Application Note 6

Solid Phase Microextraction of Semivolatile Compounds

An SPME fiber coated with 7µm of polydimethylsiloxane is ideal for extracting semivolatile compounds from water. The SPME technology eliminates the use of solvents in extracting water samples for organic compound monitoring.

Key Words:
- semivolatile organic compounds
- solid phase microextraction • water analysis

US Environmental Protection Agency (US EPA) methods for extracting semivolatile organic compounds from water and waste samples specify liquid-liquid extraction procedures using methylene chloride as a solvent. The EPA and other environmental bodies are attempting to find alternative extraction methods that minimize the use of solvents. As part of this effort, Supelco has introduced an exciting alternative — solid phase microextraction (SPME)■, a solventless sample preparation technique for extracting organic compounds in water. Developed at the University of Waterloo in Ontario, Canada, this technique eliminates most drawbacks in sample extraction. Problems associated with solvent use and disposal are largely eliminated.

The SPME unit consists of two elements: a length of coated fused silica fiber bonded to a stainless steel plunger; and a holder. The fiber is introduced into the sample or headspace (1), and organic analytes adsorb in the phase and establish equilibrium. The analytes are desorbed from the fiber to a capillary GC column in the heated chromatograph injection port, where they are focused on the inlet of the capillary column. No solvents or complicated apparatus are required. The fiber is reusable.•

SPME can be used to concentrate volatile, semivolatile, or nonvolatile compounds in either liquid or gaseous samples. It can be used with any gas chromatograph or GC-mass spectrometer, with split/splitless or on-column injection. The technique is quick (equilibration is reached in only 2 to 30 minutes) and highly sensitive (parts per trillion detection limits have been attained with an ion-trap detector).

We used a 7µm polydimethylsiloxane (PDMS) fiber to evaluate the extraction of the polynuclear aromatic hydrocarbon (PAH) compounds listed in US EPA methods 625 and 8100 and the phthalate esters in methods 625 and 8060. We extracted the semivolatile PAH and phthalate compounds from spiked water samples ranging from 10 to 200ppb (Table 1). The similarity in response factors for the individual concentrations indicates good linearity. The relative standard deviation (RSD) represents the linearity of the five concentrations. The small standard deviations for most of the compounds indicates excellent reproducibility, and illustrates the ability of SPME to provide desirable results.

Table 1. Response Factors for PAHs and Phthalates by SPME, Using a 7µm Bonded PDMS Fiber

Compound	Concentration (ppb in 4mL Water) 10	25	50	100	150	Mean	Std. Dev.	%RSD
Naphthalene	0.99	1.08	1.01	0.96	1.16	1.04	0.07	6.8
Acenaphthylene	0.87	1.00	0.93	1.00	1.14	0.99	0.09	9.2
Dimethylphthalate	0.01	0.01	0.02	0.01	0.01	0.01	0.00	20.7
Acenaphthene	0.96	1.02	1.04	0.95	1.02	1.00	0.03	3.5
Fluorene	0.52	0.49	0.54	0.68	0.63	0.57	0.07	12.3
Diethylphthalate	0.01	0.01	0.01	0.02	0.01	0.01	0.00	26.8
Phenanthrene	1.03	0.93	0.90	1.07	1.02	0.99	0.06	6.4
Anthracene	1.11	0.98	0.97	1.16	1.09	1.06	0.07	6.9
Di-n-butylphthalate	1.05	1.00	0.78	0.98	1.13	0.99	0.12	11.8
Fluoranthene	1.38	1.12	1.08	1.23	1.34	1.23	0.12	9.6
Pyrene	1.48	1.17	1.15	1.29	1.40	1.30	0.13	9.8
Benzyl butylphthalate	0.47	0.41	0.36	0.44	0.51	0.44	0.05	11.5
Benzo(a)anthracene	1.19	0.88	0.85	1.04	1.06	1.00	0.13	12.6
Chrysene	1.00	0.86	0.81	0.95	1.03	0.93	0.08	9.0
Bis(2-ethylhexyl)phthalate	0.99	0.76	0.85	0.81	0.86	0.85	0.08	9.1
Di-n-octylphthalate	1.29	1.01	1.05	1.21	1.39	1.19	0.15	12.2
Benzo(b)fluoranthene	1.14	1.04	1.10	0.90	1.00	1.04	0.08	8.0
Benzo(k)fluoranthene	1.17	0.89	1.13	0.93	1.10	1.04	0.11	10.6
Benzo(a)pyrene	1.06	0.78	0.78	0.88	0.99	0.90	0.11	12.4
Indeno(1,2,3-cd)pyrene	0.78	0.66	0.72	0.74	0.88	0.75	0.07	9.9
Dibenz(a)anthracene	0.57	0.52	0.62	0.60	0.71	0.60	0.06	10.5
Benzo(ghi)perylene	0.80	0.61	0.73	0.74	0.79	0.73	0.07	9.1

The more polar compounds (dimethylphthalate and diethylphthalate) exhibited poor recovery on the nonpolar polydimethylsiloxane fiber. A polar fiber (polyacrylate) phase coating is needed to effectively extract these compounds.

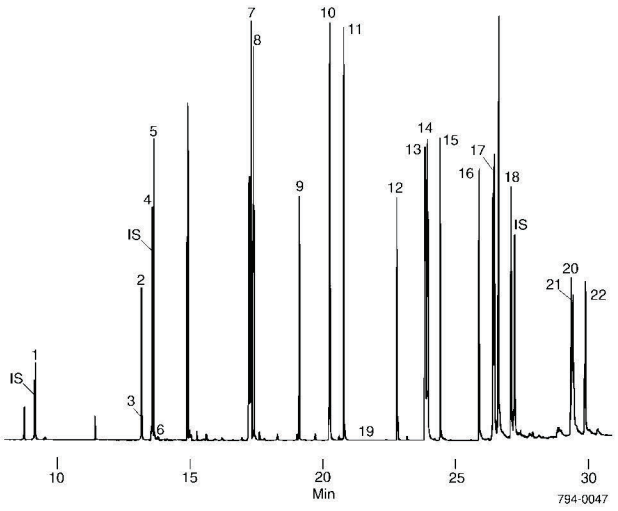
Using a narrow bore capillary column produces a desirable low flow rate, which provides high resolution of the PAHs and phthalates. We used a narrow bore PTE™-5 fused silica capillary column (30m x 0.25mm ID x 0.25µm film) with a Finnigan Incos GC/MS system.

Our analysis (Figure A) resulted in excellent peak-to-baseline return, indicating a good sample transfer from the fiber to the head of the column.

Figure A. PAHs and Phthalates by SPME

Sample:	water spiked with PAHs and phthalates
SPME Fiber:	**7µm polydimethylsiloxane film**
Cat. No.:	**57302**
Sampling:	4mL, 15 min
Inj.:	split/splitless, 280°C (closed 4 min)
Column:	**PTE-5, 30m x 0.25mm ID, 0.25µm film**
Cat. No.:	**24135-U**
Col. Temp.:	60°C (3 min) to 320°C at 10°C/min
Carrier:	helium, 40cm/sec at 60°C
Det.:	MS, Scan Range m/z = 45-465 at 0.6 sec/scan

		M/Z			M/Z
IS	Naphthalene-d8	136	12.	Benzyl butylphthalate	149
1.	Naphthalene	128	13.	Benzo(a)anthracene	228
2.	Acenaphthylene	152	IS	Chrysene-d12	240
3.	Dimethylphthalate	163	14.	Chrysene	228
IS	Acenaphthene-d10	164	15.	Bis(2-ethylhexyl)phthalate	149
4.	Acenaphthene	154	16.	Di-n-octylphthalate	149
5.	Fluorene	166	17.	Benzo(b)fluoranthene	252
6.	Diethylphthalate	149	18.	Benzo(k)fluoranthene	252
IS	Phenanthrene-d10	188	19.	Benzo(a)pyrene	252
7.	Phenanthrene	178	IS	Perylene-d12	264
8.	Anthracene	178	20.	Indeno(1,2,3-cd)pyrene	276
9.	Di-n-butylphthalate	149	21.	Dibenz(a)anthracene	278
10.	Fluoranthene	202	22.	Benzo(ghi)perylene	276
11.	Pyrene	202			



■ Technology licensed exclusively to Supelco. US patent no. 5,691,206; European patent #0523092.

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

Ordering Information:

Description	Cat. No.
SPME Fiber 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▲ or SPME/HPLC interface	57331
SPME Fiber Assembly (pk. of 3)	
100µm polydimethylsiloxane coating for volatiles	
For manual sampling	57300-U
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	57301
30µm polydimethylsiloxane coating for nonpolar semivolatiles	
For manual sampling	57308
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	57309
7µm polydimethylsiloxane coating for intermediate to nonpolar semivolatiles	
For manual sampling	57302
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	57303
65µm polydimethylsiloxane/divinylbenzene coating for polar volatiles	
For manual sampling	57310-U
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	57311
60µm polydimethylsiloxane/divinylbenzene coating for nonvolatiles	
For SPME/HPLC interface	57317
65µm Carbowax®/divinylbenzene coating for polar analytes	
For manual sampling	57312
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	57313
50µm Carbowax/templated resin coating for surfactants	
For SPME/HPLC interface	57315
75µm Carboxen™/polydimethylsiloxane coating for gases and low molecular weight analytes	
For manual sampling	57318
For Varian 8100/8200 AutoSampler or SPME/HPLC interface	57319
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 — please see our catalog) 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
SPME/HPLC Interface	
With Valco® valve	57350-U
With Rheodyne® valve	57353

▲ Requires Varian SPME upgrade kit.

For additional fibers, fiber kits, and SPME accessories, please see our current catalog.

Reference

1. Zhang, Z., and J. Pawliszyn, *Anal. Chem.* **65**: 1843-1852 (1993).

Reference not available from Supelco.

Trademarks

Carbowax — Union Carbide Corp.
Carboxen, PTE — Sigma-Aldrich Co.
Rheodyne — Rheodyne, Inc.
Valco — Valco Instruments Co., Inc.

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

Note 6

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