SPME Sample Prep Made Easy

Winter 1999/2000

How to Choose the Proper SPME Fiber

A continuation of reports discussing SPME parameters, begun in the Fall 1999 SPME newsletter

The most common question we receive concerning SPME[1] is, naturally, "Which fiber should I use for extracting my specific analyte?". Recently, we evaluated the abilities of currently available SPME fibers to extract organic analytes of various classes and molecular weights. From the results, we hoped to make some general recommendations.

First we focused on volatile analytes with similar size (molecular weight 58-89) and structure, but different functionalities (Table 1). We introduced these analytes into water at 1ppm each, extracted them, using 6 different fibers, then determined absolute responses for each analyte, extracted by each fiber. Table 1 lists the best fibers for extracting each of these analytes. Where possible, the three best choices are given.

For extracting analytes with molecular weights of less than 90, regardless of functionality, the clear choice is the 85µm Carboxen™/polydimethylsiloxane (PDMS) StableFlex™ fiber. For nearly all of

(contd. on page 2)

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Table 1. Best SPME Fiber Choices for Extracting Analytes

Analyte	Mol. Wt.	1st Choice	2nd Choice	3rd Choice
Acetone	58	Carboxen™/PDMS		
Propanal	58	Carboxen/PDMS		
Isopropanol	59	Carboxen/PDMS		
Isopropylamine	59	DVB/Carboxen	Carboxen/PDMS	PDMS/DVB
Acetic acid	60	Carboxen/PDMS		
Propionitrile	68	Carboxen/PDMS		
Pentane	72	Carboxen/PDMS		
Methylacetate	74	Carboxen/PDMS		
Dichloromethane	84	Carboxen/PDMS	DVB/Carboxen	
Dioxane	88	Carboxen/PDMS		
Nitropropane	89	Carboxen/PDMS		
Toluene	92	Carboxen/PDMS	DVB/Carboxen	PA
Aniline	93	Carbowax®/DVB	PA	DVB/Carboxen
Phenol	94	Carboxen/PDMS	Carbowax/DVB	PA
Benzaldehyde	105	Carboxen/PDMS	DVB/Carboxen	Carbowax/DVB
Xylene	106	DVB/Carboxen	Carboxen/PDMS	PA
Anisole	108	Carboxen/PDMS	DVB/Carboxen	PA
Benzoic acid	122	PA	Carbowax/DVB	Carboxen/PDMS
p-Nitroaniline	138	Carbowax/DVB	PA	PDMS/DVB
p-Nitrophenol	139	PA	Carbowax/DVB	
Acenaphthene	154	DVB/Carboxen	PA	100µm PDMS
N-Nitrosodi-n-butylamine	159	DVB/Carboxen	Carbowax/DVB	PDMS/DVB
Dimethylphthalate	163	DVB/Carboxen	Carboxen/PDMS	Carbowax/DVB
1,3,5-Trinitrobenzene	213	DVB/Carboxen	PA	PDMS/DVB
Chrysene	228	Carbowax/DVB	30µm PDMS	100µm PDMS
Decachlorobiphenyl	499	30µm PDMS	PA	DVB/Carboxen

Carboxen/PDMS: 85µm Carboxen/PDMS (StableFlex fiber)
DVB/Carboxen: 50µm/30µm divinylbenzene/Carboxen-PDMS (StableFlex fiber)
Carbowax/DVB: 70µm Carbowax/divinylbenzene (StableFlex fiber)
PDMS/DVB: 65µm polydimethylsiloxane/divinylbenzene (StableFlex fiber)
PA: 85µm polyacrylate

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

Choose the Proper SPME Fiber *(contd. from page 1)*

these analytes, responses for the Carboxen/PDMS fiber were more than 100 times greater than responses for any other fiber. Apparently, the porous Carboxen particles retain any small analyte that comes in contact with the pores. The Carboxen/PDMS fiber extracts these analytes by adsorption, as opposed to absorption, the extraction mechanism of fibers coated solely with liquid phase. The only analyte that did not follow the pattern was isopropylamine. Divinylbenzene (DVB) fibers have a high affinity for small amines. Consequently, the combination coating of DVB over Carboxen was the best choice for isopropylamine. However, the Carboxen/PDMS fiber and the PDMS/DVB fiber also were suitable for extracting isopropylamine.

Next, we extracted larger analytes, again from varied organic classes (Table 1). We introduced these analytes into water at 75ppb each, extracted them at 3 pH levels, using 8 coated and uncoated SPME fibers, analyzed the extracts by GC/MS, and compared the absolute responses for each analyte extracted by each fiber at each pH.

Unlike the results for the volatile analytes, often there was no clear choice of SPME fiber for a particular larger analyte (Table 1). Because liquid phases can retain larger analytes as effectively as porous materials, the effect of porosity was not as great. For larger analytes, the effect of polarity becomes more significant. Both Carbowax/DVB and polyacrylate (PA) fibers were suitable for polar analytes. The DVB/Carboxen fiber also was excellent for extracting many of the higher molecular weight analytes; larger analytes concentrate in the DVB layer and smaller analytes concentrate in the Carboxen layer. For some analytes, such as dimethylphthalate and N-nitrosodi-n-butylamine, there were more than three choices: all of the DVB-containing fibers, the PA fiber, the Carboxen fiber, and the 100µm PDMS fiber were suitable.

A surprising result was the ability of polyacrylate (PA), a fairly polar fiber, to extract nonpolar analytes, apparently through pi bonds. The results also indicate that Carboxen does not easily desorb larger analytes, particularly PAHs. It is interesting that the Carboxen fiber was effective for extracting decachlorobiphenyl. Perhaps the large chlorine groups prevent the molecule from becoming too tightly attached to the Carboxen particles. These latter observations point out that generalizations can be made concerning fiber selection, but ultimately the best fiber for a particular application should be determined by testing.

For a complete report on this investigation of fiber choice to a specific analyte, request a copy of Bob Shirey's 1999 EAS paper entitled *Selecting the Appropriate SPME Fiber for Your Application Needs* (T499232). Use the reply card on page 4 of this newsletter.

New Books on SPME

Solid Phase Microextraction: A Practical Guide

Sue Ann Sheppers Wercinski, ed., 1999, 242 pp.

This reference book contains extensive descriptions of proven sampling methods for chemical analyses, focusing on SPME applications.

Cat. No. **26610-U**

Applications of Solid Phase Microextraction

Janusz Pawliszyn, 1999, 653 pp.

A compilation of 46 invited chapters describing applications of SPME for foods, forensics, environmental samples, and other areas.

Cat. No. **26611-U**

Recent SPME Papers

These talks were presented at the
International AOAC Meeting
Houston, TX, Sept. 27-29, 1999.

Solid Phase Microextraction for the Enantiomeric Analysis of Natural AMD Synthetic Flavor in Foods and Beverages

Susan E. Ebeler, University of California, Davis, Gay Sun, Aerojet Fine Chemicals, Rancho Cordova, CA, Meera Datta, Allen K.Vickers, & Phil Stremple, J&W Scientific., Folsom, CA

Temperature/Time Effects on SPME Efficiency of Volatile Contaminants from Lipids Using Carboxen-Based Fiber Coatings

B. Dennis Page, Gladys M.-A. LaCroix, Health Canada, Canada

The following talks are scheduled for presentation at the
Water Quality Conference (WQT)
Tampa, FL, Monday, Nov. 1, 1999.

Session M3
New Taste and Odor Detection

Faster, Better, Cheaper Use of Solid Phase Microextraction (SPME) for Taste and Odor Analysis

Andrew Eaton, Dat. Ngunyen, Lely Suhady,
Montgomery Watson Laboratories

Determination of Taste and Odor Compounds Using Solid Phase Microextraction and Gas Chromatography/Mass Spectrophotometry

John Nanci, Stephen Foster, Christine Owen
Tampa City Water Department

Session M8
Technical Innovations:
Equipment Demonstration

SPME Holder and Fibers, Monitoring for Odors Geosmin and Methyl Isoborneol

Raymond Mindrup, Supelco

Upcoming Exhibits

Water Quality Conference (WQT)

Tampa, FL, Oct. 31-Nov. 2

New AWWA Method 6040, for determination of odors in drinking water by SPME, is currently under review by the AWWA odor committee. Method 6040 simplifies the determination of odor concentration at a less costly approach than traditional closed-loop stripping techniques.

Stop by **Supelco Booth #304** and ask about our new odor and carbamate standards for drinking water analysis. Also, request your free copy of the new SPME Application Guide, a compilation of literature references for nearly 400 technical articles on SPME.

Eastern Analytical Symposium (EAS)

Somerset, NJ, Nov. 15-18

- Stop by **Supelco Booth #318** to discuss your SPME application.

  While visiting, pick up a copy of the SPME Applications Guide.

- Be sure to attend the SPME Symposium, *Advances in Solid Phase Microextraction*, on Tuesday Morning, Nov. 16. Following is a list of the scheduled talks.

9:00am	*Introduction.* James D. Stuart, Dept. of Chemistry, U-60, University of Connecticut, 55 North Eagleville Rd., Storrs, CT 06269-3060.
9:05am	*New Developments in SPME.* J. Pawliszyn, J. Koziel, H. Lord, H. Yuan, H. Kataoka and X. Yu, Dept. of Chemistry, Univ. of Waterloo, Ontario, Canada N2L 3G1.
9:45am	*Selecting the Appropriate SPME Fiber for Your Application Needs.* Robert Shirey, Supelco, Supelco Park, Bellefonte, PA 16823-0048.
10:20am	Break
10:40am	*Forensic and Toxicology Applications: Accelerants, Explosives and Drug Analysis by SPME.* José R. Almirall, Dept. of Chemistry and The International Forensic Research Institute, Florida International University, University Park, Miami, FL 33199.
11:00am	*Use of SPME Fibers for Measurement of Vapor Signatures of Buried Landmines.* Thomas F. Jenkins, U.S. Army Cold Regions Research and Engineering Laboratory, 72 Lyme Rd., Hanover, NH 03755 and Thomas A. Ranney, Science and Technology Corporation, 72 Lyme Rd., Hanover, NH 03755.
11:20am	*Quantitation of Aroma and Flavor Volatiles Using Headspace SPME Techniques.* Alan D. Harmon, McCormick & Co., Inc., Technical Innovation Center, 204 Wight Ave., Hunt Valley, MD 21031.
11:40am	*Applications of SPME in Personal Care Product.* Richard K. Payne, Colgate-Palmolive Co., Corporate Research Center, 909 River Road, Piscataway, NJ 08855-1343.

New Products

Products for Odor Determination in Drinking Water

50/30µm Divinylbenzene/Carboxen/PDMS Stableflex Fibers

For manual sampling. 2cm fiber length.
Pack of 3. Cat. No. **57348-U**

40mL Headspace Vials

Clear glass, 29 x 81mm.
Pack of 100. Cat. No. **27184**

40mL Vial Holder

Five-position holder for headspace sampling of volatiles and odors. The aluminum block is used for heating and stirring in SPME headspace extractions.
Cat. No. **33313-U**

StableFlex™ Coated SPME Fibers Exhibit the Same Performance as Our Original Fibers, But with Less Breakage

Many of our SPME fibers now are available with a coating of StableFlex material. StableFlex fibers are more flexible than our original fibers, and are much less likely to break. StableFlex fibers also exhibit longer lifetime (more injections can be made on a single fiber), greater stability, and less bleed.

Choose StableFlex SPME fibers with either a standard needle (24 gauge) or with a 23-gauge needle (for use with the Merlin Microseal™ sealing system for a proper seal with Microseal septa). Fiber length 1cm unless otherwise indicated. Sold in packs of 3.

	For Manual Sampling		For Automated Sampling[2] or HPLC	
StableFlex SPME Fiber Assemblies[1]	**Standard Needle** $160.00	**23 Gauge Needle** $170.00	**Standard Needle** $160.00	**23 Gauge Needle** $170.00
65µm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) Ideal for many polar analytes, especially amines.	**57326-U**	–	**57327-U**	–
85µm Carboxen/Polydimethylsiloxane (CAR/PDMS) Ideal for gaseous/volatile analytes, high retention for trace analysis.	**57334-U**	–	**57335-U**	–
70µm Carbowax/Divinylbenzene (CW/DVB) For polar analytes, especially for alcohols, low temperature limit.	**57336-U**	**57338-U**	**57337-U**	**57339-U**
50/30µm Divinylbenzene/Carboxen/PDMS (DVB/CAR/PDMS) Ideal for broad range of analyte polarities, good for C3-C20 range.	**57328-U** **57348-U**[3]	– –	**57329-U** –	– –

[1] Requires an SPME fiber holder (see the Supelco catalog).
[2] Use with AutoSampler requires Varian SPME upgrade kit (available from Varian).
[3] 2cm fiber.

To Order:
Phone **800-247-6628** or **814-359-3441**
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