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Solid Phase Microextraction of Alcohols and Small Polar Analytes for Capillary GC

R. Shirey, V. Mani (Supelco, Inc.)
M. Butler (State of North Carolina)

SPME is a simple, solventless extraction procedure in which a phase-coated fused silica fiber is immersed into a liquid sample or is exposed to the headspace above a solid or liquid sample. Analytes adsorb to the phase, and then are thermally desorbed in the injection port of a gas chromatograph and transferred to a capillary column. A new Carbowax/divinylbenzene-coated SPME fiber extracts alcohols from samples at ppm to ppb concentrations.

Since the introduction of solid phase microextraction (SPME)* in 1993, interest in developing this procedure for polar analytes has steadily increased. Extractions of polar analytes are enhanced by using an SPME fiber coated with a polar phase or a porous polymer material. A new fiber coated with a 65µm film of Carbowax®/divinylbenzene is well suited to extracting volatile polar analytes.

We extracted alcohols and other polar analytes from water using two sampling techniques — heated headspace sampling and direct fiber immersion (Table 1). The pH was neutral and the solution was saturated with sodium chloride. With headspace sampling, alcohol extractions were linear from 0.25ppm to 100ppm (0.05ppm to 50ppm for ethyl acetate).

Detection for all analytes except ethyl acetate and acetone was much more sensitive with headspace sampling. In fact, detection was below the minimum detection limit of 50ppm specified in US Environmental Protection Agency (US EPA) Method 1671 for direct injection analysis of non-purgeable polar analytes. Except for acetone, all %RSDs were smaller by headspace extraction. Generally, extraction was more efficient by headspace SPME.

We used the new fiber to extract alcohols from the headspace of water and analyzed the compounds by gas chromatography using mass spectometry (MS) and flame ionization detection (FID). Conditions are summarized in Figures A and B. The initial baseline rise in Figure A was from water. Although the mass range was above the molecular weight of water, this compound caused a response in the ion source. Using selected ions for quantitation, however, we found water interference was not a problem. FID yielded an improved baseline (Figure B), but at reduced sensitivity.

In forensic analyses, SPME offers a quick and inexpensive method of absolute confirmation of biological specimens. Investigators for the Office of the Chief Medical Examiner of North Carolina (Chapel Hill, NC, USA) used SPME to confirm volatile compounds by GC/MS. Chemist Michael G. Butler and Chief Toxicologist William H. Anderson, Ph.D. performed analyses on blood containing standard blood alcohols (Figure C). Traditional blood alcohols were readily extractable and identifiable. Ethanol was quantitated in the range

Table 1. Alcohols and Small Polar Analytes by SPME

Detection limit by GC/MS quadrupole with selected ion monitoring

Analyte	Ions Monitored	Response Factor*	%RSD	Range (ppm)	Min. Det. Limit (ppm)	Data Points
Direct Immersion						
Methanol	31	0.004	10.6	0.75 - 100	0.75	n=8
Ethanol	31	0.005	10.0	0.75 - 100	0.75	n=8
Acetonitrile	41	0.010	4.4	0.75 - 100	0.50	n=8
Acetone	43	0.020	2.7	0.5 - 100	0.25	n=9
Isopropanol	45	0.018	2.0	0.75 - 100	0.10	n=8
n-Propanol	31	0.036	11.6	0.75 - 100	0.10	n=8
Ethyl acetate	43	0.916	18.7	0.01 - 10	0.005	n=7
Heated Headspace (50°C)						
Methanol	31	0.018	1.6	0.25 - 100	0.1	n=8
Ethanol	31	0.025	5.8	0.25 - 100	0.1	n=8
Acetonitrile	41	0.027	2.4	0.25 - 100	0.1	n=8
Acetone	43	0.078	10.1	0.25 - 100	0.25	n=8
Isopropanol	45	0.088	1.2	0.1 - 100	0.05	n=9
n-Propanol	31	0.076	5.6	0.1 - 100	0.05	n=9
Ethyl acetate	43	0.410	9.2	0.05 - 50	0.01	n=8

*RF = response factor ($counts_{analyte}$ x $conc._{IS}$) / ($counts_{IS}$ x $conc._{analyte}$)
Internal standard — 3-methyl-2-butanone at 2.5ppm.

Figure A. 1ppm Alcohols in Water by Headspace SPME

SPME Fiber: **Carbowax/divinylbenzene**
Cat. No.: **57312** (manual unit)
Sample: polar analytes , 27% NaCl, pH 7
Extraction: headspace, 1.5 min, 50°C, 2.5mL in a 4mL vial
Desorption: 3 min at 250°C

Column: **SPB-1 SULFUR, 30m x 0.32mm, 4.0µm film**
Cat. No.: **24158**
Oven: 50°C (2 min) to 150°C at 10°C/min
Carrier: helium, 40cm/sec
Injection: splitless/split, closed 3 min, 250°C
Detection: GC/MS quadrupole, selected ion mode

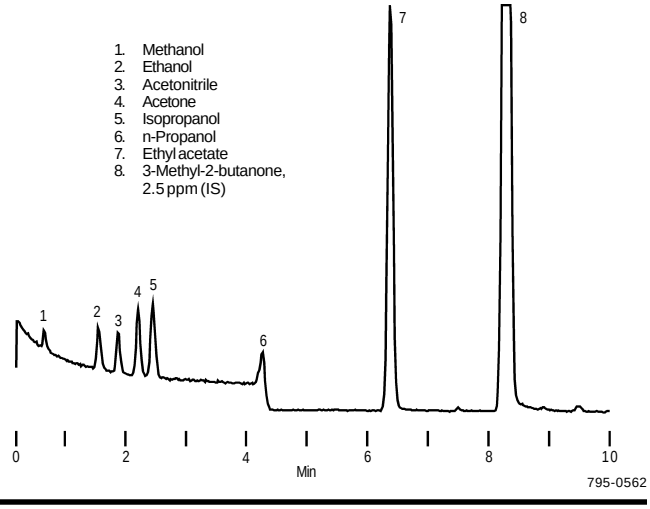


Figure B. 4ppm Alcohols in Water by Headspace SPME

SPME Fiber: **Carbowax/divinylbenzene**
Cat. No.: **57312** (manual unit)
Sample: polar analytes, 27% NaCl, pH 7
Extraction: headspace, 1.5 min, 50°C, 2.5mL in a 4mL vial
Desorption: 3 min at 250°C

Column: **Nukol, 30m x 0.25mm, 0.25µm film**
Cat. No.: **24107**
Oven: 50°C
Carrier: helium, 30cm/sec
Injection: splitless/split, closed 3 min, 250°C
Detection: FID, 260°C

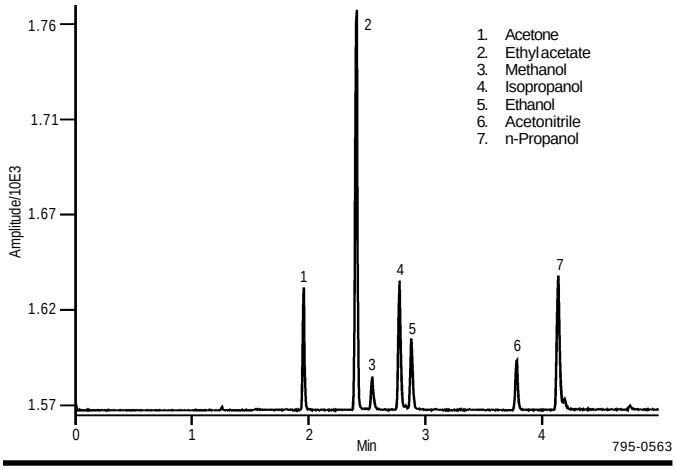
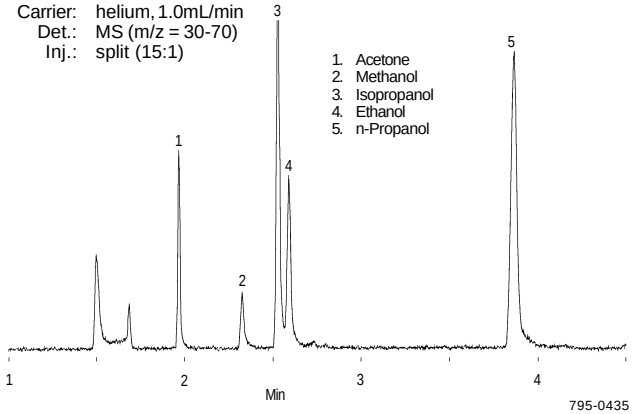


Figure C. Alcohols in Blood

Sample: 100µL blood spiked with alcohols at 200mg/dL, acetone at 100 mg/dL, saturated with NaCl
SPME Fiber: **Carbowax/divinylbenzene, 60µm film**
Cat. No.: **57312**
Extraction: headspace, 4 min, 60°C
Desorption: 30 sec, 250°C

Column: **SUPELCOWAX 10, 30m x 0.2mm ID, 0.2µm film**
Cat. No.: **24169**
Oven: 55°C
Carrier: helium, 1.0mL/min
Det.: MS (m/z = 30-70)
Inj.: split (15:1)



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of 25mg/dL; a correlation coefficient of $r^2 = 1.00$ was obtained. The coefficient of variance for a 100mg/dL blood specimen was 2.2%. The concentration of the samples and the extraction efficiency of the Carbowax/divinylbenzene fiber warranted a split of the samples, preventing column overload and improving chromatography.

Additional forensic analyses using SPME included the identification and quantification of diethyl ether and 2,2,2-trichloroethanol. Also, ethylene glycol in blood has been extracted and identified recently at a concentration of 25mg/dL.

With the development of porous polymer and polar fiber coatings, semivolatile polar analytes such as anilines and benzidines can be extracted from spiked water at low (10ppb) concentrations (1). Continued development of new fiber coatings will afford linear extractions of these analytes at lower concentrations.

Ordering Information:

Description	Cat. No.
SPME Holder**	
For manual sampling	**57330-U**
For Varian 8100/8200 autosampler (requires Varian SPME upgrade kit)	**57331**
65µm Carbowax/Divinylbenzene Fiber, pk. of 3	
For manual sampling	**57312**
For Varian 8100/8200 autosampler	**57313**
SPME Fiber Assembly Kit	
One fiber assembly each: 100µm polydimethylsiloxane (for volatile analytes), 7µm polydimethylsiloxane (for nonpolar–intermediate polarity semivolatiles), 85µm polyacrylate (for polar semivolatiles)	
For manual sampling	**57306**
For Varian 8100/8200 autosampler	**57307**
Capillary Columns	
SPB™-1 SULFUR 30m x 0.32mm ID, 4.0µm film	**24158**
Nukol™ 30m x 0.25mm ID, 0.25µm film	**24107**
SUPELCOWAX™ 10 30m x 0.20mm ID, 0.20µm film	**24169**

Reference

1. Shirey, R., and V. Mani, *New Developments in Solid Phase Microextraction — Polar Analytes and Fast Analysis*, presented at the 1995 Pittsburgh Conference (available from Supelco; request publication T495014).

For a complete explanation of solid phase microextraction and descriptions of many applications, request SPME applications package T498316.

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

**Initially you must order both holder and fiber assembly. Holder is reusable indefinitely.

Trademarks

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