Subtask 1.11 - Spectroscopic Field Screening of Hazardous Waste and Toxic Spills

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TABLE OF CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	ii
1.0 INTRODUCTION	1
2.0 OBJECTIVES	2
3.0 WORK PERFORMED AND RESULTS	2
3.1 Review of Published Work	2
3.2 EFAS Concept	2
3.3 Evaluation of Polymeric Solid Phase for SPME	3
3.4 Evaluation of the EFAS Design	9
3.5 Spectroscopic Sensor Conceptual Design	10
3.6 Fiber-Optic SPME-IR Probe Optical Design	11
4.0 CONCLUSIONS	12
5.0 REFERENCES	13
BIBLIOGRAPHIC DATABASE LISTING	Appendix A
FIELD SCREENING SYMPOSIUM SUMMARY	Appendix B

LIST OF FIGURES

1	Analyte partitioning versus temperature	4
2	Analyte partitioning versus time	5
3	Absorbance spectra of Paraflint H-1, Hoechst PE-520, and candle waxes	7
4	Absorbance spectra of Microwax 155 and 195 and Paraflint C-2 waxes	8
5	4-hr headspace extraction of test compounds with various solid phases	8
6	Concept of spectroscopic sensor	10
7	Soil probe incorporating FT-IR detection with solid-phase preconcentration	11
8	Fiber-optic SPME-IR probe prototype optical layout	12

LIST OF TABLES

1	Calibration Data	3
2	Calibration Data for Hydrocarbon-Soil Matrix	6
3	Calibration Data for Hydrocarbon-Sand Matrix	6
4	Commercially Available Waxes Tested	7
5	Comparison of Extraction Capabilities for Different Solid Phases	9

TASK 1.11 - SPECTROSCOPIC FIELD SCREENING OF HAZARDOUS WASTE AND TOXIC SPILLS

1.0 INTRODUCTION

Techniques for the field characterization of soil contamination due to spillage of hazardous waste or toxic chemicals are time-consuming and expensive. Thus more economical, less time-intensive methods are needed to facilitate rapid field screening of contaminated sites. In situ detection of toxic chemicals in soil offers both time and cost advantages for field screening, with additional application to real-time site monitoring.

One method to assess soil contamination by hydrocarbons is soil gas survey. Soil gas measurements offer a rapid and relatively inexpensive means of site characterization. However, soil gas methods are subject to influences from size and age of the contaminant source, moisture and organic content of the unsaturated zone, volatility, and solubility of the volatile organic carbon (VOC) source (1). Soil gas surveys also suffer from the effects of biochemical processes, since biodegradation may remove the low-molecular-weight VOC vapors in the vadose zone (2). In addition, soil gas surveys also have inherent limitations in their spatial resolution (3).

Lieberman and coworkers have demonstrated the combination of laser-induced fluorescence spectroscopy with cone penetrometry (LIF-CPT) as a means to estimate the extent to which a region of soil has been contaminated with petroleum hydrocarbons (4). The LIF-CPT method has also been shown to overcome some of the spatial resolution limitations of soil gas measurements (5). The LIF-CPT method, however, is currently limited to detection of higher-molecular-weight aromatic hydrocarbons that fluoresce and is not sensitive to lighter, more volatile compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX) (5).

Fourier transform infrared (FT-IR) spectroscopy coupled with evanescent-mode fiber-optic sensors has been demonstrated as a means to remotely detect and classify petroleum products in water using mid-infrared (MIR) optical fibers (6). This work demonstrated that a fiber-optic evanescent field absorbance sensor (EFAS) could be used to classify petroleum contamination into categories such as crude oil, kerosene, No. 2 fuel, and residual distillates using the MIR spectral range. Conzen and coworkers utilized silicone-clad silica optical fibers coupled with near-infrared (NIR) spectroscopy to remotely detect dichloromethane, chloroform, and trichloroethylene (TCE) in aqueous solution (7). Klunder and Russo used NIR spectroscopy with optical fibers to monitor diffusion of VOCs into a silicone rubber cylinder (8). They obtained both qualitative and quantitative information on TCE, 1,1-dichloroethylene, and benzene in aqueous solution and vapor phase.

An in situ method based on the concepts presented above would employ an EFAS similar in design to that proposed by Conzen and coworkers, but coated with a polymer to allow solid-phase extraction of analytes to improve the method's sensitivity. The fiber optic will have cladding that is hydrophobic and oleophilic such as that suggested by Klunder and Russo (8). Additionally, the process by which the detection system of the EFAS collects VOCs should be quantitative and, if possible, reusable. Work has shown that the partitioning of organic species into thin polymeric films is reversible, quantitative, and possesses the selectivity for extraction of VOCs from aqueous

solution and vapor phase when used in solid-phase microextraction (SPME) (9-11). Spectroscopic studies in the mid-infrared range have shown polymeric materials to be useful coatings for infrared attenuated total reflectance (IR-ATR) measurements (12,13) of chlorinated hydrocarbons in aqueous solution.

2.0 OBJECTIVES

The overall objective of this project is to study the feasibility of using an EFAS FT-IR spectroscopic sensor coupled with CPT as a field screening method. The FT-IR-CPT will be developed by building on the work cited above. The specific objectives of this project are as follows:

- Design an accessory for use with FT-IR that interfaces the spectrometer to a cone penetrometer.
- Characterize the response of the FT-IR accessory to selected hydrocarbons in a laboratory-simulated field environment.
- Determine the ability of the FT-IR-CPT instrument to measure hydrocarbon contamination in soil by direct comparison with a reference method (e.g., Soxhlet extraction followed by gas chromatography) to quantify hydrocarbons from the same soil.

3.0 WORK PERFORMED AND RESULTS

3.1 Review of Published Work

A literature search was done to obtain a list of published work relating to the project objectives. Bibliographic information for the articles currently on file is stored in a computer database. A complete listing is contained in Appendix A.

Recently published work on spectroscopic applications using optical fibers and SPME has been reviewed in order to apply this knowledge to the project goals.

A member of the project team attended the Fourth International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals organized by the U.S. Environmental Protection Agency (EPA) and the Air & Waste Management Association. Several presentations at this conference described either development or application of field screening methods employing fiber-optic technology with spectroscopic methods. A summary of the sessions attended is included in Appendix B. Proceedings from this conference will be available near the end of July 1995.

3.2 EFAS Concept

The proposed sensor will use fiber-optic evanescent field absorption as a means of spectroscopic detection. The EFAS will have a polymeric cladding in the active sensor region that

possesses the desired characteristics described above. Thus, the EFAS will utilize SPME to extract and concentrate analytes on the EFAS, allowing MIR spectroscopic detection of VOCs in aqueous and vapor phases. The sensor is being developed with the goal of being able to mount the EFAS into commercially available cone penetrometers. This will allow the EFAS to be deployed in the field for in situ screening of hazardous and toxic chemical spills.

3.3 Evaluation of Polymeric Solid Phase for SPME

A candidate material for cladding the EFAS has been selected based on a previous study of its capability for direct SPME of VOCs in aqueous solution (14). The material is an inexpensive commercially available film typically used for sealing laboratory sample vials and jars.¹ Work performed under this contract has collected data on the extraction capabilities of Parafilm-M® for aqueous solutions of TCE, ethylbenzene (ETB), and *m*-xylene (MXY).

An experiment similar in principle to that of Zhang and Pawliszyn (10) was devised to evaluate the characteristics of Parafilm-M® for use as an SPME solid phase for headspace sampling. Our experiment differed in the geometry and type of the solid phase (Parafilm-M®). We extract the VOCs from the headspace with the Parafilm-M® and analyze the components directly in the solid phase via MIR absorbance spectroscopy. This is unlike conventional SPME, where the analytes are thermally desorbed from the solid phase directly into an instrument such as gas chromatography-flame ionization detection (GC-FID) or GC-mass spectroscopy (MS).

For each of the test compounds TCE, ETB, and MXY, calibration curves were determined. These data sets represent the ability of Parafilm-M® to quantitatively extract analytes in the headspace over aqueous solutions. For all three compounds, the regression of analyte concentration against MIR absorbance shows excellent linearity and repeatability, as shown by the data in Table 1.

TABLE 1

Parameter	Calibration Data		
	MXY	ETB	TCE
Calibration Range, ppm	1-35	2-50	5-100
R Square	0.9988	0.9995	0.9997
Standard Error	0.5088	0.4316	0.6561
No. of Observations	7	7	7
Slope, ppm/AU	209.16	500.13	1158.17
%RSD @ Concentration	0.47 @ 1.75	1.22 @ 4.99	2.41 @ 10

It being established that quantitative extraction is possible with Parafilm-M®. Work was initiated to determine the optimum temperature at which the solid phase collects analytes. This work used the same general procedures as that of the calibration experiments. MIR absorbance

¹PARAFILM-M® - American National Can, Greenwich, CT 06836.

versus temperature curves were collected in headspace over aqueous solutions of 10 ppm for TCE, ETB, and MXY using an exposure time of 90 min. Data were collected at five temperatures ranging from 20° to 50°C. A plot of absorbance versus temperature for all analytes is shown in Figure 1. In order to plot the data for all three compounds on a common set of axes, the MIR absorbance was normalized to the maximum value obtained.

As shown in Figure 1, as the temperature increases, the extraction efficiency increases in direct proportion to temperature up to 37°C. Detailed analysis of the MIR spectra obtained from these experiments revealed that at approximately 50°C, thermally induced structural changes in the solid phase occur, causing distortions in the spectrum baseline. Therefore, 37°C has been selected for a temperature at which an acceptable compromise is reached between extraction efficiency and thermal degradation effects in the stationary phase.

Since SPME is a diffusion-based method, it will show a strong dependence on temperature and time. Experiments were carried out to determine partitioning of analytes into Parafilm-M® as a function of exposure time at a fixed temperature and analyte concentration. Partitioning curve data (MIR absorbance versus time) were collected for TCE, ETB, and MXY at a temperature of 37°C and a fixed concentration (TCE = 10 ppm, ETB = 10 ppm, *m*-xylene = 5 ppm). A graph depicting the data collected is shown in Figure 2. As with the temperature data of Figure 1, the data are calculated to a common Y-axis by normalization to the maximum value obtained for the compound.

As with the extraction temperature study, an exposure time was selected based on a compromise between practical and theoretical considerations. For practical reasons, the extraction time should be minimized. However, if too small an extraction time is chosen, analyte detection limits will increase, reducing measurement sensitivity. Figure 2 shows that as expected, the amount

Figure 1. Analyte partitioning versus temperature.

Figure 2. Analyte partitioning versus time.

of analyte that has diffused into the Parafilm-M® increases with time. A subtle break appears in the partitioning curves of Figure 2 at approximately 180 to 200 min of exposure time. Past this point, the slope of the partitioning curves decreases. Therefore, 180 min has been chosen as an extraction time in this preliminary work.

The work described above provided a preliminary evaluation of the ability of Parafilm-M® to quantitatively extract hydrocarbons from headspace over aqueous solution, with sensitivities in the low parts per million (ppm) range. Headspace extraction capabilities of Parafilm-M® were evaluated over hydrocarbon-spiked sand and soil matrices. Procedures used for the sand and soil tests are the same as those used for the aqueous solution tests performed in the work described above, except a hydrocarbon-sand matrix or hydrocarbon-soil matrix is substituted for the hydrocarbon-water matrix. The sand used in these experiments was Ottawa Sand Standard (Fisher Scientific S23-3), and the soil samples were obtained locally from the Grand Forks, North Dakota, area. Experiments to determine partitioning times for the test compounds (MXY, ETB, and TCE) were carried out, and 120 min was determined as the optimal partitioning time for both soil and sand matrices. Calibration curves for each test compound were determined for both soil and sand matrices using a 120-min partitioning time, as listed in Tables 2 and 3, respectively.

For each of the test compounds, TCE, ETB, and MXY, calibration curves were determined. These data sets represent the ability of Parafilm-M® to quantitatively extract analytes in the headspace over soil and sand matrices. For all three compounds, the regression of analyte concentration against MIR absorbance shows excellent linearity and good repeatability, as shown by the data in Tables 2 and 3.

TABLE 2

Calibration Data for Hydrocarbon-Soil Matrix			
Parameter	ETB	MXY	TCE
Calibration Range, ppm	2.6-102	2.6-102	4.3-173
R Square	0.9887	0.9918	0.9799
Standard Error	4.6475	3.7005	9.7684
No. of Observations	6	7	7
Intercept, ppm	2.67	1.52	7.28
Slope, ppm/AU	785.17	461.53	611.73
RSD @ Concentration	15.37 @ 5.17	21.69 @ 5.15	0.55 @ 8.62

TABLE 3

Calibration Data for Hydrocarbon-Sand Matrix			
Parameter	ETB	MXY	TCE
Calibration Range, ppm	1.4-54	1.4-54	2.2-90
R Square	0.9832	0.9954	0.9806
Standard Error	2.7690	1.4522	5.0079
No. of Observations	7	7	7
Intercept, ppm	1.53	0.77	B0.19
Slope, ppm/AU	242.77	105.24	107.29
RSD @ Concentration	3.78 @ 2.71	2.29 @ 2.70	29.16 @ 4.53

During on-line testing of the new spectroscopic sensor design, it was found that the solid-phase material used (Parafilm-M®) did not provide the needed structural rigidity for this application. Therefore, work continued focused on evaluation of different solid-phase materials for analyte extraction and preconcentration for use with infrared detection. It was determined through analysis of the composition of Parafilm-M® that a large fraction of its chemical components are paraffins, so work was initiated to evaluate commercially available waxes as preconcentrating media.

Several solid-phase materials were evaluated for structural rigidity. Results of this testing provided the idea for a support structure that enables construction of solid-phase coupons, allowing different film thickness to be deposited onto a substrate. The substrate used is wire screen; the mesh size of the wire screen is selected based on the spectral range of interest (e.g., UV or MIR), viscosity of the solid phase at room temperature, and desired solid-phase thickness. For the initial suite of tests, the wire screen support for the solid phase was 18 mesh (18 holes per in.), since all materials tested are solid at room temperature. Table 4 lists the solid-phase materials tested and whether or not they are optically clear enough in the MIR for the analytical application.

TABLE 4

Commercially Available Waxes Tested	
Wax Type (trade name)	Usable in MIR?
Parafilm	Yes
Microwax 155	Yes
Microwax 195	Yes
Paraflint C-2	Yes
Paraflint H-1	Yes
Hoechst PE-520	Yes
Candle Wax	Yes
Beeswax	No
Hoechst Wax F	No
Japan Wax	No
Paraflint A-1	No
Carnauba Wax	No

Figures 3 and 4 depict the MIR absorbance spectra of the waxes that exhibit good optical clarity in the fingerprint region. For comparative purposes, each figure contains a spectrum of Parafilm-M®. It should be noted that since the wax materials have less chemical functionalities with MIR absorbance features in the fingerprint region, they provide a better medium for optical detection of the extracted hydrocarbons.

Figure 3. Absorbance spectra of Paraflint H-1, Hoechst PE-520, and candle waxes.

Figure 4. Absorbance spectra of Microwax 155 and 195 and Paraflint C-2 waxes.

Each of the solid phases listed in Table 4 as being usable in the MIR was tested with each of three test compounds, TCE, ETB, and MXY. The test involved a 4-hr headspace extraction of the test compound from Ottawa sand at a concentration of 50 $\mu\text{g/g}$. Figure 5 shows a comparison of the instrument responses of each solid phase for each of the three test compounds.

Figure 5. 4-hr headspace extraction of test compounds with various solid phases.

As can be seen in Figure 5, quite a range of instrument responses results from the different solid phases when the same concentration of analyte is extracted. Some of the variation is due to differences in film thicknesses, but more of the variations are due to the different partitioning coefficients for the solid phases tested. Table 5 compares the extraction data for each solid phase and test compound on a basis normalized to the solid phase that produced the most intense instrument response.

TABLE 5

Comparison of Extraction Capabilities for Different Solid Phases			
Wax Type	TCE, % of best	MXY, % of best	ETB, % of best
Parafilm	90	74	72
Microwax 155	100	100	100
Microwax 195	35	31	39
Paraflint C-2	16	12	14
Paraflint H-1	19	14	18
Hoechst PE-520	74	80	79
Candle Wax	63	59	51

The work above determined Microwax 155 employing wire mesh as a support structure to be applicable to the SPME-IR application with headspace extraction of test compounds TCE, MXY, and ETB. Further work extended proof of the capabilities for Microwax 155 solid-phase material applied to headspace extraction of a test compound-contaminated soil and direct extraction from test compound-contaminated water. SPME-IR testing of Microwax 155 for headspace extraction over soil and direct extraction from contaminated water were carried out using test procedures established for Parafilm-M®. Calibration of the SPME-IR system using Microwax 155 for all test compound-contaminated sand, soil, and water matrices gave detection limits and linear dynamic range performance comparable to those determined for Parafilm-M®.

3.4 Evaluation of the EFAS Design

As discussed in the introduction and objectives, we propose to design a soil probe capable of detecting hydrocarbon contamination using an MIR fiber-optic-based evanescent field absorbance sensor, building on previous work done by other researchers in the NIR range. Experiments were carried out to evaluate the capabilities of an MIR spectral region EFAS sensor.

The EFAS was built from 650- μ m-core-diameter, unclad, chalcogenide optical fiber 10 cm in length. The EFAS was fitted with SMA connectors to allow connection to the FT-IR fiber-optic interface. The EFAS was wrapped with Parafilm-M®, which serves as the preconcentrating solid phase used to enhance the evanescent field detection of analytes. The optical alignment and coupling were optimized to allow maximum throughput of infrared energy for the EFAS and FT-IR optical system.

In order to test the ability of the EFAS to detect analytes in the headspace over sand or soil matrices, a device was built that allows the EFAS to be mounted in a temperature-controlled enclosure that houses the analyte-containing soil or sand matrix. The temperature-controlled enclosure allows exposure of the EFAS to a sample matrix while still being connected to the FT-IR spectrometer, allowing on-line detection of analytes. Several tests were conducted to determine the sensitivity of the device to the test compounds (MXY, ETB, and TCE). Results of the tests indicated that the EFAS was not nearly sensitive enough for application to detection of hydrocarbon contamination in soil.

A theoretical model of the optical system was developed and geometric optics approximations were done to evaluate the EFAS. Through theoretical analysis, it was determined that the mismatch of refractive indices at the core-solid phase interface was the major factor in the loss of sensitivity for the EFAS. In other words, the loss of sensitivity was in part due to the fact that for optimum internal reflection conditions in the EFAS, the refractive index of the optical fiber core must be greater than the medium adjacent to it, but a large differential in refractive indices causes less than optimal conditions for internal reflection. For the case of the EFAS built at the EERC, one has a nominal optical fiber core refractive index of 2.8 (in the MIR region), and for the Parafilm-M cladding, the refractive index is approximately 1.5. This produces unfavorable optical conditions at the core-solid-phase interface for internal reflection, which results in less sampling of the solid phase by the evanescent field, resulting in reduced sensitivity to analytes.

3.5 Spectroscopic Sensor Conceptual Design

Because of the lack of sensitivity in the preliminary EFAS design, a new design utilizing fiber optics and transmission spectroscopy was developed. Figure 6 illustrates the basic concept. The sensor (the middle section) consists of a small, thin film of a solid-phase polymer that will

Figure 6. Concept of spectroscopic sensor.

function as the preconcentration/sensing portion. Infrared-transmitting fiber-optic cables (e.g., chalcogenide core material or silver halide) will be used to provide radiant energy to the sensor and to collect the unabsorbed energy for transmission to the spectral analyzing device (an FT-IR spectrometer). The entire fiber-optic probe assembly will be designed so that it can be easily interfaced to any commercially available FT-IR spectrometer.

The analytes will be detected by direct transmission measurement of the solid phase (e.g., Parafilm-M®). As shown in Figure 6, the solid phase will preconcentrate analytes in the path of the infrared energy from the spectrometer. IR energy impinging on the solid phase will pass through it, and depending on which analytes are present, some wavelengths of the IR light will be absorbed and not be collected by the detector-side optical fiber, which routes the energy back to the detector mounted in the FT-IR spectrometer. Figure 7 shows a detail of how the spectroscopic sensing device may be incorporated into a soil probe such as that used in cone penetrometry.

Preliminary testing of the IR transmission detection scheme depicted in Figure 6 has been done to assess the feasibility of the design. Sensor responses to test analytes have been obtained, indicating great improvements in the sensitivity of the new device over the previous EFAS design.

3.6 Fiber-Optic SPME-IR Probe Optical Design

The prototype SPME-IR probe optical design depicted below was modified. Rather than using two lengths of optical fibers, one to transmit the IR light to the solid-phase preconcentrated sample and one to collect transmitted light and return it to the FT-IR spectrometer for detection, the design employs a recently developed MIR lamp as a remote IR source located in the SPME sampling area, with one length of optical fiber to collect and return the transmitted light to the FT-IR for detection. Figure 8 depicts the optical geometry of the probe design.

Figure 7. Soil probe incorporating FT-IR detection with solid-phase preconcentration.

Figure 8. Fiber-optic SPME-IR probe prototype optical layout.

The $\frac{5}{8}$ -inch-diameter MIR lamp is located at the sample extraction region so that IR light from the lamp impinges directly on the SPME coupon. Light transmitted through the SPME coupon is collected and focused onto a 750- μ m-diameter chalcogenide optical fiber using a plano convex lens fabricated from arsenic/selenium/sulfide (AMTIR) glass. The planoconvex lens has a diameter of 1 in. and a focal length of 1 in.

4.0 CONCLUSIONS

Past work by other researchers has shown that construction of a spectroscopic method utilizing an evanescent field absorption sensor based on fiber optics and solid-phase microextraction using NIR spectroscopy is possible. Further development of this technology will allow evaluation of its use for field screening applications using cone penetrometry. Work in this project investigated the applicability of MIR spectroscopic detection of analytes using the EFAS concept. Due to limitations of the materials (MIR optical fibers, solid-phase materials) it is recommended that the designs investigated in this work not be considered practical at this time, the major problems being 1) obtaining adequate lengths of optical fiber for in situ applications and 2) the partitioning time associated with solid-phase material to obtain adequate detection limits may be excessively long for some applications.

The data presented here show Parafilm-M® is a useful solid phase for extraction of hydrocarbons from the headspace above hydrocarbon-contaminated soil or sand matrices. The data also show that MIR spectroscopy is applicable to analytes collected on the solid phase. Further development of an EFAS sensor has been ruled out at this time owing to its poor sensitivity to analytes. Transmission-mode spectroscopic detection using solid-phase preconcentration has proven

to be a possible alternative to the EFAS concept. The work presented here indicates the feasibility of using SPME-IR as a laboratory or field technique for ex situ sample characterization. This technique offers the following advantages over conventional methods: 1) samples can be analyzed in the field, 2) compound identification can be made using MIR techniques, 3) sample preparation is minimal, 4) analysis time is less than 2 hr per sample. Therefore, it is recommended that this technique be developed further for field screening applications using ex situ sample analysis.

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APPENDIX A
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APPENDIX B

FIELD SCREENING SYMPOSIUM SUMMARY

**Summary Report on Fourth International Symposium on Field Screening
Methods for Hazardous Wastes and Toxic Chemicals**

February 22-24, 1995

Tropicana Hotel

Las Vegas, NV

Attendee:

David C. Tilotta

Department of Chemistry

University of North Dakota

Attendance Dates:

February 22-23, 1995

General. Although there were many excellent papers presented at this meeting, (out of ca. 100), I was only able to attend approximately 25 because of their overlapping presentation times and because I was unable to attend the last day of the conference. The papers I attended can be grouped into four categories: fiber optic remote sensing, open path FT-IR, in situ sparging, and miscellaneous. It should be noted that all references in this report refer to specific papers in the "proceedings" book for this conference. Only the most relevant papers are discussed here.

Fiber-optic remote sensing. The papers at this conference seemed to focus extensively on the use of fiber -optics for remote sensing. It was evident that there are general needs for field analytical methods for most contaminants at a variety of concentration levels (ppt to percent). Aggarwal presented work from the Naval Research Laboratory on the development of a fiber optic remote sensing system for fuel hydrocarbons in soil based on chalcogenide fiber optics and Fourier transform spectrometry.(1) Because his system utilized sapphire optical windows, his spectral range was limited to the C-H stretching area (3-4 μm). Thus, he was able to determine only fuel aromatics (because of the spectral interference of the soil matrix). Nevertheless, he reported detection limits of ca. 50 ppm of diesel on soil at distances of 30 feet. However, these studies were limited to the laboratory and have not been field tested.

Denton summarized his results of applying Raman spectrometry to fiber optic remote sensing.(2) Even though he utilized a CCD array for the optimum signal-to-noise ratio, he reported that the best detection limits to date for benzene (in water) were ca. 25 ppm. He stated that he expects these detection limits to improve by an order of magnitude when new monochromator technology (e.g., holographic edge filters) is refined.

Earley reported results of the ROST (rapid optical screening tool) developed at Unisys and NDSU.(3) This ultraviolet-based, laser-induced fluorescence instrument was

applied to a gasoline dump site and the results were compared to standard field sampling methods (e.g., spoon sampling and organic vapor screening). They discussed the development of a wavelength/time matrix for speciation (based on the fact that different compounds fluoresce for different lengths of time). The ROST system costs \$24/foot (a typical study costs ca. \$21,000) and is designed to be used in a conventional cone penetrometer (CP) system. The maximum depth of penetration is currently ca. 100 ft, and the detection limits are typically in the mg/kg range.

Open path FT-IR. Rather than use CP technology to determine subsurface organics, several researchers reported on their on-going work on open path FT-IR. In these approaches, the organics are determined at sites (on the surface) by examining the infrared absorption of molecules over long distances. For example, Griffiths reported on the use of a low resolution FT-IR for such open path work.(4) He reported that 16 cm⁻¹ resolution was sufficient for most analyses. At this resolution, the signal-to-noise ratio appeared to be optimized for the FT-IR he was using. In addition, monostatic reflection (one reflection mirror with the source and detector side-by-side) appeared to yield the best performance. He also reported his efforts at developing mirrors for such work. He reported that cube corner reflectors reflected the most light (in comparison to cone or focussing reflectors).

In-situ Sparging. Another approach to in-situ analyses involves subsurface sparging. Doskey et al. discussed the development of an in-situ sparging system for CP use that would be useful for VOCs in water.(5) Briefly, their concept involves pushing tubing into the ground in the center of a CP. Once the CP is at the proper depth, they utilize warm air to sparge the VOCs from the water back to the surface. Standard collection and analysis methods are then used to analyze the effluent. Their system has been field tested down to 200 ft depths (with CPs that have 1 inch diameters) at an actual dump site. They report detection limits in the ppb range. In addition, they stated that the temperature of the water as well as the relative humidity of the effluent significantly influenced the analytical properties (i.e., linearities and recoveries) of the measurements. In a similar vein, Myers et al. discussed an in-situ sparging system for BTEX compounds and TCE in soil.(6) As in the work by Doskey, they sparged the VOCs (however, from the soil) using warm air. These sparged VOCs were then transferred to the surface for analysis by GC. They reported that relative humidity and the type of tubing used to transport the organics to the surface was important for good recoveries. They reported detection limits at ca. 5 ppb.

Miscellaneous. Of the myriad other field methods discussed at this conference, several were of note. The Petrosense, introduced by FCI technology, was discussed in two papers.(7,8) Although proprietary, the Petrosense is a NIR analyzer that measures the absorption of organics partitioned into an unspecified coating. Although the petrosense boasts detection limits in the 200-500 ppb range, it is non-specific (i.e., speciation is not possible). Furthermore, the calibration procedure is difficult, and the field results often must be compared to laboratory standards.

A fiber optic Raman vapor sensor was described that worked on the basis of partitioning. Specifically, Ewing et al. fixed a C-18 coating to the end of a fiber optic cable and guided a laser to it (with the fiber optics).(9) Organics partitioned into the C-18 coating and then were detected by fiber optic Raman spectroscopy. They reported detection limits for benzene at 200 ppm.

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