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Task 2 - Extraction and Analysis of Pollutant Organics From Contaminated Solids Using Off-Line Supercritical Fluid Extraction (SFE) and On-Line SFE-Infrared Spectroscopy

Semi-Annual Report

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1.0 INTRODUCTION/BACKGROUND

1.1 Methodology

This activity will result in a commercialized version of a field-portable instrument for performing supercritical fluid extraction (SFE) with on-line Fourier transform infrared (FT-IR) detection. The Energy & Environmental Research Center (EERC) has developed an SFE field-portable method for quantitatively extracting organic pollutants (e.g., polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], total petroleum hydrocarbons [TPHs]) from soils and sludges under U.S. Environmental Protection Agency (EPA) funding. FT-IR is a detector that can yield quantitative and compound-class information for organic pollutants and is excellent for survey uses, since virtually all organic compound classes can be monitored. A laboratory prototype SFE–FT-IR instrument has been developed at the EERC and the University of North Dakota (UND) Department of Chemistry. The commercial instrument will be field-portable (requiring only generator electricity) and able to extract and measure organic pollutants from soils and sludges, identify the compound classes present, and provide quantitative or semiquantitative results at detection limits relevant to regulatory needs (e.g., parts per million). The SFE–FT-IR approach is particularly advantageous for very hazardous samples (e.g., determination of organics in solids contaminated with radioactive components), since SFE–FT-IR analysis generates no waste solvents. The instrument will also be configured to allow collection of "positive" extracts for analysis by other confirmatory (e.g., gas chromatography–mass spectroscopy [GC–MS]) methods.

1.2 DOE Environmental Management Focus Areas

The instrument fulfills the Environmental Management (EM) needs for extracting and measuring organic pollutants ranging from volatiles (e.g., halogenated solvents, benzene, toluene, ethylbenzene, xylenes) to semivolatiles (e.g., PAHs, PCBs, and petroleum hydrocarbons). Relevant samples will be solids and semisolids such as soils and waste sludges. The instrument will be applied in several of the EM Focus Areas, including Contaminated Landfill, Mixed Wastes, Decontamination and Decommissioning and, possibly, for Tank Wastes. Crosscutting areas include Characterization, Monitoring, and Sensor Technology (primary area), with strong applicability to Pollution Prevention.

1.3 EERC Core Competency

The EERC and the UND Department of Chemistry jointly developed and constructed the first SFE–IR and SFE–FT-IR interfaces. Both systems have been shown to have excellent analytical characteristics for organic pollutants in soil sludges. Field demonstrations of prototype systems are currently being conducted. Dr. Steven Hawthorne (EERC) is considered a world leader in the use of SFE for the extraction of organic pollutants, and Professor David Tilotta (Department of Chemistry, UND) is known for his development of rapid analysis techniques by coupling solventfree extraction and spectroscopic methods. The commercial partner (Suprex Corporation, Pittsburgh, PA) is widely recognized as a leading supplier of analytical SFE instrumentation.

2.0 OBJECTIVES

The major objective is to develop, test, and construct a commercial version of the fiber optic SFE–FT-IR interface in conjunction with Suprex Corporation. The specific objectives for this year are:

- To evaluate optical fibers for optical clarity and chemical inertness to determine the optimal fibers for the commercial interface.
- To develop, construct, and test a prototype of the high-pressure optical cell.
- To produce prototype interfaces for "beta site" testing.

3.0 ACCOMPLISHMENTS/WORK PERFORMED

3.1 Development of Commercial Prototype for an SFE–IR Interface

An agreement was reached with Suprex Corporation (Pittsburgh, PA) to commercialize the SFE–FT-IR interface. A prototype commercial SFE–FT-IR interface has been produced and tested. The original plan was for final development and production of the commercial version and field demonstrations to be performed in the second year (FY97). However, the recent purchase of Suprex Corporation by a leading SFE competitor (ISCO of Lincoln, Nebraska) may alter the proposed FY97 schedule.

3.2 Evaluation of Fiber Optics

Problems in choosing optical fibers for evaluation include 1) reluctance of manufacturers to supply small quantities, 2) large variations in the quality of so-called "identical" fiber materials, and 3) large differences in the materials used for cladding the optical fibers. Fortunately, two suitable fiber optics have been procured: one based on chalcogenide material and one based on silver halide. Both are suitably clear through the desired IR spectral range. Both have been mounted in the prototype commercial interface and undergone continuing evaluation. Based on these evaluations, the chalcogenide material was chosen because it displayed better sensitivity and because of the tendency of the silver halide fiber to corrode under some experimental conditions.

3.3 Development of Fiber Mounting Methods

Because of the variations in fiber cladding material, different approaches to fiber mounting are needed. We have developed two approaches that have performed reliably over large pressure ranges (up to 450 atm). The first approach uses a stainless steel tube which has been drilled to close specifications that allow the fiber to be inserted with a small amount of sealing epoxy resin (used for the chalcogenide fiber). The second approach uses a 15% graphite/85% polyimide predrilled ferrule and standard 1/16-inch high-pressure fittings (for the silver halide fitting). This approach has been tested for ca. 1 month at pressures up to 450 atm with no failures.

Both approaches have been designed to be compatible with standard high-pressure fittings to reduce manufacturing costs and increase reliability. Mr. Ray Houck (Suprex) has expressed his satisfaction that these mounting methods are sufficiently developed that Suprex will be responsible for making additional modifications (if any) needed for the commercial version.

3.4 Development of the Prototype Commercial Optical Cell

Commercially available, low dead volume crosses were found that reduce both the size and the number of connections needed by ca. 1/3 the number needed by the initial prototype version. Only minor modifications (e.g., drilling the optical path through the union) have been needed. The prototype commercial version of the interface has been developed based on these commercial crosses. An additional advantage is their relatively low cost (ca. $60 each). Ray Houck (Suprex) also approved this simple approach during his visit in April.

3.5 Development of the Optical Cell Stage

A second prototype commercial version of the optical cell mounting stage was developed which incorporates three dimensions of adjustment, provisions for a cell heating chamber, and additional developments to include the focusing lenses. Suggestions made by Ray Houck (Suprex) were incorporated in this final version of the prototype interface and cell stage.

3.6 Development of the Cell Heater

Suprex has supplied a prototype heating chamber for the optical cell which is controlled by existing connections and software on the SFE instrumentation. This heater has been installed and appears to work well.

3.7 Testing the Prototype Commercial Version of the SFE–IR Interface

Preliminary robustness testing was initially performed with the silver halide fiber optics described above. Because of the selection of the chalcogenide fiber material (discussed above), additional robustness testing was performed. Both interfaces performed reliably for ca. 1 month over the target pressure range (e.g., up to 450 atm). Several "real-world" samples have been extracted, and the interface appears to have little or no memory (e.g., contaminant carryover) from sample to sample.

The sensitivity of the interface using the silver halide fibers was not as low as desired for the commercial version. Therefore, additional work focused on optimizing the factors controlling sensitivity, including optical alignment of the cell and focusing lenses, optimizing cell path length (i.e., the distance between the optical fibers in the cell interior), and optimizing the transfer of extracted analytes from the extraction cell to the optical cell. In addition, the chalcogenide fiber was found to be more sensitive (higher light throughput) and was used to replace the silver halide fiber.

With the final interface, the sensitivity goal (1 ppm for petroleum hydrocarbons) was achieved. In addition, the SFE–FT-IR system has demonstrated good linearity over two to three orders of magnitude and usable calibration response over a wider concentration range. An example of a typical calibration curve is shown in Figure 1. The calibration was achieved by spiking diesel fuel onto 10 grams of sand and analyzing the sample by SFE–FT-IR in the same manner as used for a real sample. As shown in Figure 1, the calibration is very linear from the detection limit (ca. 1 ppm) to ca. 1600 ppm. At higher concentrations, the calibration curve is no longer linear, but semiquantitative results are still possible.

Quantitative applications of the final SFE–FT-IR interface are demonstrated in Table 1. Samples contaminated with gasoline or diesel fuel were extracted using SFE conditions similar to those of the promulgated Environmental Protection Agency (EPA) method for total petroleum hydrocarbons. Quantitative determinations were based on the SFE–FT-IR response for the EPA calibration standard (a mixture of chlorobenzene, isooctane, and hexadecane). As shown in Table 1, the SFE–FT-IR determinations give good agreement with the known concentrations of the fuel contaminants.

TABLE 1

SFE–FT-IR Determinations of Fuel Concentrations on Contaminated Sand

	% Recovery (%RSD)
Gasoline	100 (4)
Diesel Fuel	98 (3)

3.8 Additional Modifications of the Interface

Ray Houck (Suprex) visited our lab in early April to work on integrating and optimizing the use of the prototype commercial interface with the Suprex SFE system. His suggestions and comments were valuable in modifying our present design to make the interface robust and "user friendly" for the commercial market. His suggested modifications were incorporated into the final prototype interface and optical stage. With these modifications, Mr. Houck has stated that he is comfortable that the interface is sufficiently well developed to allow Suprex to produce the commercial version with continued technical support from the EERC.

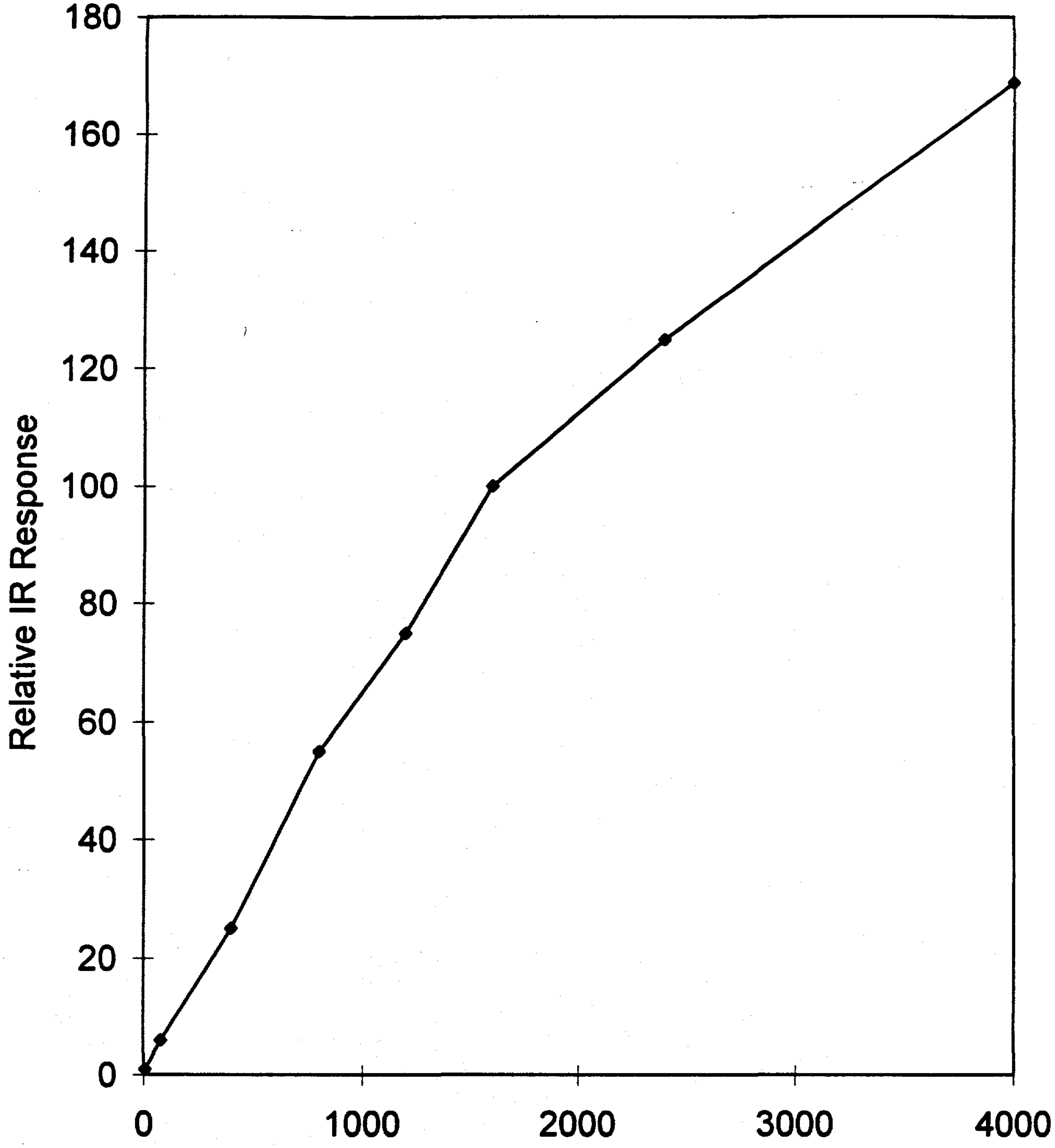

Figure 1. SFE–FT-IR calibration curve for total petroleum hydrocarbons.

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FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

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1. Program/Project Identification No. DE-FC21-94MC31388	2. Program/Project Title EM Task 2 - Extraction and Analysis of Pollutant Organics	3. Reporting Period 7/1/96 through 9/30/96
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 9/30/94 6. Completion Date 9/29/99

7. FY	8. Months or Quarters	b. Dollar Scale	1st			2nd			3rd			4th		
95/96	Quarters		OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP

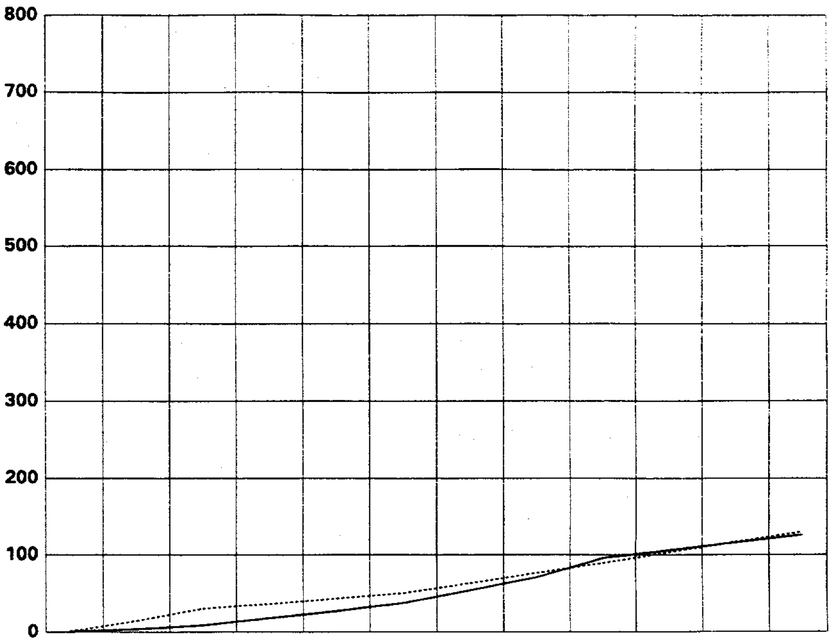
9. Cost Status a. Dollars Expressed In Thousands

10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	30	20	40	40	130	380
	A	9	28	59	30	126	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		30	20	40	40	130	380
Total A		9	28	59	30	126	
Variance		21	(8)	(19)	10	4	

P = Planned A = Actual

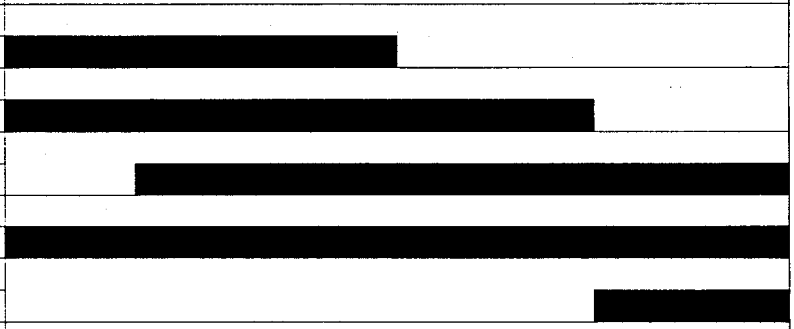
Total Planned Costs for Program/Project
$380



c. Cumulative Accrued Costs

	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP
Planned			30			50			90			130
Actual			9			37			96			126
Variance			21			13			(6)			4

11. Major Milestone Status	Units Planned Units Complete
2.1 Selection of Field Sites	P C
2.2 Testing of Field-Portable Off-Line SFE and GC Instrumentation	P C
2.3 Analysis of Off-Line SFE with Portable GC	P C
2.4 Conversion of SFE-IR Laboratory Apparatus to Field Apparatus	P C
2.5 Testing of Prototype On-Line SFE-IR	P C
	P C
	P C
	P C
	P C



12. Remarks

13. Signature of Recipient and Date 10/30/96	14. Signature of DOE Reviewing Representative and Date

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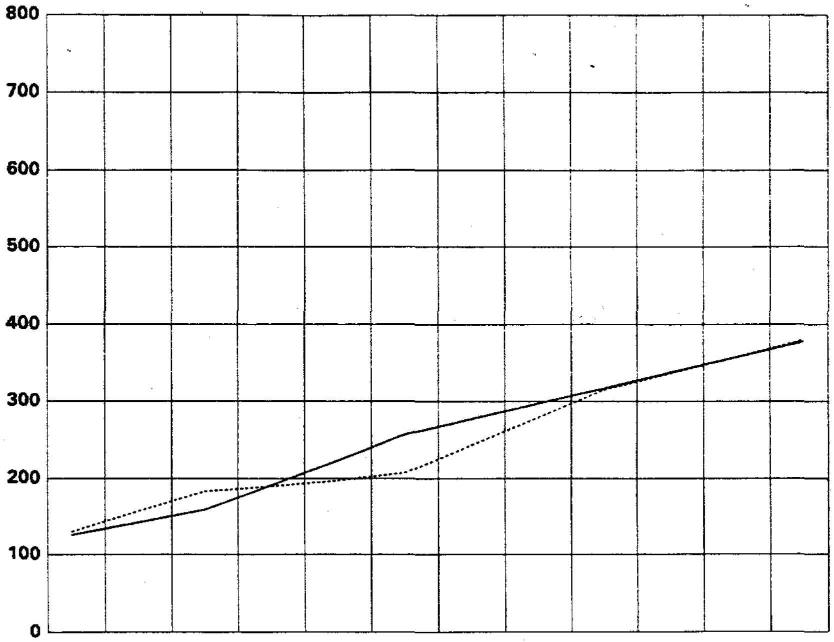
9. Cost Status a. Dollars Expressed In Thousands



10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	53	24	108	65	380	380
	A	33	98	60	61	378	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		53	24	108	65	380	380
Total A		33	98	60	61	378	
Variance		20	(74)	48	4	2	

P = Planned A = Actual

Total Planned Costs for Program/Project
$380

c. Cumulative Accrued Costs

	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP
Planned			183			207			315			380
Actual			159			257			317			378
Variance			24			(50)			(2)			2

11. Major Milestone Status	Units Planned Units Complete	
2.1 Evaluation of Optical Fibers For Optical Clarity and Chemical Inertness	P	
	C	
2.2 Development and Testing of the Prototype High-Pressure Optical Cell	P	
	C	
2.3 Producing Prototype Interfaces for "Beta-Site" Testing	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks

13. Signature of Recipient and Date 10/30/96	14. Signature of DOE Reviewing Representative and Date

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Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Year 1				
2.0	Extraction and Analysis of Polutant Organics from Contaminated Solids Using Off-Line SFE-IR			
2.1	Selection Of Field Sites	3/95	3/95	100%
2.2	Testing of Field-Portable Off-Line SFE and GC Instrumentation	6/95	6/95	100%
2.3	Analysis of Off-Line SFE with Portable GC	9/95	9/95	100%
2.4	Conversion of SFE-IR Laboratory Apparatus to Field Apparatus	9/95	9/95	100%
2.5	Testing of Prototype On-Line SFE-IR	9/95	9/95	100%
Year 2				
2.1	Evaluation of Optical Fibers for Optical Clarity and Chemical Inertness	8/96	8/96	100%
2.2	Development and Testing of the Prototype High-Pressure Optical Cell	10/96	9/96	100%
2.3	Producing Prototype Interfaces for "Beta-Site" Testing	12/96	9/96	100%