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New Applications for SPME/Capillary GC: Screening for Amphetamines in Urine; Identifying Tobacco Varieties; Monitoring Nitrogen-Containing Herbicides in Water

R.F. Mindrup

This article summarizes the work of three groups of investigators who have developed new solid phase microextraction (SPME) techniques. In screening for methamphetamine and amphetamine in urine, heated headspace SPME offers a 20-fold increase in sensitivity, relative to conventional heated headspace sampling. Sampling the headspace over a tobacco sample affords a fast, sensitive means of identifying the variety, through comparison of individual analytes. SPME coupled with GC/FID, GC/NPD, or GC/MS was used to monitor 22 nitrogen-containing herbicides in water at concentrations of 0.1 to 1000ng/mL. Limits of detection were at microgram/liter to sub-nanogram/liter levels; values were precise to within $\pm 2\%$ to $\pm 20\%$.

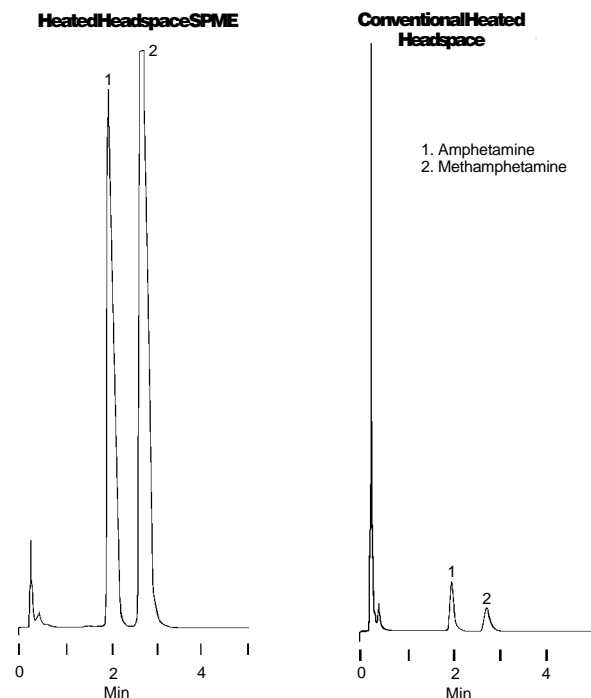
Applications for the new sample preparation technique of solid phase microextraction (SPME)* are being described with increasing frequency at conferences and in the literature. This article summarizes three recently developed applications for SPME: detecting methamphetamine and amphetamine in urine, identifying tobacco varieties through comparison of individual analytes, and monitoring nitrogen-containing herbicides in water. Additional details concerning these applications are supplied in Application Notes #83, #84, and #85, respectively.

Fast, Accurate Detection of Amphetamines in Urine

Staff members of the Departments of Legal Medicine of Hiroshima University School of Medicine and Fukuoka University School of Medicine have developed an accurate, simple, and rapid method for analyzing urine for methamphetamine (MA) and its principal metabolite, amphetamine (AP), using heated headspace SPME (1). A 1mL urine sample, with internal standard (5 μ g pentadeuterated methamphetamine, prepared according to reference 2) and 0.7g potassium carbonate added, is sealed in a 12mL vial and heated at 80°C for 20 minutes in a block heater. An SPME fiber coated with a 100 μ m film of polydimethylsiloxane is exposed to the headspace above the sample for 5 minutes, then thermally desorbed in the injection port of a capillary gas chromatograph. In a system equipped with mass spectrometry/chemical ionization selected ion monitoring (GC-MS/CI-SIM), this analysis was 20 times as sensitive as a method incorporating conventional headspace extraction (Figure A). Correlation coefficients for MA and AP, based on d₅-MA, were 0.9999 for concentrations from 0.2 to 10mg/liter and 0.9970 for concentrations from 5 to 100mg/liter. Coefficients of variation for 5mg/liter of AP and MA in urine were 7.0% and 5.1%, respectively.**

Figure A. SPME Is Effective for Detecting Methamphetamine and Amphetamine in Urine

Sample: 1mL urine + 100 μ g each analyte, 5 μ g d₅-methamphetamine, 0.7g K₂CO₃ in 12mL vial
 SPME Fiber: 100 μ m polydimethylsiloxane
 Cat. No.: 57300-U (manual sampling)
 Extraction: headspace, 80°C, 5 min (after 20 min sample warming period)
 Desorption: 3 min, 250°C
 Column: poly(dimethylsiloxane), 15m x 0.53mm ID, 2.0 μ m film
 Oven: 110°C
 Carrier: nitrogen, 25mL/min
 Det.: FID, 250°C
 Inj.: splitless, 250°C



795-0595, 0596

Figure provided by M. Yashiki, T. Kojima, T. Miyazaki, N. Nagasawa, and Y. Iwasaki, Hiroshima University School of Medicine, Hiroshima, Japan and K. Hara, Fukuoka University School of Medicine, Fukuoka, Japan.

In addition to speed, simplicity, and accuracy, the headspace SPME method can, under some circumstances, reduce the potential for interference by co-administered drugs. Chlorpromazine and its metabolites can cause false positive results in an immunoassay for MA/AP (3), but these compounds did not interfere with the headspace SPME extraction.

Figure B. Tobacco Varieties Identified from SPME/GC Profiles

Sample: 1.00g tobacco (12% moisture) + 3.0mL 3M KCl in 20mL headspace vial
 SPME Fiber: **100µm polydimethylsiloxane**
 Cat. No.: **57300-U** (manual sampling)
 Extraction: headspace, 95°C, 30 min
 Desorption: 1 min, 250°C
 Column: 5% phenylmethylsiloxane, 30m x 0.25mm ID, 0.25µm film
 Oven: 40°C (1 min) to 250°C at 6.0°C/min, hold 2 min
 Carrier: helium, 30cm/sec
 Det.: MSD, 280°C transfer line
 Inj.: splitless, 250°C (0.75mm ID injector liner)

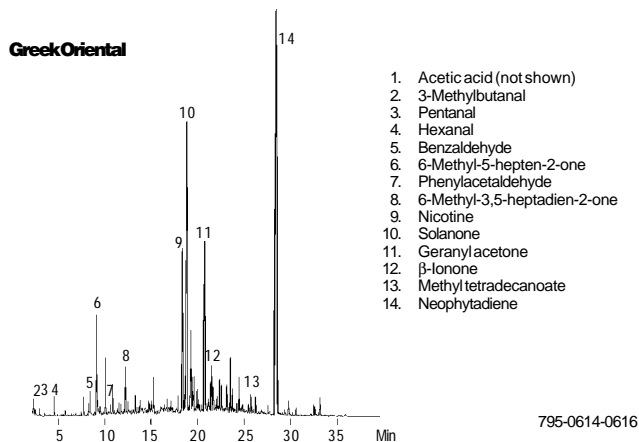
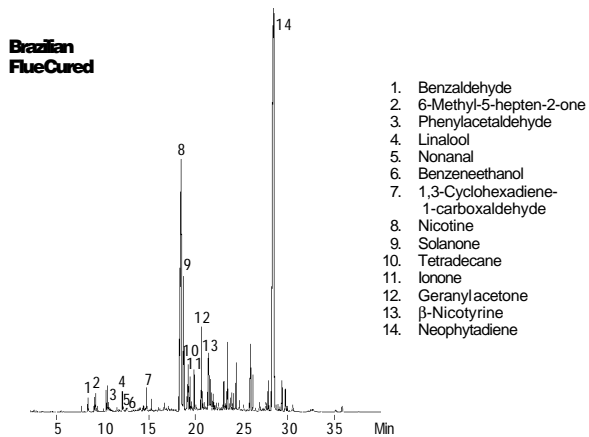
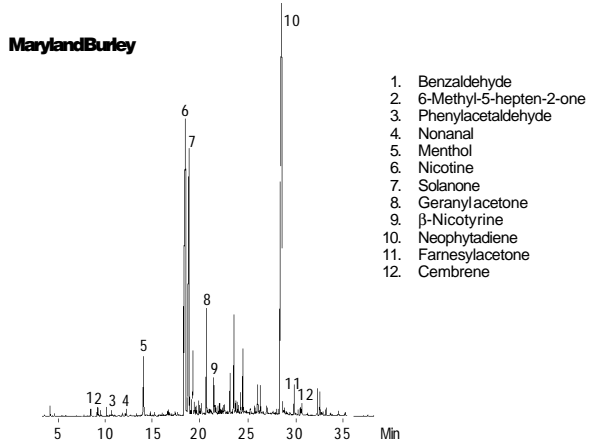


Figure provided by T. J. Clark and J. E. Bunch, Liggett Group Inc., Durham, NC 27702 USA.

Identification of Tobacco Varieties

Investigators at the Liggett Group have found that SPME offers several advantages over other headspace analyses of tobacco varieties: simpler technique and equipment, less carryover of impurities (purge and trap methods require long trap bake times), greater sensitivity (less sample is required, relative to purge and trap methods), and faster analyses (at least a 2 hour purge at 95°C is required to provide data comparable to SPME by the method described here). An SPME fiber coated with a 100µm film of polydimethylsiloxane is more selective for sampling nonpolar components than is purge and trap using a Tenax® material (MS spectra are less complex and the analysis is much simpler).

In the headspace SPME/GC analysis, tobacco samples are cut and adjusted to 12% moisture. A 1.00g subsample and 3.0mL of 3M KCl are sealed in a 20mL headspace vial and heated to 95°C in a block heater during the extraction. Differences among the

Figure C. Nitrogen-Containing Herbicides Extracted from Water

Sample: 4mL (water + 1g/mL NaCl + 100ng/mL each analyte), pH 2, in 4.6mL vial
 SPME Fiber: **85µm polyacrylate**
 Cat. No.: **57304** (manual sampling)
 Extraction: immersion, ambient temp., 50 min (constant stirring)
 Desorption: 5 min, 230°C
 Column: **PTE-5, 30m x 0.25mm ID, 0.25µm film**
 Cat. No.: **24135-U**
 Oven: 40°C (5 min) to 100°C at 30°C/min, to 275°C at 5°C/min
 Carrier: helium, 40cm/sec, set at 40°C
 Det.: MS (Ion Trap Manifold: 250°C; Mass Scan Range: m/z = 45-400 at 0.6 sec/scan)
 Inj.: splitless, 230°C

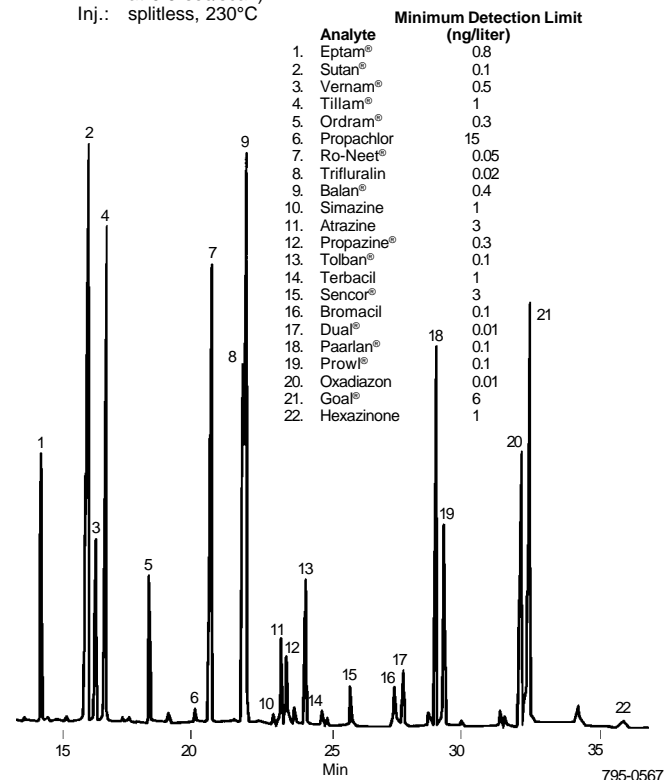


Figure provided by A. Boyd-Boland and J. Pawliszyn, University of Waterloo, Waterloo, Ontario, Canada.

components of various tobacco varieties are easily detected, as shown in Figure B. (All identifications in this figure were made by the investigators, based on mass spectral data, retention times and, for major components, SPME/GC/FTIR.) The KCl solution and the 95°C temperature enhance the volatility of the minor components and thus improve detection.

Nitrogen-Containing Herbicides in Water

Chemists at the University of Waterloo used a polyacrylate-coated SPME fiber to monitor a mixed group of 22 nitrogen-containing herbicides, including thiocarbamates, triazines, nitroanilines, and other compounds, in water samples (4). Responses for flame ionization detection, nitrogen-phosphorus detection, and ion trap mass spectrometry were calculated for each analyte at a minimum of five concentrations. Minimum detection limits ranged from 200-19,000ng/liter (FID) to 10-6000ng/liter (NPD) to 0.01-15ng/liter (MS). For almost every analyte, detection was more sensitive by SPME/GC/MS (16 of 16 analytes) or SPME/GC/NPD (12 of 16 analytes) than by the procedures described in US EPA Method 507/508. Correlation coefficients for all but 1 (hexazinone) of the 22 analytes were greater than 0.99 by linear regression analysis, both when the y intercept was allowed to vary and when the intercept was fixed at zero. Extractions of most of the analytes were precise to within $\pm 2\%$ to $\pm 20\%$, values well within the US EPA requirement of $\pm 30\%$.

The investigators added various concentrations of pesticides to water containing 1g/mL NaCl and compared results for SPME times ranging from 10 to 120 minutes, at room temperature, with constant stirring. The added salt generally increased the amount of each analyte extracted, with the exception of the nitroanilines, Goal, and oxadiazon. Varying the pH from 4 to 11 had no significant effect on extraction of any of the analytes, but at pH 2 extraction of the nitroanilines and Goal was enhanced. The combination of pH 2 and salt in the sample was effective for extracting most triazines, substituted uracils, and thiocarbamates, but was less effective than salt addition alone. The combination also was detrimental to the extraction of nitroanilines, Goal, and oxadiazon, which were most effectively extracted at neutral pH or at pH 2, without salt. Conditions for GC/MS analysis are shown in Figure C; for GC/FID or GC/NPD the temperature program was 100°C (5 min) to 300°C at 10°C/min (hold 5 min), and the carrier gas flow rate was 1.0mL/min.

SPME is fast and easy, and eliminates the costs and hazards associated with using organic solvents. Under consistent sampling conditions, analytes can be extracted with good precision over wide ranges of concentrations, ensuring reliable results for screening samples or in quantitative analyses. If you want to reduce the time and expense of sample concentration in your analyses, these diverse applications show that SPME is an approach well worth investigating.

Trademarks

Balan, Paarlan — Eli Lilly & Co.
Dual, Tolban — Ciba-Geigy AG
Eptam, Ordram, Ro-Neet, Sutan, Tillam, Vernam — Stauffer Chemical Co.
Goal — Rohm and Haas Co.
Prowl — American Cyanimid Co.
Sencor — Bayer AG
PTE, SPB, SigmaChrom — Sigma-Aldrich Corp.

Ordering Information:

Description	Cat. No.
SPME Holder	
Initially you must order both holder and fiber assembly. Holder is reusable indefinitely.	
For manual sampling	57330-U
For Varian 8100/8200 AutoSampler requires Varian SPME upgrade kit	57331
100µm polydimethylsiloxane fiber, pk. of 3	
For manual sampling	57300-U
For Varian 8100/8200 AutoSampler	57301
85µm polyacrylate fiber, pk. of 3	
For manual sampling	57304
For Varian 8100/8200 AutoSampler	57305
Capillary GC Columns	
SPB™-1, 15m x 0.53mm ID, 2.0µm film (polydimethylsiloxane)	available on request
SPB-5, 30m x 0.25mm ID, 0.25µm film (5% phenylmethylsiloxane)	24034
PTE™-5, 30m x 0.25mm ID, 0.25µm film	24135-U

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- Boyd-Boland, A. and J. Pawliszyn, manuscript submitted to *Analytical Chemistry* (1995).

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Acknowledgments

The amphetamines investigation was conducted by Mikio Yashiki, Tohru Kojima, Tetsuji Miyazaki, Nobuyuki Nagasawa, and Yasumasa Iwasaki, Department of Legal Medicine, Hiroshima University School of Medicine, 1-2-3 Kasumi, Minami-ku, Hiroshima 734, Japan and Kenji Hara, Department of Legal Medicine, Fukuoka University School of Medicine, 7-45-1 Nanakuma, Jonan-ku, Fukuoka 814-01, Japan.

The tobacco investigation was conducted by T. Jeffrey Clark and John E. Bunch, Liggett Group Inc., 710 West Main Street, Durham, NC 27702 USA.

The herbicides investigation was conducted by Anna Boyd-Boland and Janusz Pawliszyn, University of Waterloo, Waterloo, Ontario, Canada.

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

****NOTE:** These investigators have developed a similar procedure for monitoring amphetamines in blood (N. Nagasawa, M. Yashiki, Y. Iwasaki, K. Hara, and T. Kojima, *Rapid Analysis of Amphetamines in Blood Using Head Space-Solid Phase Microextraction and Selected Ion Monitoring* manuscript submitted to *Forensic Science International*). In place of potassium carbonate, 0.5mL 1N NaOH is used to drive the analytes into the headspace.

Many example extractions, and additional types of SPME fibers, are described in applications package 498316 (available on request).