**Task 1.12 - Solid-Phase Microextraction (SPME) Coupled
with Optical Spectroscopy for Near-Real-Time
Determination of Fuel and Related Pollutants in Water
Samples**

**Topical Report
February 1995**

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Federal Energy Technology Center
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*Two reprints removed for
separate processing*

SUBTASK 1.12 - SOLID-PHASE MICROEXTRACTION (SPME) COUPLED WITH OPTICAL SPECTROSCOPY FOR NEAR-REAL-TIME DETERMINATION OF FUEL AND RELATED POLLUTANTS IN WATER SAMPLES

1.0 INTRODUCTION

The measurement of organic pollutants in water requires that samples be collected, transported to a laboratory, extracted (usually with large volumes of hazardous chlorinated solvents), and analyzed using chromatographic techniques. Such limitations make rapid determinations in the field (e.g., for emergency response and/or for survey investigations) very expensive with analytical turnaround times requiring several days. Similar limitations exist for the collection and analysis of organic pollutants in air. An alternative approach is being developed at the Energy & Environmental Research Center (EERC) that has been demonstrated to yield good sensitivities (ppb to ppm) and be easily adapted for rapid (< 30 minutes) and inexpensive field surveys. This new approach is based on the preconcentration of organic pollutants in optically clear sorbent media followed by measurement with either ultraviolet (UV) spectroscopy or Fourier transform infrared spectrometry (FT-IR). Investigations using sorbent media including methylsilicone gums (for UV spectroscopy) and "Parafilm" (for FT-IR) have shown that quantitative determinations of aromatic fuel components, such as benzene and alkylbenzenes (BTEX), can be achieved using UV spectrometry, and of common solvents (e.g., chloroform and other chlorinated solvents) can be achieved using FT-IR. Sample concentration and spectroscopic steps can be performed in a few minutes using the combination of solid-phase sorption followed by spectroscopic measurements. This work has demonstrated that the approach can yield low-ppm to low-ppb detection limits for organic pollutants in water without the negative influences of water matrix components (e.g., dissolved humic material) that prohibit the use of direct spectroscopic measurements. A good potential for real-time air monitoring of organic pollutants also exists. Additional advantages of the technique are that no organic solvents are used and that a simple (and very inexpensive) "dipstick" device was constructed that can be used with conventional (and portable) spectroscopic instrumentation.

The results of this project demonstrated that the method can be used as a solvent-free and rapid survey method in the lab or in the field.

2.0 DELIVERABLES

The deliverables for this subtask are as follows:

- 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.
- Prototype dipstick devices will be constructed with the best of the sorbent films.

- Analytical characteristics of the sorbent films (e.g., selectivity, ability to perform quantitative determinations) for organic pollutants (e.g., aromatic fuel hydrocarbons and chlorinated solvents) in real water will be reported.

3.0 ACCOMPLISHMENTS

Many of these investigations were performed in parallel with Subtask 1.11. For the sake of clarity, this report will focus on the experiments performed with UV spectroscopy, while the report for Subtask 1.11 will focus on the experiments performed with FT-IR and mid-IR spectroscopy.

3.1 Evaluation of Sorbent Materials

Several sorbent films were evaluated for their potential use as sorbents for concentrating organic pollutants from water and allowing the determination of pollutant concentrations based on UV spectroscopy. Evaluations included physical stability and handling characteristics, optical clarity, and the potential to selectively concentrate organic pollutants (e.g., aromatic fuel hydrocarbons) in preference to typical matrix (nontarget) organics such as dissolved humic material. Table 1 shows the results of the evaluation as well as relevant characteristics of the sorbent materials. In general, the sorbents tested all failed to exhibit any practical characteristics superior to OV-1. Thus the selection of OV-1 for the initial studies conducted prior to the sorbent evaluations was fortuitous, since none of the sorbent materials tested had superior characteristics. Therefore, subsequent studies focused on the use of OV-1 as the sorbent material.

3.2 Development of a New SPME-UV Method for Determining Aromatic Fuel Components in Water

The preliminary investigations with OV-1 sorbent material (polydimethylsiloxane) and UV detection were promising enough that further development of the system was performed (in conjunction with a parallel project supported by the U.S. Environmental Protection Agency [EPA]). A method was developed to cast $2 \times 4 \times 10$ -mm "chips" of the sorbent phase which could then be inserted into a standard UV cell for the determination of absorbed analytes. For UV spectroscopy, the OV-1 sorbent is particularly well-suited because it causes little loss of the UV light (mostly from light scattering), even with the 2-mm-thick sorbent path. In addition, OV-1 is an excellent sorbent for nonpolar organics (such as the aromatic components of fuels) from water. Finally, OV-1 is the same sorbent phase used for the gas chromatographic methods (which use a commercially available, syringe-mounted sorbent), which allows our results to be compared to those determined by independent solid-phase extraction methods.

With this system, the extraction of organic pollutants from water is performed by simply placing a sorbent chip into a water sample and shaking the sample for several minutes (typically 45 minutes for quantitative determinations). The initial investigations into determining fuel components in contaminated water were reported in the June 30 quarterly report. These studies have been expanded and completed and were accepted for publication as two articles in *Analytical Chemistry* (please refer to the attached copies of these manuscripts for details). In summary, the sorbent chip method using OV-1 has the following characteristics for determining fuel contamination in environmental water samples:

TABLE 1

Evaluation of Potential Sorbent Films for Determining Aromatic Organic Pollutants in Water Samples by UV Spectroscopy

Film	Chemical Type	Physical Stability	Extraction Test*	UV Clarity
OV-1	Methylsilicone	Fair	Pass	Good
OV-225	50% Cyanopropylphenyl/methylsilicone	Poor	Fail	Good
OV-351**	Nitroterephthalate-modified polyethylene glycol	Poor	Fail	Good
OV-1701	14% Cyanopropylphenyl/methylsilicone	Poor	Fail	Good
Microwax 155	Alkane wax	Good	Fail	Good

* Note: The "extraction test" is based on obtaining a high-quality UV-Vis spectrum for gasoline after 1 hour of sorption of a 10-ppm solution of gasoline in water into the test sorbent film.

** OV-351 dissolved in the water.

- The method requires no organic solvent, generates essentially no wastes, and can easily be performed in the field using very simple and inexpensive instrumentation.
- Quantitative and semiquantitative determinations of aromatic hydrocarbons require 45 minutes for sample extraction (by simply placing the sorbent chip in a water sample and mixing), and <5 minutes for the UV determination.
- The method has very good detection limits; typically in the 1-to 12-ppb ($\mu\text{g}/\text{liter}$) range for individual compounds, and 5-to 17-ppb for typical fuels including gasoline, JP-4 jet fuel, and No. 1 diesel fuel. Reproducibility is also sufficient for environmental measurements, with relative standard deviations of replicate measurements, typically in the 5% to 10% range.
- The method is highly selective for typical fuel aromatic hydrocarbons and does not show interference from dissolved aromatics (e.g., dissolved humic acids) typically found in surface waters. This selectivity makes the OV-1 method excellent for determining fuel-derived aromatics in surface waters having high natural organic content (e.g., marsh and wetland waters).

3.3 Construction of Simple and Robust Sorbent Coupons

The OV-1 sorbent method described above and in the attached manuscripts showed very good analytical characteristics. The most significant disadvantage of the method is that the sorbent chips are rubbery and were therefore somewhat difficult to align properly in the spectroscopic cell. This problem has been solved by casting the chips in a screen "sandwich" made by casting the OV-1 sorbent between two sheets of stainless steel screen (note that the same approach is being used for Task 1.11). The screen does not cause any appreciable loss in UV light and therefore does not reduce the sensitivity of the method. A further refinement to the method includes orienting the chip perpendicular to the UV light (rather than collinear to the light as described in the attached manuscripts). This makes the chip alignment much less critical and much easier to perform, while only yielding a small (ca. three-fold) loss in sensitivity. The use of this approach is demonstrated in Figure 1 by the UV-Vis determination of 100-ppm of gasoline in water. As shown in Figure 1, the gasoline in water was virtually nondetectable without the sorbent concentration step ("10-mm cuvette" plot). The OV-1 sorbent mounted in the screen showed good optical clarity before exposure to the contaminated water ("before extraction" plot). Finally, the screen-mounted sorbent was exposed to the contaminated water for 1 hour and showed a good UV-Vis spectrum for gasoline ("after 1-hour extraction" plot).

Figure 1. UV-Vis spectra of a 100-ppm solution of gasoline in water.

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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																																																																						
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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	
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12. Remarks	
13. Signature of Recipient and Date 2/3/92	14. Signature of DOE Reviewing Representative and Date

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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 (optional)	P	
	C	
1.13.4 Summary Final Report of Information Collected	P	
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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			