Application Note 17

Polyacrylate Film Fiber for Solid Phase Microextraction of Polar Semivolatiles from Water

Our polyacrylate-coated fiber used in the solid phase microextraction technique effectively extracts difficult polar compounds, such as phenols, from water samples. This fiber overcomes the problems of removing polar analytes from a polar matrix. SPME is a simple, practical, and cost-effective extraction technique that meets US EPA specifications.

Key Words:
- solid phase microextraction • polyacrylate
- semivolatile compounds • polar compounds • phenols

Extracting polar semivolatile compounds from water samples can be a difficult operation for the environmental chemist. Attempts to isolate phenols and other polar semivolatiles using conventional extraction methods (liquid-liquid extraction, solid phase extraction, and supercritical fluid extraction) require either high-priced instrumentation or extensive training and time, and often are not successful.

Solid phase microextraction■ (SPME) is a simple, cost-effective, time-saving extraction technique developed by Janusz Pawliszyn and associates at the University of Waterloo, Ontario, Canada. In SPME, a phase-coated fiber contained within a syringe is exposed to the sample, allowing the analytes to adsorb in the fiber coating. Adsorption equilibrium is attained in 2 to 15 minutes. After sample adsorption, the fiber is withdrawn into the needle, and the needle is removed from the sample vial and introduced into the GC injector, where the adsorbed analytes are thermally desorbed and analyzed.

SPME has important advantages. It is quick, highly sensitive, and versatile (SPME can be used with any gas chromatograph or GC-mass spectrometer, with split/splitless or on-column injection). No solvents or complicated apparatus are required. Any problems associated with solvent use and disposal are largely eliminated.

Supelco offers an SPME fiber assembly coated with 85µm of polyacrylate that easily extracts polar analytes, such as phenols, from water in less than 20 minutes.

To obtain good extraction efficiency, it is essential to lower the sample pH to 2 and saturate the sample with sodium chloride. These modifications can increase response by 10- to 500-fold by driving the equilibrium toward the fiber. Under these conditions, an 85µm polyacrylate film fiber was used to extract phenols at 50ppb from a 1.8mL sample (Figure A). High desorption temperatures resulted in sharp peaks. Our low volume injection port liner (0.75mm ID) allowed rapid transfer of the phenols to the GC column, contributing to the excellent quality of the peak shapes. Using low-bleed, pre-drilled Thermogreen™ LB-2 septa reduced septa coring that can cause extraneous peaks.

Table 1 shows the response factors over a concentration range of 5 to 200ppb. Note that the standard deviation is improved if the calibration curve is calculated from 10 to 200ppb. US Environmental Protection Agency (US EPA) methods 604 and 8040 list tables showing %RSDs in the 20s and 30s. SPME yielded excellent %RSDs, under 20 for most of the analytes. The only compound with %RSDs greater than 30 was the more polar 2,4-dinitrophenol.

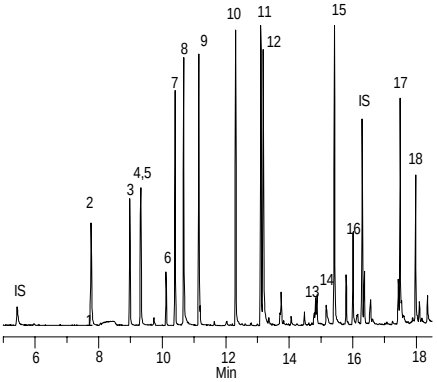
The reproducibility of the SPME extraction technique is illustrated in Table 2. Conducting this evaluation with three fibers demonstrated the consistency between fibers and precision of the analysis. Except for the nitro-substituted phenols, the %RSDs were quite low.

In addition to the polyacrylate-coated fiber, Supelco offers SPME fiber assemblies with polydimethylsiloxane (PDMS) film. Our 100µm PDMS fiber effectively extracts volatile, low molecular weight organic compounds. A 7µm PDMS fiber offers faster equilibration of less volatile analytes and a higher desorption temperature limit (320°C vs. 280°C). Other phases are available for different types of applications.

The SPME devices can be used in both manual and autosampling modes. All are reusable.●

Figure A. Phenols Extracted at 50ppb, Using an 85µm Polyacrylate SPME Fiber

Sample:	50ppb phenols in 1.8mL saturated salt water, pH 2
SPME Fiber:	**polyacrylate, 85µm film**
Cat. No.:	**57304**
Sampling:	direct in water, 20 min
Desorption:	splitless, 280°C (closed 3 min)
Column:	**PTE™ -5, 30m x 0.25mm ID, 0.25µm film**
Cat. No.:	**24135-U**
Oven:	40°C (4 min) to 260°C at 12°C/min
Carrier:	helium, 40cm/sec at 40°C
Det.:	MS, Scan Range m/z = 45-465 at 0.6 sec/scan



IS 2-Fluorophenol (int. std.)
1. Phenol
2. 2-Chlorophenol
3. 2-Methylphenol
4. 3-Methylphenol
5. 4-Methylphenol
6. 2-Nitrophenol
7. 2,4-Dimethylphenol
8. 2,4-Dichlorophenol
9. 2,6-Dichlorophenol
10. 4-Chloro-3-methylphenol
11. 2,4,5-Trichlorophenol
12. 2,4,6-Trichlorophenol
13. 2,4-Dinitrophenol
14. 4-Nitrophenol
15. 2,3,4,6-Tetrachlorophenol
16. 2-Methyl-4,6-dinitrophenol
IS 2,4,6-Tribromophenol (int. std.)
17. Pentachlorophenol
18. Dinoseb

794-0199

Table 1. Summary of Calibration Curve Response Factors for Phenols by SPME*

	5ppb to 200ppb			10ppb to 200ppb		
	Avg.	S.D.	%RSD	Avg.	S.D.	%RSD
2-Fluorophenol (int. std.)						
Phenol	0.33	0.04	11.4%	0.32	0.02	7.5%
2-Chlorophenol	1.15	0.05	4.6%	1.15	0.06	4.9%
2-Methylphenol	0.69	0.03	5.1%	0.68	0.03	5.1%
3- & 4-Methylphenol	1.18	0.08	6.9%	1.19	0.08	7.1%
2-Nitrophenol	0.29	0.08	25.8%	0.30	0.07	22.7%
2,4-Dimethylphenol	1.15	0.10	8.6%	1.14	0.10	8.8%
2,4-Dichlorophenol	1.32	0.14	10.8%	1.34	0.13	9.7%
2,6-Dichlorophenol	1.33	0.14	10.5%	1.35	0.13	9.5%
4-Chloro-3-methylphenol	0.98	0.08	7.9%	0.98	0.08	8.3%
2,4,5-Trichlorophenol	1.01	0.06	6.3%	1.00	0.07	6.6%
2,4,6-Trichlorophenol	1.01	0.09	8.4%	1.00	0.08	8.3%
2,4-Dinitrophenol	0.08	0.04	50.3%	0.08	0.04	44.7%
4-Nitrophenol	0.20	0.03	17.5%	0.20	0.03	15.6%
2,3,4,6-Tetrachlorophenol	0.70	0.13	18.7%	0.68	0.12	18.1%
2-Methyl-4,6-dinitrophenol	0.26	0.09	36.1%	0.28	0.08	30.2%
2,4,6-Tribromophenol (int. std.)						
Pentachlorophenol	0.31	0.09	29.3%	0.29	0.08	27.9%
Dinoseb	0.27	0.08	29.1%	0.29	0.07	25.0%

Table 2. Summary of Response Factors for Phenols at 50ppb*

Triplicate extractions for 3 fibers (n = 9)

	Avg.	S.D.	%RSD
2-Fluorophenol (int. std.)			
Phenol	0.44	0.05	12.3%
2-Chlorophenol	1.60	0.17	10.5%
2-Methylphenol	0.81	0.10	13.0%
3- & 4-Methylphenol	1.77	0.22	12.5%
2-Nitrophenol	0.49	0.05	10.1%
2,4-Dimethylphenol	1.60	0.23	14.2%
2,4-Dichlorophenol	1.06	0.13	12.7%
2,6-Dichlorophenol	1.02	0.12	12.1%
4-Chloro-3-methylphenol	0.74	0.09	11.8%
2,4,5-Trichlorophenol	0.79	0.09	11.3%
2,4,6-Trichlorophenol	0.83	0.09	10.8%
2,4-Dinitrophenol	0.06	0.02	25.5%
4-Nitrophenol	0.14	0.03	21.0%
2,3,4,6-Tetrachlorophenol	0.69	0.08	11.9%
2-Methyl-4,6-dinitrophenol	0.18	0.02	13.2%
2,4,6-Tribromophenol (int. std.)			
Pentachlorophenol	0.42	0.09	21.3%
Dinoseb	0.27	0.04	14.3%

* Extracted from saturated salt water, pH 2.

Ordering Information:

Description	Cat. No.
SPME Holder	
First time users must order both holder and fiber assembly.	
Holder is reusable indefinitely.	
For manual sampling	**57330-U**
For Varian 8100/8200 AutoSampler[s] or SPME/HPLC interface	**57331**
SPME Fiber Assembly (pk. of 3)	
85µm polyacrylate coating for polar semivolatiles	
For manual sampling	**57304**
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	**57305**
Fiber Assortment Kit 1 (other kits available)	
One fiber each of 85µm polyacrylate coating, and 100µm and 7µm polydimethylsiloxane coating.	
For manual sampling	**57306**
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	**57307**

▲ Requires Varian SPME upgrade kit.

■ Technology licensed exclusively to Supelco (US patent 5,691,206; European patent # 0523092).

● Fiber lifetime depends on conditions of use. 100+ uses have been achieved.

Contact our Technical Service Department (phone 800-359-3041 or 814-359-3041, FAX 800-359-3044 or 814-359-5468) for expert answers to your questions.