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

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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 detection of 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 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 trichloroethylene, 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 MIR 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 method will be developed by building on the work cited above. The specific objectives of this project are:

- To design an accessory for use with FT-IR that interfaces the spectrometer to a cone penetrometer.
- To characterize the response of the FT-IR accessory to selected hydrocarbons in a laboratory-simulated field environment.
- To 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

Continued evaluation of applicable solid-phase materials using wire mesh support structures (14) was carried out. A prototype design for a device capable of remotely sensing hydrocarbons preconcentrated using SPME and detected by MIR spectroscopy was completed.

3.1 Evaluation of Solid-Phase Materials

Previous work (14) determined Microwax 155 employing wire mesh as a support structure to be applicable to the SPME-IR application with headspace extraction of test compounds trichloroethylene (TCE), m-xylene (MXY), and ethylbenzene (ETB). Work completed during this reporting period extended proof of the capabilities for Microwax 155 solid-phase material applied to headspace extraction of a test compound (TCE, MXY, or ETB) 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 (15,16). Calibration of the SPME-IR system using Microwax 155 for each test compound-contaminated sand, soil, and water matrices gave detection limits and linear dynamic range performance comparable to those determined for Parafilm (15,16).

3.2 Fiber-Optic SPME-IR Probe Optical Design

A prototype SPME-IR probe optical design was developed. 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 1 depicts the optical geometry of the probe design.

The $\frac{5}{8}$ -inch-diameter MR 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- μm -diameter chalcogenide optical fiber using a plano convex lens fabricated from arsenic/selenium/sulfide (AMTIR) glass. The plano convex lens has a diameter of 1 inch and a focal length of 1 inch.

Figure 1. Fiber-Optic SPME-IR probe prototype optical layout.

4.0 FUTURE WORK

Work during the next quarter will involve breadboarding and testing of the SPME-IR probe design using test procedures previously established during this work. If the performance prototype design is adequate for the application, design modifications will be done to construct a SPME-IR device which can be housed in a cone penetrometer probe.

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Page 1 of 3

1. Program/Project Identification No. DE-FC21-93MC30097		2. Program/Project Title TASK 1.0 WASTE MANAGEMENT				3. Reporting Period 10-1-96 through 12-31-96															
4. Name and Address Energy & Environmental Research Center University of North Dakota PO Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000		5. Program Start Date 01-12-93																			
		6. Completion Date 12-31-97																			
7. FY 96/97	8. Months or Quarters Quarters	b. Dollar Scale	1st JAN	2nd FEB	3rd MAR	4th APR	5th MAY	6th JUN	7th JUL	8th AUG	9th SEP	10th OCT	11th NOV	12th DEC							
9. Cost Status		a. Dollars Expressed In Thousands																			
10. Cost Chart																					
Fund Source		Quarter				Cum. to Date	Tot. Plan														
		1st	2nd	3rd	4th																
DOE	P	38	34	34	64	170	235														
	A	0	61	57	26	144															
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Total P			38	34	34	64	170	235													
Total A			0	61	57	26	144														
Variance			38	(27)	(23)	38	26														
P = Planned A = Actual																					
Total Planned Costs for Program/Project \$235																					
			c. Cumulative Accrued Costs																		
Planned					38			72			106			170							
Actual					0			61			118			144							
Variance					38			11			-12			26							

11. Major Milestone Status	Units Planned	
	Units Complete	
1.7 Hot-Water Extraction of Organics, Metals and Halogens from Coal and Contaminated Soils	P	
	C	
1.11 Spectroscopic Field Screening	P	
	C	
1.12 Solid-Phase Microextraction (SPME)/Spectroscopy	P	
	C	
1.13.2 CCT Byproduct Management Workshop (optional)	P	
	C	
1.13.3 Revised Final Report on CCB Utilization	P	
	C	
1.13.4 Summary Final Report of Information Collected	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks	
13. Signature of Recipient and Date 2/3/97	14. Signature of DOE Reviewing Representative and Date

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10. Cost Chart																			
Fund Source		Quarter				Cum. to Date	Tot. Plan
		1st	2nd	3rd	4th														
DOE	P	35	30			170	235												
	A					0													
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	A																		
	P																		
	A																		
Total P		35	30	0	0	170	235												
Total A		0	0	0	0	144													
Variance		35	30	0	0	26													
P = Planned A = Actual																			
c. Cumulative Accrued Costs																			
Total Planned Costs for Program/Project \$235		Planned				205			235			235			235				
		Actual				0			0			0			0				
		Variance				205			235			235			235				

11. Major Milestone Status	Units Planned	
	Units Complete	
1.7 Hot-Water Extraction of Organics, Metals and Halogens from Coal and Contaminated Soils	P	
	C	
1.11 Spectroscopic Field Screening	P	<div></div>
	C	
1.12 Solid-Phase Microextraction (SPME)/Spectroscopy	P	
	C	
1.13.2 CCT Byproduct Management Workshop (optional)	P	
	C	
1.13.3 Revised Final Report on CCB Utilization (optional)	P	<div></div>
	C	
1.13.4 Summary Final Report of Information Collected	P	<div></div>
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks

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				6. Completion Date 12-31-97	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Subtask 1.7	Hot-Water Extraction of Organics, Metals, and Halogens from Coal and Contaminated Soils				
a	Extraction efficiencies and selectivities for model systems	6/96		100%	
b	Extraction efficiencies and selectivities for real samples	12/96		100%	
Subtask 1.11	Spectroscopic Field Study				
a	Fabrication of SPME-IR soil probe completed	6/96		90%	
b	SPME-IR soil probe calibration data collection	8/96		90%	
c	Correlation of SPME-IR probe measurements to reference method	11/96		0%	
Subtask 1.12					
a	The relative advantages and disadvantages of three to five polymeric sorbent films for their optical clarity with UV and/or FT-IR spectroscopy and for their ability to concentrate model organic pollutants from water will be reported	8/96		100%	
b	Prototype dipstick devices will be constructed with the best of the sorbent films	10/96		100%	
c	Analytical characteristics of the sorbent films (e.g., selectivity, sensitivity, ability to perform quantitative determinations) for organic pollutants (e.g., aromatic fuel hydrocarbons and chlorinated solvents) in real water samples will be reported	12/96		100%	
Subtask 1.13.2	CCT Byproduct Management Workshop (optional)	12-31-97			
Subtask 1.13.3	Revised Final Report on CCB Utilization	6-30-97			
Subtask 1.13.4	Summary Final Report of Information Collected	6-30-97			

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