mixing and resuspension continue to be active in Tannery Bay. In addition, the high inventories of ^{210}Pb in the 0-20 cm zone show that surface runoff from the waste piles has not contributed significantly to the recent sediment record. The lack of a significant ^{137}Cs horizon in the sediments indicates that groundwater is discharging in this region; however, the linkage with chromium mobility requires further investigation. While traditional chemical analyses provide important information for determining the spatial extent of contamination, additional techniques are required to describe chemical fate and transport. Stratigraphy and radiometric analysis using ^{210}Pb can provide critical information related to sediment stability, depositional patterns, and chemical flux that is essential for the analysis of remediation alternatives.

REFERENCES

Appleby, P.G., G.F. Oldfield, R. Thompson, P. Huttunen, and K. Tolonen. 1979. Pb-210 dating of annually laminated lake sediments from Finland. Nature 280:53-55.

Appleby, P.G. and F. Oldfield. 1983. The assessment of ^{210}Pb data from sites with varying sediment accumulation rates. Hydrobiologia 103: 29-35.

Binford, M.W. 1990. Calculation and uncertainty analysis of ^{210}Pb dates for PIRLA project lake sediment cores. J.

Paleolim. 3:253-267.
Bolattino, C. and R. Fox. 1995. White Lake Area of Concern: 1994 sediment assessment. EPA Technical Report. Great Lakes National Program Office, Chicago.
EPA, 1994. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods. US. Environmental Protection Agency.* SW-846, 3rd Edition.
Fisher, M.M., M. Brenner, and K.R. Reddy, 1992. A simple, inexpensive piston corer for collecting undisturbed sediment/water interface profiles. Journal of Paleominology 7:157-161.
Hassan, S.M. and A.W. Garrison. 1996. Distribution of chromium species between soil and porewater. Chemical. Speciation and Bioavailability. 8:(3/4)85-103.
James, B.R. and R.J. Bartlett. 1983. Behavior of chromium in soils. V. Fate of organically complexed Cr(lll) added to soils. J. Environ. Qual. 12:169-172.
Kaczynski, S. E, and R.J. Kiebler. 1994. Hydrophobic C_{18} bound organic complexes of chromium and their impact on the geochemistry of chromium in natural waters. Environ. Sci. Technol. 28:799-804.
Palmer, C.D. and R.W. Puls. 1994. *Natural Attenuation of Hexavalent Chromium in Groundwater and Soils.* U.S. Environmental Protection Agency. EPA/540/5-94/505.
Robbins, J.A., D.N. Edgington, and A.L.W. Kemp. 1978. Comparative ^{210}Pb, ^{137}Cs, and pollen geochronologies of sediments from Lakes Ontario and Erie. Quat. Res. 10:256-278.
Robbins, J.A., and L.R. Herche. 1993. Models and uncertainty in ^{210}Pb dating of sediments. Int. Ver. Theor. Angew. Limnol. Verh 25:217-222.
Rediske, R.R., G. Fahnensteil, C. Schelske, P. Meier. T. Nalepa, and M. Tuchman, 1998. Preliminary Investigation of the Extent and Effects of Sediment Contamination in White Lake near the Whitehall Leather Tannery. Final Report to U. S. EPA. Great Lakes National Program Office. Chicago, Il.
Schelske, C.L., A. Peplow, M. Brenner, and C.N. Spencer. 1994. Low-background gamma counting: Applications for ^{210}Pb, dating of sediments. J. Paleolim. 10:115-128.
Schelske, C.L. and D. Hodell. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Eric. Limnol. Oceanogr. 40:918-929.
Wolfe, B., H.J. Kling, G.J. Brunskill, and P. Wilkinson. 1994. Multiple dating of a freeze core from Lake 227, and experimental fertilized lake with varied sediments. Can. J. Fish. Aquat. Sci. 51:2274-2285.

ACKNOWLEDGEMENTS

This work was supported by an Interagency Agreement (IAG) #DW13947766-01between the Environmental Protection Agency Great Lakes National Program Office (GLNPO) and the National Oceanic and Atmospheric Administration (NOAA) Great Lakes Environmental Research Laboratory (GLERL). Other funding was provided by NOAA/GLERL and Grand Valley State University (GVSU) Water Resources Institute (WRI). The authors would also like to acknowledge the assistance of the following individuals:

NOAA/GLERL	C. Beckman, S. Beattie, R. Stone, and G. Carter
GVSU	A. Stiop, F. Winkler, J. Oxford, D. Graeber, T. Hudson, and K. Onwuzulike
University of Florida	Dr. Jaye Cable
R/V *Mudpuppy* (USEPA)	J. Bonam

AIR-FORCE WIDE BACKGROUND CONCENTRATIONS OF INORGANICS OCCURRING IN GROUND WATER AND SOIL

Philip M. Hunter
Air Force Center for Environmental Excellence, Consultant Operations Division,
3207 North Road, Brooks AFB, Texas 78235

ABSTRACT

Background concentrations of naturally occurring inorganics are important to site characterization, establishing cleanup levels, conducting risk assessments, designing and operating long-term monitoring programs, and the like. The Air Force Center for Environmental Excellence (AFCEE) has streamlined the process for determining background concentrations by using computer algorithms that interrogate the Air Force's Environmental Resources Program Information Management System (ERPIMS). Analysis of this database reveals that there are a wealth of

existing sampling locations that are known to be uncontaminated and available for use in these important calculations. Air-Force wide background concentrations for ground water and soil have been calculated for inorganics using all available sampling data from the ERPIMS Database. Insight can be gained by using these concentrations as a representative baseline of numbers for ongoing and future investigations concerned with monitoring and remediation of inorganic contamination.

INTRODUCTION

Analysis of the ERPIMS database reveals that most contamination across the Air Force is organic in nature and is typically associated with chlorinated solvents and fuels (i.e. BTEX and related compounds). The presence of key organics detected in groundwater and soil samples is a good indicator of both inorganic and organic contamination. Often Air Force resources are expended needlessly to perform a separate background investigation at individual installations using newly-captured data rather than relying on existing data. AFCEE-developed computer algorithms were used to automate the process of identifying background locations using ERPIMS data. Over 10 years worth of project data is available as an existing resource for background determinations at installations across the Air Force. This methodology reduces and some cases eliminates the need to perform a separate background investigation which can cost hundreds of thousands of dollars to accomplish. This paper will discuss AFCEE's automated approach for identifying background locations, the statistical methodology used to calculate Air-Force wide background concentrations, and the nature of these background concentrations for both ground water and soil.

ERPIMS DATABASE

ERPIMS (previously known as IRPIMS) stores some 12.5 million analytical sampling results from 196 Air Force installations. Data from 40,000 distinct sampling locations (wells, borings, etc.) is captured by the system. The ERPIMS hardware consists of a Digital Equipment Corporation (DEC) Alpha® 4100 computer that runs Oracle® 7.3 on a VMS operating system. The system has been operational since 1987 and is managed by AFCEE/MSC.

DETERMINATION OF BACKGROUND LOCATIONS

Even when investigations specifically target contamination by drilling wells and borings into areas known to be hazardous waste sites, the non-detect (ND) rates for organics are surprisingly high. For example, the ND rates for TCE, which is highly mobile and known to be the most ubiquitous constituent found on Air Force installations, are on the order of 65% in ground water. For most other organic constituents, the ND rates are approximately 90% for ground water. For soil, the ND rates for organics tend to be even higher. As a result, a wealth of existing sampling locations are known to be uncontaminated and available for use as locations for background calculations. This knowledge was used to construct a computer algorithm that identifies background locations across the entire Air Force. The algorithm, which was written in Structured Query Language (SQL), searches out all locations that have been sampled for both inorganics and organics. Sampling locations showing evidence (i.e. detects) of organic contamination are then eliminated from the search and those remaining are retained for further consideration as background locations. Both upgradient, downgradient, and sidegradient locations could potentially be identified as background sampling locations. There were substantially more background locations identified for soil as opposed to ground water. On average, at least 25 background well locations and 50 background borehole locations per Air Force installation have been identified using these procedures. As indicated in the next section that follows, the magnitude of distinct sample locations and the sample sizes generated from these locations will more than adequately meet the requirements for the statistical calculations used to determine background levels.

DATA ANALYSIS AND CALCULATION OF BACKGROUND LEVELS

For calculation of background levels at individual installations and sites, AFCEE's approach and statistical methodology are similar to guidance published by EPA (EPA 1989, 1992), ASTM (1996), and Gibbons (1994). Using this guidance, normal 95% confidence 95% coverage upper tolerance limits are used. Depending on the distribution of individual data sets and the percentage of detects, nonparametric tolerance limits are also typically used. AFCEE, like EPA and others, requires at least 2 sampling locations to minimally account for spatial variability and a total sample size of at least 8 (n = 8 for each constituent) to provide ample statistical power for the background calculations. However, Air-Force wide inorganic data is complicated by multiple detection limits, diverse hydrogeologic terranes, variability over 3-dimensional space, a variety of types of hazardous waste sites, multiple Air Force bases, different waste handling practices, and the like. All of these issues force one ultimately to discriminate background levels across more than one hydrostratigraphic unit or more than one soil horizon. As a result and for the purposes of this investigation, the 95th percentile (Prc95) of the data associated with each analyte was used as the statistic of choice to best represent background. This approach parallels AFCEE's guidance for individual installations in that the 95% upper tolerance limit

focuses on the 95th percentile of the data (i.e. a tolerance limit is similar to an upper confidence limit on a specified percentile or coverage of the data, in this case the 95th percentile). Calculation of the median and the 99th percentile of background levels for analytes detected in both ground water and soil were also calculated and can be found in Tables 1 and 2. These tables also provide information that qualifies the results of the background calculations including: sample size, the number of distinct background well locations, the number of Air Force bases having background locations, and the detection frequency. All statistical analysis was performed using SAS® statistical software.

Table 1. Air-Force Wide Background Levels of Inorganics in Ground Water
As of May 1998

Analyte	Sample Size	Wells Sampled	AF Bases	Detection Freq (%)	Median (mg/L)	Prc95 (mg/L)	Prc99 (mg/L)
Aluminum	5656	2493	86	54	0.0735	44	201
Antimony	5839	2843	97	7	ND	0.014	0.2
Arsenic	7259	2996	107	32	ND	0.044	0.171
Barium	6828	2750	98	83	0.07715	0.6	2.03
Beryllium	5891	2843	98	9	ND	0.002	0.009
Boron	812	461	26	65	0.042	1.46	12
Cadmium	7153	3202	110	9	ND	0.0049	0.017
Chromium	7892	3169	112	35	ND	0.195	1.52
Cobalt	5121	2538	83	13	ND	0.031	0.12
Copper	6412	2873	102	29	ND	0.086	0.371
Cyanide	1796	987	49	2	ND	ND	0.015
Fluoride	2132	1351	60	61	0.24	2.263	4.9
Iron	6844	2838	93	78	0.56	54.4	240
Lead	8916	3552	118	33	ND	0.047	0.23
Manganese	6465	2718	92	83	0.0708	2.840	9.2
Mercury	6017	2808	105	9	ND	0.00036	0.0017
Molybdenum	3481	1779	58	17	ND	0.021	0.147
Nickel	6471	2915	104	25	ND	0.2	0.83
Nitrate	1788	1074	61	67	0.8	24.600	67
Nitrite	662	468	33	6	ND	0.02	1.1
Potassium	6561	2750	91	98	27.4	452	4050
Selenium	6794	2934	105	12	ND	0.0081	0.1
Silver	6812	3165	108	4	ND	ND	0.0155
Sodium	6561	2750	91	98	27.4	452	4050
Strontium	31	22	2	100	0.17	3670	9070
Sulfate	3175	1794	77	92	36.09	430	2420
Sulfide	176	122	14	11	ND	0.14	9.3
Thallium	5698	2780	97	4	ND	ND	0.16
Vanadium	5378	2443	84	37	ND	0.11	0.464
Zinc	6820	2863	104	67	0.02	0.33	1.67

BACKGROUND LEVELS FOR GROUND WATER

The universe of distinct monitoring wells that were sampled simultaneously for both inorganics and organics across the Air Force is approximately 4000 wells as of this writing. The query used to identify the background data set resulted in the analysis of over 145,000 analytical records. Depending on the analyte, the number of background wells used in the analysis varied from 22 (strontium) to 3552 (lead) and sample sizes varied from 31 (strontium) to 8916 (lead). Background data was captured from as many as 118 Air Force installations for lead and as little as 2 installations for strontium. Potassium and sodium were detected 98% of the time while cyanide was detected 2% of the time. Other analytes such as strontium and sulfate were detected over 90% of the time; however, the detection frequency for strontium was represented by only 2 Air Force bases and 22 monitoring wells. Some constituents were not typically detected at background locations. The following analytes had median concentrations that were below the method detection limit (MDL): antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, cyanide, lead, mercury, molybdenum, nickel, nitrite, selenium, silver, sulfide, thallium, and vanadium. The 95th percentile of the data sets for cyanide, silver, and thallium were also below MDL. This indicates that they are rarely detected in ground water and was substantiated by detection frequencies that were found to be in the neighborhood of 2% - 4%. Conversely, some inorganic constituents were detected frequently and at levels that exceeded important

environmental thresholds such as Maximum Contaminant Levels (MCLs) or Action Levels for drinking water. The following analytes had background levels (95th percentile) that exceeded MCLs: antimony, chromium, and nitrate. The background level for lead exceeded the Action Level of 0.015 mg/L set for drinking water measured at the tap. This may suggest that some regulatory limits are placed artificially close to observed background levels.

Table 2. Air-Force Wide Background Levels of Inorganics in Soil
As of May 1998

Analyte	Sample Size	Wells Sampled	AF Bases	Detection Freq (%)	Median (mg/L)	Prc95 (mg/L)	Prc99 (mg/L)
Aluminum	13077	4840	80	99	6,510	23700	84600
Antimony	15051	5683	90	8	ND	5.5	29.3
Arsenic	17212	6165	101	66	1.6	13.8	43.3
Barium	15290	5765	98	98	56.25	332.64	995
Beryllium	14724	5513	89	64	0.3	1.1	2.4
Boron	790	396	16	63	24.7	108	201
Cadmium	17464	6738	103	20	ND	2.56	10
Chromium	17549	6689	103	93	9.1	51.8	388
Cobalt	11815	4359	81	60	3	15.2	28.4
Copper	15396	5764	89	83	7.9	53	230
Cyanide	3220	1299	47	5	ND	0.155	2.3
Fluoride	1270	224	8	79	3.4	9.9	17
Iron	13719	4939	82	99	9180	33600	82900
Lead	20784	7523	113	76	5	54	340
Manganese	13495	4837	80	99	187	856	2380
Mercury	15465	5492	94	8	ND	0.11	0.58
Molybdenum	10584	3581	56	8	ND	1.8	7.99
Nickel	15167	5677	92	68	6.1	38.3	160
Nitrate	1400	273	12	47	ND	7.95	42.75
Nitrite	107	30	4	50	0.008	0.499	1.1
Selenium	16966	6019	99	8	ND	0.87	23.3
Silver	17600	6598	103	7	ND	0.93	7.35
Sodium	12161	4466	81	64	120	1300	3260
Strontium	92	24	2	100	25.1	111	8020
Sulfate	1416	273	7	96	13	200	1340
Sulfide	204	162	10	12	ND	24	99.7
Thallium	15186	5580	89	6	ND	0.352	19
Vanadium	12342	4645	80	97	18.6	66.6	142
Zinc	16017	5996	90	98	25.2	111	540

BACKGROUND LEVELS FOR SOIL

The universe of distinct boreholes sampled for both inorganics and organics across the Air Force was approximately 8100 boreholes. The query used to identify the background data set resulted in the analysis of over 325,000 analytical records. Depending on the constituent, the number of background boreholes used in the analysis varied from 24 (strontium) to 7523 (lead) and sample sizes varied from 92 (strontium) to 20784 (lead). Background data was captured from as many as 113 Air Force installations for lead and as little as 2 installations for strontium. Since inorganics tend not to be particularly mobile in ground water, it is not surprising that they are detected at higher frequencies in soil vis a vis ground water. The following constituents had detection frequencies exceeding 95%: aluminum, barium, chromium, iron, manganese, strontium, sulfate, vanadium, and zinc. The high detection frequencies for strontium and sulfate, however, are misleading since the number of Air Force bases represented is 2 and 7, respectively. Strontium, in particular, had only 24 boreholes that were sampled and identified as background locations across the Air Force. Some analytes were not commonly detected at background locations. The following analytes had median concentrations that were below MDLs: antimony, arsenic, cadmium, cyanide, mercury, molybdenum, nitrate, selenium, silver, sulfide, and thallium. These same constituents also had median concentrations below MDLs for ground water. None of the 95th percentiles of any of the data sets for soil fell below MDLs, unlike the situation found for ground water. The following analytes had detection frequencies that were below 10%: antimony, cyanide, mercury, molybdenum, nitrate, selenium, silver, sulfide, and thallium. On rare occasion, inorganic constituents were detected at levels that exceeded important environmental thresholds (using residential

criteria) such as Preliminary Remediation Goals (PRGs), Human Health Screening Levels (HHSLs), and Risk-Based Concentrations promulgated by various EPA regions. The background level for both arsenic and beryllium exceeded the PRGs and HHSLs for EPA Region 9 and Region 6, respectively. Iron exceeded both the HHSLs and the PRGs for EPA Regions 6 and 9, respectively. As in the case for ground water, these results also suggest that regulatory limits may be artificially placed too close to observed background levels.

SUMMARY

Computer algorithms developed by the Air Force were used to automate the process of identifying background locations for inorganics occurring in ground water and soil. These procedures identified large numbers of background locations and a more than adequate sample size which was used to determine Air-Force wide background levels for some 30 inorganic constituents. This baseline of numbers which was calculated in this study provides insight on the nature of background variability across the Air Force and gives decision makers a "feel" for representative background levels. The 95th percentile statistic calculated from individual constituent data sets is believed to best represent background levels given the inherent complexities associated with analyzing these large and diverse data sets. Potassium and sodium were highly detected in ground water; while aluminum, barium, chromium, iron, manganese, strontium, sulfate, vanadium, and zinc were frequently detected in background soil. Some constituents were not commonly detected at background locations across the Air Force. The following analytes were not typically found in ground water: antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, cyanide, lead, mercury, molybdenum, nickel, nitrite, selenium, silver, sulfide, thallium, and vanadium. For background soil, the following analytes were not typically detected in soil: antimony, cyanide, mercury, molybdenum, nitrate, selenium, silver, sulfide, and thallium. The results of this investigation suggest that some regulatory limits may be placed too close to observed background levels for selected analytes. Analytes that may fall into this category include antimony, chromium, and nitrate for ground water; and arsenic, beryllium, and iron for soil. Background levels of these constituents were found to exceed important environmental thresholds. This automated approach of performing background investigations using existing data which has already been paid for, affords the Air Force many cost benefits. Use of this methodology can eliminate the need to conduct a separate background investigation for individual sites or at the installation level and can save hundreds of thousands of dollars that would otherwise be needlessly spent.

REFERENCES

American Society for Testing Materials (ASTM), 1996, Provisional Standard Guide for Developing Appropriate Statistical Approaches for Ground-Water Detection Monitoring Programs, Designation: PS 64 - 96.

EPA, Office of Solid Waste, 1989, Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Interim Final Guidance.

EPA, Office of Solid Waste, 1992, Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance.

EPA Region 6, 1996, Human Health Media-Specific Screening Levels.

EPA Region 9, 1996, Preliminary Remediation Goals (PRGs).

EPA Region 3, 1997, Risk-Based Concentrations.

Gibbons, Robert D., 1994, Statistical Methods for Groundwater Monitoring; John Wiley & Sons.

NEW TOOLS FOR LIQUID SAMPLING
"Evaluation and Comparison of the Performance of Liquid Sampling Devices In Stratified Liquids"

James D. Hoover
Department of Civil and Environmental Engineering,
Washington State University Tri-Cities, 100 Sprout Road, Richland, WA 99352
509-372-6972
Scott R. Somers
Advanced Concepts & Design, Inc., 77 Symons Street, Richland, WA 99352
509-943-1431

EXECUTIVE SUMMARY

Systematic differences in sampling performance were found to exist between the Drum Thief, COLIWASA, and ACD liquid sampling devices in laboratory tests simulating the containerized sampling of stratified liquids. The study involved two phases of testing: (1) the collection of 250 samples with these devices using water and corn oil at a ratio of 1:1 by 17 professional and 35 inexperienced sampling personnel, and (2) the collection of 216 test samples at water:oil ratios ranging from 95:5 to 5:95 by a single user. Both small volume (≤250 ml) and large volume (≈1000 ml) device models were evaluated. Statistically significant differences in the accuracy, precision, spillage, and time of sampling were found to exist among these devices. The relative performance of the devices were also found to coincide with the rating of the devices by 52 volunteer users.

Nearly all differences in sampling performance were found to vary systematically with device type. Differences in sampling accuracy between devices range from 18% to 175%, and sampling accuracy was found to be highly dependent on the liquid ratio for some devices. Sampling accuracy with tile COLIWASA and Drum Thief decreased sharply when the proportion of either liquid was <30%, indicating that there are limits on the liquid proportions that can be sampled with these devices. Sampling reproducibility among users also varied systematically with device type, but when used by a single individual, precision was >97% for all devices. The amount of spillage associated with sampling ranged from zero with some devices to as much as 10% of the sample volume with others. Sampling time among devices differed by as much as 300%.

The performance of the small volume and large volume models of the ACD devices exceeded that of the other devices in essentially all categories of evaluation. Nearly all aspects of sampling performance appear to be dominated by differences in the inherent design and function of the devices, which cause some devices to also be more user intensive than others. Among the devices tested, sampling performance with the ACD devices was found to be the least dependent on user factors, including experience. The ACD devices also received the highest ratings in the user survey.

These results have important implications for the sampling of liquids that is routinely performed for the purpose of characterizing their composition and potential hazard. These implications include health, safety, economic, legal, and practical considerations for the handling and disposition of the sampled liquids. These results also provide a quantitatively basis for comparing the performance of liquid sampling devices used in the environmental industry and to provide a basis for improving sampling performance and sampler design.

PURPOSE AND BACKGROUND

The sampling of liquids is an activity that is performed thousands of times daily by numerous federal, state, and local and agencies for the purpose *of* characterizing type, nature, and/or hazard of unknown liquid substances. Environmental regulations also require that essentially all liquid waste materials be sampled and appropriately characterized for the purposes of appropriate handling, transportation, treatment and/or disposal. Although a relatively small number of sampling devices are used to collect these samples, there is little documented information regarding the performance of these sampling devices or a quantitative comparison to serve as a benchmark for assessing quality control or product improvement

These studies were undertaken to assess the performance of five liquid sampling devices, The purpose of these studies was to establish a quantitative baseline for the evaluation and comparison of liquid samplers used in the acquisition of representative samples of stratified liquids. These studies were motivated by the need to establish a quantitative basis for evaluating the quality of samples that are obtained with various sampling devices.

The sampling and analysis of waste materials, contaminated media, and other materials of unknown composition are integral components of many environmental activities including regulatory compliance in accordance with the Resource Conservation and Recovery Act (RCRA; 1976) and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA; 1980). Sampling protocols have been established to ensure uniformity in the generation on of sampling data (e.g., Environmental Protection Agency's (EPA's) Office of Solid Waste and Emergency Response (OSWER (e.g., EPA, 1986). Although general guidelines and procedures for liquid sampling exist (e.g., ASTM 1994; EPA 1991), there are no standards pertaining to sample quality (e.g., accuracy), and essentially no information on the quality of the samples that call be obtained with various types of sampling devices.

EXPERIMENTAL DESIGN AND TEST METHODS

This Study focused on the evaluation of three types of liquid sampling devices for the sampling of stratified liquids

from containers such as drums. The three types of liquid sampling devices evaluated were the Drum Thief, the COmposite Liquid WAste SAmpler (COLIWASA), and a new product, the Advanced Concepts & Design (ACD) liquid samplers. Further description of the sampling devices is provided in Attachment 1. These liquid sampling devices were chosen because they have all been recognized by the standards organizations as devices appropriate for liquid sampling (e.g., ASTM 1994, 1995, 1996, 1998; EPA 1986). The Drum Thief and the COLIWASA have also been the most commonly used liquid sampling devices in the collection of composite liquid samples. The Drum Thief and small volume models of the other two devices (COLIWASA-S and ACD-S) were evaluated for the collection of small volume liquid samples ≤250-ml. The COLIWASA-L and ACD-L models were evaluated for the collection of larger volume samples (i.e., 1000 ml).

Conditions of stratified liquid sampling were chosen because most data quality issues in containerized liquid sampling involve representative sampling of segregated liquids with different physical and chemical properties. Two essentially immiscible liquids, distilled water (=1.0) and more viscous corn oil (=0.9), were used in these tests to simulate simplified test conditions for stratified liquids. The evaluation involved two phases of study. In the first phase of testing, accuracy, precision, spillage, and sampling time were evaluated for samples collected from simulated waste drums containing equal proportions of water and oil (ratio - 1:1). Phase II tests involved the assessment of the accuracy and precision of the sampling devices for seven different water:oil ratios ranging from 95:5 to 5:95.

Test Conditions

All samples were collected under controlled laboratory conditions simulating the sampling of stratified liquids from 55-gallon waste drums. In the Phase I tests, 17 professional and 35 inexperienced volunteers collected samples with each of the five sampling devices from simulated waste drums under the supervision of laboratory personnel. The simulated waste drums consisted of cut-away 55-gallon barrels fitted with 4" ID acrylic cylinders 34" in length (5.6 liter capacity per cylinder) sealed on the bottom and mounted below the bung hole. In the Phase II tests, samples were collected from freestanding acrylic cylinders by a single individual. Measured volumes of water and corn oil were placed into the cylinders to simulate stratified liquid conditions. A user survey was also conducted in conjunction with the Phase I tests to obtain all independent assessment of the overall performance of each device from the perspective of user personnel. Details regarding, the experimental procedures of the Phase I and II tests are described in Attachment 2.

RESULTS

Nearly all aspects of liquid sampling performance were found to differ with the type of device used. Systematic under-sampling and/or over-sampling, of the liquids (bias) and spillage occurred with some devices. Most aspects of device performance appear to be attributable to the inherent design of the devices and the extent to which device performance is affected or influenced by the user. The magnitude of sampling error and spillage with some devices also appears to depend on the viscosity and proportions of the liquids.

Accuracy

The more viscous of the two liquids (oil) was systematically under-sampled with the Drum Thief and COLIWASA devices. Systematic differences in the accuracy of the sampling devices were observed across the range of water:oil ratios investigated (Figure 1a,b; Figure 2). Sampling accuracy with the Drum Thief and COLIWASA was found to be highly dependent on the water:oil ratio. The differences in sampling accuracy among the devices ranged to 18% at a water:oil ratio of 1:1 (Figure 2), and increased as the fraction of either liquid became smaller. The largest errors and differences in sampling accuracy occurred with the smallest liquid fractions (5%). At a water:oil ratio of 5:95, samples obtained with the COLIWASA-S were nearly 90% *larger* than the actual the proportion of water, and about 85% *smaller* with the Drum Thief (Figure 1a,b). This pattern of antipodal bias typically occurred with the Drum Thief and COLIWASA. Sampling accuracy was routinely high with the ACD devices among all users for both small and large volume models, with >96% accuracy across most of the range of water:oil ratios. For tests performed with a water:oil ratio of 1:1, under-sampling of one liquid resulted in complementary oversampling, of the other liquid by an equivalent amount. Sampling biases for tests performed at other ratios were not complementary (Figure 1).

Precision

Measurement reproducibility, i.e., precision, varied systematically with device type among multiple users, but varied little when used by a single individual. For the tests performed with a water:oil ratio of 1:1, the ACD devices produced the greatest precision among both experienced and inexperienced users. For the tests with a water:oil ratio of 1:1, measurement uncertainty (at the 95% confidence interval) with the Drum Thief and COLIWASAs were about twice as

large as that with the ACD devices (Figure 2). However, when all samples were collected by a single user, the sampling precision (at the 95% confidence interval) for all devices was >97% for all water:oil ratios. Thus, the level of precision produced by an individual user was significantly better that that produced among multiple users. Sampling precision appears to be only slightly influenced by user experience and to be generally insensitive to differences in liquid ratios.

Spillage

The amount of spillage from sampling and the variability in the spillage measurements differed systematically with device type. The average spillage with the small volume devices ranged from essentially zero with the ACD device (0.006 ml, 1 = 0.02 ml), to as much as 10% of sample volume (24 ml, 1 =13 ml) with the Drum Thief (Figure 3). For the tests with large volume devices. the COLIWASA-L yielded the greatest spillage and variability (up to 11 ml, 1 =6.7ml), and the ACD-L yielded the least spillage and variability (0.02 ml, 1 =0.07 ml) (Figure 3). The variability in spillage was generally observed to increase with the volume spilled. User experience resulted in reduced spillage only with the Drum Thief (by about 30%).

Sampling Time

The time required to collect samples with each of the devices varied systematically with the type of device used, and was lower among experienced users. Average sampling times for the devices ranged from 40 seconds to 120 seconds. The small volume samples obtained by inexperienced users were collected fastest with the ACD device. The COLIWASA-S required about 30% longer, and the Drum Thief took nearly three times as long (Figures 4). The same pattern of device performance was found for samples collected by experienced users, but with a 20%-30% reduction in sampling times with all devices. The sampling times with the larger volume devices required only about 10-15 seconds longer. Sampling with the ACD-L was consistently about 10 seconds (10-12%) faster than with the COLIWASA-L.

User Ratings

The ratings of specific devices by experienced and inexperienced users were nearly identical. The small and large volume ACD devices received the highest ratings (4.2 and 4.3 out of a maximum of 5.0: Figure 5). The two COLIWASA devices received the second highest ratings; about 3.0 for the smaller device. and 2.7-3.2 for the larger device. The Drum Thief was ranked lowest by both groups of users, receiving average scores of 1.3-1.5. The average ratings and the 95% confidence intervals for these scores are shown in Figures 5.

Other Comparisons

It was hypothesized that some aspects of sampling performance may be related to factors such as the height of the user and/or arm length for devices requiring 42" tubes to be lifted clear of the sampling vessel for the collection of the sample. However, no obvious correlation was found between any of the sampling performance parameters and physical characteristics of the user including height, user stature, or sex.

SUMMARY AND INTERPRETATIONS

The relative performance of the five liquid sampling devices evaluated in these tests is summarized in Table 1. As indicated in Table 1, the performance of the ACD-S device exceeded that of the Drum Thief and COLIWASA in essentially all categories of evaluation for small volume sampling devices, and the performance of the ACD-L exceeded that of the COLIWASA-L for large volume devices. The performance of the COLIWASA-S was somewhat better than that of the Drum Thief for most test parameters, but the accuracy obtainable with these two devices appears to vary from user to user. The relative performance of all five devices is also consistent with the ranking of device performance based on the survey of 17 professional and 35 inexperienced users. The two ACD devices received the highest ratings, followed by the two COLIWASA devices, with the Drum Thief receiving the lowest user ratings.

The systematic differences in sampling performance among the devices can largely be attributed to their design and function. Design factors that affect performance include the relative size of the opening through which liquids enter the sampler, closing mechanisms, and the tendency for sample leakage. These factors also appear to control the extent to which device performance is affected by the user.

Much of the sampling error with the COLIWASA and Drum Thief is related to the relatively small diameter opening on the sampling tube, which causes disproportionate amounts of the liquids to enter the tube. The magnitude of this error appears to depend on the opening diameter, the rate of insertion of the sampling tube into the liquids, and on

the proportions and viscosities of the liquids sampled. Although the guidelines for use of the COLIWASA and Drum Thief recommend a slow insertion, the rate of insertion necessary to minimize this error is never known in blind sampling. In practice, disproportionate amounts of water and oil were obtained with these devices by all users. These relationships are discussed further in manuscripts being prepared for publication.

Another important manifestation of this source of bias is the dependency of sampling accuracy on the water:oil ratio with the Drum Thief and COLIWASA because this error is magnified as the proportion of a liquid becomes smaller. Although sampling accuracy for all devices was >80% when the proportions of both liquids were greater than 10%, accuracy with the COLIWASA and Drum Thief decreased substantially when the fraction of the liquid was less than 30% (Figure 1a,b). At extreme water:oil ratios (e.g., 95:5) the accuracy with these two devices was as low as 10%. These results indicate that there are limits on the proportions of a liquid that can be sampled with these devices. Sampling accuracy with the ACD devices, however, was >96% for most liquid ratios and >85% for extreme liquid proportions. Although there may also be sampling limits with the ACD devices for other testing conditions, these limits appeal to be much smaller than those for Drum Thief and COLIWASA. Liquid viscosity is expected to affect the accuracy and limits of sampling with all these devices at some point. However, it is indicated from the results of this study that sampling accuracy with the ACD devices should be significantly greater than with the Drum Thief or COLIWASA for most sampling conditions.

These design and function factors also affect sampling accuracy with the Drum Thief and COLIWASA because they cause performance of these devices to vary from user to user. It is possible for individual users to obtain highly reproducible results with the COLIWASA and Drum Thief, whether or not they are accurate. But it is indicated from the results of this study that the uncertainty in sampling accuracy among users is two to three times higher with the COLIWASA and Drum Thief than with the ACD devices. The Drum Thief appears to be the most prone to user errors. The high sampling accuracy and precision obtained with the ACD devices among all users indicates that sampling quality with these devices is essentially independent of user factors, including user experience.

Design-related performance factors unique to the Drum Thief include the leakage of liquid from tire Drum Thief and the small tube volume necessitating multiple strokes for the collection of samples. Spillage and the potential for sampling error related to spillage is greatest with the Drum Thief because significant leakage of liquid from this device during transfer is inherent to its' use. Although leakage is negligible with the COLIWASA and ACD devices, spillage resulting from liquid on the outside of the sampling tube occurs with both the COLIWASA and Drum Thief. This Source of spillage occurs because the 42-inch tubes must be removed from the vessel being sampled, and lifted above eye-level to transfer the liquid to a sample container. With the Drum Thief, both types of spillage are compounded because multiple strokes are required to obtain a sufficient sample volume all forms of spillage are essentially eliminated with the ACID devices because they are designed for transfer of the liquid directly to a sampling container without removal of the tube from the vessel (e.g., drum). These factors also affect the time required to collect a sample. Samples were systematically collected more rapidly with the ACD devices than with the COLIWASA or Drum Thief because direct transfer of samples requires less time than removal of the tube for transfer. Sampling times with the Drum Thief are also up to three times longer because multiple strokes are required to obtain samples.

Although statistically significant differences were found in the performance of liquid samplers, these differences are specific to these test conditions. Based on the evaluation of these results, similar patterns of performance are expected for most other sampling conditions. The magnitude of the differences in device performance is expected to vary systematically with changes in physical properties of liquids such as viscosity and density. However, these relationships, and the effects of other factors such as suspended solids oil device performance are not presently known, and are the subject of further investigations.

There are many potentially important implications for the results obtained in this study. Although the practical significance of the differences in device performance must be assessed oil a case-by-case basis, these results have a number of broad implications for liquid sampling. The implications for significant differences in sampling accuracy are important because the objective of sampling is to determine the types and amounts of liquids present so they can be properly (and legally) handled and dispositioned. Representative sampling has safety, economic, legal, and practical implications because the accuracy of sampling determines, correctly or incorrectly, the type and level of hazards associated with the liquids. Errors in sampling accuracy have direct and indirect economic implications involving billings and associated costs that are based on the amounts of specific chemicals that must handled or

otherwise dispositioned. The level of sampling accuracy required also depends on the inherent hazard of the materials which is usually not known prior to sampling. Thus, sampling should be carried out in a manner capable of providing the highest practicable accuracy. The indication that the proportion limits on sampling with the Drum Thief and COLIWASA are relatively high (5%-30%) is especially notable because this implies that liquid fractions smaller than 30% are subject to significant sampling errors with these devices. Sampling precision requirements may also vary from case to case, but it is important that the quality of sampling be comparable and reproducible from user to user. Spillage has direct implications for worker safety and for the costs of handling spillage and any subsequent contamination in accordance with regulatory requirements Sampling time differences of up to 300% can have cost-benefit implications, but only if the quality of sampling is not compromised. Sampling time and ease of use can also be important when sampling must be performed in personal protection equipment (PPE) or under adverse (e.g., weather) conditions. Long-term implications of sampling performance also include the integrated cost savings associated with improved sampling efficiency and minimizing the negative implications of poor quality sampling.

CONCLUSIONS & RECOMMENDATIONS

Systematic differences in sampling performance were found between the Drum Thief, COLIWASA, and ACD liquid sampling devices in tests simulating the sampling of stratified liquids. Accuracy and precision were found to be highest, and spillage and sampling time least, with the small volume (⩽ 250 ml) and large volume (1000 ml) ACD devices. Sampling accuracy with the COLIWASA and Drum Thief appear to depend on the relative proportions of the liquids, viscosities, and on the users themselves. The ACD devices were found to be largely independent of user factors, including user experience for the test conditions evaluated, and to exhibit high sampling accuracy for proportions ranging from 5% to 95% of each liquid. The Drum Thief and COLIWASA appear to have limitations on proportion of a liquid that can be reliably sampled between 5%-30%. The overall performance of the devices based on a survey of 17 professional samplers and 35 inexperienced nolunteer samplers indicate that both groups of users rated the ACD devices highest followed by the COLIWASA, and the Drum Thief.

These results have potentially important implications for the handling and disposition of potentially hazardous liquids, and immediate implications for sampling efficiency and the reduction of risk to sampling personnel from spillage. The results provide a baseline for quantitatively comparing the performance of liquid sampling devices, for matching sampling needs with product performance, and also provides a basis for the improvement of sampling performance and sampler design.

Although these tests are specific to the test conditions used, these results provide insight regarding the factors that affect liquid sampling under these and other conditions. Tests with liquids over wider range of densities, viscosities, and liquid conditions including suspended solids, and numbers of liquids, will be required to establish functional relationships for the performance of these devices over the range of sampling conditions encountered in the field. Based on the results of this study, the ACD devices appear to provide significantly better sampling performance and data quality than the COLIWASA and Drum Thief for most conditions of stratified liquid sampling.

REFERENCES

American Society for Testing and Materials, 1994, Standard Practice for Sampling With a Composite Liquid Waste Sampler (COLIWASA), ASTM D5495-94, 2pp.

American Society for Testing and Materials, 1995, Standard Practice for Sampling Single or Multilayered Liquids, With or Without Solids, in Drums or Similar Containers, ASTM D5743-95, 5pp.

American Society for Testing and Materials, 1996, Standard Guide for Sampling of Drums and Similar Containers by Field Personnel, ASTM D6063-96, l8pp.

American Society for Testing and Materials, 1998, Standard Practice for Sampling Single or Multilayered Liquids, With or Without Solids, in Drums or Similar Containers, ASTM D5743-98, 7pp.

Coin prehensive Environmental Response, Compensation, and Liability Act (Superfund), 42 USC 9601 et seq., 1980.

EPA, 1986, Compendium of ERT Waste Sampling Procedures, EPA/540/P-91/008, U.S. Environmental Protection Agency, Washington, D.C.

EPA, 1991, Test Methods for the Evaluation of Solid Waste Physical/Chemical Methods, SW-846, 3rd ed., U.S. Environmental Protection Agency, Washington, D.C.

The Resource Conservation and Recovery Act of 1976, 42 USC 6901 et seq., 1976.

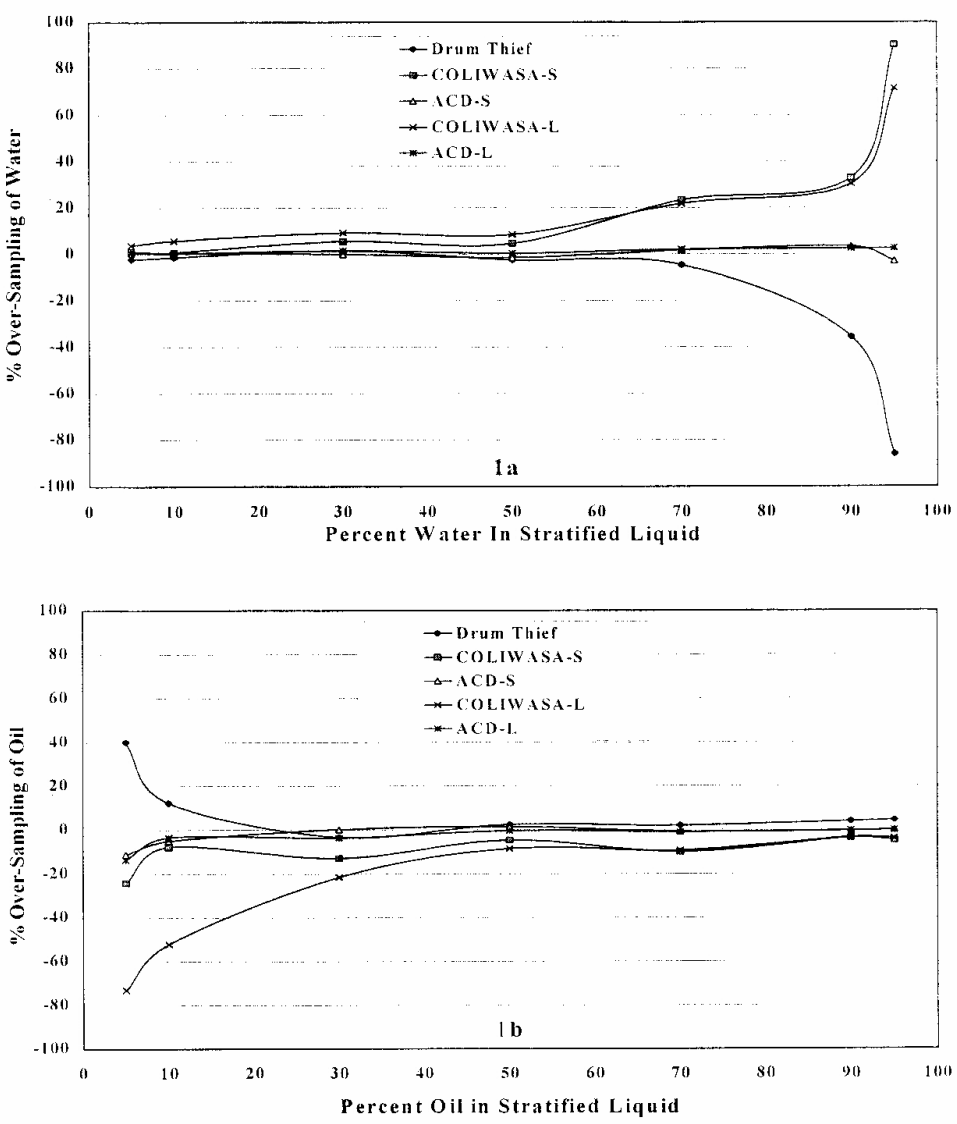


Figure 1a,b. Accuracy for test results at various water:oil ratios.
Accuracy of sampling for five liquid sampling devices at water:oil ratios ranging from 5:95 to 95:5. Sampling accuracy is indicated by the percent of over-sampling or under-sampling (bias); e.g., zero bias corresponds to 100% accuracy. Figure 1a shows the amount of over-sampling and/or under-sampling of water obtained with each device as a function of the amount of water present in the stratified liquids that were sampled. Figure 1b shows the amount of over-sampling and/or under-sampling of oil obtained with each device as a function of the amount of oil present in the stratified liquids that were sampled.

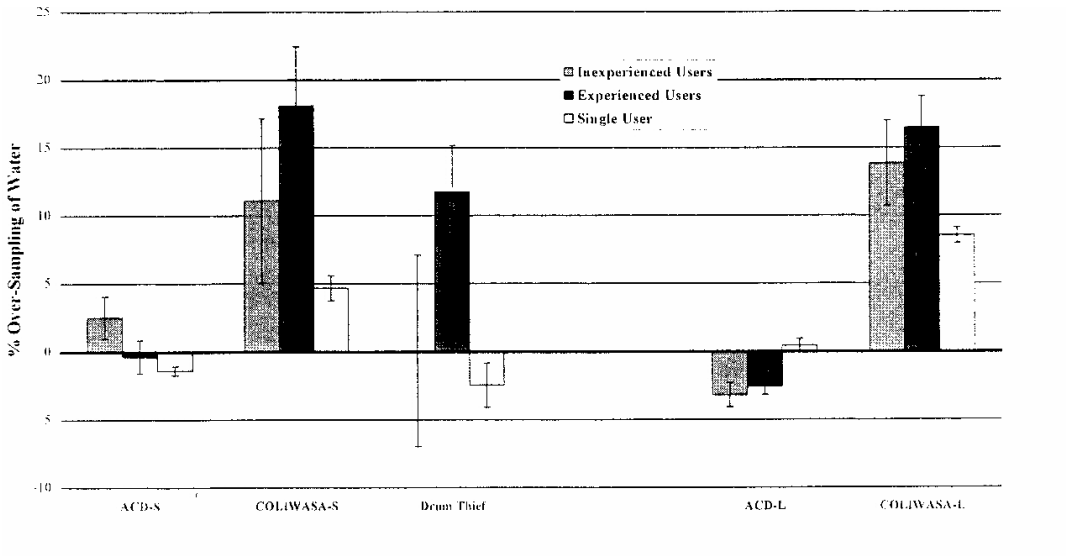


Figure 2. Accuracy and precision test results.
Accuracy and precision for liquid samples collected with five sampling devices by experienced inexperienced, and individual users. Sampling accuracy is indicated in terms of the average percent of over-sampling and/or under-sampling (bias) for water at a water:oil ratio of 1:1. Zero over-sampling corresponds to 100% accuracy. Bias levels for water mirror bias levels for oil (i.e., 10% over-sampling of water corresponds to 10% under-sampling of oil). The vertical lines at the top of each bar represent tile precision of the measurements at the 95% confidence interval (i.e., 95% confidence that the mean values lies within the range of these error bars).

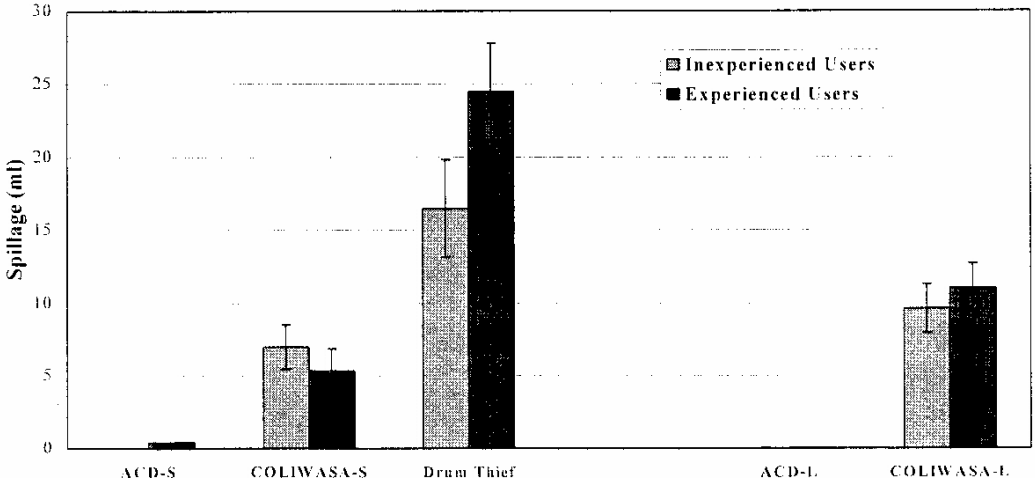


Figure 3. Spillage Test Results.
Amount of spillage resulting from the collection of liquid samples with five sampling devices. The height of the columns denote the average volume of liquid spilled (ml) by experienced and inexperienced in the process of collecting samples from simulated waste drums. Vertical lines at the top of each bar represent the 95% confidence intervals for the measurements.

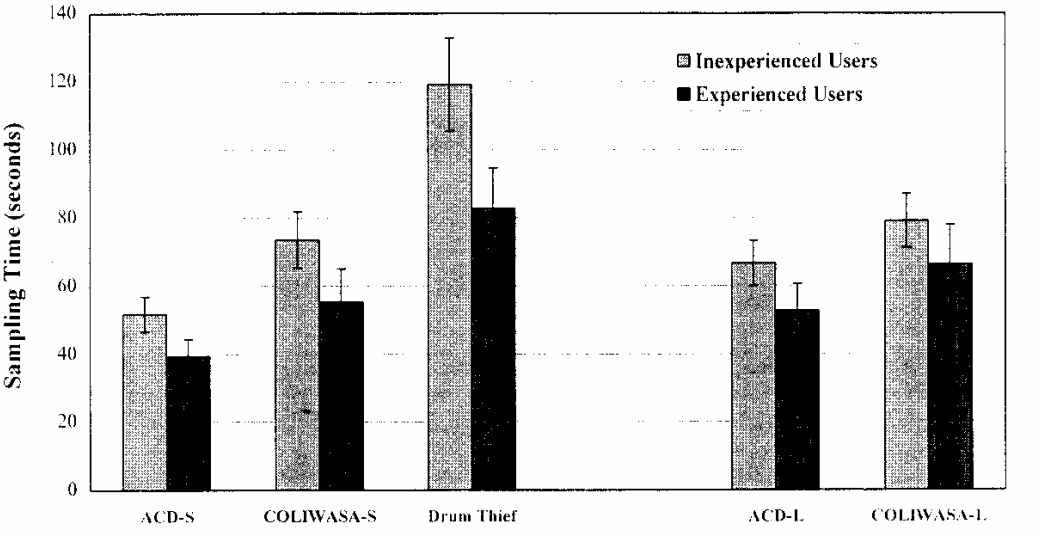


Figure 4. Sampling Time Test Results.
Time required for the collection of a sample with each of five sampling devices. The height of the columns denote the average time (in seconds) required for experienced and inexperienced users to collect a liquid sample from a simulated waste drum and transfer the liquid to a sampling container. Vertical lines at the top of each bar represent the 95% confidence intervals for these measurements.

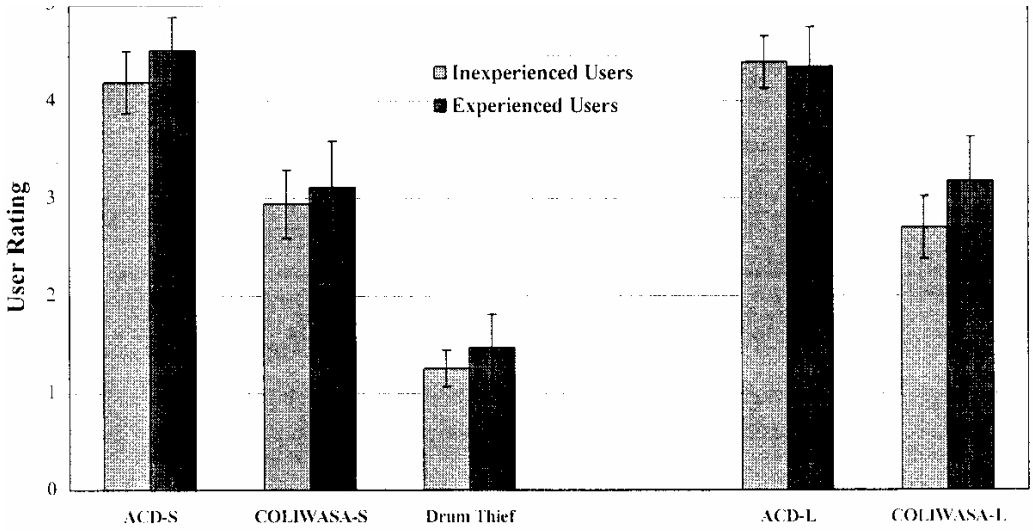


Figure 5. User Rating Results
Results of a survey of 17 professional and 35 inexperienced users regarding the performance of five liquid sampling devices. After collecting samples with each device, users scored each device on a scale of 1 to 5, with 5 = best, and 1 = worst. The heights of the columns denote the average user score. Vertical lines at the top of each bar represent 95% confidence intervals for the mean values.

	SMALL VOLUME SAMPLERS			LARGE VOLUME SAMPLERS	
	ACD-S	COLIWASA-S	Drum Thief	ACD-L	COLIWASA-L
EXPERIENCED USERS (n=17)					
Accuracy	○	●	◎	○	◎
Precision	○	●	◎	○	◎
Spillage	○	◎	●	○	◎
Sampling Time	○	◎	●	○	◎
User Ratings	○	◎	●	○	◎
INEXPERIENCED USERS (n=35)					
Accuracy	○	◎	○	○	◎
Precision	○	◎	●	○	◎
Spillage	○	◎	●	○	◎
Sampling Time	○	◎	●	○	◎
User Ratings	○	◎	●	○	◎
SINGLE USER (n=80)					
Accuracy					
Fraction = 1:1	○	◎	○	○	◎
Fraction 10% to 90%	○	●	◎	○	●
Fraction <10% or >90%	○	●	●	○	●
Precision (all ratios)	○	◎	◎	○	○

○ High Performance

◎ ⇩

● Low Performance

Table 1. Performance Summary for Liquid Sampler Tests.
Summary of results for tests with five liquid sampling devices. Level of performance of the three small-volume and two large-volume devices in each of the categories shown are indicated by symbols defined in the legend.

ATTACHMENT 1
Devices Tested
The liquid sampling devices evaluated in this study are all commercially available and were not modified or altered.

Drum Thief
The Drum Thief is a small diameter hollow tube (typically 0.42" ID) manufactured by Wheaton Scientific Products, which is used essentially like a large capillary tube or pipette. The Drum Thief model used in these tests was 42 inches long. Samples are collected with the Drum Thief by inserting the tube into a liquid container and liquid is allowed to enter the tube. The sample is collected by covering the exposed end of the tube with a finger/thumb or stopper, removing the tube from the container, and transferring the sample to an empty container. The sample volume varies with the size of the device, but about 75-100 ml of liquid can be obtained per stroke with the 42 inches long model. Multiple aliquots are collected if larger volume samples are required.

COLIWASA
The COLIWASA, an acronym for COmposite LIquid WAste Sampler, manufactured by Wheaton Scientific Products, is constructed as a larger diameter open tube with a closure mechanism at the lower end. The COLIWASA is typically 42" long and 0.7" ID for the small volume model (~200 ml), and 1.5" for the larger volume (~1000 ml) models. The tube is tapered at the lower end, or fitted with a reduction plug about half of the tube diameter. Liquid samples are collected with the COLIWASA in a similar manner as with the Drum Thief, except that lower end of the tube is manually closed from inside the tube using a tapered plug attached to a small diameter tube (or rod) somewhat longer than the collection tube. After liquid has entered the collection tube and the lower end plugged, the

device is removed from the container, and the sample is drained into a sample jar.

ACD Samplers
The third type of sampling device tested was a product developed and manufactured by Advanced Concepts & Design (AC&D), Inc. The ACD devices are essentially have an open tube design (0.87" and 1.5" ID) in which fluid in the sample tube is manually drawn by pulling a small cone-shaped plastic plunger upward from the bottom of the tube using an attached rod or cord extending the length of the collection tube. A sample container (jar) adapter is attached at the upper end of the tube to receive the sample. Samples are obtained with this device by lowering the collection tube into the liquid and transferring the liquid from the tube to the sampling container (jar) by pulling the plunger up through the tube with the rod or cord, essentially pumping the liquid from the tube into the aligned sample jar without removing the collection tube from the sampled vessel (e.g., drum).

The COLIWASA and the ACD devices both have small volume (~200-250 ml) and large volume (~1000 ml) models. All three devices are available in glass and high density polyethylene (HDPE) models.

ATTACHMENT 2
Laboratory Procedures
Phase I Testing
Samples were collected with each of the five sampling devices from simulated waste drums under the supervision of laboratory personnel. The simulated waste drums consisted of cut-away 55-gallon barrels fitted with 4" ID acrylic cylinders 34" in length (5.6 liter capacity per cylinder) sealed on the bottom and mounted below the bung hole. Sampling was performed by two groups of volunteer. A total of' 250 samples were collected by 17 experienced (professional) samplers, and 35 inexperienced participants with no prior sampling experience. A description of the study and procedures for the use of each device was provided to each participant (herein referred to as users) prior to testing. Each user was tasked with drawing a sample from each of five simulated waste drums using one of the five liquid sampling devices at each drum station, and transferring the samples to clean sampling containers (jars) placed on top of the drum.

Data on the sample volume, liquid ratios, sampling time, and spillage were obtained for each sample collected. Pre-weighed drip trays and absorbent material (e.g., paper towels) were placed on the top of the barrels to capture spillage associated with the transfer of liquid from the drum to the sampling jars. At the conclusion of each sampling series, laboratory personnel measured the water:oil volume ratio and total volume in each sampling jar in graduated cylinders. The drip trays were then re-weighed to quantitatively assess the spillage associated with each device. The sequence in which the devices were used was rotated randomly between users to minimize bias due to the sequence in which the devices were used. All devices and testing materials were thoroughly cleaned between sampling series, liquid columns refilled and recalibrated, and pre-measured spill trays replaced.

All participants completed a user survey at the conclusion of their sampling series. In the survey, users rated each device in terms of overall performance, and commented on device features, attributes, and shortcomings. Users also provided personal information on experience and physical characteristics such as height, sex, and age. Measurements were also made of wrist girth and forearm length to assess correlation between sampling performance and physical characteristics of the users.

Phase II Tests
Sampling procedures similar to those used in the Phase I tests were employed in the Phase II tests. However, all samples were collected from freestanding acrylic cylinders by a single individual. Multiple samples were collected with each sampling device for water:oil ratios ranging from 95:5 to 5:95. A total of 216 samples were collected in Phase II testing. The following are the water:oil ratios, and the number of measurements made at each ratio.

<u>Numbers of samples collected in Phase II testing at each water:oil ratio</u>
Preliminary test, were performed with glass and plastic models of the COLIWASA and Drum Thief to assess performance among these models of the same brand. The samples were collected with each of the seven device models at a water:oil ratio of 50:50, including ten single-stroke and double-stroke samples with both of the COLIWASA-S models. The best performing models of the Drum Thief and COLIWASA-S were then used in tests at other water:oil ratios. The glass model of the Drum Thief was selected based on slightly better sampling accuracy than the high-density polyethylene (HDPE) model. The COLIWASA-S with the (HDPE) plunger head was selected

for use in the remaining tests because its' sampling accuracy was slightly better than that with the model with a borosilicate plunger head. The COLIWASA-L and ACD devices tested were all composed of HDPE. Single stroke measurements were also made for the purpose of independently evaluating the accuracy and uncertainty of samples obtained from multiple stroke composites.

RATIO	COLI WASA-Small - Glass head - Plastic head		Drum Thief - Glass model - Plastic model		COLIWASA Large	ACD Small	ACD Large
water/oil	Single stroke	Double stroke	Single stroke	Five stroke	Single stroke	Single stroke	Single stroke
95/5	3	3	3	3	3	3	3
90/10	3	3	3	3	3	3	3
70/30	3	3	3	3	3	3	3
50/150	10	10	10	10	10	10	10
30/70	3	3	3	3	3	3	3
10/90	3	3	3	3	3	3	3
5/95	3	3	3	3	3	3	3

The following steps were routinely followed in the conduction of Phase I and Phase II testing:

- Each sampler was cleaned before use.
- The plunger head was consistently lifted to a height of 4-inches prior to inserting tile sampling tube into the liquid-filled acrylic cylinder.
- A constant insertion rate of approximately 0.5 inches per second was used with all devices.
- Sampling devices were closed and sample transfer was initiated immediately after the head of the sampling tube reached the bottom of the acrylic cylinder.
- The Drum Thief and COLIWASA samplers were removed from the acrylic cylinder by pulling them up through a rag to wipe out excess fluid on the outside surface.
- Samples obtained with the Drum Thief and COLIWASA devices were transferred directly to graduated cylinders.
- Samples obtained with the ACD-S and ACD-L devices were first collected in 250ml and 1000ml jars respectively, and then transferred to graduated cylinders. The jars were allowed to drain into the graduated cylinders for up to 60 seconds so that transfer loss was negligible.
- Sufficient amount of time (up to 20 minutes) was allowed for the sample in the graduated cylinder to be segregate into layers of water and oil prior to recording the total volume and water and oil volumes of.
- Ambient room temperature was recorded at the beginning of each series of tests. An ambient room temperature from 19-21^{o}C was maintained for all tests.
- The density of oil in each simulated waste cylinder was determined on daily basis at the beginning of each experiment. Distilled water was used in all tests.

ANALYSIS OF CHEMICAL WARFARE AGENT DECONTAMINATION BRINES FOR LEWISITE DEGRADATION PRODUCTS USING GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTION

Kevin M. Morrissey, Theresa R. Connell, and Jeffrey Mays
EAI Corporation, 1308 Continental Drive, Suite J, Abingdon, Maryland 21009
Tel: (410) 612-7332/Fax: (410) 612-7317
E-mail: kmmorris@eaicorp.com
H. DuPont Durst
US Army, CBDCOM, Edgewcod Research, Development, and Engineering Center, Edgewood, Maryland 21009
Tel: (410) 671-5270/Fax: (410) 671-2081
E-mail: hddurst@cbdcom.apgea.army.mil

Bulk chemical warfare agent (CWA) storage containers which contain decontaminated CWA waste are stored at several locations throughout the United States. Most of these containers have been in storage since the mid 1970's, and little analytical work has been performed to characterize the contents. This work reports on the efforts to determine whether these ton containers may have contained Lewisite (L, 2-chlorovinylarsonous dichloride, CAS No. 541-25-3), an arsenic containing CWA. This work summarizes the efforts at analyzing 250 ton containers stored at a single location.

In the presence of water, Lewisite quickly hydrolyzes to 2-chlorovinylarsenous acid (CVAA, CAS No. 159939-86-3), and this hydrolysis product is not directly amenable to gas chromatographic analysis. The CVAA was derivatized with 1,3-propanedithiol (PDT, CAS No. 109-80-8), and analyzed by gas chromatography/atomic emission detection (GC/AED). Quantitation was accomplished using response in the arsenic channel, with supporting data collected in the sulfur and carbon channels. Spike recovery experiments were performed at 7 different levels, and data will be reported. In addition, total arsenic was determined by ICP/MS, and supporting techniques of GC/MSD, LC/MS and CE were used to confirm the presence of CVAA and other L hydrolysis products.

Detectable levels of total As were observed in 25 of the ton containers by ICP/MS. The total As values ranged from just over the detection limit of 1 ppm, to well over 7800 ppm. Detectable levels of CVAA were observed in 17 of the ton containers by GC/AED. The CVAA levels ranged from just over the detection limit of 0.008 ppm to 2.4 ppm. In addition to the CVAA, additional organo-arsenic compounds were detected in several of the ton container samples. These additional organo-arsenicals may be indicative of the presence of other As containing CWA, interaction of CVAA with sulfur mustard (HD, CAS No. 505-60-2) hydrolysis products, or As containing industrial waste. Correlations will be made between the presence of CVAA and other CWA hydrolysis products.

EPA'S ENVIRONMENTAL MONITORING RESEARCH PROGRAM

INTRODUCTION, SESSION SCOPE AND PURPOSE

William Stelz
US EPA, Office of Research and Development, 401 M St., SW, Washington, DC

NO ABSTRACT AVAILABLE

BIOAVAILABILITY AND RISK ASSESSMENT OF COMPLEX MIXTURES

K.C. Donnelly, W.R. Reeves, T.J. McDonald, L.-Y. He and R.L. Autenrieth
Departments of Veterinary Anatomy & Public Health and Civil Engineering,
Texas A&M University, College Station, TX

There is an urgent need to develop an accurate method to assess the risk associated with contaminated soils and complex mixtures. Perhaps more importantly, this method should provide a means of defining acceptable residue levels to allow a more cost effective approach to site remediation. This research program is developing a methodology which can be used to estimate bioavailability. Two soils have been prepared for evaluating the bioavailability extraction method. One soil is a Weswood silt loam amended with model chemicals, including chrysene, pyrene, phenanthrene and anthracene; while the second soil is a Weswood silt loam amended with 10% (wt/wt) wood preserving waste (WPW). The soil was spiked with either the model chemicals or the complex mixture and samples collected immediately after spiking, as well as after 60 and 360 days of incubation (note day 360 samples will be collected in the fall of 1998). Soil was extracted with pH 7 water or a 1:1 methanol:water mixture. Other solutions to be tested will include a gastric solution (pH 2) and an intestinal solution (pH 7) and a 3:1 methanol:water mixture. Extractions are performed by shaking 40 g of soil with a 200 mL volume of extracting solution for 2, 3, or 5 hours (depending on the extractant) at 37ºC. Recoveries were determined using GC-FID. In addition, these extractions will be compared to results from desorption kinetics studies. Results from the digestive fluid extractions indicate that the stomach to intestinal fluid conversion (GI) extracted only 5.4% and 0.11% of that recovered by standard methods for chrysene and pyrene, respectively. Using these numbers as an estimate, the hypothetical excess lifetime cancer risk for the hexane:acetone extraction would be 7.1E-5, while the estimate for the GI fluid was 1.3E-7. The desorption study reveals two compartments: one slowly desorbing and solubility limited, and one limited by desorption/diffusion, which increases in size as the soil ages. An animal study is planned for this summer using the soil from this study as a means of evaluating these methods in a rodent model. This research is supported by USEPA Grant No. R825408.

FIELD DETERMINATION OF ORGANICS FROM SOIL AND SLUDGE USING SUB-CRITICAL WATER EXTRACTION COUPLED WITH SPME AND SPE

Steven B. Hawthorne, Carol B. Grabanski, Arnaud J.M. Lagadec, Martin Krappe,
Cedric L. Moniot, and David J. Miller
Energy and Environmental Research Center, University of North Dakota,
Grand Forks, North Dakota, USA 58202

We have demonstrated that subcritical water (hot water maintained as a liquid by a few bar pressure) is an excellent solvent to quantitatively extract polar and non-polar organics from soils and sludges. Subcritical water extractions can be highly selective; polar organics extract at lower temperatures (e.g., phenols and amines extract at 50 to 100 ºC), and non-polar organics extract at high temperatures (e.g., 200 to 250 ºC). By heating water under low pressure, solubilities of polar organics increase dramatically, and even non-polar organics such as PAHs can increase solubilities by > 10^6-fold.

For water samples, both SPE (solid phase extraction) and SPME (solid phase microextraction) can be used to extract and concentrate organics in the field for subsequent analysis (e.g., field-portable GC), but are not applicable to extracting organic pollutants from solid samples. If organic pollutants on soils and sludges could be efficiently transferred to water, both SPE and SPME could be very useful for field determinations of organic pollutants from solids. The primary purpose of the proposed investigations is to couple SPE and SPME with subcritical water extraction of soils and sludges to allow field-portable water methods to be applied to contaminated solids.

We have coupled subcritical water extraction with SPME using very simple, inexpensive, and field-portable equipment. The method uses a static extraction (no pump), no flow restrictor, and no organic solvent. Soil, water, and internal standards are placed in an extraction cell and heated for 15-60 minutes. The cell is then cooled and the water extracted using a SPME fiber followed by direct desorption in a GC injection port. Although the method involves multiple partitioning steps (water/soil, and water/SPME), quantitative results can be obtained using proper internal standards, e.g., deuterated PAHs are added to calibrate for PAH determinations. Methods have been developed for PCBs, PAHs, and aromatic amines which give good quantitative comparisons to conventional (Soxhlet) extraction. Typical sample preparation time is < 1 hour, and detection limits of < ppb are obtained.

In contrast to the multiple partitioning steps involved in the coupled subcritical water/SPME method, coupling subcritical water with SPE discs (e.g., "Empore" discs) should allow quantitative extraction and collection of organic analytes. For example, when a static extraction cell contains the soil, water, and an SDB disc, PAHs extract from the soil into the water during the 250 ºC heating step, but then are efficiently collected (ca. 90 %) on the sorbent disc as the extraction cell is cooled to room temperature. The PAHs are then eluted from the disc in a few mL of solvent, and the extracts analyzed by conventional GC methods. Similar approaches are being developed for PCBs. In addition, the use of subcritical water to aid in derivatization reactions for the SPME or SPE collection and analysis of more polar solutes (e.g., acid herbicides, natural pyrethrins) will be presented.

A FIELD PORTABLE CAPILLARY LIQUID/ION CHROMATOGRAPH

T. Scott Kephart, C. Bradley Boring and Purnendu K. Dasgupta
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061
James N. Alexander, IV
Rohm and Haas Company, 727 Norristown Road, P.O. Box 904, Spring House, Pennsylvania 19477-0904

INTRODUCTION

The need for on-site, real time characterization of environmentally hazardous sites has led to a considerable interest in the development of self-contained field-portable instrumentation. Presently, two factors limit the use of field portable instruments for environmental analysis. First, most portable instruments do not compare favorably to laboratory-based instruments with respect to reliability and performance. Second, the availability of stand-alone field portable equipment is limited primarily to chemical analyzers or sensors which measure a single physicochemical property such as pH, temperature, or UV/VIS absorbance, although more sophisticated instruments such as X-ray fluorescence analyzers, mass spectrometers, and Fourier transform IR systems have recently been developed[1]. Bringing samples collected in the fields back to the laboratory for analysis results in a time lag that can compromise sample integrity as well as delay any needed response prompted by the analytical result.

Analysis in the field often requires the separation of multiple analyte species before detection and quantitation. For the environmental analyst, liquid chromatography (LC), including ion chromatography (IC), and gas chromatography (GC) remain the primary techniques of choice. Although field portable GC systems have been commercially available for some time, field portable LC systems are virtually non-existent. If used in the field, LC systems typically have to be located in a mobile laboratory, making them at best only moderately portable.

The practice of capillary LC has undergone extensive development since its introduction twenty years ago[2]. The primary advantages of moving from conventional size columns ($\geq$ 4 mm i.d.) into the capillary domain include higher

efficiencies, higher mass sensitivities, low eluent consumption, and a very small sample requirement. LC hardware components other than the absorbance detector have been miniaturized with the development of capillary chromatography. Fully automatable injection valves are available down to 20 nL; small, compact, and inexpensive syringe pumps with very low power requirements have been developed.

Recently, we described a capillary IC with suppressed conductometric detection for anion analysis[3]. The miniaturization of LC hardware components in combination with the excellent performance of this bench-top capillary IC, led us to investigate the feasibility of a field portable capillary IC/LC system.

In this paper, we present a fully computer controlled, stand-alone field portable capillary IC. Further, we describe a dual syringe pump capillary LC system that is in the process of being prepared for field use. The construction and performance of each of these capillary systems is reported.

EXPERIMENTAL

The layout of the capillary IC and capillary HPLC systems are shown in Figure 1a and 1b, respectively. The pumps used were fully computer controlled 48 000 step, motor driven syringe-type dispensers (Model 50300, Kloehn Inc., Reno, NV) equipped with syringes of appropriate size. A 500 µL glass syringe was used for capillary IC; stainless steel syringes (constructed in-house) were used for capillary HPLC because operating pressures are well above 1000 psi. A stainless steel block was machined in-house with appropriately sized ports to accommodate the appropriate syringe head, a low leak dual ball and seat inlet check valve (P/N 44541, Dionex Corp., Sunnyvale, CA), and a liquid output port, A small volume eluent reservoir was affixed next to the syringe dispenser and was connected to the check valve with PEEK tubing to avoid CO_2 intrusion. A pressure sensor (Model SP70-A3000, Senso-Metrics, Simi Valley, CA) was connected to the liquid output port of the stainless steel block using 0.25 min i.d. PEEK tubing. The column backpressure was continuously monitored to insure proper system performance.

Capillary IC System

Water pumped by the syringe was passed through a mixed bed ion exchange resin to remove any impurities leached from glass and metal parts in the upstream components. A previously described microscale electrodialytic sodium hydroxide generator[3] (EDG) was used for eluent production. A mildly pressurized reservoir of 25 mM sodium hydroxide was used as the donor solution for the EDG. A 10 cm long polystyrene capillary, ~80 µm i.d., 250 µm o.d., was placed at the exit of the EDG to remove the H_2 gas in the eluent stream by permeation through this tube. The polystyrene capillary was able to perform gas removal at pressures > 900 psi at NaOH concentrations > 40 mM.

A hollow fiber suppressor, which has been previously described,[3] was deployed prior to the detector. A H_2SO_4 regenerant reservoir, mildly pressurized (< 1 psi), was connected to the suppressor using Tygon tubing. The suppressor was able to suppress NaOH concentrations ranging from 0.5 to 40 mM to a background of $\leq$ 2 µS/cm with eluent flow rates of 1.5-2.2 µL/min. A conductivity cell was connected at the suppressor exit. A bipolar pulse conductivity detection system[4] was used for the IC system. A laptop computer in combination with an executable program, written in C, provided a user interface for the data acquisition system.[5]

Capillary HPLC System

The dual syringe pump capillary HPLC system is shown in Figure 1b. The syringe pumps were coupled to a mixing chamber, having an internal volume of 2 µL, for isocratic or gradient eluent production in the capillary HPLC system. To produce a constant flow rate while operating in the gradient mode, this setup required a custom control program to be written. An executable program written in Microsoft Visual Basic® provided a user interface for instrument control. A typical gradient program utilizes a six step gradient, although more steps can easily be added. The program calculates the appropriate delay between steps for each pump, given the total flow rate, in terms of the percentage of flow necessary from each pump. The program then creates a command string with the appropriate delays for each pump and downloads this into the resident memory of the pump hardware via an RS-232 serial communication port. A Linear model UVIS 200 absorbance detector (Spectra-Physics/Thermoseparation systems), designed for on-column detection with capillaries, was used for HPLC detection. A smaller detector will be developed in the future.

An electrically actuated injection valve equipped with 20-100 nL internal sample loops (Valco Instruments, Houston, TX) was used for sample introduction.

Analytical columns, ~50 cm long, 180 µm i.d. fused silica capillaries (Polymicro Technologies), were packed in-house. The IC columns were packed with the same packing as commercially available Dionex AS-11 columns. The reverse phase HPLC columns were packed with 5 µm PRP-1 and 5 µm HSC-18 particles, respectively. A frit was made at the exit end of the column by placing several short pieces of glass wool into 0.3 mm i.d. PTFE tubing and push fitting the end of the column and a 75 µm i.d., 365 µm o.d. fused silica capillary on either side of the glass wool. No frit was needed at the front of the column. This configuration allowed the front of the column to be easily trimmed when compression of packing material at the head of a column led to a void over a period of time.

For IC experiments using sample preconcentration, the preconcentration column consisted of an ~1.5 cm long piece of 250 µm i.d. fused silica capillary packed with AS-11 packing. The exit frit was constructed by first pushing a small piece of glass fiber filter (Whatman type GF/A, Maidstone, England) into this capillary ~1 cm from the end of the packing. A 50 µm i.d., 150 µm o.d. fused silica capillary was then pushed inside the larger capillary against the glass fiber filter and epoxied into place. The total length of the preconcentrator column was ~8 cm. The electrically actuated sample injector was equipped with a six port valve (Cheminert Model C3-1006-EH, Valco Instruments Co. Inc.), having internal dead volumes of 200 nL between each port, to accommodate the preconcentrator column.

A 24 Vdc power supply (Lambda Electronics, Melville, NY) was used to power the pumps and pressure sensor. A 24Vdc-10Vdc converter was built in-house to provide the pressure sensor with 10 Vdc operating voltage. The bipolar pulse conductivity detector (capillary IC system only) used a 5 Vdc power supply for operation.

Atmospheric Sampling

The capillary ion chromatograph was interfaced to a miniaturized parallel plate diffusion denuder (PPDD) to monitor ambient levels of sulfur dioxide. The PPDD construction is shown in Figure 2. The PPDD was constructed from two Plexiglas plates, each measuring 2 x 17 cm. The active area of the PPDD (0.6 x 10 cm) was prepared by thermally pressing silica gel particles (120 mesh or smaller) onto the Plexiglas plates. The two plates were separated by 1.5 mm thick Teflon coated Plexiglas spacers, 0.7 x 17 cm, which completely cover the untreated edges of the plates. Holes were machined in the top and bottom of the silica coating to provide a liquid input and output, respectively. Stainless steel tubing (23 gauge) was push fit into these holes and epoxied to the plates to provide rigid liquid input/output ports. The two plates were clamped together along their edges. Tubing for the air inlet and air outlet was fixed by epoxy adhesive at the bottom and top of the PPDD, respectively. Hydrogen peroxide (0.5 mM, 30 µL/min flow rate) was used as the denuder liquid. The denuder effluent was loaded onto a preconcentration column at a flow rate of 18 µL/min for 10 minutes for analysis. The PPDD displayed ~100 % collection efficiency up to an air sampling rate of 0.5 standard liters per minute (SLPM). Data presented here was obtained using this sampling rate.

RESULTS AND DISCUSSION

Portable Capillary IC

System Performance

The day to day reproducibility of the portable IC is shown in Figure 3 for repeated injections of fluoride, chloride, sulfate, and phthalate. The chromatograms were obtained under isocratic conditions using an ~20 mM NaOH eluent at a flow rate of 1.5 µL/min. The relative standard deviation of retention times ranged from 0.1% to 0.7% within one day and 0.3% to 0.8% day-to-day. Peak efficiencies for chloride, sulfate, and phthalate were 27 133, 21 018, and 15 422 plates/m, respectively.

Response linearity was studied under the same chromatographic conditions as above. A sample solution containing chloride, sulfate, and phthalate over a concentration range of 10-200 µM was used; fluoride eluted near an impurity and therefore was not used for evaluating response linearity. Linear r^2 values for peak area response vs. injected concentration for chloride, sulfate, and phthalate were 0.9959, 0.9988, and 0.9974, respectively. Above a concentration of 200 µM, peak broadening resulted from column overloading.

The three constituent mixture was also evaluated in terms of attainable limits of detection (LOD) under the same isocratic conditions. The intrinsic electronic noise of the bipolar pulse detector electronics was 0.3-0.4 nS. The noise increased to 2-3 nS/cm during chromatography, regardless of NaOH concentration or flow rate employed. Based on the performance at an injection concentration near the baseline and the peak-to-peak noise level, the S/N = 3 LOD for the three anions are as follows (LOD in µM indicated in parenthesis): chloride (0.03), sulfate (0.12), and phthalate (0.25). This performance is comparable to conventional size IC systems. However, an increase of >2 orders of

magnitude in terms of mass sensitivity is realized in the present system compared to the performance of a bench-top IC using conventional size columns.

Gradient Chromatography
Incorporation of the EDG on the high pressure side of the pump also allows gradient chromatography to be performed easily. The lag time, or time required for the produced NaOH to reach the head of the column from the EDG, was measured to be 1.5 minutes using an eluent flow rate of 1.5 µL/min. Therefore, only a short time is needed for a specific programmed NaOH concentration to reach the head of the column. A gradient chromatogram of a sample containing 15 anions is shown in Figure 4. A linear gradient of ~2 mM to 38 mM NaOH from 5 min to 17 min was used for the separation. This corresponded to a current requirement of 5-95 µA using a water flow rate of 1.5 µL/min. The resulting separation was excellent. Peak efficiencies ranged from 10 648 plates/m for acetate to 240 152 plates/m for chromate, with an average of 80 000 plates/m being observed for the separation.

Miniaturized PPDD Coupled Capillary Ion Chromatography System
An air sampling rate of 0.5 SLPM was chosen for evaluation of the PPDD-capillary IC system due to the collection efficiency of the PPDD being ~100% at this sampling rate. The response linearity was studied over an SO_2 concentration range of 23 pptv to 1944 pptv (at an SO_2 concentration $\geq$ 2000 pptv, sample peak height reached the maximum value permitted with the conductivity detection system). The response linearity over this concentration range was excellent. A log-log plot of peak height vs. SO_2 concentration resulted in a linear r^2 value of 0.998. The reproducibility of the data over this concentration range was $\leq$ 3.2% RSD for each point sampled. Figure 5 shows a chromatogram resulting from the sampling of clean air and 80 pptv SO_2. These data lead to a computed limit of detection of 1.6 pptv SO_2.

Ambient Air Studies
The ambient concentration of SO_2 was studied in Lubbock, TX over a period of 48 h. The system operated over this time period without any user intervention. The results are shown in Figure 6. These results correlate well with the ambient SO_2 levels at this location.

Capillary HPLC System
Isocratic Elution
Experiments evaluating retention time reproducibility were performed on the PRP-1 column injecting samples of biological interest. A solution of 100 mM ammonium formate (pH 4.25) was contained in pump A and the same solution containing 10% acetonitrile was contained in pump B. Figure 7 shows system reproducibility for isocratic elution of 8 sample components with a 50:50 A and B mix.

The average RSD in retention times for the 8 component mixture was 0.825%. Using only a single syringe pump and employing the same eluent conditions, the average RSD in retention times was 0.921%. The fact that the dual pump system actually has a lower average RSD indicates that the main source of retention irreproducibility is not from the pumping system but comes from other components.

Gradient Elution
The gradient capabilities of the system were examined by separating a series of benzene derivatives on the HSC-18 column. Pump 1 contained a mixture of acetonitrile and water (50:50); pump 2 contained only acetonitrile. Figure 8 shows a sample chromatogram that also indicates the gradient profile. Figure 9 shows the dual pump gradient reproducibility. The average RSD in retention times under gradient conditions was 0.545%. This corresponds to a variation of 2.05 (±.88) seconds for 10 peaks eluting in under 8.5 minutes.

System performance in terms of peak efficiency for the gradient HPLC system was also evaluated. The maximum peak efficiency was observed for ethylbenzene, which had 320 000 theoretical plates per meter. The average peak efficiency for the 10 components was 220 000 theoretical plates per meter. This correlates to an average of 17 000 plates per minute.

ACKNOWLEDGMENT
This research was supported by the U. S. Environmental Protection Agency through Grant R82-5344-01-0. The manuscript has not, however, been reviewed by the agency and no endorsements should be inferred.

REFERENCES

1. Newman, A. R. *Anal. Chem* **1991**, *63,* 641A-644A.
2. Ishii, D.; Asai, K.; Hibi, K., Jonokuchi, T.; Nagaya, M. *J. Chromatogr.* **1977***,144,* 157-168.
3. Sjögren, A.; Boring, C.B.; Dasgupta, P.K.; Alexander, J.N. *Anal. Chem* **1997***, 69,* 1385-1391.
4. Kar, S.; Dasgupta, P. K.; Liu, H.; Hwang, H. *Anal. Chem* **1994***, 66,* 2537-2543.
5. Boring, C.B.; Dasgupta, P.K. and Sjögren, A. *J. Chromatogr.* **804***,* 45-54 (1998).

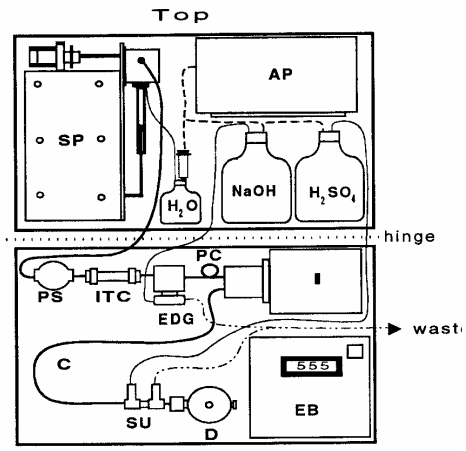


Figure 1a. Schematic layout of portable IC system. Figure designations: SP, syringe pump; AP, air pressure pump; PS, pressure sensor; ITC, ion trap column; EDG, electrodialytic sodium hydroxide generator; PC, polystyrene capillary; I, motorized injector; C, capillary column; SU, chemical suppressor; D, detector; EB, electronics box.

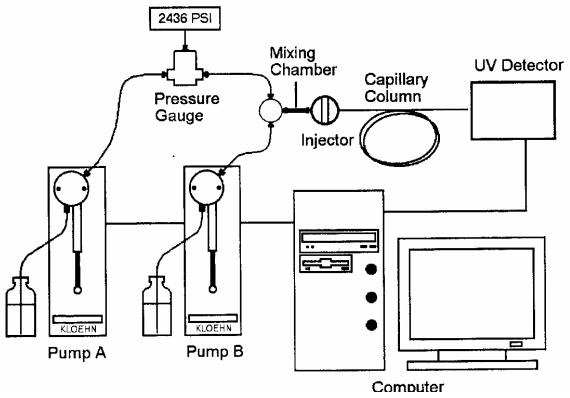
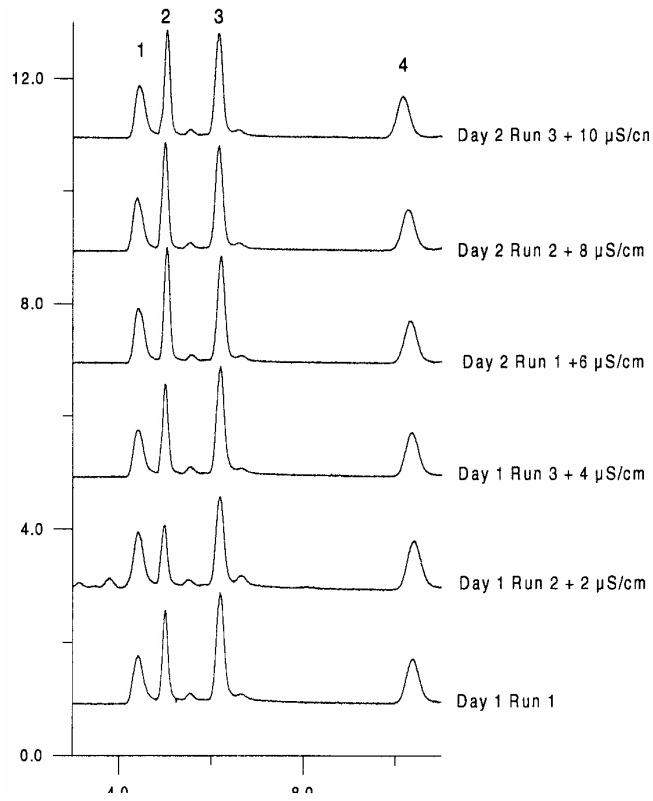


Figure 1b. Schematic layout of capillary HPLC system.



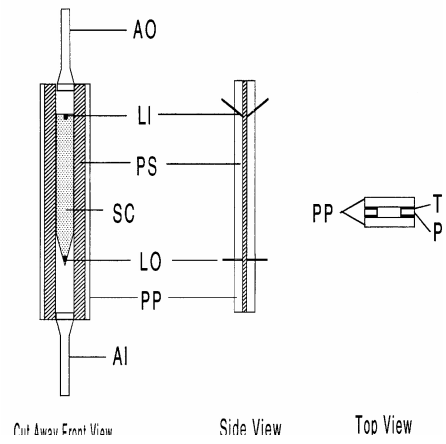


Figure 2. Wet parallel plate diffusion denuder. Figure designations: AO, air outlet; LI, liquid inlets; PS, Teflon coated Plexiglas spacer; SC, silica coating; LO, liquid outlet; PP, Plexiglas plates; AI, air inlet; TF, Teflon film

Figure 3. Day-to-day system reproducibility; repeated 100nL injections with ~20 mM NaOH eluent. Injected concentration was 20 µM for each ion. Peak identities: 1, fluoride; 2, chloride; 3, sulfate; 4, phthalate.

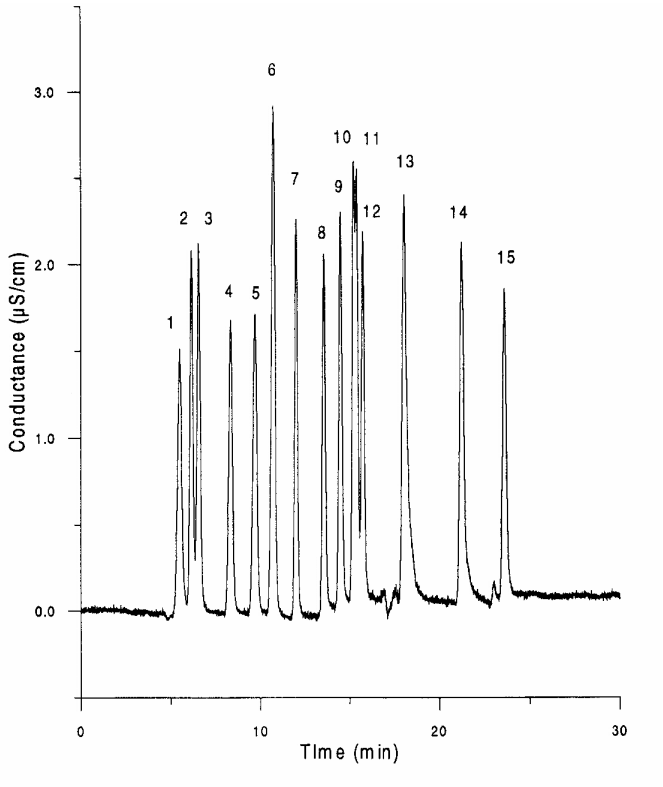


Figure 4. Background subtracted gradient chromatogram. A linear gradient from 2 mM NaOH to 38 mM NaOH from 5 to 17 minutes was used. Peak identities: 1, acetate; 2, formate; 3, methanesulfonate; 4, monochloroacetate; 5, bromate; 6, chloride; 7, nitrite; 8, trifluoroacetate; 9, dichloroacetate; 10, bromide; 11, nitrate; 12, chlorate; 13, sulfate; 14, phthalate; 15, chromate. All ions were 50 µM except dichloroacetate which was 60 µM.

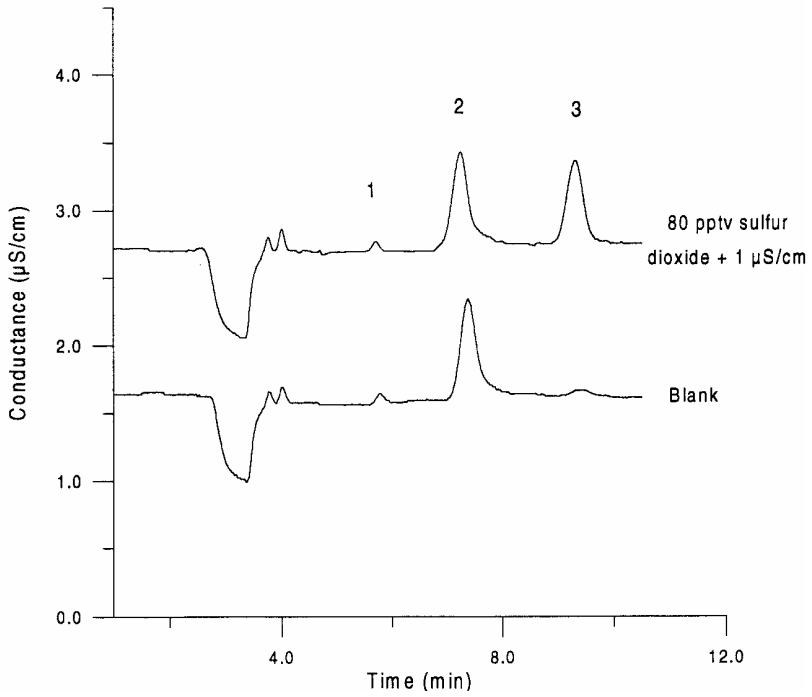


Figure 5. Chromatograms resulting from sampling blank air (lower trace) and 80 pptv SO_2 (upper trace). Peak identities: 1, chloride; 2, carbonate; 3, sulfate.

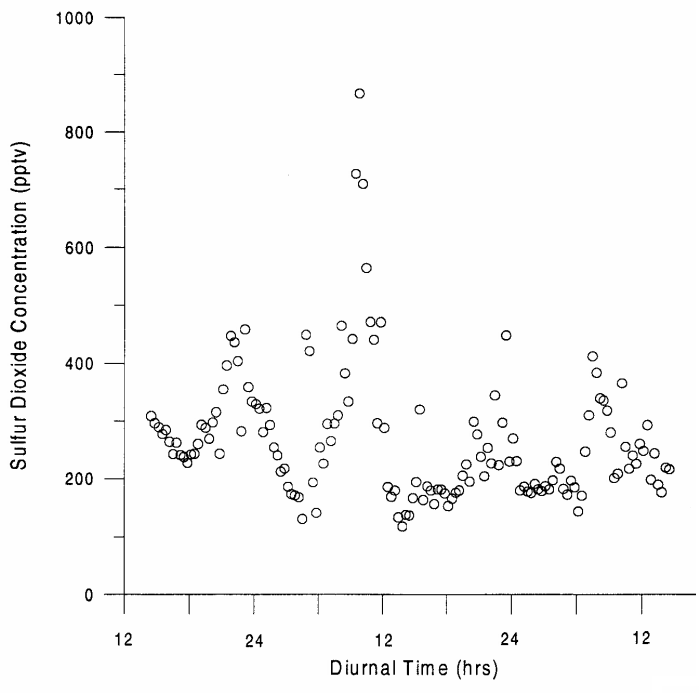


Figure 6. Ambient air levels of SO_2 in Lubbock, TX for a 48-hr period beginning in the afternoon of April 28, 1998.

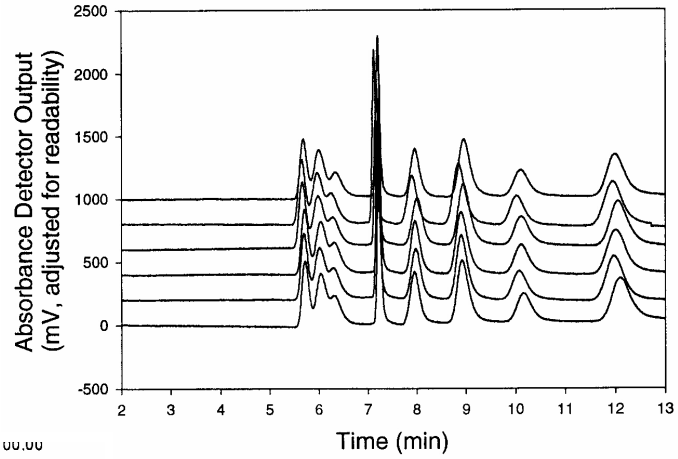


Figure 7. Sample of isocratic system reproducibility. RSD in retention time is < 1%. All samples are 500 µM. Peak identities from left to right: cytosine, uracil, adenine, uridine, thymidine, adenosine, xanthosine, and inosine.

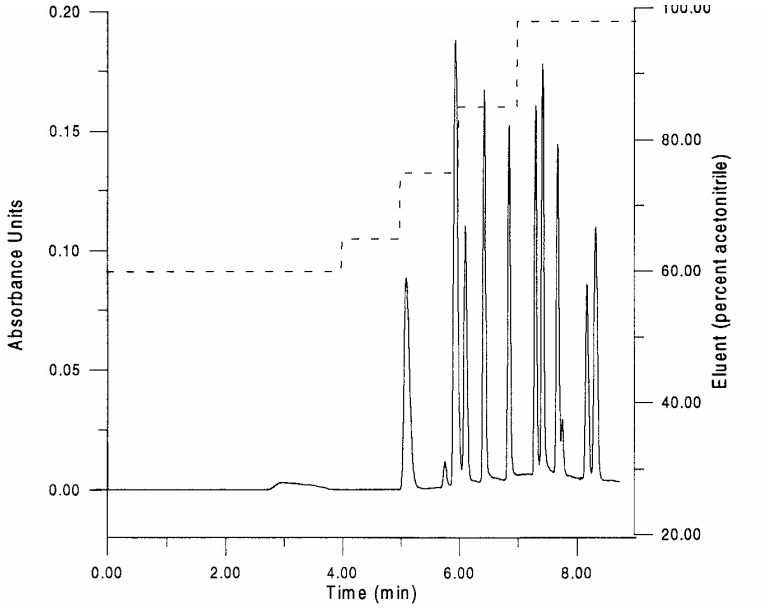


Figure 8. Sample chromatogram with gradient profile using an eluent flow rate of 5.0 µL/min. All samples are 0.5 ml / 100 ml solution in acetonitrile. Peak identities from left to right: phenol, benzaldehyde, benzonitrile, nitro-benzene, benzene, bromobenzene, toluene, ethylbenzene, propylbenzene, and t-butyl-benzene.

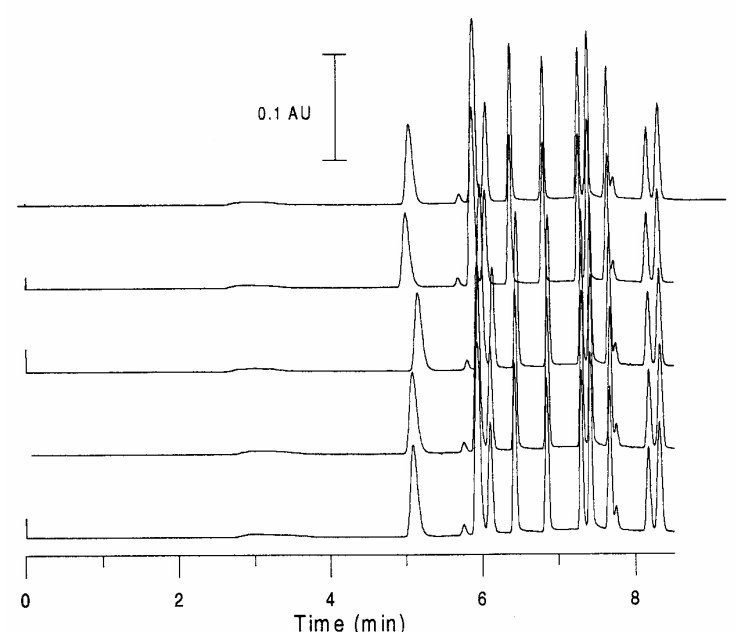


Figure 9. Dual pump gradient reproducibility. Average RSD in peak retention time is 0.545%. Peak identities from left to right: phenol, benzaldehyde, benzonitrile, nitrobenzene, benzene, bromobenzene, toluene, ethylbenzene, propylbenzene, and t-butylbenzene.

RAPID DETERMINATION OF ORGANIC CONTAMINANTS IN WATER BY SOLID PHASE MICROEXTRACTION AND INFRARED SPECTROSCOPY

David C. Tilotta, Danese C. Stahl, Sheila A. Merschman, Daniel L Heglund, and Said H. Lubbad
Department of Chemistry, P.O. Box 9024, The University of North Dakota, Grand Forks, ND 59202

The objectives of this research project are to: identify suitable solid phase films for determining organic contaminants in water by SPME/IR, determine which organic contaminants are amenable to the SPME/IR method, and adapt the basic methodology to field use.

Solid Phases

Of the 15 solid phases examined to date, three polymers have been found to be useful. for SPME/IR: Parafilm M™ (a wax-impregnated polymer/rubber composite), poly(dimethylsiloxane) (PDMS, an important solid phase material of the SPME syringe technology) and Teflon PFA™ (a perfluoroalkoxy teflon polymer).

Analyte Classes

To date, three classes of compounds have been examined for their suitability as analytes for SPME/IR using the three aforementioned films. Table 1 shows formal equilibration times, linear dynamic ranges, detection limits, and precision data (expressed as percent relative standard deviation) for these classes for the appropriate solid phase film(s). Multiple entries in this table for a given analyte imply that more than one film is useful Conversely, the absence of an entry for a given analyte/film combination indicates that that film is not suitable for the analysis.

Volatile organic compounds (VOCs) examined include the BTEX compounds (benzene, toluene, ethylbenzene, xylenes), and halocarbons such as carbon tetrachloride, chlorobenzene, chloroform. and p-chlorotoluene. Parafilm M™ and PDMS both have been useful for the analytical determination of these compounds. SPME/IR analyses using Parafilm, have demonstrated the ability of SPME/IR in distinguishing four of the six alkylbenzenes (benzene, o-xylene, m-mylene, p-xylene) in petroleum industry wastewater samples. Quantitation by simple univariate calibration based on absorbance band heights have provided good agreement with purge and trap GC/MS standard methods. Analytical determinations of ethylbenzene and toluene are, however, complicated by the spectral overlap of other components in gasoline.

Gasoline fuels include the more volatile organics such as the short chain hydrocarbons (e.g., $<C_6$) and, as previously discussed, the BTEX compounds. Teflon PFA™ has been found to successfully extract gasoline-range organics (GROs) from water and to provide a clear spectral region for identification and quantitation. SPME/IR analysis of the C-H stretching region provides a method for determining aggregate hydrocarbons. Whereas Parafilm and PDMS provides a means of identifying individual components of multicomponent mixtures, PFA is more useful for analysis of the mixture itself. The films thus compliment one another in terms of the selectivity they provide.

Analysis of pesticides and herbicides are currently underway using the SPME/IR approach. Poly(dimethy- lsiloxane) has been identified as the only solid phase that can successfully be used to determine trifluralin in aqueous solutions by SPME/IR.

Future Activities: Future SPME/IR work will involve: 1) continuing the identification of suitable solid phase films, 2) expanding the basic methodology to pesticides and herbicides, and 3) demonstrating the approach in field environments (summer, 1998).

INTRINSIC STABLE ISOTOPIC TRACERS OF ENVIRONMENTAL CONTAMINANTS

Stephen A. Macko, Peter J. Yanik, Nicole A. Cortese
Department of Environmental, Sciences, University of Virginia, Charlottesville, VA 22903
Mahlon C. Kennicutt II, Yaorong Qian
Geochemical and Environmental Research Group, Texas A&M University,
833 Graham Road, College Station, TX 77845

Abstract
The stable isotopic composition of a contaminant in the environment is the end result of a complex chain of events. Chemicals produced from disparate sources by fundamentally different processes would be expected to exhibit intrinsic isotopic compositions that could be used to identify sources. Compound specific isotope analysis (CSIA) based on gas chromatography/isotope ratio mass spectrometry (GC/C/IRMS) is being used to uniquely identify naturally occurring pollutants, such as PAH in petroleum, and synthetic or manufactured pollutants, such as pesticides and PCBs. The expected benefit to be derived from the application of CSIA to environmental questions is to be able to more accurately define the sources, fate, and transformation of pollutant mixtures in the environment. Effective environmental regulation can only be accomplished if contaminant distributions can be unambiguously linked to known processes or sources. As concerns about the quality of the environment have increased it has become clear that our ability to inventory, trace and provide a mass balance of pollutants in the environment is poor. The study presented here includes development of purification techniques, optimization of instrumental conditions, development of models based on study results, and field testing of the concepts developed. Selected polycyclic aromatic hydrocarbons, pesticides, and PCBs have been the analytes of interest. Fused silica capillary columns have been used to provide resolution of complex mixtures, minimize co-elution and background interferences, and limit column bleed during GC/C/IRMS analysis. The resolution and accuracy of the method is being determined by analyzing authentic standards, primary sources of contaminants, extracts of effluents and well-characterized pollutant occurrences. The study has had four primary objectives: (1) development of isolation techniques that produce high purity, unaltered concentrates that maintain the stable isotopic integrity of the analytes; (2) determine the stable isotopic composition of target analytes in primary sources of contaminants; (3) determine the stable isotopic composition of priority pollutants in selected processes that introduce contaminants to the environment; and (4) verify the techniques and models developed with well-characterized sites of pollutant occurrences.

Introduction
In recent years, there has been increased attention concerning the contamination of global soil, water and air. As the human population continues to increase, there is an ever-increasing strain placed on these life-sustaining reservoirs. This added strain is reflected in the quantities of and manner in which waste and potential contaminant sources are dealt with. It is inevitable that there are occasional occurrences when products, produced or processed for human

use, are released into the environment. Upon reaching the environment, the contaminants can be transported in a variety of ways until they reach a depositional end point, possibly in soils, waters or in biological tissues. Depending on the reactivity and toxicity of the contaminants, there is a multitude of possible implications for both the environment and human populations. It is necessary, therefore, to understand the nature of the contaminants, where they came from, and how they reached their depositional location. With this understanding, cleaning contaminated sites and preventing further contamination become more manageable endeavors.

There are many compound classes that have been contributors of contaminants into the environment. Of growing interest in recent decades are polycyclic aromatic hydrocarbons (PAH), organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs). PAH are of interest because they can be indicative of a variety of contaminant sources, such as petroleum spills or combustion processes and are known to be carcinogenic (LaFlemme and Hiles, 1978 and Hites *et al.,* 1980). Although some organisms, such as fish, are able to metabolize PAH, other organisms such as mollusks and crustaceans are unable to do so (Law and Biscaya, 1994; Hickey *et al.,* 1995; Roper *et al.,* 1997). Thus, PAH tend to accumulate in the tissue of these organisms. Pesticides, such as DDT, and PCBs are of interest because they not only can reside in soil and water reservoirs, but due to their lipophilic nature, they can accumulate in tissues and are known to be toxic (Killops and Killops, 1993 and Hickey *et al.,* 1995). The storage of such contaminants in tissue results in heightened concentrations in organisms residing at higher trophic levels, thus enhancing the risk to many predatory species.

In many earlier attempts at deciphering the sources of contaminants such as PAH and PCBs, the approach has been to look at absolute concentration levels and relate a concentration gradient to a point source. Another approach was to determine the concentrations of compound classes relative to one another and compare these relationships to possible source relationships. One difficulty with the first approach is that although measurable amounts of a contaminant may be located near a source known to produce such compounds, there is no absolute proof that the contaminant came from that source. Furthermore, owing to the off-site acquisition of pesticides, there is rarely a point source nearby which can serve as a possible answer to contaminant apportioning scenarios. A problem with the second approach is that chemical or biological activities such as evaporation, water washing or biodegradation could alter the concentration of one compound relative to the others. This chemical or biological alteration could change the original "signature" of the compound class that could lead to an incorrect assignment of a source (O'Malley *et al.,* 1994). In the past, traditional analytical methods using gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) have been used to characterize contamination sites. As the above arguments show however, these techniques may yield ambiguous results (Mansuy *et al.,* 1997).

A Different Technique

In recent years another approach has developed which is based on the stable isotopic composition of the compounds of interest. Carbon, for instance, has two naturally occurring stable isotopes, ^{13}C and ^{12}C. It is reasonable to assume that the ratio of the amounts of these two isotopes is unique for each compound derived from a different source. If two chemical companies were to produce the chemically identical PCBs, for instance, it is probable that the identical compounds will have isotope ratios characteristic of different feedstocks or different manufacturing processes. Upon entering the environment, therefore, a contaminant should be able to be linked to a source by its isotopic composition.

The technique for compound specific isotopic analysis (CSIA) involves coupling a gas chromatograph (GC) to a combustion furnace, which is then attached to an isotope ratio mass spectrometer (GC/C/IRMS). The effluent of the gas chromatograph is introduced into a microcombustion/CO_2 purification interface. Within the GC, fused silica columns have been found to be most effective because carrier gas flows are low (a few ml/min. of He), resolving power is excellent (30 to 60 meter column lengths are routine), and column bleed is minimal (bonded phase columns). The column effluent is combusted to CO_2 in the interface in the presence of CuO and water is removed by a cryogenic trap. Ion current intensities of masses 44, 45 and 46, which represent the major isotopic forms of CO_2, are recorded simultaneously using a high speed on-line acquisition system. A schematic of the system is shown below (Figure 1).

The ratio of the ion current intensities of mass 45 to mass 44 is a measure of the ratio of $^{13}C/^{12}C$ and is compared to the reference value of $^{13}Cl/^{12}C$. The reference and sample ion current intensities are measured in an alternating manner, which ensures a reliable comparison between the reference and sample isotope ratios. A computer interfaced to the instrument is used to calculate in the "per mil" (‰) notation. Isotope compositions are reported as

(delta) values, using the following formula:

$$R = {}^{13}C/{}^{12}C$$

$$^{13}C = (R_{sample}/R_{reference} - 1) \times 1000$$

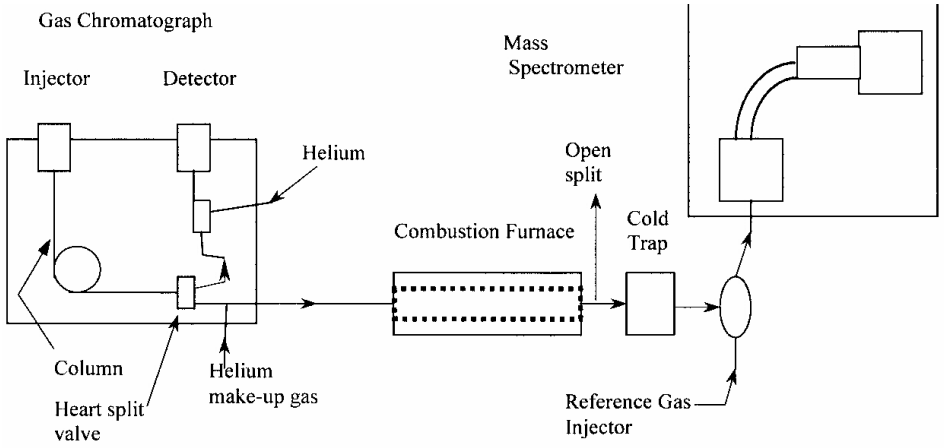


Figure 1. Schematic showing the basic structure of a GC/C/IRMS system (adapted from Freedman *et al.,* 1988).

Isotopic compositions are measured as ratios owing to the normally low absolute abundances of each chemical species of interest. Samples with more ^{13}C than the reference compound will have positive ^{13}C values, and are said to be enriched in ^{13}C. Samples with less ^{13}C than the reference compound are said to be depleted. It should be noted that currently, while there are many elements with multiple stable isotopes, the most commonly used in analyses are carbon, nitrogen, oxygen, sulfur and hydrogen. Like carbon, each of the other elements are analyzed in a similar way, with deviations occurring in the combustion and subsequent gas purification processes occurring just before mass abundances are measured. In every case, a sample with more of the heavy stable isotope is said to be enriched for that element under investigation. For instance, with respect to nitrogen, using new modifications of the combustion system, it is now possible to perform CSIA on nitrogenous compounds (Macko *et al.,* 1997). In this case, the heavy isotope is ^{15}N and the mass spectrometer measures the ion current intensities of masses 29 and 28, representingthe two most common forms of molecular nitrogen.

With a state-of-the-art instrument, reproducibility is quite good, with standard deviations on replicate measurements typically better than 0.5 ‰ (Tables 1-3).

Table 1. Average ^{13}C values (relative to PDB reference) with associated standard deviations for five PAH standards.

Compound	Average ^{13}C value	Standard Deviation (+/-)
Naphthalene	-26.2	0.4
Phenanthrene	-24.4	0.45
Anthracene	-23.7	0.44
Chrysene	-23.9	0.58
2,3,6 - Trimethylnapthalene	-22.6	0.20

Table 2. Average ^{13}C values (relative to PDB reference) with associated standard deviations for four alkane standards.

Compound	Average ^{13}C value	Standard Deviation
Decane	-29.0	0.30
Undecare	-27.1	0.30
Dodecane	-33.3	0.30
Tridecane	-32.6	0.40

Also, with a state-of-the-art instrument, performing CSIA with a GC/C/IRMS system has many advantages over other techniques for determining contaminant identities and sources. Because a GC is coupled to the mass spectrometer, there is the capability of resolving complex mixtures. Also, with such a system, there is very high sensitivity, which

can be a very important consideration when dealing with trace contaminants. With a GC/C/IRMS system, detection is possible in the sub nM region.

Table 3. Average ^{15}N values (relative to atmospheric N_2 reference) with associated standard deviations for four nitrogen-containing compounds.

Compound	Average ^{15}N value	Standard Deviation
Pyrazine	0.7	0.12
Tripropylamine	9.5	0.55
Quinoxaline	-0.6	0.16
Nicotine	-1.7	0.41

The Approach

In applying CSIA to the problem of tracing environmental contaminants, measures must be taken to determine whether the techniques are viable under natural conditions. As was mentioned above, using GC/IRMS to measure isotopic compositions for the purpose of tracing contaminants seems to be an exciting alternative to traditional methods. The first steps taken toward application of the technique must be field tests, however. This can be stated in a series of objectives:

1) Establish extraction, isolation, and purification techniques for the contaminants of interest. Of particular importance is obtaining high purity samples that have not been altered in isotopic composition.

2) Determine the stable isotopic composition of the compounds of interest obtained from primary sources, such as manufacturers, petroleum suppliers and chemical storage locations.

3) Determine the stable isotopic composition of the contaminants at locations where they are introduced into the environment. Possible locations include combustion areas (automobile exhaust and industrial exhaust), industrial emission, agricultural runoff, urban runoff and sewage effluent.

Once the first three objectives are fulfilled, the next step is to apply them to well-characterized sites where pollution sources and times of occurrence are well known. In this initial phase, carbon isotopes have been the focus, and within this framework, early efforts have concentrated on the most common PAH, OC pesticides and PCBs (Table 4). The reasons for first analyzing the most common contaminants are two-fold. First, in trying to determine the validity and applicability of this technique, it is undesirable to be sample-limited. From a sample extraction and purification standpoint, it is necessary to deal with sufficient sample quantities. Once the method proves successful, samples of lower of concentration can be addressed. The second reason for focusing on the most common contaminants is time constraints. This approach is fairly time consuming, and thus only a limited number of samples can be analyzed during the study. Choosing the most abundant contaminants for analysis should allow for the greatest chance of success.

Methods

In this study, the matrices of interest are soil and biological tissue. Typically, the first step is the extraction process. Soil samples are Soxhlet extracted with methylene chloride and then separated based on compound class with an alumina/silica column. Aliphatic hydrocarbons are eluted from the column with 50 ml of pentane. Aromatic hydrocarbons, PCBs and OC pesticides are eluted with 150 ml of pentane/methylene chloride (1:1). The second fraction is further separated on a silica column. PCBs are eluted with an additional 90 ml of pentane. High performance liquid chromatography (HPLC) using a cyano/amino bonded phase column as per Killops and Readman (1985) is used to purify the PCBs from fraction 2. Pentane is used as the eluting solvent. Purity is then checked with gas chromatography/electron capture detector (GC/ECD) and GC/MS systems. Fraction two from the silica column is separated into several subfractions, with the aromatic compounds being separated based on the number of double bonds they contain (Killops and Readman, 1985). A pentane and methylene chloride gradient is used for the elution. It should be noted that others have shown that aromatic species can also be separated with molecular sieves based on the arrangement of any alkyl substitutions present (Ellis *et al.,* 1992; 1994). If need be, this is another viable alternative.

For the tissue samples, 20-30 grams of wet tissue are mixed with approximately 50 g of anhydrous sodium sulfate. The extraction is performed with three 100 ml methylene chloride aliquots while macerating with a homogenizer. The combined extract is then separated as described above except there is not an aliphatic hydrocarbon component to contend with. Before analyzing by GC/C/IRMS, if the samples still are not pure enough, thin layer chromatography

(TLC) can be utilized for further purification.

Table 4. List of contaminants that are initially being investigated.

Contaminant	
PAH	Naphthalenes
	Fluorenes
	Phenanthrenes/Anthracenes
	Dibenzothiophenes
	Fluoranthenes/Pyrenes
	Benzanthracenes
	Benzofluoroanthenes
	Benzopyrenes, Dibenzanthracenes
	Perylene
Pesticides	Aldrin, Heptachlor, Endrin, Mirex
	DDT, Dieldrin, Transnonachlor
PCBs	Dichlorobiphenyls
	Trichlorobiphenyls
	Tetrachlorobiphenyls
	Pentachlorobiphenyls
	Hexachlorobiphenyls
	Heptachlorobiphenyls
	Octachlorobiphenyls
	Nenachlorobiphenyls

Upon final separation and purification, the analytes of interest are taken up in an appropriate solvent (pentane and methylene chloride, for example) to a concentration in the 5-100 ng/µl range, depending on the sensitivity of the instrument for a particular compound class. Samples are then analyzed for isotopic composition by the GC/C/IRMS system as described above.

Other Considerations

The stable isotopic composition of a contaminant in the environment is the end-result of a complex chain of events. Naturally occurring pollutants such as spilled crude oil are most easily traced in the environment because the starting material is usually readily available for analysis. Furthermore, intrinsic tracers in spilled crude oil would also be directly reflected in environmental samples since few complicating processes would intervene. Many synthetic materials are produced from petrochemical precursors through manufacturing processes such as distillation, catalytic cracking, chlorination and polymerization to name a few. A change in isotopic composition might occur during the manufacturing process if catalysis or high temperature is involved. Next the product is applied for its intended purpose which could include combustion (gasoline), lubrication (lube oils), pesticide application (DDT), or use as a transformer oil (PCBs) for example. These applications may cause an additional shift in isotopic and molecular composition. During the application, either intentionally or indirectly, some portion of the contaminant is released to the environment (such as soot from combustion or the disposal of waste materials). Once released to the environment, the contaminant is then subjected to redistribution throughout various matrices including air, water, sediments, and biological tissue depending on its chemical properties and stability. The partitioning of the chemical among various phases might be accompanied by a shift in isotopic composition as well as chemical transformation. Environmental transformations are brought about by physical, chemical and microbiological processes. Each process defines an independent set of isotopic and compositional changes. The complex history of a pollutant suggests that a combination of compositional and stable isotopes can be linked to a specific series of events and processes (Figure 2). Chemicals of identical structure may have different isotopic composition if they have witnessed different histories from manufacture to environmental deposition. By analyzing contaminant samples at different stages of transport it should be possible to understand the dominant processes acting on them and to elucidate the complex chain of events which led to the isotopic composition of the contaminants at their environmental end point.

The issue of complex mixtures

As was mentioned above, compound specific isotopic analysis using GC/C/IRMS has the potential to handle complex mixtures. It is inevitable, however, that during some analyses, there are two or more chemical species present in a mixture that are similar chemically and therefore coelute. Perhaps in some of the separated fractions there could be additional compounds present other than the desired analytes of interest that are similar to the desired compounds. If there is only one other compound present, temperature programs for the GC could be altered, columns could be changed, either in length or composition, or additional separation steps could be added to alleviate this problem. When there is a high amount of background, however, owing to more than one additional chemical species being present, the problem is more difficult to handle. The coelution will lead to erroneous isotopic results because what was thought to be the composition of one compound is actually the combined isotopic composition of two or more compounds. This issue is complicated further by the fact that isotope fractionation occurs during

elution, with portions of the peak varying dramatically in isotopic composition (Figure 3). Although the isotope values can be averaged across a peak, with coelution, the modifying effect of the additional species can also vary across the peak if the analyte of interest and the additional species do not elute at exactly the same time. Some researchers have used internal standards in their analyses to monitor the degree to which unresolved complex mixtures (UCM) or other coelution problems affect the results of the isotopic analyses. By knowing how much the isotopic values of compounds of known composition have shifted, corrections can be made for the unknowns (Mansuy *et al.,* 1997). Other researchers have relied on certain separation techniques to try to keep the problem to a minimum (Ellis *et al.,* 1994). Also, within some software packages, monitoring of the background is possible, along with the subsequent subtraction of unwanted contributions to a peak. Based on the above discussion, it is obvious that this issue will require careful monitoring in order to insure results are as accurate as possible.

Initial Applications

Extraction, purification, and analysis on some of the analytes of interest has already been performed (Table 5). PAH mixtures from two sediment sites as well as a sample of creosote were analyzed by GC/C/IRMS yielding variable carbon isotope values. This variability could indicate different sources of the PAH influence into the various reservoirs.

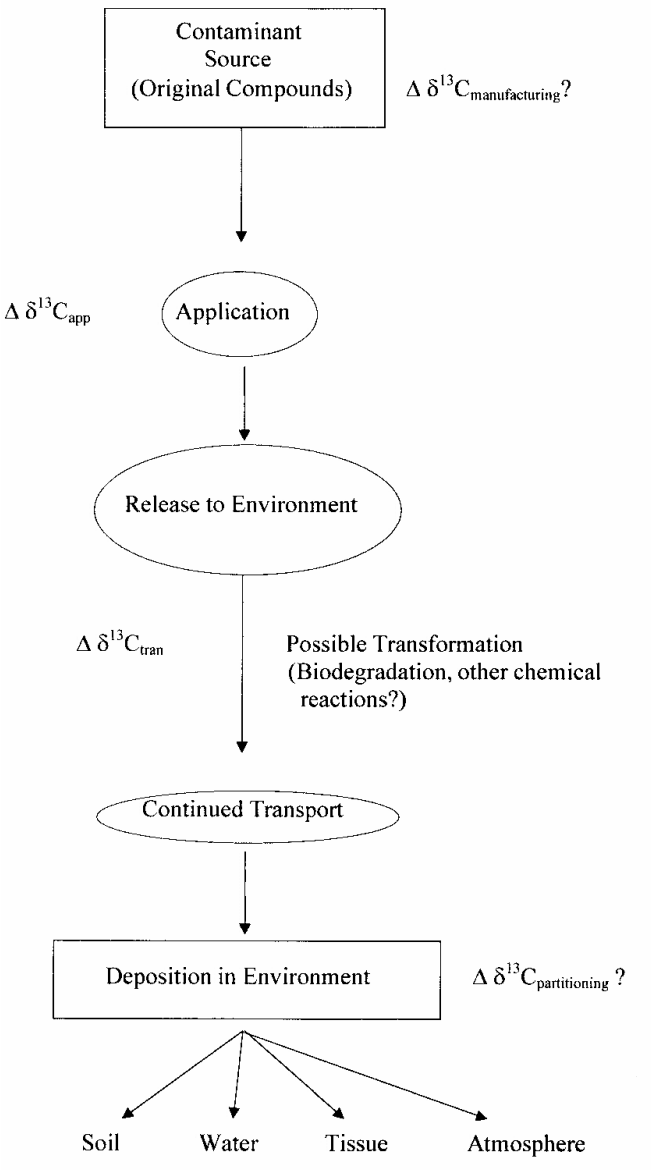


Figure 2. Schematic representing possible pathways for contaminants that enter the environment.

Table 5. ^{13}C values (relative to PDB reference) for PAH mixtures derived from three different sources.

Compound	Oregon Inlet Sediment	Creosote	Casco Bay Sediment
Naphthalene	-27.1	-23.5	
2-Methylnaphthalene	-27.8	-23.1	-27.9
1-Methylnaphthalene	-28.2	-21.2	-29.5
Biphenyl	-28	-21.4	-26.4
2,6-Dimethylnaphthalne	-28.8		
Acenaphthalene	-27.4		
Fluorene	-27.7	-18.4	
Phenanthrene	-25.6	-24.3	
1-Methylphenanthrene	-25.8		
Fluoranthene	-24.6	-25.2	
Pyrene	-23.0	-25.2	
Chrysene	-23.0		

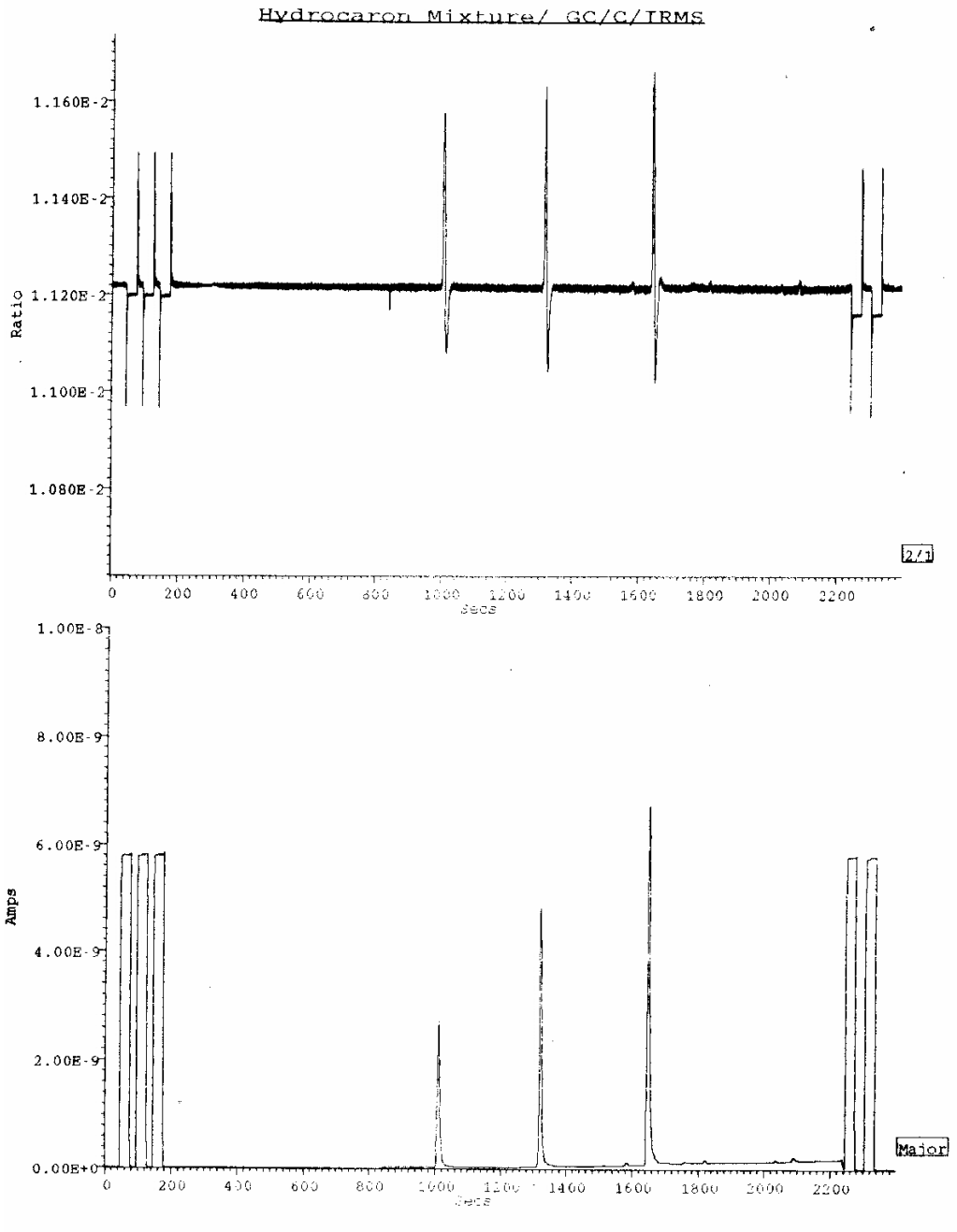


Figure 3. Plot of the carbon isotope signal of three hydrocarbon species. The upper trace is the ratio of ion current intensities of masses 45 and 44. The lower trace is the ion current intensity of mass 44. Note the changing isotope ratio across the peak.

Stable Isotopic Analysis as a Versatile Tool

In recent years, more attention has been focused on stable isotopic analysis, and in recent years, on compound specific isotopic analysis. While traditional molecular approaches are still in active use today, stable isotope analysis has gained popularity as a complement to other techniques or a stand-alone technique when other approaches are ineffective or too time consuming. Furthermore, as more attention is paid to stable isotopic analysis, the versatility of the technique has become more evident. As was mentioned in the above discussion, stable isotope analysis can be used as an effective tracer or method to apportion sources of compounds to a site. GC/C/IRMS has been used to distinguish oils based on the isotopic composition of alkane and isoprenoid constituents present in the

oil (Bjoroy *et al.,* 1991). This technique has been applied to oil spills as well; even under conditions where some of the oils have been weathered (Mansuy *et al.,* 1997). With respect to the analytes of interest in this study, CSIA has been used to not only trace the transport of PAH in aerosols (Ballentine *et al.,* 1995) but to distinguish between biomass burning and fossil fuel burning sources of PAH (Ballentine *et al.,* 1996). Also, sources of PAH have been identified along with the relative amount of influence of each in marine soils. (O'Malley *el al.,* 1994). With respect to PCBs, it was discovered that individual compounds tend to be more depleted in ^{13}C the more chlorine atoms there are present in the structure (Jarman *et al.,* 1998). Stable isotopic analyses have also been used in groundwater studies, both as a source apportioning tool (Kelley *et al.,* 1997) and also as a means of tracing compounds during groundwater flow (Dempster *et al.,* 1997). Perhaps one of the most unique characteristics of stable isotope analysis is that is has been applied to many different scientific areas. Two areas that are utilizing this approach more and more are biology and ecology. Characteristics of food webs, from trophic structure to influences on the diet on individual organisms have found application in stable isotope analysis (Fang *et al.,* 1993 and Jarman *et al.,* 1996). As has been shown, beyond the realm of just contaminant studies, compound specific stable isotope analyses has a wide range of applicability. This should prove very beneficial as the call for more interdisciplinary science continues.

Conclusions

With the current heightened awareness of the need to understand and control contamination sites and sources, the demand for powerful and accurate analytical tools to answer these questions is very high. Compound specific isotopic analysis has been suggested as a new tool to be used to answer these questions. Upon purifying contaminant fractions, GC/C/IRMS can be used to determine the isotopic composition of the individual components in these fractions. These stable isotope compositions can compared to the isotopic compositions of different source materials and contaminants entering the environment through various pathways. With this information, the analyst can begin decipher together the history of the contaminants, linking the source and the process of introduction to the contaminants of interest. Whereas first only being applied to well characterized sites, upon finding that the techniques are valid, the methodology can be applied to sites of unknown composition and influence. Compound specific isotopic analysis could then be used to complement other analytical methods or as a stand-alone technique where the other methods prove to be ineffective.

Works Cited

Ballentine, D.C., Macko, S.A., Turekian, V.C., Gilhooly, W.P. and B. Martincigh. 1995. Transport of biomass burning products through compound specific isotope analysis, *Selected Papers from the 17th International Meeting on Organic Geochernistry,* 644-646.

Ballentine, D.C., Macko, S.A., Turekian, V.C., Gilhooly, W.P. and B. Martincigh. 1996. Compound specific isotope analysis of fatty acids and polycyclic aromatic hydrocarbons in aerosols: implications for biomass burning, *Organic Geochemistry,* **25***,* 97-104.

Bjoroy, M., Hall, K., Gillyon, P. and J. Jumeau. 1991. Carbon isotope variations in *n*-alkanes and isoprenoids of whole oils*, Chemical Geology,* **93***,* 13-20.

Dempster, H.S., Sherwood Lollar, B. and S. Feenstra. 1997. Tracing organic contaminants in groundwater: a new methodology using compound specific isotopic analysis, *EnvironmentalScience and Technology,* **31***,* 3193-3197.

Ellis, L., Alexander, R., and R.I. Kagi. 1994. Separation of petroleum hydrocarbons using dealuminated mordenite molecular sieve-II. Alkylnapthalenes and alkylyphenanthrenes, *Organic Geochemistry,* **21***,* 849-855.

Ellis, L., Kagi, R.I., and R. Alexander. 1992. Separation of petroleum hydrocarbons using dealuminated mordenite molecular sieve. I. Monoaromatic hydrocarbons, *Organic Geochemistry,* **18**, 587-593.

Fang, J., Abrajano, T.A., Comet, P.A., Brooks, J.M., Sassen, R. and I.R. MacDonald. 1993. Gulf of Mexico hydrocarbon seep communities XI. Carbon isotopic fractionation during fatty acid biosynthesis of seep organisms and its implications for chemosynthetic processes, *Chemical Geology,* **109***,* 271-279.

Freedman, P.A., Gillyon, E.C.P. and E.J. Jumeau. 1988. Design and application of a new instrument for GC-isotope ratio MS, *American Laboratory,* **June***,* 114-119.

Hickey, C.W., Roper, D.S., Holland, P.T. and T.M. Trower. 1995. Accumulation of organic contaminants in two sediment-dwelling shellfish with contrasting feeding modes: deposit- *(Macomona liliana)* and filter-feeding- *(Austrovenus stutchburyi), Archives of Environmental Contamination and Toxicology,* **29**, 221-231.

Hites, R.A., LaFlamme, R.E., Windsor, Jr., J.G., Farrington, J.W., and W.G. Denser. 1980. Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode Island, USA), *Geochim. Cosmochim. Acta,* **44**, 873-878.

Jarman, W.A., Hobson, K.A., Sydeman, W.J., Bacon, C.E., and E.B. Mclaren. 1996. Influence of trophic position and feeding location on contaminant levels in the Gulf of Farallones food web revealed by stable isotope analysis,

Environmental Science and Technology, **30**, 654-660.
Jarman, W.M, Hilkert, A., Bacon, J.W., Ballschmoter, K. and R.W. Risebrough. 1998. Compound specific carbon isotopic analysis of Aroclors, Clophens, Kaneclors, and Phenoclors, *Environmental Science and Technology,* **32**, 833-836.
Kelley, C.A., Hammer, B.T. and R.B. Coffin. 1997. Concentrations and stable isotope values of BTEX in gasoline-contaminated groundwater, *Environmental Science and Technology,* **31**, 2469-2472.
Killops, S.D. and V.J. Killops. 1993. An introduction to organic geochemistry, Longman Scientific and Technical, 265 pp.
Killops, S.D. and J.W. Readman. 1985. HPLC fractionation and GC-MS determination of aromatic hydrocarbons from oils and sediments, *Organic Geochemistry,* **8***,* 247-257.
LaFlamme, R.E. and R.A. Hites. 1978. The global distribution of polycyclic aromatic hydrocarbons in recent sediments, *Geochim. Cosmochim. Acta,* **42**, 289-303.
Law, R.J. and J.L. Biscaya. 1994. Polycyclic aromatic hydrocarbons (PAH)-problems and processes in sampling, analysis and interpretation, *Marine Pollution Bulletin,* **29**, 235-241.
Macko, S.A., Uhle, M.E., Engel, M.H. and V. Andrusevich. 1997. Stable nitrogen isotope analysis of amino acid enantiomers by gas chromatography/combustion/isotope ratio mass spectrometry, *Analytical Chemistry,* **69**, 926-929.
Mansuy, L., Philp, R.P. and J. Allen. 1997. Source identification of oil spills based on the isotopic composition of individual components in weathered oil samples, *Environmental Science and Technology,* **31**, 3417-3425.
O'Malley, V.P., Abrajano, Jr., T.A., and J. Hellou. 1994. Determination of the $^{13}C/^{12}C$ ratios of individual PAH from environmental samples: can PAH sources be apportioned?, *Organic Geochemistry,* **21**, 809-822.
Roper, J.M., Cherry, D.S., Simmers, J.W. and H.E. Tatem. 1997. Bioaccumulation of PAHs in the Zebra mussel at Times Beach, Buffalo, New York, *Environmental Monitoring and Assessment,* **46***,* 267-277.

RECENT DEVELOPMENTS IN IMMUNOBIOSENSORS & RELATED TECHNIQUES FOR THE DETECTION OF ENVIRONMENTAL POLLUTANTS

M. Masila, H. Xu, E. Lee, O.A. Sadik*
Department of Chemistry, State University of New York at Binghamton,
P.O. Box 6016, Binghamton, New York 13902
Fax: (607)777-4478
E-mail: osadik@binghamton.edu

ABSTRACT
This paper describes inimunobiosensors and other related multianalyte detection methods of identification and quantitation of various environmental compounds and metabolites. It presents the synthesis and characterization of polymers, biological conjugates and metabolites for the detection of a range of toxic chemicals, including chlorinated phenols, s-triazine herbicides, polychlorinated biphenyls, and heavy metals. A new multi-analyte detection technique utilizing polypyrrole derivatives was developed for the detection of chlorinated phenols and other organics. The detection of polychlorinated biphenyls (PCBs), volatile and semivolatile, halogenated organic compounds of environmental interest was conducted using the new polymer sensors. A new promising approach for heavy metal detection is described that utilizes *o*-hydroxypyridylazo metal-protein conjugates which may also be used in the development of nonradioactive immunosensor labels for environmental compliance monitoring and clinical applications.

INTRODUCTION
Very few analytical methods for environmental monitoring that are fast, low-cost and continuous are currently available. The monitoring of residue or contamination in soil, water and air can be classified into two main categories. These are: (i) screening or diagnostic techniques in which only a yes-or-no (qualitative) answer is required, and (ii) semi-quantitative or quantitative techniques in which the detection of unwanted chemicals, and the testing of whether or not the residues of the contaminants are within permissible levels are required. It is possible for the former methods to generate false positive or negative results if the sensitivities are insufficient for the detection of the threshold levels.

The successful coupling of suitable transducers (e.g. electrochemical, optical or mass) with biomolecular systems is of great importance in the search for novel sensing technologies that are inexpensive, highly selective and capable of generating early warning signals in the presence of toxic environmental chemicals. The emergence of on-site chemical and immunochemical biosensors for environmental pollutant monitoring has tremendous potentials due to their small size, low costs and the case of analytical signal generation in real time. These sensors represent a step forward over the conventional laboratory analytical methods.

In recent years, biosensors; that can detect a range of analytes in environmental samples have been developed[1,2]. Basically, a sensor consists of a chemically selective layer, a transducer, and a signal processor. If the selective layer utilizes a biological or biochemical species, then it can be classified as a biosensor. Thus, an immunosensor is a subset of biosensor since it comprises either an antibody or an antigen. Each sensor has a number of desirable characteristics depending on its applications. Essentially, a practical biosensor for the monitoring of environmental pollutants must be specific, reversible, able to provide fast response time, and capable of direct detection of an immunoreaction with minimal sequential addition of immunoreagents. Also, the sensor should be capable of continuous flow measurements and capable of determining multiple analytes in complex samples with little or no need for sample preparation steps. Finally, the sensor must be able to process signals, or capable of being integrated into other devices that can exercise real-time feedback as required for pollution monitoring or surveillance studies. Although, a number of pollutant measurement techniques have been reported, only few possess these specific requirements.

One of the major objectives of our research is to develop field-portable sensors that meet or exceed the above sensor requirements for use in the assessment of toxic chemical residues in various environmental media. This paper discusses sensors developed in our laboratory for the identification and quantitation of environmental contaminants.

MATERIALS AND METHODS

Instrumentation

The following instruments were used to conduct the experiments described in this paper: A Hewlett-Packard Diode-array UV/Vis spectrophotometer was used for the characterization of all protein conjugates. ELX 800 UV Plate Reader (from Bio-Tek Instruments) was used for all of the enzyme-linked immunosorbent assay (ELISA) experiments. EG&G PAR potentiostat/galvanostat Model 263A and EG&G 270 software were employed for the electrochemical experiments with silver/silver chloride reference electrode, platinum wire counter electrode and gold (A = 0.2 cm^2) as working electrode. Quartz crystal microbalance (QCM) measurements were carried out using EG&G quartz crystal analyzer (Model QCA917). A 9MHz EG&G At-cut quartz crystals was sandwiched between two gold electrodes (A = 0.186 cm^2). AromaScanner Model A32S (from AromaScan, Inc., NH) was used for the multiarray electronic nose experiments.

Sensor Preparation and Characterization

Immobilization on Quartz: The Au-coated quartz crystal was initially pretreated by cycling the potential between 1.4 and 0.0V for a minimum of 15 minutes in 0.2M perchloric acid. The cell was then rinsed with copious amount of water, and one surface of the crystal was soaked in a 0.02 M cystamine solution. The Au surface was thoroughly rinsed with water to remove any physically adsorbed cystamine before being soaked in 3mM cyanazine hapten solution containing 0.01M HEPES (N-[2-Hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid) buffer solution (pH = 7.3) using 10mM 1-ethyl-3-(3-dimethylamino-propyl) cabodimide EDC coupling reagent.

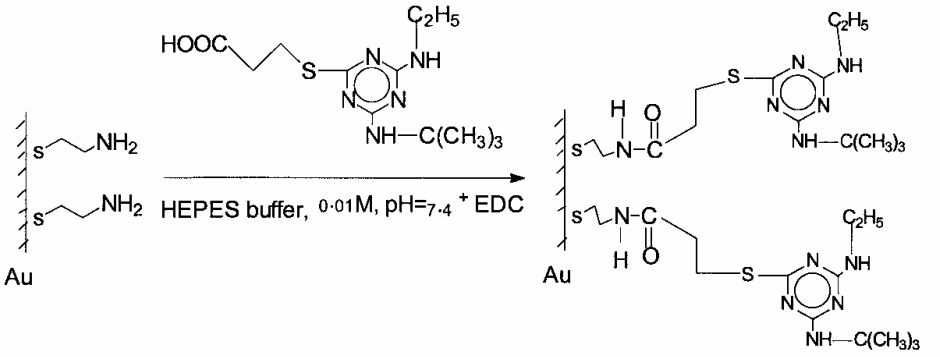
Electrochemical Immobilization: The Au electrode was pretreated as described above before being modified with the cyanazine hapten using EDC as the coupling reagent. The modified electrode was used in the electrochemical analysis, first without soaking in an antibody solution. Later the electrode was incubated in an anti-cyanazine antibody solution at 35ºC using a thermostated water-bath. All cyclic voltammetry experiments were conducted at the same temperature. The other electrochemical immobilization procedures were as recently reported[3,4].

Polymer Synthesis: Various pyrrole derivatives were polymerized by electrochemical oxidation to enable the conducting polymer films to be used for conductivity, electrochemical, and mass measurements. Some selective electrodes for phenols, PCBs and *s*-triazines were prepared by the electropolymerization of pyrrole onto platinum electrodes in the presence of tetrabutyl ammonium perchlorate. The selectivities were comparable to a range of structurally similar organic compounds, including 2,3,5,6-tetra chloroanisole, 2,3,4-trichloroanisole, 2-chloroanisole, 2,4,5-trichlorophenol, simazine, cyanazine, and substituted benzenes.

Antibody Production: The design and preparation of analyte analogs and immunogens are essential steps in the development of low molecular weight immunosensors. Triazine analogs were obtained from Dr. J.R. Fleeker's laboratory. These were prepared from active esters of the carboxylic acid analog of the triazine haptens using N-hydroxysuccinamide[5]. The triazines were coupled to a high molecular weight carrier, bovine serum albumin (BSA), or keyhole limpet hemocyanin (KLH) which were used for the production of the antibodies. The antibodies were purified by gel filtration and protein-A immunoaffinity columns, and were subsequently characterized using ELISA and nuclear magnetic resonance (NMR) techniques. By using these antibodies, sensors for *s*-triazine were developed based on the antibody inhibition of the current generated by the ferricyanide mediator on antigen-immobilized gold electrodes.

Pesticide Immunosensors

Several pesticides and herbicides are routinely used to improve crop harvesting and pest-control. Due to the growing concern about health effects, several investigations have been conducted in order to understand how pesticides and herbicides degrade in the environment[6,7]. Current methods of monitoring pesticides include liquid chromatography and gas chromatography with mass spectrometry. The high costs and labor involved in the chromatographic methods have led to the search for low-cost alternatives capable of providing rapid analysis. In this paper, we report on the development of immunosensors for atrazine, cyanazine, simazine and their metabolites. The sensor chemistries are shown in Scheme 1 below:



Scheme 1. The assembly of a cyanazine hapten monolayer on Au electrode.

The hapten monolayer electrode sensor assembly was used in the detection of cyanazine in a flow injection analysis mode. The interaction of the electrode with different antibody concentrations resulted in the formation of an antibody-antigen (*Ab-Ag*) complex which insulated the electrode towards the $[Fe(CN)_6]^{4-}/Fe(CN)_6]^{3-}$ redox probe, hence resulting in no charge transfer. The extent of the insulation depended on the antibody concentration and the time of exposure to the antibody solution. The decrease in the amperometric response of the antigenic monolayer to corresponding antibody solution for a fixed time produced a quantitative measurement of the antibody concentration (Figure 1). Typical voltammetric responses obtained for the cyanazine hapten monolayer electrode to different antibody concentrations are shown in Figure 2. The lowest detection limit achieved for the cyanazine sensor was 4.0 µg/ml with a response time of a few minutes and a less-than 2% cross-reactivity to atrazine, simazine and other metabolites.

Multianalyte Sensors

The presence of halogenated organic compounds in the environment has posed a great concern due to their persistent toxicity and the ability to bioaccumulate. Of all the 19 known chlorinated phenols, the most important congeners include the 2,4-Dinitrophenol (2,4-D), 2,4,5-trichlorophenol, (2,4,5-TCP) and pentachlorophenol. While these compounds can be determined using mass spectrometry and gas chromatographic techniques, the structural similarities of substituted phenols and their derivatives enable the development of a rapid, multianalyte method rather than for one or two analytes. The combination of gas sensor arrays and pattern recognition techniques has resulted in a fast and objective method for the simultaneous measurement of a wide range of volative and semi-volative organics.

A 32-array conducting polymer sensor was used for the rapid measurement of volatile and semivolatile halogenated organic compounds of environmental interest. The mathematical expressions for the microscopic polymer network model was described in a recent article[4]. A classical, nonparametric, and unsupervised technique of cluster analysis was used to discriminate between the polychlorinated organic phenol vapor response vectors in a 2-dimensional

space, and to identify clusters, or groups, to which unknown vectors were likely to belong. Consequently, the characteristic pattern for each sample was generated. The pattern was used to generate the database employed in the determination of the Euclidean distances between two given patterns and the normalized sensor response. Also, this was used to develop the 2-dimensional mapping from a multi-dimensional space to quantify the distinctions of the samples.

The resulting sensor arrays were found to recognize small molecules on the basis of their chemical structures which were related to the nature of the chemical class, the type and the position of the functional groups. Each sensor responded in varying degrees to chlorinated organic molecules with standard deviation of less than 0.05. The time averages for the sensor response databases, datamaps, response patterns, and the intensity profiles were obtained for different phenols. Tables 2 and 3 showed the representative databases obtained for 2,4,6-trichlorophenol and 2-CP created from the raw sample data files by selecting sample data between 60 and 120 sec. The limit of detection obtained for 2,4,6-trichlorophenol and 2-chlorophenols using the conducting polymer sensor array were 0.1 and 0.25 ng/mL respectively. This results demonstrated the viability of conducting polymer sensor arrays for the identification and quantitation of chlorinated organic phenols based on the differences in their Euclidean distances. The qualitative differences as defined by the Euclidean distance measurements were most clearly visible when the nature and the type of the functional groups were considered.

Direct Electrochemical Sensors for Polychlorinated Biphenyls (PCBs)

A direct electrochemical immunosensor has been developed for the determination of PCBs in water. The assay was based on the measurement of the current due to the specific binding between PCB and anti-PCB antibody-immobilized conducting polymer matrix. The linear dynamic range of the immunosensor was between 0.3-100 ng/mL with a correlation coefficient of 0.997 for Aroclor 1242. A typical flow injection analysis signal obtained for Aroclor 1254 is shown in Figure 3. Well defined responses were recorded for all aroclors. The method detection limits for Aroclors 1242, 1248, 1254 and 1016 were 3.3, 1.56, 0.39, and 1.66 ng/mL respectively, and a signal-to-noise (S/N) ratio of 3. The immunosensor exhibited high selectivity for PCBs in the presence of potential interference such as chlorinated anisoles, benzenes and phenols. The highest cross-reactivity measured for chlorinated phenolic compounds relative to Aroclor 1248 was less than 3%. The recoveries of spiked Aroclors 1242 and 1254 from industrial effluent water, rolling mill and seafood plant pretreated water at 0.5 and 50 ng/mL ranged from 103-106%. The effect of ionic compounds on the detection indicated that no significant change in immunosensor signal was observed within the uncertainty of the assay procedure. The detection method can be used for continuous monitoring of effluent such as waste streams and ground water.

Rational Design of Immunosensors: Sensors for Heavy Metals

In order to increase the sensitivity of immunosensing methods, a rational design of sensors using *o*-hydroxypyridylazo compounds was explored. The two most important of these compounds employed were 1-(2-pyridylazo)-2-naphthol (PAN) and 4-2-pyridylazo resorcinol (PAR). Both PAR and PAN have been used extensively for the analysis of metals, and they posses lots of useful spectroscopic and luminescence properties.

The use of 2-pyridylazo compounds as precursors for the preparation of protein conjugate by coupling the ligand to BSA, KLH, and ovalbumin was considered. It was anticipated that using these conjugates would lead to the development of new biosensing chemistries and transduction principles. Ultimately, any protein conjugate developed may become useful in developing novel non-radioactive molecular labels for immunoassay, molecular labeling and environmental compliance monitoring applications. The metal-chelate conjugates were tested to determine if the system was simpler and rapid for the identification and quantitation of lead and other heavy metals.

Finally, the PAR-lead-BSA, PAR-lead-Ovalbumin, and PAR-lead-alkaline phosphatase enzymes were successfully designed and synthesized[8]. These conjugates were characterized using UV/Vis, intra-red spectroscopy, NMR, and electrochemical techniques. Figure 3 shows the absorption spectrum obtained for the coupling of PAR (510 nm) and BSA (280 mn) conjugate. A preliminary test of the PAR-conjugates and the detection of lead and mercury were conducted using optical, differential pulse voltammetry and anodic stripping voltammetry techniques. The binding strategies employed include a sandwich configuration using the synthesized PAR-protein conjugates.

Pb^{2+} binding was monitored by recording the change in the cathodic reduction of the ion and the absorbance of the lead-PAR chelate. The binding affinity was controlled by an electro-optical technique which influenced the PAR-chelate's geometry. However, it is our understanding that no published literature exists on protein that utilizes

PAR metal-ion binding and the chromophoric PAR-protein conjugates. Using the electro-optical techniques, it became possible to quantitatively determine mercury and lead at approximately $3x10^{-7}$ and $1x10^{-8}$M respectively. Thus, a good knowledge of the selective interaction of the conjugates with biological macromolecules may result in new applications of metal-ion immunoselective adsorbents.

CONCLUSIONS

We have developed various sensors for the detection of pesticides, PCBs and heavy metals for environmental monitoring. Other sensors developed and their analytical characteristics are summarized in Table 3. The new metal-chelate protein conjugates reported in this manuscript could lead to the development of new immunoassay formats and instrumentation capable of providing rapid and selective environmental monitoring. Details of the design, synthesis and characterization of the conjugates and their analytical applications for metal detection are being compiled for journal publication. This work demonstrates that new and promising applications of the chemical and immunobiosensors and the emerging immunoassay labels will continue to make immunochemical methods more valuable to environmental monitoring.

ACKNOWLEDGMENTS

The authors would like to acknowledge the following: Office of Research & Development, NCERQ Advance Monitoring Program of the United States Environmental Protection Agency for funding. AromaScan Inc., NH, for loaning their AS 32A Electronic Nose instrument used in the evaluation of the chlorinated organic sensors developed in this project, and Dr. James R. Fleeker of North Dakota State University for the *s*-triazine analogs used in the pesticide sensors.

REFERENCES

1. Sadik O.A., Van Emon J.M., Designing Immunosensors for Environmental Monitoring, *ChemTech, Vol. 27* No. 6, pp. 39 - 46, June 1997.
2. Sadik, O.A., Van Emon J.M., *Biosensors & Bioelectronics,* Vol 11(8), AR1, 1996.
3. Bender Sharin, Omowunmi Sadik, "Direct Electrochemical Immunosensor for Polychlorinated Biphenyls (PCBs)," *Environmental Science & Technology*, Vol. 32, No.6, pp. 788-797, 1998.
4. M. Masila, A. Sargent, F. Yan, O.A. Sadik, "Pattern Recognition Studies of Chlorinated Organic Compounds Using Polymer Sensor Arrays," *Electroanalysis*, Vol 10, No.4, pp. 1-9, 1998.
5. Lawruk T.S., Hottenstein C.S., Fleeker J.R., Rubio F.M., Herzog D.P., *ACS Symposium Series No. 630*, Herbicide Metabolites in Surface Water and Groundwater, (M.T., Meyer and E.M., Thurman - Editors) pp 43-52,1996.
6. Roy-Keith Smith, Handbook of Environmental Analysis, 2nd Edition, Genium Publishing Corp., USA, 1995.
7. Barnett D., Laing D.G., Skopec, S., Sadik O.A., Wallace G.G., *Analytical Letters,* 27(13), 2417, 1994.
8. Hongwu Xu, E. Lee, S. Bender, O.A. Sadik, "Immunosensors Based on Metal-Chelates for Monitoring Heavy Metals," PittCon 98, New Orleans, Louisiana, March 1-5, 1998, paper #1244.
9. Sadik O.A., Wallace G.G., *Anal. Chim. Acta*, 279, 209, 1993
10. Sadik O.A., John M. J., Wallace G.G., Barnett D., Clarke C., Laing D., *Analyst*, 119, 1997, 1994.
11. Anita Sargent, Omowunmi Sadik, "Pulsed Electrochemical Technique for Monitoring Antibody-Antigen Reactions at Interfaces," *Trends in Analytical Chemistry*, 1998 (In Press).
12. Sadik O.A., Wallace G.G., *Electroanalysis*, 5, 555, 1993.

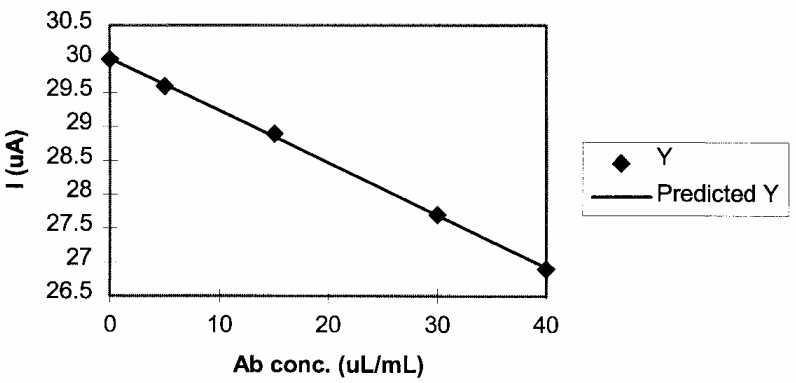


Figure 1. Cathodic peak current versus antibody concentration at constant incubation time of 5 minutes.

Table 1. Representative database obtained for 2,4,6-Trichlorophenol at conducting polymer sensor arrays

Sensor	Intensity	Pattern	SD
1	-2.560	-3.219	0.038
2	-2.450	-3.079	0.003
3	-2.710	-3.407	0.021
4	-2.700	-3.392	0.024
5	-2.540	-3.198	0.037
6	-2.460	-3.096	0.033
7	-2.730	-3.428	0.009
8	-2.600	-3.269	0.013
9	-2.490	-3.132	0.005
10	-2.700	-3.393	0.004
11	-2.320	-2.920	0.014
12	-2.450	-3.080	0.008
13	-2.310	-2.905	0.017
14	-2.720	-3.426	0.007
15	-2.310	-2.902	0.041
16	-2.260	-2.839	0.036
17	-2.150	-2.709	0.070
18	-2.500	-3.145	0.013
19	-2.720	-3.424	0.030
20	-2.790	-3.508	0.006
21	-2.570	-3.238	0.056
22	-2.170	-2.728	0.110
23	-2.300	-2.892	0.109
24	-2.120	-2.659	0.194
25	-2.070	-2.602	0.010
26	-2.440	-3.068	0.012
27	-2.520	-8.175	0.028
28	-2.350	-2.957	0.009
29	-2.430	-3.053	0.039
30	-2.700	-3.398	0.037
31	-2.810	-3.530	0.029
32	-2.570	-3.229	0.054

SD = Standard deviation, experimental conditions. relative humidity 50%, temperature 25ºC, equilibration time 30 min.

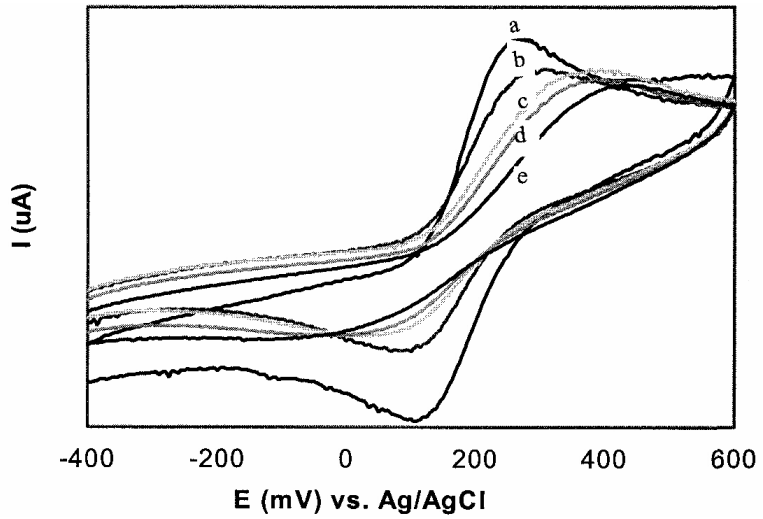


Figure 2. Voltammetric responses obtained for 1.1 mM $K_4Fe(CN)_6$ with cyanazine hapten monolayer electrode using different concentrations of anti-cyanazine antibody at 5-minute incubation time interval. (a) Blank (phosphate buffer), (b) 5µL/ml; (c) 15 µL/ml; (d) 30gL/ml; (e) 40µL/ml.

Table 2. Representative database obtained for 2-Chlorophenol at conducting polymer sensor arrays

Sensor	Intensity	Pattern	SD
1	-0.21	-3.63	1.11
2	-0.08	1.26	0.51
3	-0.15	-2.58	0.85
4	-0.15	-2.59	0.8
5	-0.17	-2.94	0.86
6	-0.18	-3.1	0.99
7	-0.08	-1.56	0.58
8	-0.12	-2.06	0.59
9	0.11	-1.66	0.66
10	-0.05	-0.97	0.62
11	-0.08	-1.36	0.37
12	-0.09	-1.56	0.5
13	0	0.1	0:090
14	-0.09	-1.62	0.55
15	-0.17	-3.09	1.03
16	-0.18	-3.16	1.04
17	0.32	4.77	1.03
18	0.46	6.05	4.58
19	0.02	0.43	0.1
20	0.36	5.44	1.51
21	-0.24	-4.31	1.49
22	0.6	8.45	3.39
23	0.73	10.09	4.38
24	0.81	11.67	3.26
25	-0.04	-0.59	0.16
26	-0.03	-0.64	0.42
27	-0.11	-1.96	0.61
28	-0.01	-0.15	0.14
29	-0.17	-3	0.9
30	-0.11	-2.07	0.72
31	-0.09	-1.65	0.47
32	-0.24	-4.22	1.45

SD = Standard deviation, experimental conditions: relative humidity 50%, temperature 25ºC, equilibration time 30 min.

Table 3. Immunobiosensors & Chemical Sensors Developed

Compound	MDL	Detection TechniquelRemarks	Ref.
Chlorinated Phenols	0.25 µg/ml	R	2
PCBs	0.05 ng/ml	FIA mode	1-3
Cyanazine	4.0 µg/ml	[Ab]	b
Heavy metals		absorbance measurement	b
Cyanide	low ppt	Fluorescence	b
Anions	3 X 10^{-8}M	Current	12
Atrazine	4.0 ng/ml	[Ab]	b
HSA	3 X 10^{-7}M	*Regenerable*	*9*
P-Cresol	0.5 mg/l	Dynamic range 3 orgers of magnitude, reusable	7
P-Athau	0.01 mg/ml	Regenerable	10

* MDL = Method Detection Limit. The MDL was computed using MDL = $t_{(n-1*1-\ =0.99)}$ * S, where t = the students t value, S = standard deviation of the replicate analyses.

[b] Currently under investigation.

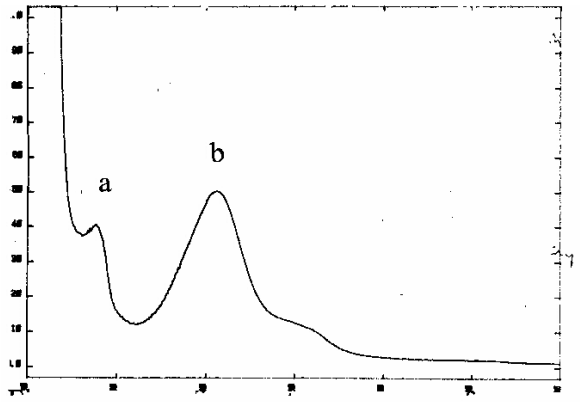


Figure 3. UV/Vis Spectrum recorded for the coupling of BSA (labeled A at 280 nm) and PAR (labeled B at 510 nm) conjugate.

MULTIPLEXED DIODE LASER GAS SENSOR SYSTEM FOR IN-SITU MULTI-SPECIES EMISIONS MEASUREMENTS

R. Hanson

NO ABSTRACT AVAILABLE

OVERVIEW/FUTURE OF NCERQA RESEARCH PROGRAM

Bala Krishnan
US EPA, Office of Research and Development, 401 M St, SW, Washington, DC

NO ABSTRACT AVAILABLE

ADVANCED ANALYTICAL METHODS FOR THE DIRECT QUANTIFICATION AND CHARACTERIZATION OF AMBIENT METAL SPECIES IN NATURAL WATERS

Janet G. Hering and Joon H. Min
California Institute of Technology, Environmental Engineering Science,
1200 E. California Blvd. (138-78), Pasadena, CA 91125

Neither the biogeochemical cycling of trace metals nor their ecotoxicological effects can be fully understood without careful consideration of metal speciation. Investigations of metal speciation in natural waters have demonstrated that, for many metals (particularly Cu, Zn, and Fe), the predominant ambient metal species are nonreactive in chemical and/or biological assays. However, the methods commonly used to monitor metal speciation cannot provide definitive information on the nature of ambient metal species.

Electrospray-mass spectrometry (ESMS) offers a powerful tool for the investigation of ambient metal species. Unlike more common GC-MS techniques, ESMS can be applied to non-volatilizable species and the comparatively gentle

ionization in ESMS allows compounds to be analyzed with minimal fragmentation thus preserving the molecular ion signature.

Preliminary studies with model compounds have been performed to investigate the application of ESMS for analysis of metal-organic complexes. Work to date with the strong organic complexing agent EDTA (ethylenediaminetetraacetic acid) has demonstrated that both uncomplexed EDTA and metal-EDTA complexes can be detected in the positive ion mode as protonated species with a single positive charge. Despite the extreme conditions imposed by the electrospray interface, protonation (and, in the case of uncomplexed EDTA, formation of the Na+ adduct) appears to be the only perturbation of the initial distribution of EDTA species. Molecular ions were detected for EDTA and its complexes with Cu, Pb, Cd, Al, and Fe(III). In the case of the Pb-EDTA complex, the isotopic signature of Pb was also observed. Based on this work, the application of ESMS for the detection of ambient metal species in natural waters appears promising but is limited by the sensitivity of the technique and by variable response to different compounds. Detection limits for EDTA and its metal complexes are approximately micromolar though better sensitivity has been reported for other metal-organic complexes.

Work is in progress to characterize the ESMS response to organic ligands of varying structures (and their metal complexes) and to improve the sensitivity of the technique. The instrument currently in use is a Hewlett Packard Series 1100 LC/MSD; adjustable instrumental parameters include drying gas flow rate and temperature, capillary and fragmentor voltages, gain and nebulizer pressure. The effects of the sample matrix (e.g., pH and methanol concentration) on sensitivity will also be tested for selected model compounds. Model compounds have been selected to include a range structural characteristics including: type of heteroatom(s) and complexing functionalities, metal-ligand stoichiometry, and ligand charge and hydrophobicity. Preliminary, screening studies will be performed to examine ESMS response to reference humic and fulvic acids.

RADICAL BALANCE IN URBAN AIR

Robert J. O'Brien
Chemistry Department
Linda A. George
Center for Science Education
Thomas M. Hard
Chemistry Department, Portland State University, PO Box 751, Portland, Oregon 97207

Atmospheric free radicals hydroxyl and hydroperoxyl (OH and HO_2, collectively HO_x) are the catalysts which cause secondary or photochemical air pollution. Chemical mechanisms for oxidant and acid formation, on which expensive air pollution control strategies are based, must accurately predict these radical concentrations. We used the FAGE technique to carry out the first simultaneous, in-situ, measurements of these two radicals in highly polluted air at downwind sites in the Los Angeles airshed.

To compare the measured OH and HO_2 concentrations with photochemical models, a complete suite of simultaneous ancillary measurements was necessary, and was obtained during each measurement campaign. The suite included speciated hydrocarbons, carbonyl compounds, carbon monoxide, nitric oxide, nitrogen dioxide, ozone, and meteorological parameters. With this suite as input, we tested the ability of a lumped chemical mechanism to accurately predict the measured OH and HO_2 radical concentrations.

Due to the short photochemical lifetime of HO_x (less than 1 minute), this test of radical balance in urban air depends directly and quantitatively on the measured parents and reaction partners of the radicals, and only indirectly on the upstream history of the sample.

Results of the measurements, and of the radical balance tests, will be presented, with acknowledgments to the organizations and scientists who provided assistance.

ENVIRONMENTAL APPLICATIONS OF NOVEL INSTRUMENTATION FOR MEASUREMENT OF LEAD ISOTOPE RATIOS IN ATMOSPHERIC POLLUTION SOURCE APPORTIONMENT RESULTS

Keeler

NO ABSTRACT AVAILABLE

REMOTE SAMPLING PROBE WITH FAST GC/MS ANALYSIS: SUBSURFACE DETECTION OF ENVIRONMENTAL CONTAMINANTS

Albert Robbat, Jr.
Center for Field Analytical Studies & Technology, Chemistry Department,
Tufts University, Medford, Massachusetts 02155

ABSTRACT
This paper describes the results of an in situ sampling probe that is capable of thermally extracting volatile and semivolatile organics bound to soil from depths of 30 ft. The organic vapor is swept to the surface by an inert carrier gas and trapped (volatiles) or condensed (semivolatiles) in appropriate sampling tubes. The organics are subsequently thermally desorbed into a gas chromatograph/mass spectrometer and analyzed in under 5 minutes.

INTRODUCTION
The EPA estimates that the cost for hazardous waste site cleanups will exceed $300 billion over the next 10 years,[1] with the cost for Superfund alone exceeding $26 billion since 1980, The following questions can be posed: Do inadequate site investigations and, therefore, a lack of understanding with respect to the chemical and physical dynamics affecting the cleanup contribute to these costs? Can field-based analytical instrumentation and methods give on-site project engineers the kind of data needed that will lead to faster, better, and cheaper cleanups?

Toward this end, research is leading to the development technology and methods that can produce quantitative analysis of environmental contaminants in minutes by thermal desorption gas chromatography/mass spectrometry (TDGC/MS). The analysis is based on a ballistically heated thermal desorber to achieve large volume sample introduction *and* mass spectral data analysis algorithms that can "look through" complex matrix signals to identify and quantify target compounds.[2] The TDGC/MS when used in a dynamic workplan framework can provide data fast enough to influence the on-site decision making process.[3] We have shown that on-site chemical analyses employing dynamic workplans can reduce the time and cost of hazardous waste site investigations.[4]

Cone Penetrometer (CP) systems can collect samples at much faster rates than can traditional drilling rigs. Figure 1 depicts the sampling probe used to collect subsurface soil and water samples. Typically, 5 cm o.d. pipes are threaded together and pushed underground by truck weights of up to 40 tons. The challenge therefore, is to design 1) a flexible heated, 300 ºC, transfer line that can be woven through each pipe section and 2) a programmable thermal extraction sample collection probe that can heat the soil to at least 350 ºC. These target temperatures are based an past studies aimed at developing direct measuring thermal desorption gas chromatography (TDGC) sample introduction system.[5,6,7,8,9] The design of a thermal extraction cone penetrometer (TECP) system for subsurface sampling of soil-bound organics from depths of up to 25 m is described in this paper as well as a new data analysis system that provides unique compound identification and quantification capabilities under fast TDGC/MS conditions.

MATERIALS
Heated Transfer Line
The materials used to fabricate the heated transfer line include: deactivated fused silica lined stainless steel tubing 30 in x 1 mm, i.d. 0.76 mm Silcosteel® (Restec Corp., Bellefonte, PA); Nextel 312 thermal insulation sleeving and Viton shrinkable tubing (Omega, Stamford, CT), heat shrinkable Teflon tubing (Patriot Plastics, Woburn, MA);

aluminum foil with silicon adhesive backing (COMCO), polyimid moisture insulation tape (Newark Electronics, Chicago, IL); thermal insulated fiber glass cloth tape (Fisher Scientific, Pittsburgh, PA). The heated transfer line is heated by connecting high temperature power lead wires (Newark Electronics) to both ends of the Silcosteel® tube. Temperature was measured using Thermocouples C01-K and C02-K (Omega).

Heated Probe

The probe was made from a 1 m x 4.5 cm, 2.5 cm i.d., threaded steel pipe. A 20 mm i.d. hole was cut in the pipe at one-third the distance from the bottom. The heat was supplied by inserting an aluminum casing into the pipe, which contained a 10 cm x 1.5 cm heating cartridge L4A712, 240V/1000W. The same model Thermocouples used to measure the transfer line temperature were used in the Probe.

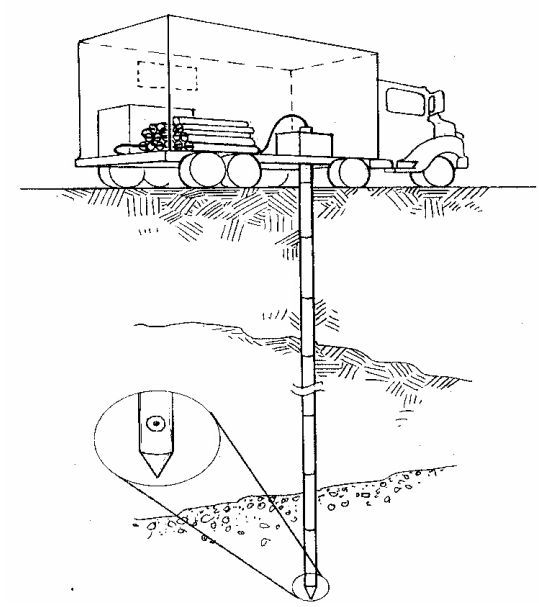


Figure 1. Cone penetrometer and thermal extraction sampling probe.

Equipment

The Silcosteel® was heated by passing current through the tube using an electrical isolation step-up transformer (Grainger, Haverhill, MA) with power and temperature controllers model DCIP-50245-F00 and model 988A-10FD-AARG, respectively (Watlow, St. Loius, MO). A Hewlett Packard (Palo Alto, CA) model 5972 mass spectrometer was ruggedized for the field and used in combination with a Tufts University (Medford, MA) designed thermal desorption gas chromatograph. All GC/MS total ion current chromatograms (TIC) were acquired by HP's data acquisition system. A new mass spectrometry data analysis software developed at Tufts was used to identify and quantify polycyclic aromatic hydrocarbons (PAHs). The Ion Fingerprint Detection™ software is available from Ion Signature Technology (Cambridge, MA).

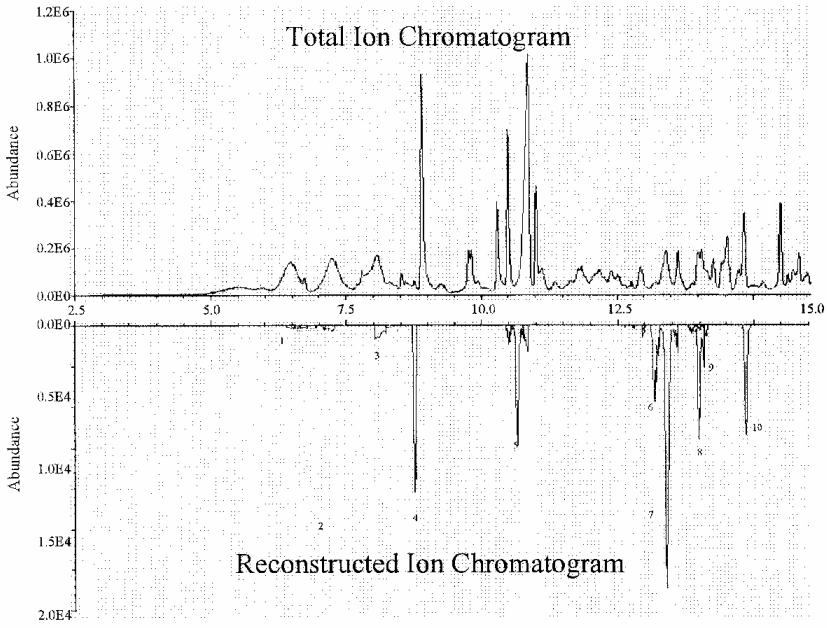


Figure 2. GC/MS analysis of a soil sample collected from Hanscom Air Force Base (Bedford, MA); compounds found: 1) 1,1,1-trichloroethene, 2) methylene chloride, 3) 1,1-dichloroethene, 4) 1,4-difluorobenzene (surrogate), 5) toluene-d_8 (internal standard), 6) ethylbenzene, 7) m/p-xylene, 8) o-xylene, 9) styrene, 10) 4-bromofluorobenzene (surrogate).

RESULTS

Two key breakthrough technologies have been developed that meet the EPA data quality measurement objectives and EPA Soil Screening Level quantitation levels under fast GC/MS conditions. First is the mass spectral data analysis software. The software extracts between three and ten characteristic fragment ions for each targeted organic and then, based on a patented set of algorithms, compound identity and concentration are determined. Algorithmic details can be found elsewhere.[2] Although all MS systems can extract ions, they cannot handle the amount of extracted ion information and determine compound presence using current statistical or library matching

routines when high levels of interferents are present in the sample. For example, the software can provide compound identification in complex environmental samples without the need for extensive sample cleanup. The second technology breakthrough is the thermal desorber. Unlike other commercially available units, the TD can be ballistically heated from subambient temperatures to 320 ºC in 8-sec. The TD uses a standard Tenax tube for trapping VOCs and an empty glass sleeve for semivolatiles that have been swept from depth to the surface by the carrier gas. Direct desorption of organics from solid materials or an organic extract into the GC is made by placing known quantities into an empty glass sleeve.

Figure 2 illustrates a representative total ion current chromatogram (TIC) and a reconstructed ion current (RIC) chromatogram where the data analysis software was able to "see through" the matrix. Note that the internal standard (peak #5) and target compounds 1,1,1-trichloroethene and 1,1-dichloroethene (peaks 1 and 3) are buried within the matrix and that their corresponding signals are 10^2 to 10^4 times smaller than the matrix signal. Typically, analysts would dilute this sample prior to analysis based on visual inspection of the petroleum present in the sample. This practice will result in the loss of low level target compounds such as the chlorinated solvents found in this sample.

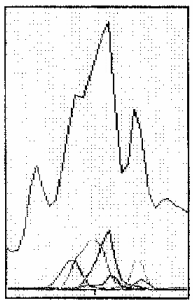


Figure 3 shows the TIC and RIC chromatograms produced from a 10-min TDGC/MS analysis of a standard mixture of polychlorinated biphenyls (PCBs, Aroclor 1248), polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, and engine oil (25% v/v). A total of 1,000-ng PCBs was thermally desorbed into a 15-m GC column along with 19 chlorinated pesticides (20-ng/compound), 16 PAHs (40-ng/compound), and pyrene-d_{10} (50-ng) added as an internal standard. An expanded view of the RIC chromatogram between 6.7 min and 6.9 min is shown here. Note that there are six compounds that elute within this time domain. Compound identification was made based on a set of algorithms that extracted 3-6 fragment ions per compound from the TIC and computed their match against standard reference spectra in seconds. Each compound's RIC signal, based upon preselected quantitation ions, are then used to produce the RIC chromatogram and to quantify compound concentration. The algorithms and results will be presented documenting measurement accuracy, precision, and sensitivity.

Figure 4 depicts the schematic of the heated transfer line and the electronic circuitry used to control the power and temperature. The figure shows the various layers including moisture, electrical, and thermal insulation sleeves as well as the fused silica coated stainless steel tube Silcosteel® The goal was to heat the transfer line to 300 ºC and achieve a 15 cm bend radius so that the pipes in the truck could be stacked efficiently. This feature is important since cone penetrometer systems can reach subsurface depths of up to 60 m when the geology is amenable. Based on the design shown in the figure a 10 cm bend radius was obtained, with the Silcosteel® temperature programmable from ambient soil temperatures up to 300 ºC. To date, a 30 m transfer line has been made, which can be woven through ten 1 m pipe sections to achieve subsurface depths of 10 m. The transfer line is heated by passing direct current through the stainless steel tube. Imbedded in the transfer line are the electrical and thermal couple wires needed to carry current to the probe head and to monitor both the transfer line and probe temperatures.

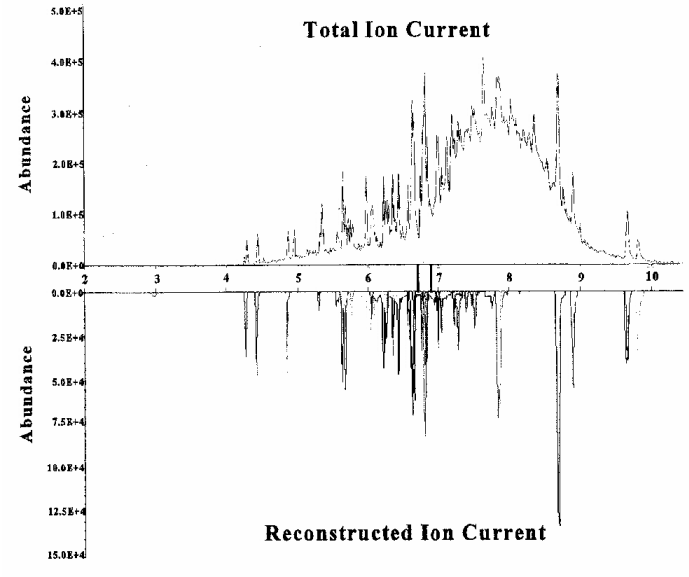


Figure 3. 10-min TDGC/MS analysis of a soil sample fortified with a standard mixture of PCBs, PAHs, pesticides and gasoline/engine oil (1:3 by vol).

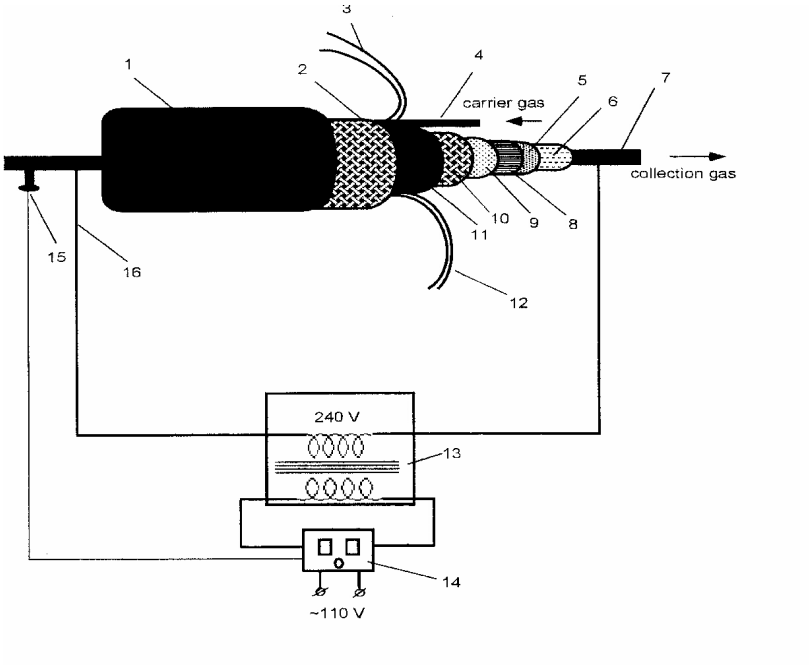


Figure 4. TECP system, which includes 1) heat shrinkable sleeve, 2) fiber glass insulation, 3) high temperature electrical wires, 4) Viton shrinkable tubing, 5) heat shrinkable Teflon tubing, 6) Nextel 312 thermal insulation sleeving, 7) deactivated fused silica lined stainless steel tubing 30 m x 1 mm, i.d. 0.76 mm Silcosteel® 8) aluminum foil with silicon adhesive backing, 9) polyimid moisture insulation tape, 10) thermal insulated fiber glass cloth tape, 11) polyimid moisture insulation tape, 12) thermocouple wire, 13) isolation step-up transformer, 14) temperature and power controllers, 15) transfer line thermocouple, and 16) high temperature electrical wires.

Table 1. Material Balance of Closed Chamber
(Re_m = 5700; V_o = 32; w_g = 0.6 m/s; dry sand)

	250 ºC			300 ºC		
	% Rec	% Soil	% Ads	% Rec	% Soil	% Ads
Naphthalene	5	ND	ND	15	ND	ND
Acenaphthylene	61	ND	ND	63	ND	ND
Acenaphthene	74	ND	3	78	ND	ND
Fluorene	72	ND	2	75	3	0.6
Phenanthrene	76	5	2	83	5	2
Anthracene	75	6	3	78	6	2
Fluoranthene	79	5	3	80	4	3
Pyrene	86	9	2	83	6	1
Benzo(a)anthracene	56	42	2	67	30	1
Chrysene	50	40	2	61	31	1
Benzo(b)fluoranthene	41	53	6	55	40	4
Benzo(k)fluorarthene	41	53	6	55	40	4
Benzo(a)pyrene	65	31	4	65	23	3
Dibenz(a,h)anthracene	NA	NA	NA	37	59	2
Indeno(1,2,3-ed)pyrene	NA	NA	NA	37	59	2
Benzo (g,h,i)perylene	NA	NA	NA	23	67	4

ND - not detected; NA - not analyzed

Little degradation of the silica lining is observed as long as air is purged from the system. Air is flushed from the transfer line by nitrogen prior to transfer line heating. After the Silcosteel® has been conditioned the gas valve is switched to re-direct nitrogen into the carrier gas line. At this point, a vacuum pump is turned on to collect the soil/organic vapor at the collection window and to transport the organics to the surface through the Silcosteel® tube. The valve can then be re-positioned to cleanse the transfer line tube when high levels of sample are collected. This step is intended to eliminate sample carry over from one sample location to the next. Work is in progress to automate the TECP system to control the probe and transfer line temperatures as well as the carrier, flush, and collection gas lines.

Material balance experiments were conducted to determine the thermal extraction efficiency for PAHs at 250ºC and 300ºC, see Table 1. At optimum conditions, i.e., soil temperature, carrier gas flow rate, collection volume, and under closed cell conditions, greater than 55% recovery was obtained. Closed cell conditions represent the maximum amount that can be extracted, as opposed to the TECP, since none of the organic vapor produced is lost to the

environment and all soil is uniformly heated. The organic vapor is efficiently flushed from the cell into Tenax for VOCs or the cold trap for semi-VOCs. Note that less than 4% of the collected organics remained in the transfer line after collection. Research is in progress to chemically modify the surface to minimize (eliminate) organic absorption. Nonetheless, back-flushing for 5-min reduced the percent adsorbed to non detectable levels.

Table 2. Comparison of TECP vs. Closed System
T_{pipe} = 450 ºC; T_{soil} = 280 ºC; Re_m = 6000; w_g = 1.2 m/s; L/d = 15

	TECP % Recovery						Closed Chamber % Recovery	% Diff
	50-ppm	25-ppm	15-ppm	5-ppm	Ave Rec	% RSD		
Naphthalene	20	37	26	37	30	23	18	68
Acenaphthylene	34	36	36	33	35	5	62	44
Acenaphthene	41	39	33	30	36	18	77	53
Fluorene	49	36	38	37	40	17	73	46
Phenanthrene	37	32	35	34	35	7	80	57
Anthracene	37	32	34	34	34	7	77	56
Fluoranthene	65	53	48	36	50	34	80	37
Pyrene	64	53	45	68	47	15	85	32
Chrysene	27	37	31	41	34	16	57	40
Benzo(a)anthracene	49	37	36	41	40	12	62	36
Benzo(b&k)fluoranthene	29	27	29	23	27	12	48	44
Benzo(a)pyrene	25	23	36	24	27	26	65	58
Indeno(1,2,3-ed)pyrene	26	19	20	23	22	14	65	31
Dibenz(a,b) anthracene	26	19	19	23	22	14	62	32
Benzo(g,h,i)perylene	17	16	16	16	10	4	20	19

Note: % Difference is between Average TECP Recovery and Closed Chamber Recovery

The TECP and closed cell data comparison study is shown in Table 2. Recall that the closed system represents maximum recovery of analyte while the TECP is what one should expect to achieve in the field. The TECP measurement precision determined over an order of magnitude for PAHs is excellent. The results are remarkable and are as good or better than what is achievable through soil/solvent extraction. The accuracy for the TECP approximates one-half that of the closed (ideal) system. Results will be presented illustrating collection efficiency as a function of soil type, probe depth and moisture content.

Table 3. TECP Field Study, Berlin Vermont
T_{pipe} = 450 ºC; T_{soil} = 280 ºC; $T_{tr.line}$ = 280 ºC; Re_m = 6000; w_g = 1.6 m/s

	TECP Measured PAH/Soil Concentration				
	Boring 1		Boring 2		
	97-cm	142-cm	130-cm	155-cm	190-cm
Naphthalene	2	2	4	ND	ND
Acenaphthylene	9	6	14	ND	5
Acenaphthene	2	2	3	2	3
Fluorene	7	3	10	4	3
Phenanthrene	11	5	5	2	4
Anthracene	11	5	7	2	4
Fluoranthene	44	3	6	2	3
Pyrene	29	4	6	5	4
Benzo(a)anthracene	45	11	6	3	2
Chrysene	45	11	6	3	2
Benzo(b)fluoranthene	5	0.4	0.5	ND	ND
Benzo(k)fluoranthene	6	0.3	0.5	ND	ND
Benzo(a)pyrene	12	0.6	ND	ND	ND
Dibenz(a,h)anthracene	2	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	3	ND	ND	ND	ND
Benzo(g,h,i)perylene	6	ND	ND	ND	ND

The TECP and heated transfer line was tested in the field employing ARA's CPT in Berlin, Vermont. The location was a Vermont state central maintenance facility known to contain petroleum hydrocarbon contamination. The TECP

was tested for mechanical ruggedness and its ability to collect subsurface bound organics. The vertical profile of two borings are shown in Table 3. PAHs were found at depths of 97-cm and 142-cm at boring one and 130-cm. The hot organic vapor was cooled by dry ice and collected in an empty glass sleeve attached to the transfer line. Total collection and analysis time required at each depth location was approximately 15-min per sample inclusive of sample collection, transfer line back flushing, and analysis time. Unfortunately, comparison measurements between the TECP measured concentrations and actual soils collected at depth and analyzed by standard GC/MS methods were not possible since ARA was unable to re-enter the hole with a soil sample collection probe without breaking the CP rod. The results produced to date are promising suggesting that direct on-line chemical measurements of subsurface contaminants may be possible within a couple years.

REFERENCES

1. Cleaning Up the Nation's Waste Sites: Markets and Technology Trends, Office of Solid Waste and Emergency Response, U.S. EPA, Washington, DC, 1993, EPA 542-R-92-012, 164 pp.
2. Y. Gankin, A. Gorshteyn, S. Smarason, and A. Robbat, Jr., Anal. Chem, 70: 1655-1663 (1998).
3. A. Robbat, Jr., "Field Analytics, Dynamic Workplans" The Encyclopedia of Environmental Analysis and Remediation, ed. by R.A. Meyers, John Wiley & Sons, Inc. New York, NY., July 1998.
4. A. Robbat, Jr., "A Dynamic Site Investigation Adaptive Sampling and Analysis Program for Operable Unit 1 at Hanscom Air Force Base, Bedford, Massachusetts", U.S. Environmental Protection Agency, Region I, October 1997; see http://clu-in.com/char1.htm#regional.
5. A. Robbat, Jr., T-Y Liu, and B. Abraham, Anal. Chem., 64:358-364 (1992).
6. A. Robbat, Jr., C. Liu, and T.-Y. Liu, J. Chromatography, 625: 277-288 (1992).
7. A. Robbat, Jr., C. Liu, and T.-Y. Liu, J., Anal. Chem., 64: 1477-1483 (1992).
8. K M. Abraham, T-Y Liu, and A. Robbat, Jr., Hazardous Waste & Management, 10: 461-473 (1993).
9. K. Jiao and A. Robbat, Jr., J. of AOAC International, 79: 131-142 (1996).

AN INTEGRATED NEAR INFRARED SPECTROSCOPY SENSOR FOR *IN-SITU* ENVIRONMENTAL MONITORING

Roland A. Levy and John F. Federici
New Jersey Institute of Technology, University Heights, Newark, NJ 07102
Tel. (973)-596-3561

The monitoring of environmental organic contaminants currently involves off-site methods which prohibit optimal usage. This study explores the possibility of combining the principles of interferometry with that of near infrared evanescent wave absorption spectroscopy to produce a novel integrated sensor technology capable of monitoring and determining *in-situ* the concentration of numerous organic analyte species simultaneously. This novel sensor promises to be non-intrusive and to provide accurate, rapid, and cost effective data. The overall instrument is envisioned to be compact, portable, rugged, and suitable for real time monitoring of organics. The sensor consists of a symmetric, single mode Mach-Zehnder interferometer with one arm (sampling) that is either exposed directly to the analyte or coated with a thin hydrophobic layer that enhances the binding of pollutant molecules onto its surface. A glass buffer layer protects the second arm (reference) from the influence of pollutants. Light is coupled into the waveguide and split between the sampling and reference arms using a Y-splitter configuration. Changes in the refractive index caused by the presence of organic contaminants result in a measurable phase difference between the sampling and reference arm. Selectivity of the sensor is achievable by utilizing evanescent wave absorption spectroscopy in the near infrared, a technique which measures wavelength dependent refractive index changes. The waveguide structures used in this study are fabricated on 10 cm silicon wafers. V-grooves are first formed in the silicon substrate to hold the fibers which couple to the ends of the Mach-Zehnder interferometer. A 10 μm thick SiO_2 film is synthesized by low pressure chemical vapor deposition (LPCVD) to act as cladding material for the waveguide and prevent light from coupling with the underlying silicon. A 4 μm thick phosphorus-doped (7.5 wt% P) LPCVD SiO_2 film is then deposited to act as core material for the waveguide. This layer is patterned using standard lithographic exposure and plasma etching techniques and subjected to a 1050 ºC anneal to cause viscous flow and round off the edges. This rounding-off procedure is necessary to minimize coupling losses between fiber and waveguide. The