The Use of Solid-Phase Microextraction–Gas Chromatography in Forensic Analysis

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Abstract

A thorough review of the application of solid-phase microextraction (SPME) combined with gas chromatography for the analysis of forensic specimens is presented, including experimental results for several recent applications. The SPME applications covered in this comprehensive review include ignitable liquid residues (also referred to as accelerants), explosive traces, drugs and poisons from biological specimens, and other forensic applications. Recently developed SPME methods are also presented, including the analysis of ignitable liquid residues on human skin, odor signatures, and several drug applications such as free-fraction antipsychotic drug levels, blood alcohol casework, drink-tampering analysis, and gamma-hydroxybutyrate identification without the need for derivatization. SPME is shown to be an inexpensive, rapid, and sensitive method for the analysis of a variety of forensic specimens.

Introduction

Solid-phase microextraction (SPME) has proven to be an important sample preparation technique for the analysis of forensic specimens because of the many advantages that the technique offers when it is applied to these types of samples (1). SPME is often faster than traditional techniques; can be readily automated; and allows for multiple sampling, preservation of the sample, and minimization of the risk of sample contamination caused by the simplicity of the technique. Also, the lower detection limits generally attributed to SPME allow for the confirmation of positive samples that previously went undetected. An additional benefit of SPME is the elimination of solvents, which can save forensic science laboratories money and reduce or eliminate the risk of analysts being exposed to toxic substances. This article reviews the application of SPME for the analysis of forensic specimens including ignitable liquid residues (often referred to as accelerants), explosive traces, drugs, and poisons from biological specimens and other forensic applications. Recently developed SPME methods are also presented, including novel methods for the analysis of ignitable liquids on human skin, odor signatures, and several drug applications such as free-fraction antipsychotic drug levels, blood alcohol casework, drink-tampering analysis, and gamma-hydroxybutyrate (GHB) identification without the need for derivatization. An overview of the forensic applications of SPME is shown in Figure 1. The major areas that will be discussed are drug analysis for toxicology, bulk drug analysis, trace analysis (including high explosives and ignitable liquids), and sampling from various matrices and a number of SPME sampling modes.

Experimental

Buffer solutions and all standard chemicals used were purchased from Fisher Scientific (Pittsburgh, PA). Valproic acid and caprylic acid were obtained from Sigma (Sigma Chemical Co., St. Louis, MO). Compressed helium (UHP–zero grade) was purchased from Air Product and Chemicals, Inc. (Allentown, PA). SPME fibers were obtained from Supelco Co. (Bellefonte, PA). Plasma was obtained from the American Red Cross (Miami, FL). A Millipore Centricon YM-30 was purchased from Amicon, Inc.

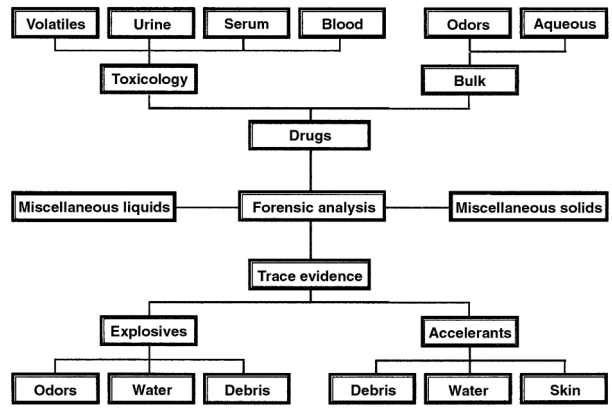

Figure 1. Several forensic applications of SPME–GC.

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(Beverly, MA). The 2-mL autosampler vials were purchased from National Scientific Co. (Lawrenceville, GA). A Varian (Varian Associates, Walnut Creek, CA) Star 3400CX gas chromatograph (GC) equipped with a Varian 8200CX autosampler and a Varian Saturn 2000 GC–mass spectrometer (MS)–MS were used in this study. The GC–MS used a Supelco Nukol capillary column (30 m × 0.25 mm) with a film thickness of 0.25 µm. The GC–flame ionization detector (FID) work-employed a Hewlett Packard (Wilmington, DE) model 5890 series II GC with a DB-5ms, 30-m column (0.25-mm i.d., 0.25-µm film thickness) (J&W Scientific, Folsom, CA).

Discussion

Ignitable liquid residues

A coated-wire adsorption technique was being applied to the recovery of ignitable liquid residues the same year SPME was being introduced (2). This early technique involved the heated headspace (70 or 80°C) adsorption of ignitable liquids onto a carbon-coated aluminum or copper wire, followed by *n*-pentane elution with ultrasonic vibration (3). The first report of SPME being applied to the recovery of ignitable liquid residues was in 1994 (4) in which SPME demonstrated improved sensitivity for the recovery of ignitable liquid residues with reduced analysis times and the elimination of toxic solvents when compared with the established activated charcoal strip–solvent elution method (5). The SPME analyses of gasoline and kerosene have been compared with headspace, cold-trap, and solvent extraction methods and shown to provide accurate information with less interference peaks (6).

Headspace SPME has also been applied to the analysis of flammable and combustible substances in human body fluids (7,8). A detailed study of the recovery of gasoline residues confirmed the utility of the SPME technique with lack of interference problems in the presence of wood or plastic pyrolysis products and the ability to provide reproducible multiple analyses from a single sample (9). The recovery of ignitable liquids directly from aqueous solvents has also been demonstrated, with SPME proving to be more than one order of magnitude more sensitive than the conventional solvent extraction method for 500-ppb preparations (allowing for positive identification of diesel fuel in aqueous samples) (10). SPME has also been used to identify the presence of gasoline in a real arson-suspected fire debris sample—conventional methods lacked the adequate sensitivity for identification (11).

SPME methods have been optimized for a variety of ignitable liquids and conditions (12,13) and applied to the recovery and identification of ignitable liquids from human skin (14). The SPME method developed for the recovery of ignitable liquid residues from human skin uses 100-µm polydimethylsiloxane (PDMS) fibers and gentle heating for 5 min, followed by 10 min of sampling from a plastic bag shrouding the suspected hand. The recovery was found to be dependent on the initial amount, environmental conditions, ignitable liquid type, and time since application (14). Figure 2 shows a chromatogram of gasoline

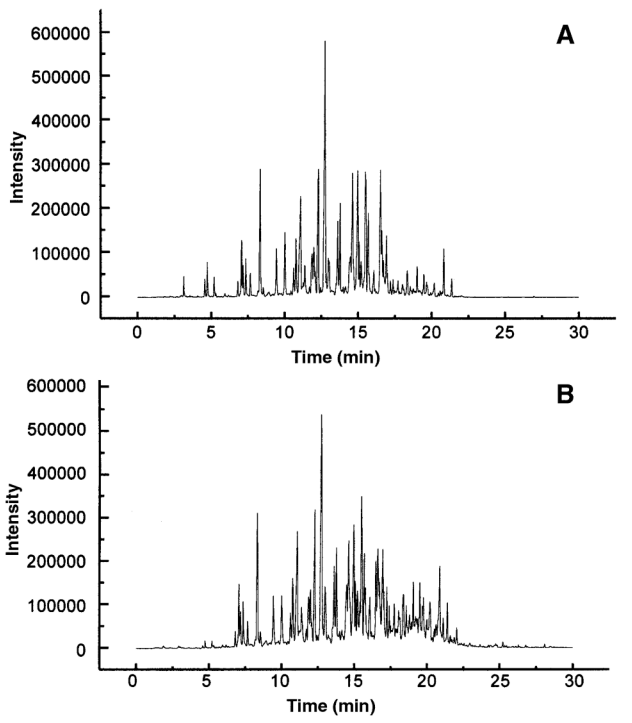

Figure 2. The headspace SPME–GC–FID of 97% evaporated gasoline. One microliter was applied on kimwipes inside a 1-L can sampled for 15 min (A) and the chromatogram from a hand that was contaminated with gasoline for 5 s then covered by a fire debris bag and performed SPME for 15 min with the first 5 min heating using a heat lamp (B).

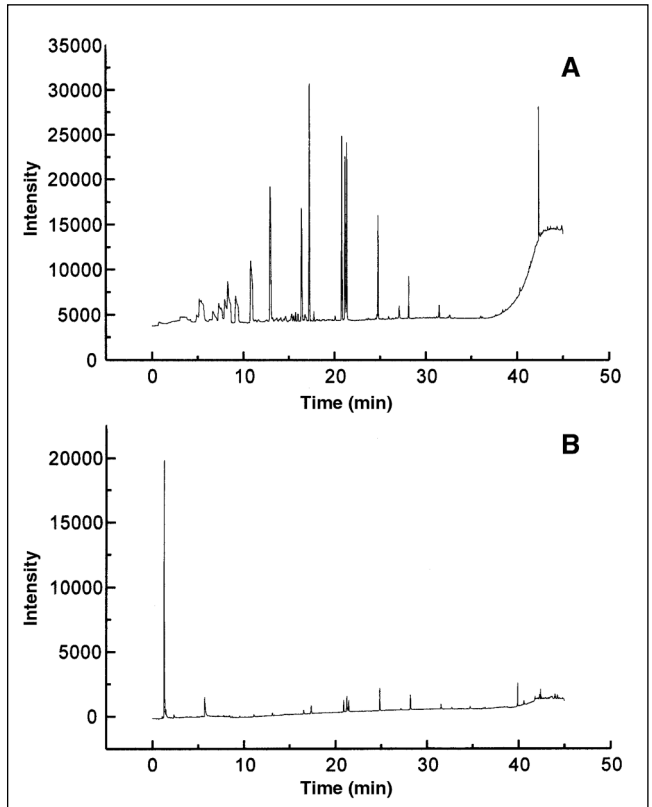

Figure 3. The GC of accelerants of the second 2 min. Desorption of Carboxen fiber after adsorption for 15 min (A) and after the second 10-s desorption of the Carbowax fiber and adsorption for 15 min (B).

evaporated 97% by SPME (Figure 2A) compared with that obtained from the hand of a subject contaminated with gasoline and sampled by a small plastic bag pierced with a 100-µm PDMS headspace SPME–GC–FID using a 15-min extraction with the first 5 min heated by a heat lamp (Figure 2B). The use of a larger bag or heating throughout the extraction process reduced recoveries. Different fiber chemistries yielded significantly different recoveries and also required significantly different desorption times to prevent carryover. For example, although the use of 75-µm Carboxen–PDMS fibers increased the recoveries of some of the hydrocarbons when compared with the 100-µm PDMS fiber, desorption times of several minutes were required to prevent carryover (as shown in Figure 3A) as opposed to the 65-µm Carbowax–divinylbenzene (DVB), which showed lower recoveries than the 100-µm PDMS fiber but required less than 10 s for complete desorption (as shown in Figure 3B). A proposed comprehensive SPME scheme for detecting ignitable liquid residues in suspect arson cases used a low-temperature Carboxen–PDMS SPME, followed by an elevated-temperature PDMS step. This demonstrated simplified sample preparation and high recovery efficiency when compared with headspace charcoal adsorption and solvent extraction methods (15). A review of contemporary sample-preparation methods (including SPME) that were used for the detection of ignitable liquids in suspected arson cases was recently published (16).

Explosives analysis

The analysis of semivolatile compounds including nitrobenzene and dinitrotoluenes (DNTs) in water has been reported using a PDMS fiber and GC–FID analysis with detection limits reported at 9–15 ng/mL (17). Headspace and direct aqueous-immersion SPME using PDMS–DVB fibers followed by GC–MS and liquid chromatography (LC)-ultraviolet detection were used to recover 14 explosives with varying results depending on the extracted explosive (18). An optimized headspace SPME–GC–MS method has been published using polyacrylate resin with 30-min adsorptions at 100°C and desorptions at 200°C with reported detection limits of 0.5–10 ng/750 mL headspace for ethylene glycol dinitrate, nitroglycerin, pentaerythrite tetranitrate, trinitrotoluene (TNT), and hexahydrotrinitrotriazine (RDX) (19). Trace explosive signatures have been determined from World War II unexploded undersea ordinances using direct-immersion SPME–GC–MS and SPME–GC–reversal electron attachment detection. This yielded improved extractions over SPE with sensitivities of 10 ppt for DNT and TNT for 15-min extractions using PDMS–DVB fibers (20). Direct-immersion SPME using a Carbowax–DVB fiber with 10 min of sampling followed by a GC–ITMS analysis yielded limits of detection of 10–325 ppt for TNT, RDX, and amino-DNTs in seawater (21). Direct-immersion SPME–GC, SPME–LC, and SPME–capillary zone electrophoresis methods have been optimized, compared, and successfully applied to actual postexplosion debris samples (22,23). Headspace SPME has also been applied to the characterization of odor signatures, including explosive odor signatures (24). The relative effects of major controllable variables for the SPME recovery of explosives and ignitable liquid residues has been reviewed for analyte chemistry, sampling modes (direct, headspace, and partial headspace), fiber chemistry, adsorption times, adsorption temperatures, desorption temperatures, desorption times, and matrix effects (including water content relative to sample container size) (25).

Toxicological analysis

The extraction of poisons from biological specimens such as urine, serum, and blood continues to be a difficult and time-consuming task. Increasingly, traditional liquid–liquid extraction techniques have been improved and replaced with newer methods, such as SPE and supercritical fluid extraction (26). Most recently, SPME has emerged as a promising alternative for the rapid recovery of poisons from biological matrices (12,27). Its recent applications for urine, blood and plasma, and unconventional poisons will be discussed.

Urine

The greatest number of toxicology applications with SPME has involved the recovery of drugs from urine, followed by recovery from blood and serum. SPME–GC has been successfully applied to the recovery of methadone, benzodiazepines, cannabinoids, phencyclidine, methaqualone, amphetamines, and their metabolites in urine, but was not as successful for the recovery of cocaine or opiates and their metabolites at pH 12 using 20-min direct ion-immersion SPME at 40°C with PDMS and polyacrylate fibers (28). A direct-immersion SPME method for the detection of cocaine at a level of 6 ng/0.5 mL in human urine has been reported using a PDMS fiber with 30 min of sampling with added NaF followed by GC–nitrogen–phosphorous detection (NPD) (29). An SPME method has been developed for the determination of benzoylecgonine in urine with hexyl chloroformate derivatization using a 100-µm PDMS fiber for 10 min at 55°C and ion-trap MS detection (30).

The determination of amphetamine, methamphetamine (MA), and dimethamphetamine in urine has been performed by 100-µm PDMS SPME–GC–MS that sampled for 30 min at pH 12.4 with 30% salt added (31). MA and amphetamine were detected at levels of approximately 10 ng/mL using PDMS–DVB fibers to extract the drugs from urine treated with 1 g/mL Na_2CO_3 for 30 min at 65°C followed by GC–NPD analysis (32). Another method for the recovery of MA and amphetamine used 100-µm PDMS fibers from urine treated with NaCl (0.5 g/mL) adjusted to pH 12 and extracted for 20 min followed by a NaOH–H_3BO_4 buffer wash prior to GC analysis with reported sensitivity 10–100 times greater than headspace methods, including SPME (33). Amphetamines and inflammable compounds in urine and blood have been analyzed using a 100-µm PDMS fiber immersed in basic solutions for 5 min at 80°C with analysis by GC–MS (34). The automated determination of amphetamines and methylenedioxymethamphetamine (MDMA) in urine has been reported using 100-µm PDMS fibers immersed at pH 10 for 16 min followed by analysis by GC–NPD or GC–MS (35).

Although sometimes less sensitive (depending on the volatility of the drug) headspace SPME has the advantage of yielding cleaner extracts from biological samples. A 5-min headspace SPME–GC–chemical ionization-MS procedure with 100-µm PDMS fibers for amphetamines from urine containing potassium carbonate at 80°C was shown to be 20 times more sensitive than the conventional headspace method (36). Another headspace SPME–GC–MS procedure using 100-µm PDMS fibers for 15 min

compared with containing NaCl at 75°C was shown to be sensitive enough for a routine confirmation of positive enzyme multiplied immunoassay technique and radioimmunoassay results for amphetamine and its analogs MA, MDMA, and methylenedioxyethylamphetamine (37). A headspace SPME–GC–FID method has also been reported for the analysis of amphetamines in clinical urine samples using 100-µm PDMS fibers for 15 min at 60°C with further method development and derivatization suggested for conclusive differentiation between the various types of amphetamines (38). A screening procedure for 21 amphetamine-related compounds has been developed using 100-µm PDMS headspace SPME–GC–MS with a 10-min extraction at 80°C with salt added (39). Finally, the rapid analysis of amphetamine, MA, methylenedioxyamphetamine, and MDMA has been reported using 100-µm PDMS headspace SPME–GC–MS with a 10-min extraction at 100°C with 2 N NaOH followed by direct on-fiber derivatization for 20 min at 60°C using trifluoroacetic anhydride (40).

Methadone has been quantified in urine using a 100-µm PDMS fiber for 15 min at pH 7.7 followed by GC–MS quantitation (41). Nicotine and cotinine in urine have been analyzed at 5 and 300 ng/mL, respectively, using 100-µm PDMS headspace SPME–GC–MS with a 5-min extraction at 80°C with the addition of potassium carbonate (42). Tricyclic antidepressants in urine have been analyzed at 24–38 ng/mL using 100-µm PDMS headspace SPME–GC–FID with a 15-min extraction at 100°C with the addition of sodium hydroxide (43). Meperidine in urine and blood has been analyzed at 20 and 100 ng/mL, respectively, using 100-µm PDMS headspace SPME–GC–FID with a 30-min extraction at 100°C with the addition of sodium hydroxide and sodium chloride (44). There have recently been several reports of the determination of benzodiazepines and metabolites using direct immersion methods. One method using a 65-µm PDMS–DVB sampling for 30 min followed by GC–FID analysis was applied to the detection of benzodiazepines in urine (45). Another method for determining benzodiazepines in urine used a 65-µm Carbowax–DVB sampling for 60 min at 45°C with salt added followed by GC–FID and GC–MS analysis (46). The analysis of benzophenones for the detection of benzodiazepines in urine has been reported using 100-µm PDMS SPME–GC–electrochemical detection (ECD) with a 30-min extraction at pH 9.4 with the addition of potassium hydroxide (47). The analysis of benzophenone and metabolites in water and human urine has been reported using 65-µm Carbowax–DVB SPME–GC–MS with a 45-min immersion time (48). Barbiturates have been determined in urine using 65-µm Carbowax–DVB SPME–GC–MS with a 20-min immersion time (49).

Nonroutine volatiles including methylene chloride and petroleum products were confirmed in urine and in a gastric sample using 100-µm PDMS headspace SPME–GC–MS with a 10-min extraction at 60°C with the addition of sodium chloride (50). The absence of an air peak in the GC–MS made possible by the SPME procedure offered a tremendous advantage in the identification of the unknown volatiles, which proved to be crucial evidence in the investigation of traffic fatalities (51). Headspace SPME using 100-µm PDMS fibers for 15 min at 60°C has been used to determine benzene, toluene, ethylbenzene, and xylenes (BTEX) in urine with GC–MS (52). An immersion method using 100-µm PDMS fibers for 5 min with added NaCl has been used to analyze urinary toluene and xylene from workers using organic solvents with GC–FID (53). The analysis of chlorophenols in urine has been accomplished using 85-µm polyacrylate SPME–GC–MS with a 50-min extraction at pH 1 (53). Another method for the analysis of chlorophenols in the urine of subjects exposed to chlorobenzene used 85-µm polyacrylate SPME–GC–MS with a 30-min extraction with salt added (54).

Blood and plasma

The free concentration of valproic acid in human plasma has been determined at 1000 ng/mL using 100-µm PDMS direct-immersion SPME–GC–FID with a 3-min extraction from a sample previously dialyzed for 25 min and adjusted to pH 2.5 (55). A calibration curve for valproic acid recovered from plasma samples centrifugally purified to remove proteins followed by direct-immersion SPME–GC–MS with a 65-µm Carbowax–DVB fiber for 10 min is shown in Figure 4. Caprylic acid (7.5-µg/mL internal standard) was added to plasma solutions containing valproic acid (1.25–12.5 µg/mL) at pH 6.86. Two milliliters of each plasma sample was pipetted into a 2-mL Centricon YM-30 cell and then centrifuged for 30 min in order to obtain a 1-mL filtrate followed by SPME and desorption into the GC inlet for 5 min at 250°C. Figure 4 demonstrates the excellent linearity of this SPME method for quantifying the free-fraction concentration of this drug.

Antidepressant drugs and metabolites in human plasma have been analyzed at 90–200 ng/mL using 100-µm PDMS headspace SPME–GC–NPD with a 10-min extraction at 22°C with high protein binding appearing to be the limiting mechanism for better extractions (56). Four tricyclic antidepressants in blood have been analyzed at 61–2000 ng/mL using 100-µm PDMS headspace SPME–GC–FID with a 60-min extraction at 100°C with the addition of sodium hydroxide (57). The analysis of antidepressants in blood and urine have been analyzed, including an analysis in a fatal intoxication case using 100-µm PDMS headspace SPME–GC–MS with a 45-min extraction at 120°C with the addition of sodium hydroxide (58,59). MA and amphetamine in blood have been analyzed at 10 ng/mL using 100-µm PDMS headspace SPME–GC–MS with a 5-min extraction at 80°C with the addition of sodium hydroxide (60). Phencyclidine has been recovered from whole blood and urine analyzed at 1.0 ng/mL and 0.25 ng/mL,

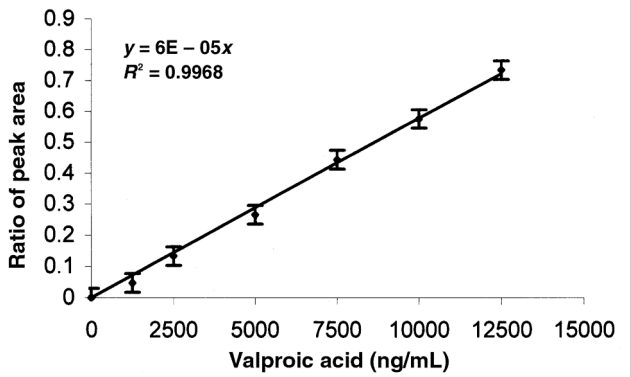

Figure 4. Aqueous calibration curve for valproic acid in pH 6.8 buffer using caprylic acid as an internal standard analyzed by SPME–GC–MS.

respectively, using 100-µm PDMS headspace SPME–GC–surface ionization detection with a 30-min extraction at 90°C with the addition of sodium hydroxide and K_2CO_3 (61). Methadone and its metabolites have been recovered from plasma by 100-µm PDMS direct-immersion SPME–GC–MS using a 30-min extraction at pH 7.7 (62). Diphenylmethane in blood and urine has been analyzed by 100-µm PDMS headspace SPME–GC–FID using a 10-min extraction at 98°C with 10 N NaOH added (63). Diazepam in human plasma has been determined using a 85-µm polyacrylate direct-immersion SPME–GC–flame photometric detector with a 4-min extraction at pH 5.5 with 1-octanol added (64). The authors applied a method using 100-µm PDMS SPME–GC–MS with 5 min of immersion at 25°C to confirm a suspected drink-tampering case using the equivalent of 10 tablets containing 2 mg of diazepam each added to a whiskey bottle (shown in Figure 5).

Steroids have been analyzed in human serum using 85-µm polyacrylate direct-immersion SPME–GC–MS with a 30-min extraction followed by headspace derivatization with *N*,*O*-bis[trimethylsilyl] trifluoroacetamide (65,66). Caffeine metabolites have been recovered from blood and urine by 65-µm Carbowax–DVB SPME–GC–NPD using a 60-min extraction at 40°C with acid added (67). SPME has been successfully applied to the detection of ethanol in human body fluids, including urine and blood at 10 and 20 µg/mL, respectively, using 65-µm Carbowax–DVB headspace SPME–GC–FID with a 15-min extraction at 70°C with the addition of $(NH_4)_2SO_4$ (68). An automated headspace SPME method for the analysis of blood alcohol concentration using 65-µm Carbowax–DVB headspace SPME–GC–FID with 3-min exposures showed excellent precision and linearity having results in close agreement with the conventional static headspace method (69). An improved method for the recovery of ethanol from blood and urine employed 75-µm Carboxen–PDMS headspace SPME–GC–FID using a 15-min extraction at 60°C with the addition of $(NH_4)_2SO_4$ and sodium dithionite, improving sensitivity by 1–3 orders of magnitude compared with previous methods (70). The analysis of methanol in whole blood has also been reported using headspace SPME–GC–FID with a Carboxen–PDMS fiber and 10-min exposures at 60°C (71). An example of SPME analysis of a blood alcohol casework sample analyzed by 65-µm Carbowax–DVB headspace automated SPME–GC–MS using 3-min headspace adsorption at 25°C is shown in Figure 6.

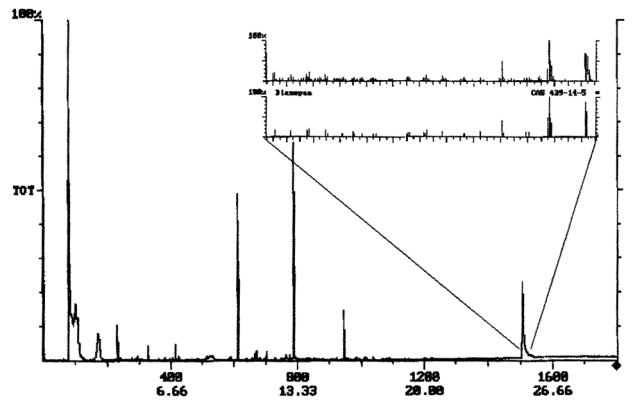

Figure 5. SPME analysis of a forensic case sample taken from a 1.75-L bottle of 80-proof whiskey suspected of tampering with a poison. SPME analysis using 100-µm PDMS SPME–GC–MS confirmed the equivalent of 26 mg of diazepam or approximately ten 2-mg sedative tablets added to the bottle.

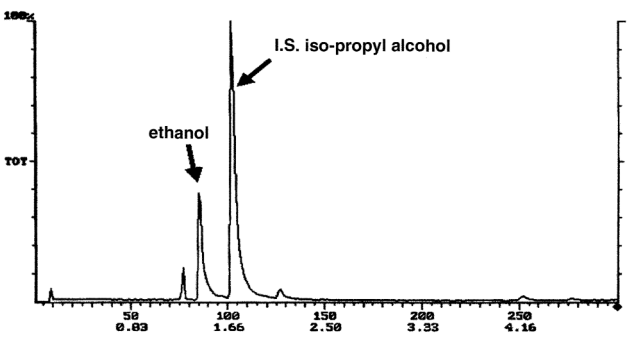

Figure 6. SPME analysis of a blood alcohol casework sample analyzed by 65-µm Carbowax–DVB headspace automated SPME–GC–MS using 3-min headspace adsorption at 25°C and 1-min desorption at 250°C.

Unconventional poisons

Although the most common toxicological analysis involves drug extraction and recovery, drugs actually represent only approximately 60% of the more than 1500 poisons that are possible (31). The second largest class of poisons are pesticides (representing approximately 30% of the compounds possible), followed by anions, metals, gases, and volatiles, which comprise a total of less than 10% of the poisons possible (31). Organophosphate pesticides in blood and urine have been analyzed at 5–80 ng/mL and 2–24 ng/mL, respectively, using 100-µm PDMS headspace SPME–GC–NPD with a 20-min extraction at 100°C and (for blood) the addition of HCl only and (for urine) the addition of HCl, NaCl, and $(NH_4)_2SO_4$ (72). The common organophosphorous pesticide, malathion, has been detected in blood at 1000 ng/mL using 100-µm PDMS headspace SPME–GC–MS with a 5-min extraction at 90°C and the addition of $(NH_4)_2SO_4$ and H_2SO_4 (73). Six carbamate pesticides in blood and urine have been analyzed at 100–500 ng/mL and 10–50 ng/mL, respectively, using 100-µm PDMS headspace SPME–GC–NPD with a 30-min extraction at 70°C and the addition of NaCl (74). Phenothiazines have been detected using 100-µm PDMS headspace SPME–GC–FID with a 40-min extraction at 140°C and added NaCl (75). Dinitroaniline herbicides have been analyzed using 100-µm PDMS SPME–GC–ECD with 30-min extractions at 70°C for water and 90°C for blood (76). The analysis of parathion in blood has also been reported using headspace SPME–GC–MS (77). The natural insecticide, nereistoxin, has been analyzed using 65-µm PDMS–DVB headspace SPME–GC–MS with a 30-min extraction at 70°C and added NaCl (78).

A headspace SPME–GC–MS method has been developed for the analysis of toluene, xylenes, and hydrocarbons at 100–1000 ng/mL in human blood and applied to the medico-legal autopsy of a fire victim with kerosene substances detected (79). The analysis of thinner components in whole blood and urine at 1 ng/mL has been performed using 100-µm PDMS headspace SPME–GC–FID with a 5-min extraction at 80°C (80). Cresol and phenols have been detected using 85-µm polyacrylate headspace SPME–GC–FID with a 30-min extraction at 100°C and NaCl added (81). Benzene and toluene in human blood have also been monitored

using 65-µm Carboxen–PDMS headspace SPME–GC–MS with a 30-min extraction at 20°C (82). Headspace sampling of BTEX in the blood and urine of cyclists exposed to air pollutants employed 75-µm Carboxen–PDMS SPME–GC–MS with a 30-min extraction at 50°C (83). Tetrachloroethylene and trichloroethylene have been analyzed in serum tissue and urine in a fatality using 100-µm PDMS headspace SPME–GC–ECD with a 1-min extraction at 60°C (84).

Local anesthetics have been analyzed at 58–830 ng/mL using 100-µm PDMS headspace SPME–GC–FID with a 40-min extraction at 100°C from human blood deproteinized with perchloric acid and sodium hydroxide and added $(NH_4)_2SO_4$ (85). The recovery of local anesthetics from human blood has also been accomplished with a direct immersion using 100-µm PDMS SPME–GC–FID with a 40-min extraction (86). Another recent method for the recovery of local anesthetics employed 100-µm PDMS headspace SPME–GC–MS using selected-ion monitoring (SIM) with a 45-min extraction at 120°C and added NaOH (87). The analysis of the highly toxic methylmercury in aqueous and tissue samples has been reported using 100-µm PDMS headspace SPME–GC–atomic fluorescence spectrometry (AFS) and simultaneous extraction–derivatization with sodium tetraethylborate at 25°C and pH 4.5 with an acetate buffer (88). The simultaneous determination of mercury, alkylmercury, lead, and tin in human body fluids was accomplished using 100-µm PDMS headspace SPME–GC–MS–MS and derivatization with sodium tetraethylborate for 10 min at pH 5.3 (89). Methylmercury in biological samples has also been reported using headspace SPME–GC–atomic absorption spectrometry (AAS) and hydride derivatization (90). Cyanide in blood has been analyzed using 65-µm Carbowax–DVB headspace SPME–GC–NPD with a 45-min extraction at 50°C and Na_2SO_4 added (91). Lead in blood and urine has been analyzed below 10 ppb using 65-µm PDMS–DVB headspace SPME–GC–FID with a 15-min extraction–derivatization time with sodium tetraethylborate at 25°C and pH 4.0 with an acetate buffer (92).

Miscellaneous applications

A modified SPME device has been developed that is capable of detecting down to 5.8 nmol/L ethanol, 1.8 nmol/L acetone, and 0.3 nmol/L isoprene in human breath using a 65-µm PDMS–DVB fiber and 1 min of sampling followed by GC–MS analysis (93). SPME has been shown to be a useful tool to determine phospholipid–water-partition coefficients and free-concentration (bioavailable) in vitro systems, which may make experimental data more meaningful for quantitative in vivo extrapolations (94). SPME has been used to determine residual organic solvents in pharmaceutical samples with an optimized method using 65-µm PDMS–DVB with 30-min headspace extraction and NaCl added (95). A method for profiling confiscated MDMA and amphetamine uses 65-µm PDMS–DVB headspace SPME–GC–NPD with a 30-min extraction at 90°C and a pH level of 5.0 with an acetate buffer (96). SPME has also been used to characterize street narcotic odors. The room-temperature recoveries of cocaine odor chemicals (including methyl benzoate) required optimized headspace extraction times of up to 12 h with the optimum fiber found to be 65-µm Carbowax–DVB (97,98). SPME has played an important role confirming the chemicals responsible for drug-detector dog alerts of suspected drug money having an SPME–GC–MS odor signature profile similar to street cocaine (shown in Figure 7), which was extracted using a 50/30-µm DVB–Carboxen on PDMS with a 2-cm fiber for 15 min at 20°C and a 1-min desorption time at 250°C. Methyl benzoate has been confirmed as one of the dominant odor chemicals used by detector dogs and has been identified as a cocaine breakdown product and a dominant nonsolvent odor chemical in street cocaine samples (making up over 10% of the volatiles in the example specimen in Figure 7). Although it has been established that most U.S. currency in circulation is contaminated with milligram-quantities of cocaine, the corresponding odor chemical (methyl benzoate) levels are shown to be well below the threshold levels of drug-detector dogs (98).

A method for determining cannabinoids in water and saliva used 75-µm Carboxen–PDMS direct-immersion SPME–GC–MS with a 10-min extraction (99). SPME has also been applied to the analysis of cannabinoids and amphetamines in hair (100,101) and used to characterize items such as cinnamon, vodka, coffee, and tobacco (102–105), which could prove to be useful investigative information. Recently, a fast and simple SPME method has been developed for the identification of GHB in aqueous samples (106). The direct injection of a GHB extraction into a GC port under

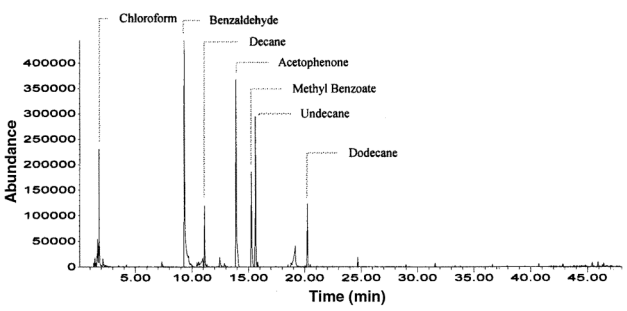

Figure 7. A headspace SPME–GC–MS chromatogram of cocaine volatiles extracted by 50/30-µm DVB–Carboxen on PDMS on a 2-cm fiber for 15 min at 20°C with 1-min desorption time at 250°C.

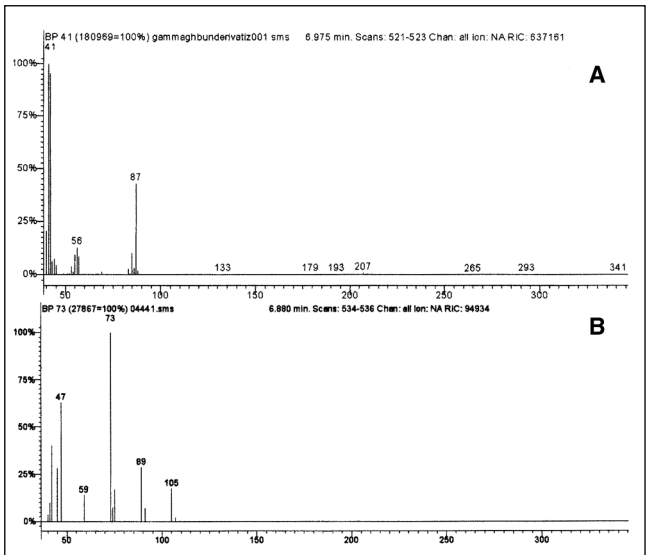

Figure 8. GC–EIMS of GHB (A) yielding an inconclusive identification of this drug compared to the SPME–GC–CIMS (B) providing improved fragmentation and a molecular ion +1 peak.

normal temperature (280°C) conditions followed by electron ionization in the MS resulting in the thermally induced intramolecular esterification that forms the butyrolactone (the EI spectra can be found in Figure 8A) prevents the positive identification of the drug. A 15-min 100-µm PDMS SPME headspace extraction at 60°C followed by a low-temperature (100°C) desorption into the injector of a GC outfitted with a short (2 m) DB-1 column and a positive chemical ionization using methanol as the reagent gas yields good fragmentation and a confirmatory molecular ion +1 peak (the CI spectra can be found in Figure 8B).

Overall, most reported SPME methods have proven to be superior to existing extraction methods with overall improved recoveries translating to lower detection limits with shorter analysis times, minimal sample handling, and the significant reduction or elimination of organic solvents. Future developments of SPME for forensic applications will likely include further improvements in automation and field sampling and analyses such as fast GC methods. Field-portable SPME–GC methods could dramatically improve law enforcement response times by providing rapid on-site confirmation of drugs, accelerants, and explosives. Obstacles to a more widespread acceptance in the forensic science community include the need for additional optimization and the establishment of standard methods (i.e., ASTM) for analyses using SPME.

Acknowledgments

Partial financial support from Supelco Inc. is gratefully acknowledged. Helpful discussions with Ray Mindrup and Robert Shirey (Supelco) and Terry L. Sheehan (Varian Associates) are also greatly appreciated.

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Manuscript accepted May 24, 2000.