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

R. E. Shirey

An 85µm polyacrylate fiber used in the recently-introduced solid phase microextraction technique effectively extracts difficult polar compounds, such as phenols, from water samples. A polyacrylate-coated fiber overcomes the problems of removing polar analytes from a polar matrix. This newest development enhances the importance of SPME as a simple, practical, and cost-effective extraction technique that meets US EPA specifications.

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.

A simple, cost-effective, time-saving extraction method is quickly gaining acceptance as the preferred technique. Solid phase microextraction■ (SPME) is the revolutionary technique developed by Janusz Pawliszyn and associates at the University of Waterloo, Ontario, Canada (Reporter Vol. 12, No. 4). In SPME, a phase-coated fiber contained within a syringe is exposed to the sample, allowing the analytes to adsorb to 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 After sample adsorption, the fiber is withdrawn into the needle, and the needle is removed from the sample vial and introduced into the GC injector, where the adsorbed analytes are thermally desorbed and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.

A recently developed SPME fiber assembly is coated with 85µm of polyacrylate. This unit easily extracts polar analytes, such as phenols, from water in less than 20 minutes.

We used an 85µm polyacrylate film fiber to extract phenols at 50ppb from a 1.8mL sample (Figure A). Lowering the sample pH to 2 and saturating it with sodium chloride greatly improved the extraction. High desorption temperatures resulted in sharp peaks. Our new 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. Low-bleed, pre-drilled Thermogreen™ LB-2 septa reduced septum 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

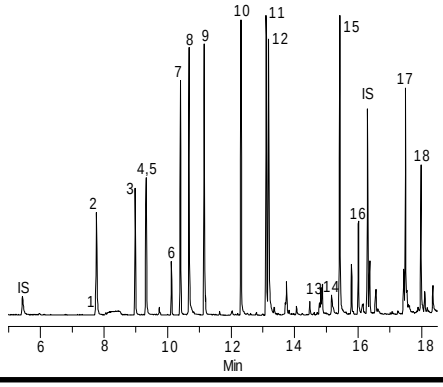
Figure A. Phenols Extracted at 50ppb, Using an 85µm Polyacrylate SPME Fiber

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**
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



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

For more information on the polydimethylsiloxane-coated fibers, request literature no. 394006 (for extracting volatile compounds) and 394011 (for mid- to nonpolar semivolatiles).

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

Compound	5ppb to 200ppb Avg.	S.D.	%RSD	10ppb to 200ppb 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

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

▲ First time users must order both holder and fiber assembly. Holder is reusable indefinitely. Use with Varian 8100/8200 AutoSampler. Requires Varian SPME upgrade kit.

Trademarks

Hewlett Packard – Hewlett Packard Corp.
PTE, Thermogreem – Sigma-Aldrich Co.

Fused silica columns manufactured under HP US Pat. No. 4,293,415.

Ordering Information:

Description	Cat. No.
SPME Fiber Assembly (pkg. of 3)	
85µm polyacrylate coating for polar semivolatiles	
For manual sampling	**57304**
For Varian 8100/8200 AutoSampler	**57305**
7µm polydimethylsiloxane coating for mid- to nonpolar semivolatiles	
For manual sampling	**57302**
For Varian 8100/8200 AutoSampler	**57303**
100µm polydimethylsiloxane coating for volatiles	
For manual sampling	**57300-U**
For Varian 8100/8200 AutoSampler	**57301**
SPME Holder▲	
For manual sampling	**57330-U**
For Varian 8100/8200 AutoSampler	**57331**
PTE-5 Fused Silica Capillary Column	
30m x 0.25mm ID, 0.25µm film	**24135**
Inlet Liners, Splitless, 0.75mm ID	
For Hewlett-Packard® instrument	
each	**26375,01**
pk. of 5	**26375,05**
pk. of 25	**26375,25**
For Varian instrument	
each	**26358,01**
pk. of 5	**26358,05**
pk. of 25	**26358,25**