

SPME/HPLC Interface Combines Fast Sample Extraction with Efficient Analysis for Explosives

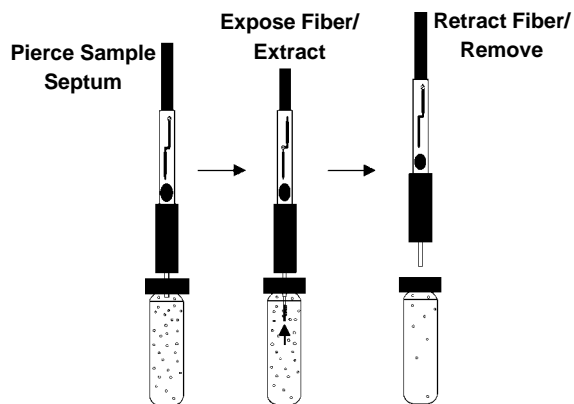
The SPME/HPLC interface enables HPLC analysts to take advantage of the time and solvent savings offered by SPME. Through the interface, mobile phase contacts the SPME fiber, removes the adsorbed analytes, and delivers them to the column for separation. Analytes can be desorbed in a moving stream of mobile phase (dynamic desorption), or the fiber can be soaked in mobile phase for a specific period of time before the material is injected onto the column (static desorption). Using the technique to analyze explosives residues in water provided peaks that were symmetric, sharp, and easily discerned, indicating efficient transfer from the SPME fiber to the HPLC column.

Key Words:

- sample preparation • SPME • explosives

Solid phase microextraction (SPME)* has rapidly been established among the practical alternatives for sample preparation for gas chromatography. Because virtually no solvent is used (Figure A), SPME saves preparation time and preparation costs, and often improves the limits of detection in an analysis. Many analytes that can be analyzed by GC have proven to be effectively extracted by

Figure A. Analyte Extraction by SPME



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SPME. However, many weakly volatile or thermally labile compounds cannot be analyzed by GC. Pharmaceutical compounds, polynuclear aromatic hydrocarbons, and numerous other analytes are more effectively monitored by HPLC but, until the introduction of the SPME/HPLC interface, there was no simple way to introduce analytes extracted by SPME onto an HPLC column.

The SPME/HPLC interface, developed at Supelco, enables HPLC analysts to take advantage of the time and solvent savings offered by SPME. The interface consists of a six-port injection valve and a desorption chamber (Figure B) that replaces the injection loop in the HPLC system. Easily installed and removed, the desorption chamber includes a PEEK needle guide, a stainless steel body and compression cap, a double-tapered VESPEL® ferrule, and a sealing clamp. The SPME fiber is introduced into the desorption chamber under ambient pressure when the injection valve is in the “load” position. After the SPME fiber is inserted through the ferrule, the unit is made leak-tight by closing the clamp and compressing the ferrule against the SPME needle. All surfaces which come in contact with the SPME fiber or the mobile phase are stainless steel or VESPEL.

In SPME/GC, analytes are thermally desorbed from the SPME fiber in the heated injection port. The SPME/HPLC interface enables mobile phase to contact the SPME fiber, remove the adsorbed analytes, and deliver them to the column for separation. Analytes can be removed in a moving stream of mobile phase (dynamic desorption) or, when analytes are more strongly adsorbed to the fiber, the fiber can be soaked in mobile phase or another, stronger solvent for a specific period of time (e.g., 1 minute) before the material is injected onto the column (static desorption). In experiments to date with our current selection of bonded phase SPME fibers, neither desorption technique was detrimental to the fiber. Pressures to approximately 5400psig did not cause leaks at the double-tapered ferrule.

Analysts at the University of Waterloo (Ontario, Canada) effectively extracted and analyzed polynuclear aromatic hydrocarbons (1) and nonylphenol ethoxylate surfactants (2) using SPME/HPLC. Chemists in Supelco laboratories evaluated the practicality of the technique for monitoring explosives residues in water. They used an SPME fiber with a 65µm polydimethylsiloxane/divinylbenzene coating to extract explosives from water containing 27% sodium chloride (20 minutes, rapid stirring). After inserting the fiber into the SPME/HPLC interface, and with the injection valve in the “load” position, they filled the desorption reservoir with 200µL of 50:50 acetonitrile:water, allowed the fiber to soak in the solvent for 1 minute, then switched the valve to the “inject” position and began integration. After 10 minutes, the valve was returned to the “load” position, the desorption chamber was flushed and refilled, using 500µL of 50:50 acetonitrile:water (200µL remains in the interface), and the SPME fiber was removed. After a 1-minute air drying period, the fiber was ready to use for the next extraction.

*SPME technology is licensed exclusively to Supelco. US patent pending; European patent #05 23092.

Figure B. Desorption Chamber of Interface

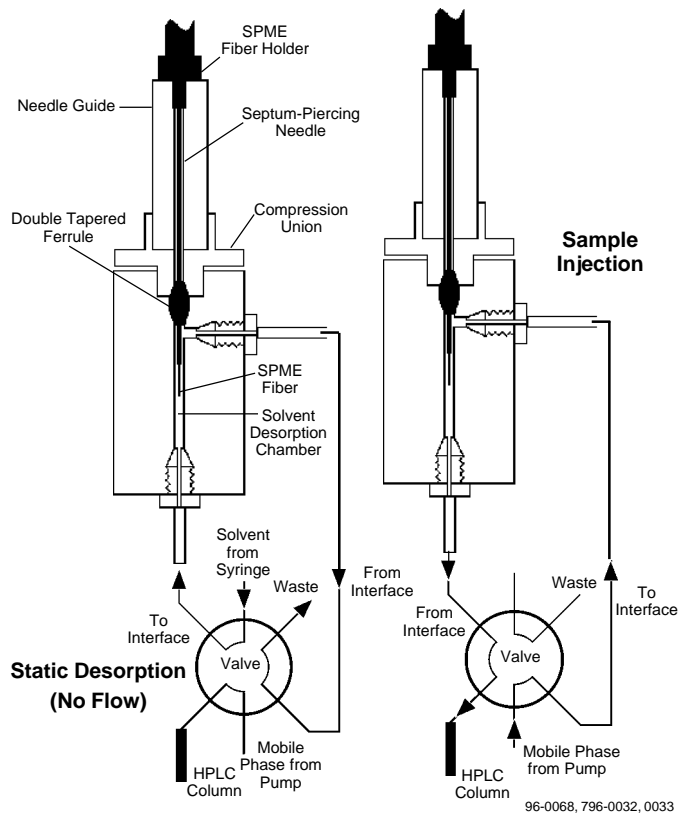
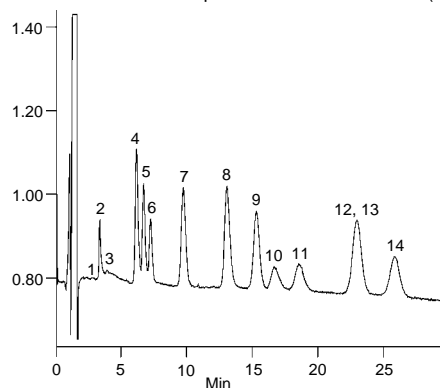


Figure C. Explosives in Water, Using SPME/HPLC

Sample: 4mL (water + 27% NaCl, pH 9.5) in 4.6mL vial, 50ppb each analyte
 SPME Fiber: 65µm polydimethylsiloxane/divinylbenzene
 Cat. No.: 57311 (autosampler/HPLC)
 Extraction: immersion, 20 min (rapid stirring)
 Desorption: static, 200µL acetonitrile:water, 50:50, 1 min
 Column: SUPELCOSIL LC-8, 15cm x 4.6mm ID, 3µm particles
 Cat. No.: 58983
 Mobile Phase: isopropyl alcohol:water, 18:82
 Flow Rate: 1.5mL/min
 Det.: UV, 254nm

- | | |
|---------------------------------------|---|
| 1. HMX [•] | 9. 2,6-Dinitrotoluene [■] |
| 2. 1,3,5-Trinitrobenzene [•] | 10. 2-Amino-Dinitrotoluene [•] |
| 3. RDX [•] | 11. 4-Amino-Dinitrotoluene [■] |
| 4. 1,3-Dinitrobenzene [•] | 12. 4-Nitrotoluene [■] |
| 5. 2,4,6-Trinitrotoluene [•] | 13. 2-Nitrotoluene [■] |
| 6. Tetryl [■] | 14. 3-Nitrotoluene [■] |
| 7. Nitrobenzene [•] | •Component of EPA 8330 Mix A (Cat. No. 47283) |
| 8. 2,4-Dinitrotoluene [•] | ■Component of EPA 8330 Mix B (Cat. No. 47284) |



The analysis was performed on a 15cm x 4.6mm ID SUPELCOSIL™ LC-8 column (3µm particles). Peaks for the analytes, present in the water sample at 50ppb each, were symmetric, sharp, and easily discerned, indicating efficient transfer from the SPME fiber to the HPLC column (Figure C).

If your HPLC analyses call for time-consuming and expensive solvent-based extractions, SPME may very well prove to be a better approach. Several investigators have already established that SPME can be effective for monitoring drugs and drug metabolites in biological fluids (for an example – amphetamines in urine – ask for free Application Note 83), and we feel the new SPME/HPLC interface will accelerate the development of new pharmacological and food and beverage applications.

References

- Chen, J. and J. Pawliszyn, *Anal. Chem.* **67**: 2530-2533 (1995).
- Boyd-Boland, A.A. and J.B. Pawliszyn, *SPME Coupled with HPLC for the Analysis of Nonylphenol Ethoxylate Surfactants in Water*. For information, contact the authors at The Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

References not available from Supelco.

Trademarks

SUPELCOSIL — Sigma-Aldrich Co.
 Rheodyne — Rheodyne, Inc.
 Valco — Valco Instruments Co., Inc.
 VESPEL — E.I. du Pont de Nemours & Co., Inc.

Ordering Information:

Description	Cat. No.
SPME/HPLC Interface	
with Valco® valve	57350-U
with Rheodyne® valve	57353
SPME Holder (Autosampler/HPLC)*▲	57331
SPME Fiber	
65µm polydimethylsiloxane/divinylbenzene, pk. of 3 For HPLC▲	57311
SUPELCOSIL LC-8 HPLC Column	
15cm x 4.6mm ID, 3µm particles	58983
Explosives Standards	
Formulated for US EPA Method 8330, 100µg/mL each analyte in acetonitrile	
EPA 8330 Mix A (8 analytes), 1mL	47283
EPA 8330 Mix B (6 analytes), 1mL	47284

*First time SPME users must order an SPME fiber holder in addition to SPME fibers. The holder is reusable indefinitely. To see our complete selection of nonpolar, intermediate polarity, and polar SPME fibers, refer to the Supelco catalog.

▲Also used with Varian 8100/8200 AutoSampler.

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