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# Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens

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## Abstract

A current review of the application of solid-phase microextraction (SPME) to the analysis of ignitable liquids and explosive residues is presented along with experimental results demonstrating the relative effects of controllable variables. Variables discussed include fiber chemistry, adsorption and desorption temperatures, extraction and desorption times, fiber sampling placement (direct, headspace, and partial headspace) and matrix effects, including water content. SPME is shown to be an inexpensive, rapid and sensitive method for the analysis of ignitable liquids and high explosives residues from solid debris samples and from aqueous samples. Explosives are readily detected at parts per trillion concentrations and ignitable liquids are reproducibly detected at levels below those using conventional methods. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction/review

In the last 5 years, solid-phase microextraction (SPME) has emerged as a powerful sample preparation technique for the analysis of chemical traces from fire and explosion debris. SPME has many advantages when applied to a variety of samples including forensic specimens [1]. SPME allows for multiple sampling and preservation of the sample while minimizing the risk of sample contamination due to the simplified sample handling afforded by the technique. SPME can yield faster case turnaround time, is often faster than traditional techniques and can be readily automated. Additionally, the often lower detection limits possible using SPME allow for

confirmation of positive samples that previously went undetected. Finally, the elimination of solvents can save forensic science laboratories money and reduce the risk of analysts being exposed to toxic substances.

In this article, we review the applications of SPME to the detection of explosive traces and ignitable liquid residues, often referred to as accelerants, and present new data. Interestingly, a coated wire adsorption technique was being applied to ignitable liquid analysis the same year SPME was being introduced [2]. This early technique involved the heated headspace (70 or 80°C) adsorption of ignitable liquids onto carbon-coated aluminum or copper wire followed by *n*-pentane elution with ultrasonic vibration [3]. The first report of SPME applied to arson analysis was in 1994 [4] in which SPME demonstrated improved sensitivity for the

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recovery of light, medium and heavy petroleum distillates with significantly reduced analysis times and the elimination of toxic solvents [4,5] when compared to the established activated charcoal strip (ACS)–solvent elution method [6]. The SPME analyses of gasoline and kerosene has been compared to headspace, cold trap and solvent extraction methods and shown to provide accurate information with less interference peaks [7].

Headspace SPME has also been applied to the analysis of flammable and combustible substances in human body fluids [8,9]. A more detailed study of the most common ignitable liquid used as an accelerant (gasoline) confirmed the utility of the SPME technique including lack of interference problems in the presence of wood or plastic pyrolysis products and the ability of SPME to provide reproducible multiple analyses from a single sample [10]. The recovery of ignitable liquids directly from aqueous solvents has also been demonstrated, with SPME proving to be more than an order of magnitude more sensitive than the conventional solvent extraction method on 500 ppb preparations and allowed for positive identification of diesel fuel in aqueous samples [11]. SPME has also been used to identify the presence of gasoline in a real arson-suspected fire debris sample, while conventional methods, such as static headspace, lacked adequate sensitivity for the analysis such that ignitable liquids were not detected [12]. The method has been optimized in recent years for a variety of ignitable liquids and conditions [13,14] and applied to the recovery and identification of ignitable liquids from human skin [15,16] as a potential field method to test suspected arson suspects. The method developed uses 100  $\mu\text{m}$  polydimethylsiloxane (PDMS) fibers with gentle heating for 5 min followed by 10 min 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 [16]. Recently, a comprehensive sample preparation scheme for detecting ignitable liquid residues in suspect arson cases using SPME has been presented including a critical comparison to traditional dynamic and headspace charcoal adsorption and solvent extraction methods [17]. The proposed two step method includes a low temperature Carboxen SPME and an

elevated temperature PDMS SPME demonstrating simplified sample preparation and high recovery efficiency [17]. A review of contemporary sample preparation methods, including SPME, for the detection of ignitable liquids in suspected arson cases has recently appeared [18].

Analysis of semi-volatile compounds including nitrobenzene and dinitrotoluenes in water has been reported using a PDMS-coated fiber [19] and GC–flame ionization detection (FID) analysis with detection limits reported as 9–15 ng/ml. Headspace and direct aqueous immersion SPME followed by GC–MS and LC–UV allows for the recovery of various explosives [20]. PDMS–divinylbenzene (DVB) yielded optimal recovery for the 14 explosives studied with varying results depending on the extracted explosive [21]. 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 EGDN, NG, PETN, 2,4,6-trinitrotoluene (TNT) and exogen (RDX) [22]. Trace explosive signatures have been determined from World War II unexploded undersea ordinance using direct immersion SPME–GC–MS and SPME–GC–reversal electron attachment detection (READ) yielding improved extractions over solid-phase extraction with sensitivities of 10 part per trillion for dinitrotoluene and TNT for 15 min extractions using PDMS–DVB fibers coupled to a bubble aeration scheme for agitation [23]. Direct immersion SPME using a Carbowax–DVB fiber with 10 min sampling (with stirring) followed by a 10 min GC–ion-trap (IT) MS analysis yielded limits of detection of 10 ppt for TNT, 325 ppt for RDX, 5–10 ppt for the metabolites 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene [24] in seawater. Recently, a method involving the modification of a commercially available SPME–HPLC interface allowing for separate optimization of the desorption step and chromatographic step (using dual columns) has shown improved precision and chromatographic resolution with complete separation of all 14 US Environmental Protection Agency (EPA) explosives [25]. Direct immersion SPME–GC, SPME–LC and SPME–capillary zone electrophoresis methods have been optimized, critically compared and successfully applied to actual post-explosion debris samples with

additional details presented later in this paper [26–28]. Headspace SPME has also been applied to the characterization of a variety of odor signatures including explosive odor signatures [29].

In this paper, we present experimental results for explosives and ignitable liquid residues demonstrating the relative effects of major controllable variables including analyte chemistry, sampling mode (direct, headspace, and partial headspace), fiber chemistry, adsorption times, adsorption temperatures, desorption temperature, desorption time, and matrix effects including water content relative to sample container. The optimized method for explosives involves the extraction of the post-blast debris with an organic solvent followed by addition of high salt content water and SPME prior to chromatographic analysis. Conditions affecting the SPME recovery of ignitable liquid residues from simulated fire debris samples are compared using a simulated ignitable liquid mixture.

## 2. Experimental

For the explosives study, the SPME fiber types used in this work were a 100  $\mu\text{m}$  PDMS, a 65  $\mu\text{m}$  partially crosslinked PDMS–DVB, a 85  $\mu\text{m}$  partially crosslinked polyacrylate, a 75  $\mu\text{m}$  partially crosslinked Carboxen–PDMS, a 65  $\mu\text{m}$  partially crosslinked Carbowax (CW)–DVB, and a 50  $\mu\text{m}$  partially crosslinked Carbowax–template resin (CW–TPR) (All SPME fibers were obtained from Supelco, Bellefonte, PA, USA). The high explosives of interest were 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), nitrobenzene (NB), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), TNT, 1,3,5-trinitrobenzene (TNB), 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT), 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT), RDX, octagen (HMX), and *N*-methyl-*N*-tetranitrobenzenamine (tetryl) (All explosives were obtained from Radian International LLC, Austin, TX, USA). The GC conditions used thermal desorption into a splitless injection port at 180°C with an HP 5890 series II GC system outfitted with an electron-capture detection (ECD) system. A J&W Scientific 30 m $\times$ 0.25 mm I.D. (0.25  $\mu\text{m}$ ) DB1701 column was used with a helium flow-rate of 57 cm/s

at an inlet pressure of 140 kPa. The ECD make-up gas was nitrogen ( $\text{N}_2$ , flow-rate 55 ml/min). The column temperature was held at 60°C for 1 min, then ramped at 12°C/min up to 240°C and held for 9 min. The HPLC conditions included the use of a SSI model HPLC pump and ISCO UV detector and dual chromatographic columns; a Supelcosil  $\text{C}_{18}$  25 cm $\times$ 4.6 mm (5  $\mu\text{m}$ ), a SPME–HPLC interface desorption reservoir (Supelco) and an Elut CN 3 cm $\times$ 4.6 mm (5  $\mu\text{m}$ ). The system was run at a flow of 1.3 ml/min under isocratic conditions with MeOH–water (50:50) as the mobile phase. The UV wavelength was set at 254 nm and a 30 min extraction from water, 25% NaCl, 0.5% acetonitrile (ACN) provided for the best direct extraction yields. The SPME–HPLC interface desorption reservoir was filled with 200  $\mu\text{l}$  of ACN–water (50:50). After 1 min of desorption, analytes were delivered at 0.2 ml/min for the first 2 min to minimize band broadening and the fiber was washed with 500  $\mu\text{l}$  of ACN–water (50:50) for 2 min.

The real post-explosion residue was collected from the resulting craters after detonating 5 g of PETN (ICI Explosives, Byron, GA, USA) conducted by the Miami-Dade Police Department Bomb Squad (Miami, FL, USA). Prior to detonation, 2-g samples of range soil were collected and analyzed as a blank. After detonation, 2-g samples of soil samples from the resulting crater were collected and washed with 5.0 ml of HPLC-grade acetonitrile in a clean glass jar manually shaken for 15 min, allowed to settle for 10 min and filtered through a 0.45  $\mu\text{m}$  filter. A 75- $\mu\text{l}$  volume of the filtered solution was added to 7.5 ml of water (containing 25% NaCl) and extracted by SPME.

For the ignitable liquids study, a simulated mixture containing the 30 major components of possible ignitable liquid types including those from light petroleum distillate (LPD) which contain from  $\text{C}_4$ – $\text{C}_{11}$  alkanes, medium petroleum distillate (MPD) ranges from  $\text{C}_8$  to  $\text{C}_{12}$ , high petroleum distillate (HPD) spreads from  $\text{C}_{10}$  to  $\text{C}_{23}$  and selected aromatic hydrocarbons using the standard ASTM method [30]. Desorption studies were conducted by placing 1  $\mu\text{l}$  of the mixture spiked on a Kimwipe inside a 1 quart can (1 quart=946.3 ml). A 200 ml volume of water was then added into the can and sealed with a lid, which contained a 2 mm diameter

Table 1  
Peak area ( $\times 10^3$ ) of headspace and aqueous immersion with 20 min extraction with a PDMS–DVB fiber

	Compounds					Tetryl
	2-NT	3-NT	4-NT	2,6-DNT	4-A-2,6-DNT	
Headspace	7.712	10.70	6.774	3.656	0	0
Aqueous immersion	185.3	375.3	387.7	1139	19.53	3.390

septum. A 100  $\mu\text{m}$  PDMS fiber was inserted (via a syringe) into the can and headspace for 15 min, then retracted and inserted into the 250°C injection port of HP 5890 chromatograph for 10 s and analyzed. After the first desorption, the same fiber was inserted into the injection port and desorbed for another 10 s and re-analyzed. The same procedure was followed using DVB, 65  $\mu\text{m}$  Carboxen, Carbowax, PDMS–DVB and polyacrylate fibers. SPME was performed by using headspace, complete immersion and a modified “partial headspace” techniques with only a portion of the SPME fiber dipped into the water (by previous

visual observation and marking of insertion depth). The influence of water was tested by using 1  $\mu\text{l}$  of the ignitable liquid mixture spiked on a Kimwipe inside a 1 quart can sampled with a 100  $\mu\text{m}$  PDMS fiber by headspace SPME for 25 min and then analyzed by GC. The same procedure as above but different amounts of water were added into the can before it was sealed. The amounts of water include: 5 drops of water which just wet the ignitable liquids, 20 ml which just covered the bottom of the can and immersed the ignitable liquid mixture and 100 ml, 200 ml and 740 ml of water. To determine the

Table 2  
The average relative recovery ratios (relative to headspace SPME) of wet ignitable liquids (740 ml water on 1  $\mu\text{l}$  ignitable liquids in 1 quart can) using a PDMS fiber and different SPME sampling methods (SPME for 15 min) at 20°C for triplicate analysis

Peak		Headspace (area) ratio	Direct immersion	Partial headspace
Compound	$t_R$ (min)	(average RSD 4.0%)	(average RSD 3.1%)	(average RSD 2.8%)
Toluene	3.18	(198) 1		
Octane	3.55	(3 381) 1	0.038	0.340
<i>p</i> -Xylene	4.70	(10 120) 1	0.010	0.318
Noncane	5.24	(27 273) 1	0.010	0.276
3-Ethyltoluene	6.88	(54 115) 1	0.007	0.266
2-Ethyltoluene	7.46	(63 312) 1	0.007	0.261
1,2,4-Trimethylbenzene	8.06	(71 978) 1	0.007	0.255
Decane	8.31	(98 600) 1	0.005	0.238
1,2,3-Trimethylbenzene	9.17	(73 905) 1	0.007	0.249
Butylbenzene	10.73	(160 478) 1	0.005	0.234
Undecane	12.73	(7 041 230) 1	0.004	0.234
Naphthalene	16.13	(72 089) 1	0.010	0.215
Dodecane	17.02	(433 713) 1	0.005	0.278
1-Methylnaphthalene	20.52	(202 080) 1	0.008	0.215
Tridecane	20.94	(471 409) 1	0.012	0.399
2-Methylnaphthalene	21.08	(171 621) 1	0.010	0.216
Tetradecane	24.52	(392 384) 1	0.034	0.620
Pentadecane	27.80	(186 451) 1	0.112	0.893
Hexadecane	30.99	(78 509) 1	0.368	1.331
Heptadecane	35.2	(21 585) 1	1.120	2.335
Pristane	35.41	(31 102) 1	1.198	2.509
Octadecane	38.43	(6 118) 1	3.138	5.272
Nondecane	39.85	(1 469) 1	9.900	16.579
Eicosane	40.85	(394) 1	18.282	30.558
Heneicosane	41.63	(541) 1	16.911	30.053

influence of container size, a similar procedure was used except that an amount of water to just cover the bottom of three containers was employed with 7 ml used for the 137 ml (45 mm ID) container, 20 ml used for the ~1000 ml (104 mm ID) container and 100 ml used for the ~5000 ml (164 mm ID) container. Different headspace SPME sampling times and temperatures included 5, 10, 15, 20, 25, 30, 40, 50 and 60 min as well as 20°C, 40°C, 60°C, 80°C and 100°C for 30 min each. For comparison, the traditional method employed a DFLEX (Cromwell, CT, USA) activated charcoal strip (9 mm×20 mm) placed along with 1 µl of the ignitable liquid mixture spiked on a Kimwipe inside a 1 quart can. The can was then sealed and extracted overnight. The charcoal strip was removed and eluted with 300 µl of CS<sub>2</sub> for 3 min, then 5 µl solution was injected into the injection port of HP 5890 chromatograph for analysis.

### 3. Results and discussion

One of the first variables to be considered was the sampling mode to employ for the recovery of analytes from a sample. In general, more volatile and more hydrophilic analytes are best recovered by headspace sampling whereas less volatile, more hydrophobic compounds are best sampled directly from aqueous samples. For the explosives studied, direct aqueous immersion yielded the highest recoveries at 20°C using the PDMS–DVB fiber and 20 min extraction times (Table 1). Higher temperatures can increase recoveries by headspace SPME such as that reported at 100°C [22], but non-volatile and thermally unstable explosives such as HMX cannot be recovered this way. For ignitable liquids, which are generally significantly more volatile than explosives, headspace sampling is the preferred mode. Table 2 compares the relative recoveries of a range of simulated ignitable liquid compounds with direct immersion and partial headspace (with only a portion of the fiber immersed in the water) compared to headspace sampling at 20°C. In general, the headspace mode yielded the best recoveries; however, partial headspace sampling yielded similar recoveries for the low-molecular-mass components with significantly enhanced recoveries for the high-molecu-

lar-mass compounds. The latter may be explained as the high-molecular-mass hydrocarbons float on the surface of water. The effect of amount of water added for ignitable liquid extractions is detailed later.

Another major variable is the choice of SPME fiber chemistry. For the explosives studied PDMS–DVB fiber yielded the highest overall recoveries of the fibers tested as seen in Fig. 1. Analytes with significantly different polarities generally require different fiber chemistries. For example, whereas the PDMS–DVB fiber was best overall, the more polar fibers CW–DVB and polyacrylate yielded higher recoveries for the more polar analyte 4-A-2,6-DNT. For this reason, optimal fibers for specific applications will often need to be blended phases with multiple chemistries on a single fiber. Fig. 2 compares the headspace SPME recoveries of different hydrocarbons (relative to the PDMS fiber) with water added at 20°C. All other fibers tested except Carboxen have lower recovery than PDMS fiber. The recovery of ignitable liquids by Carbowax fiber ranged from 20 to 30% for lower-molecular-mass components to 70% for higher-molecular-mass components compared to the PDMS fiber. The recovery of DVB fiber is about 70% that of PDMS fiber. Compared to PDMS, the recovery of polyacrylate fiber on ignitable liquids has a wide range of recoveries ranging from 6 to 89% recoveries relative to PDMS. For the Carboxen fiber the recoveries ranged from 42% to more than 200% with overall higher recoveries than by PDMS. Although the Carboxen yielded higher overall recoveries the complete desorption of extracted analytes was more difficult with the Carboxen fiber. The results of desorption time studies for the ignitable liquids indicate that PDMS, polyacrylate, DVB and PDMS–DVB fiber have the shortest desorption times and Carboxen fiber has the longest desorption time. At 250°C, only 10 s desorptions were needed to completely desorb all analytes tested from PDMS, polyacrylate, DVB and PDMS–DVB fibers. The carboxen fiber required a 15 s desorption time and even when the desorption temperature was raised from 250 to 290°C, more than 2 min were required to completely desorb analytes from the Carboxen fiber.

Optimum extraction times are affected by many variables including the sampling mode, fiber chemistry, extraction temperature and analyte type. For

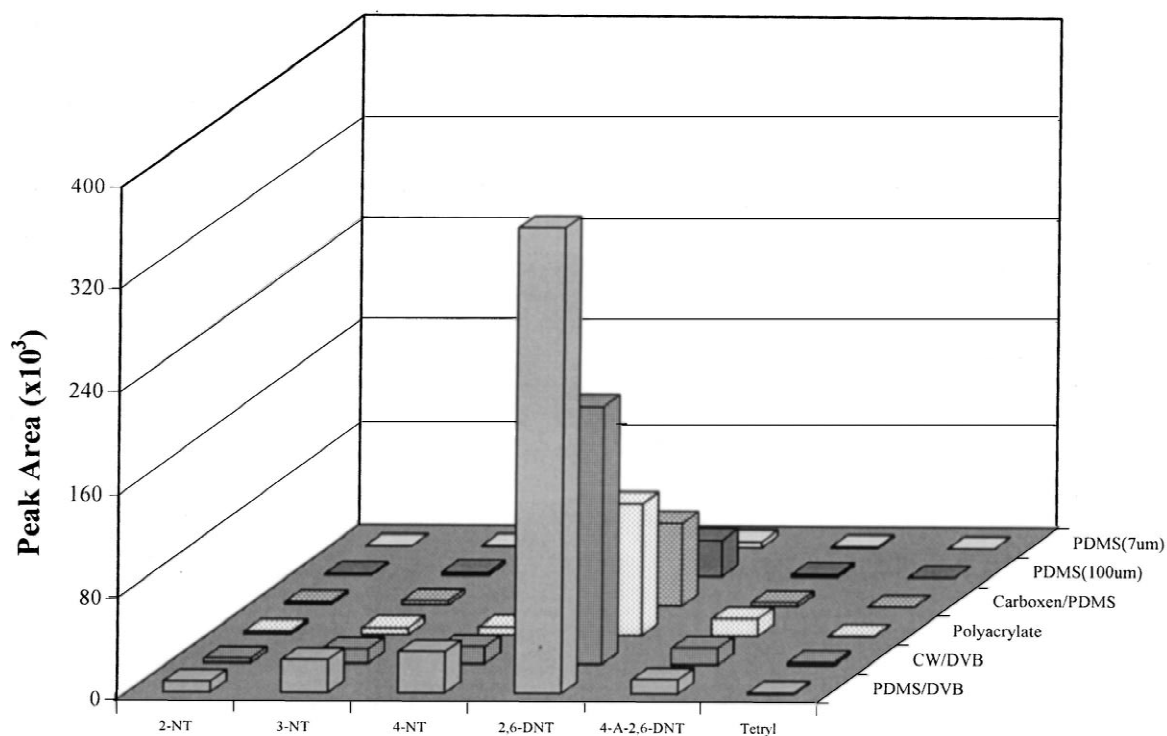


Fig. 1. Amount extracted by different SPME fiber coatings.

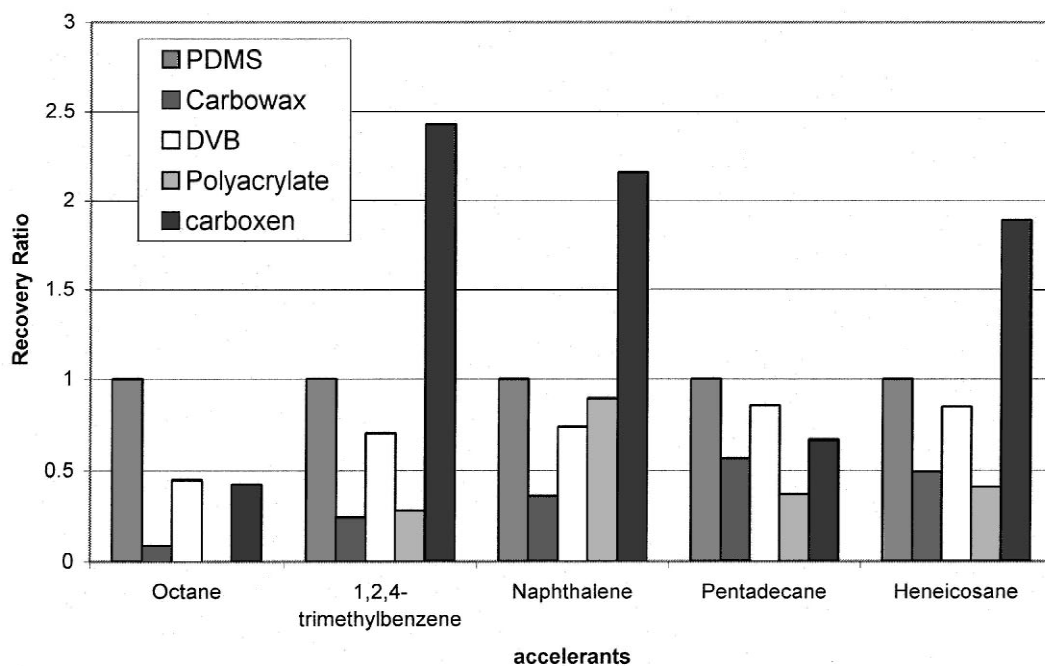


Fig. 2. Comparison of the recovery ratios (relative to the PDMS fiber) of 1  $\mu$ l of ignitable liquids with 750 ml water added using different fibers using headspace sampling at 20°C.

explosives and ignitable liquids, it was found that after a period of time, higher-molecular-mass components can begin to displace lower-molecular-mass components and a compromise extraction time at or before this point is optimal. For example, the direct immersion SPME recoveries of explosives using the

Carbowax–DVB fiber is shown in Fig. 3 with the lower-molecular-mass components, NB and NT, reaching optimal recoveries at ca. 50 min and then decreasing whereas the higher molecular–mass components continue to increase. Fortunately, SPME generally yields such high recoveries that signifi-

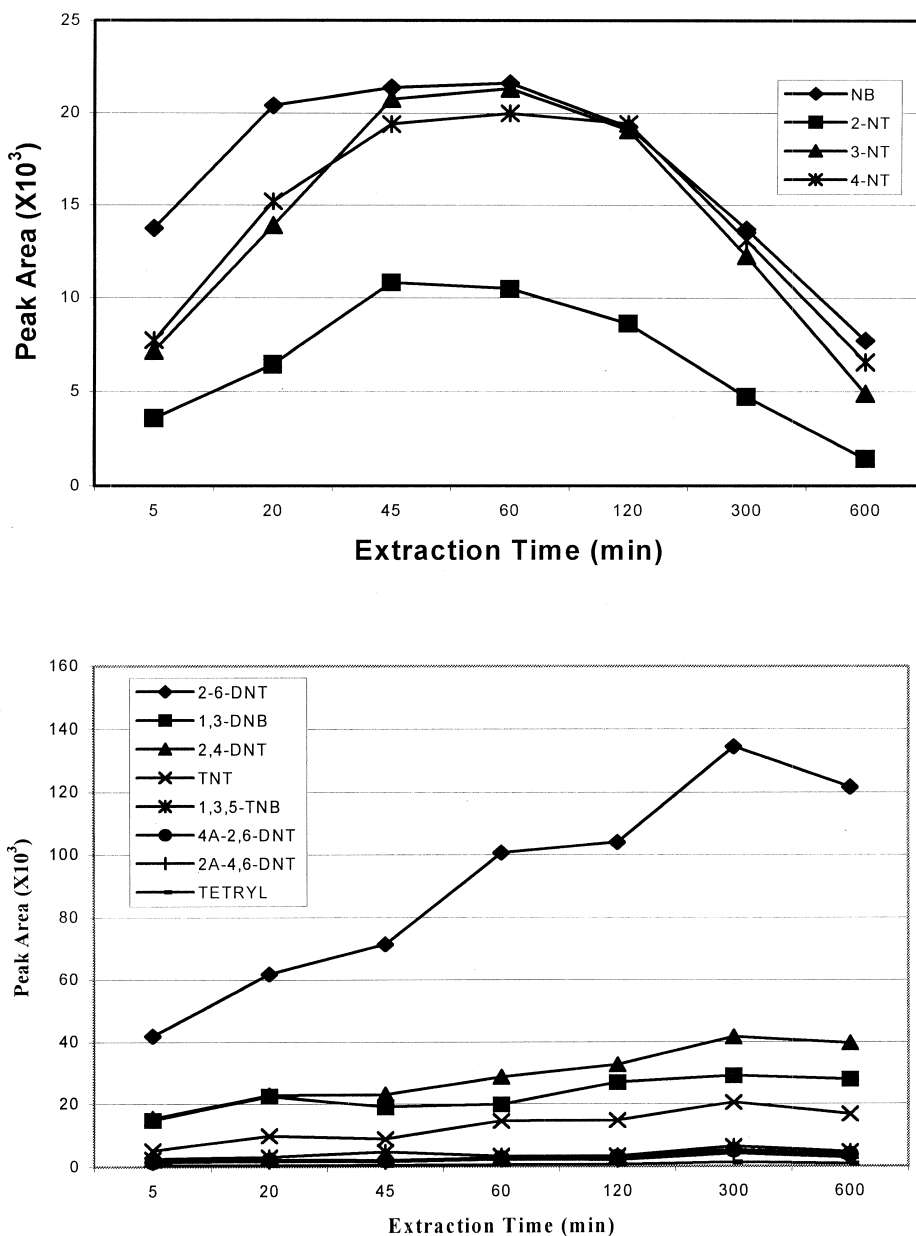


Fig. 3. Absorption time profiles for NB, 2-NT, 3-NT and 4-NT (top) and 2,6-DNT, 1,3-DNB, 2,4-DNT, TNT, 1,3,5-TNB, 4A-2,6-DNT, 2A-4,6-DNT and tetryl (bottom) at a concentration level of 2 ppm for each compound using Carbowax–DVB Fiber.

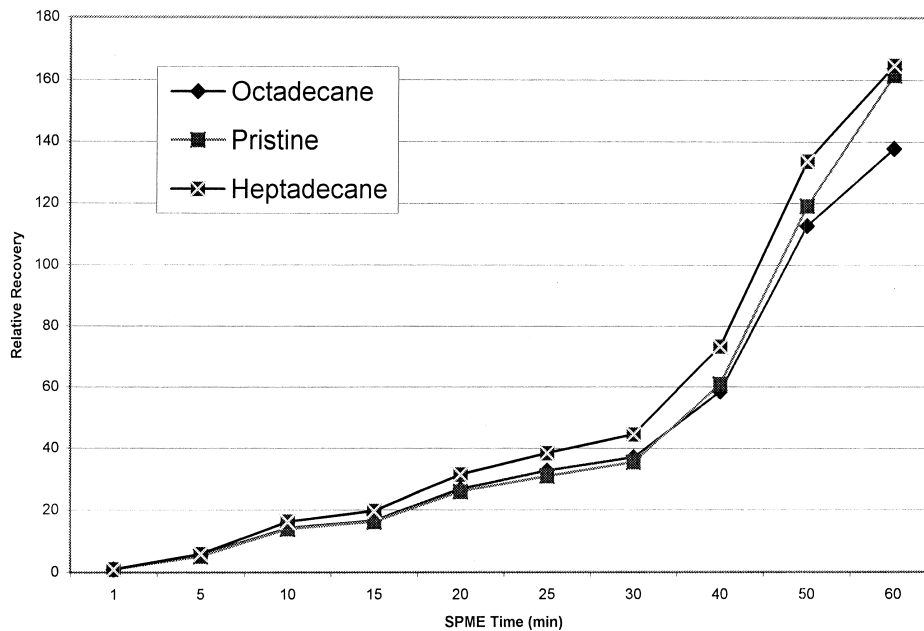
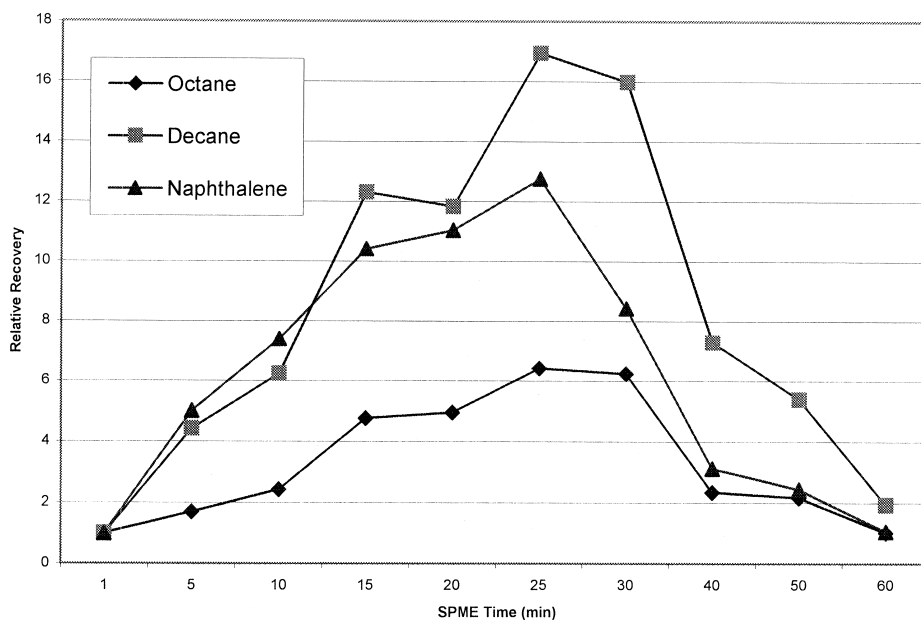


Fig. 4. The relative recovery ratio (relative to 1 min extraction) of wet ignitable liquids (740 ml water added to 1  $\mu$ l sample in 1 quart can) versus time using of headspace SPME with a PDMS fiber for low-molecular-mass ignitable liquids (top) and high-molecular-mass accelerants (bottom).



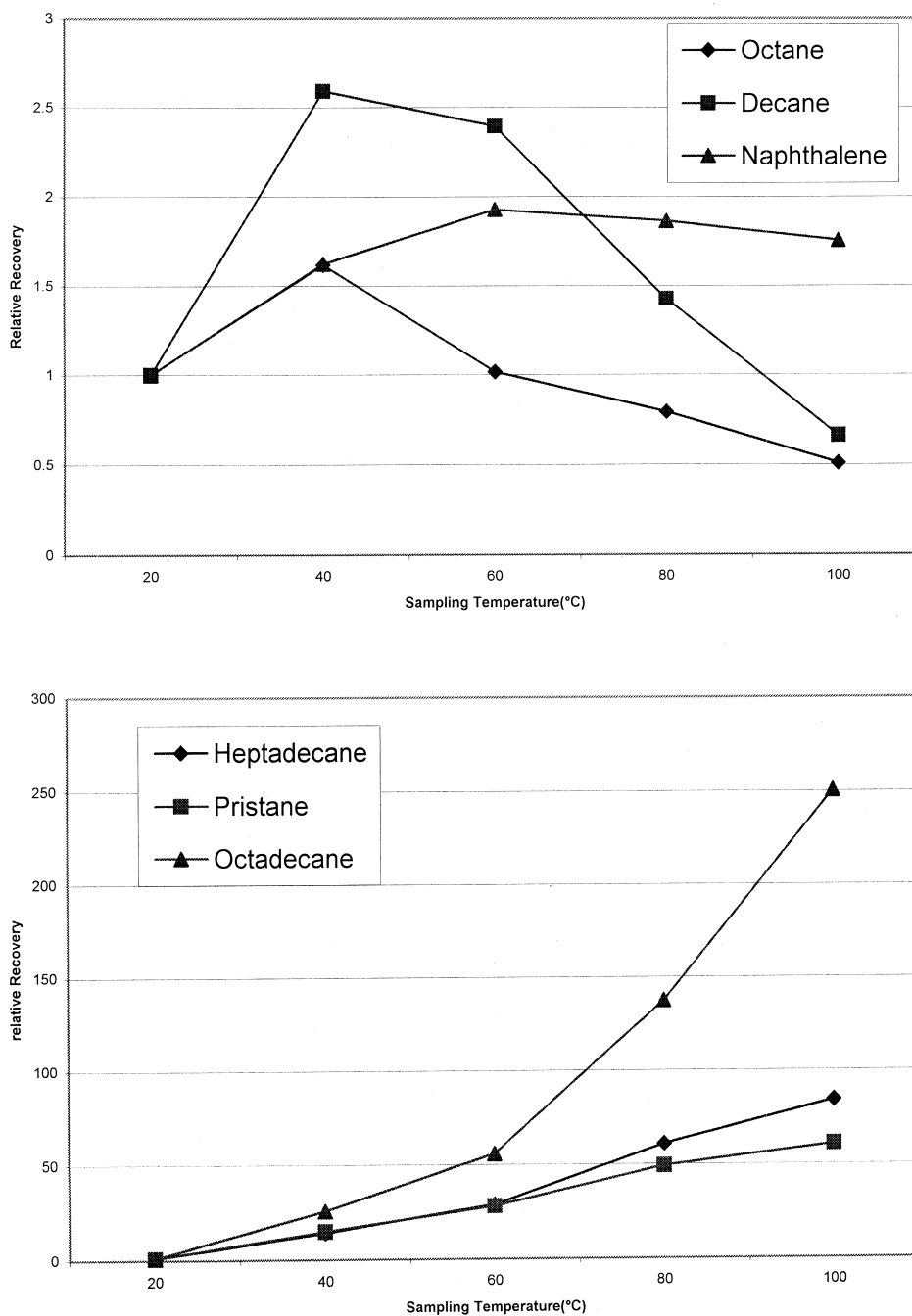


Fig. 5. The relative recovery ratio (relative to 20°C extraction) of wet ignitable liquids (740 ml water added to 1  $\mu$ l sample in 1 quart can) versus temperature using of headspace SPME with a PDMS fiber for low-molecular-mass ignitable liquids (top) and high-molecular-mass accelerants (bottom) with a 15 min extraction time.

cantly shorter extraction times can be employed while still improving sensitivity compared to traditional methods. The same effect is seen in Fig. 4 for ignitable liquid components with the lower-molecular-mass hydrocarbons reaching optimal relative recoveries at ca. 25 min and then decreasing whereas the highest-molecular-mass components continue to increase to 60 min. Relative recoveries are presented as an area ratio compared to the first data set. This effect is also seen by increasing temperature at a constant extraction time as shown in Fig. 5 with the lower-molecular-mass hydrocarbons reaching optimal recoveries at ca. 40°C and then decreasing whereas the highest-molecular-mass components

continue to increase up to the highest temperature studied of 100°C.

The addition of water on ignitable liquid sample has been shown to significantly affect the headspace SPME recovery for ignitable liquids at 20°C as seen in Table 3. The recovery changes with the addition of water is a function of chain length. Both the recovery of high-molecular-mass components and the number of components that can be recovered by headspace SPME increases with the addition of water. The recovery increase was as high as 30 times that for the dry sample and four more compounds were recovered as shown in Table 3. However, the recoveries of low- and medium-molecular-mass com-

Table 3

The average relative recovery ratios (relative to dry sample) of ignitable liquids with the addition of different amounts of water on 1  $\mu$ l sample in 1 quart can using a PDMS fiber headspace SPME for 25 min at 20°C for triplicate analysis

Compound	Dry sample: area (ratio) (average RSD 3.0%)	5 Drops (average RSD 2.7%)	20 ml (average RSD 2.6%)	100 ml (average RSD 3.1%)	200 ml (average RSD 2.8%)	740 ml (average RSD 2.9%)
Area-ratio at various amounts of water						
Heptane						
Toluene	1 118 (1)	0.869	0.675	0.420	0.440	0.216
Octane	12 911 (1)	0.705	0.455	0.391	0.355	0.352
<i>p</i> -Xylene	53 105 (1)	0.760	0.488	0.308	0.248	0.256
Noncane	109 866 (1)	0.680	0.354	0.311	0.227	0.346
3-Ethyltoluene	279 948 (1)	0.722	0.381	0.274	0.181	0.262
2-Ethyltoluene	349 374 (1)	0.727	0.380	0.264	0.170	0.244
1,2,4-Trimethylbenzene	416 923 (1)	0.722	0.368	0.254	0.158	0.231
Decane	415 806 (1)	0.675	0.319	0.286	0.181	0.328
1,2,3-Trimethylbenzene	496 577 (1)	0.726	0.358	0.237	0.138	0.196
Butylbenzene	801 461 (1)	0.695	0.329	0.270	0.162	0.267
Undecane	994 545 (1)	0.657	0.340	0.307	0.186	0.328
Naphthalene	1 928 135 (1)	0.725	0.278	0.126	0.048	0.071
Dodecane	1 253 250 (1)	0.766	0.640	0.568	0.365	0.561
1-Methylnaphthalene	1 924 974 (1)	0.833	0.505	0.331	0.150	0.165
Tridecane	566 839 (1)	1.13	1.833	1.622	1.174	1.500
2-Methylnaphthalene	1 758 696 (1)	1.843	1.516	1.332	1.151	1.156
Tetradecane	139 970 (1)	1.972	6.21	5.831	5.027	5.240
Pentadecane	27 893 (1)	2.622	13.664	13.426	14.855	12.838
Hexadecane	8 318 (1)	2.137	14.877	14.796	21.95	18.390
Heptadecane	1 700 (1)	1.874	13.536	13.729	24.515	24.798
Pristane	2 016 (1)	1.804	12.918	13.463	25.784	29.146
Octadecane	364 (1)	1.99	12.214	12.915	24.758	32.961
Nondecane			(828) 1	1.653	2.136	3.508
Eicosane			(180) 1	1.194	1.967	4.094
Heneicosane					(306) 1	1.523
Docosane						(138)
Tricosane						

pounds showed decreases with the addition of water. The relative recovery change of wet and dry samples and the number of components that can be recovered are also affected by the size of the container used to hold the ignitable liquid sample. The larger the I.D. of the container, the larger the observed influence of water present as shown in Table 4. For the 37 mm I.D. container, the recovery ratio of wet/dry for low- and medium- molecular-mass components is about 0.7, and for high-molecular-mass components it is about 3. When the container I.D. increases to 164 mm, the ratio for low- and medium-molecular-mass components is about 0.25, for high-molecular-mass

components it is about 16 and two additional ignitable liquid components are recovered compared to the smaller container (three compared to the dry sample).

The relative recoveries at 20°C using the established headspace activated charcoal strip ASTM method [6] compared with headspace SPME method with dry samples, wet samples and using partial headspace SPME are compared in Table 5. For dry samples, the standard ASTM method showed higher recoveries up to 2.5 times for octadecane but for wet samples (which is common in real samples or water can be added) the ASTM method showed lower

Table 4

The average relative recovery ratios of wet<sup>a</sup>–dry ignitable liquids at different size of containers used to hold 1 µl sample using PDMS fiber headspace SPME for 25 min at 25°C for triplicate analysis

Compound	Small container (ID 37 mm)		Medium container (ID 104 mm)		Large container (ID 164 mm)	
	Dry: (area) ratio (average RSD 2.9%)	Wet: ratio (average RSD 2.9%)	Dry: (area) ratio (average RSD 2.6%)	Wet: ratio (average RSD 3.1%)	Dry: (area) ratio (average RSD 2.7%)	Wet: ratio (average RSD 2.9%)
Heptane	(730) 1	0.97				
Toluene	(5 721) 1	0.77	(1 118) 1	0.68		
Octane	(76 215) 1	0.73	(12 911) 1	0.45	(2 301) 1	0.46
<i>p</i> -Xylene	(261 226) 1	0.72	(53 105) 1	0.49	(9 768) 1	0.37
Noncane	(535 936) 1	0.70	(109 866) 1	0.35	(20 327) 1	0.32
3-Ethyltoluene	(1 163 849) 1	0.71	(279 948) 1	0.38	(52 907) 1	0.28
2-Ethyltoluene	(1 415 600) 1	0.70	(349 374) 1	0.38	(66 901) 1	0.26
1,2,4-Trimethylbenzene	(1 590 572) 1	0.70	(416 923) 1	0.37	(79 768) 1	0.25
Decane	(1 642 942) 1	0.70	(415 806) 1	0.32	(79 492) 1	0.26
1,2,3-Trimethylbenzene	(1 798 448) 1	0.69	(496 577) 1	0.36	(96 280) 1	0.23
Butylbenzene	(2 669 680) 1	0.72	(801 461) 1	0.33	(156 186) 1	0.24
Undecane	(2 946 578) 1	0.75	(994 545) 1	0.34	(214 048) 1	0.23
Naphthalene	(4 954 493) 1	0.52	(1 928 135) 1	0.28	(446 710) 1	0.11
Dodecane	(3 159 502) 1	0.93	(1 253 250) 1	0.64	(444 108) 1	0.29
1-Methylnaphthalene	(4 592 451) 1	0.78	(1 924 974) 1	0.50	(783 319) 1	0.15
Tridecane	(1 566 916) 1	1.27	(566 839) 1	1.83	(335 596) 1	0.62
2-Methylnaphthalene	(4 061 416) 1	1.36	(1 758 696) 1	1.52	(762 867) 1	0.14
Tetradecane	(484 904) 1	1.68	(139 970) 1	6.21	(128 859) 1	2.10
Pentadecane	(99 452) 1	2.60	(27 893) 1	13.66	(26 914) 1	7.10
Hexadecane	(23 782) 1	3.58	(8 318) 1	14.87	(6 642) 1	14.53
Heptadecane	(4 975) 1	3.71	(1 700) 1	13.54	(1 611) 1	16.15
Pristane	(5 225) 1	3.33	(2 016) 1	12.92	(1 779) 1	16.14
Octadecane	(1 076) 1	2.74	(364) 1	12.21	(377) 1	15.38
Nondecane	(1 992) 1	1.23		(922) <sup>∞</sup>		(998) <sup>∞</sup>
Eicosane						(210) <sup>∞</sup>
Heneicosane						(259) <sup>∞</sup>
Docosane						
Tricosane						

<sup>a</sup> Wet sample: 5% of container volume of water was added.

Table 5

The average relative recovery ratios (relative to ASTM activated charcoal strip extraction method) of simulated ignitable liquids compared to PDMS fiber SPME for 15 min triplicate extractions at 20°C

Peak Compound	$t_R$ (min)	ASTM method compared to SPME methods (ratio of peak areas)	
		Compared to headspace SPME dry sample (average RSD 3.1%)	Compared to headspace SPME wet sample (average RSD 3.1%)
Heptane	2.50		
Toluene	3.18		(37 141) 1
Octane	3.56	0.284	0.807
<i>p</i> -Xylene	4.72	0.145	0.566
Nonane	5.25	0.154	0.444
3-Ethyltoluene	6.9	0.147	0.562
2-Ethyltoluene	7.47	0.154	0.632
1,2,4-Trimethylbenzene	8.07	0.167	0.723
Decane	8.29	0.232	0.707
1,2,3-Trimethylbenzene	9.18	0.189	0.966
Butylbenzene	10.7	0.166	0.623
Undecane	12.65	0.108	0.329
Naphthalene	16.14	0.032	0.456
Dodecane	16.88	0.085	0.152
1-Methylnaphthalene	20.49	0.018	0.110
Tridecane	20.78	0.182	0.121
2-Methylnaphthalene	21.05	0.154	0.133
Tetradecane	24.37	0.854	0.163
Pentadecane	27.71	2.786	0.217
Hexadecane	30.94	2.978	0.162
Heptadecane	35.19	3.397	0.137
Pristane	35.37	1.573	0.054
Octadecane	38.44	2.505	0.076
Nondecane	39.86		0
Eicosane	40.86		0
Heneicosane	41.64		0
Docosane	42.32		0
Tricosane	42.99		

recoveries particularly for the higher-molecular-mass components with four components not detected at all by the established ASTM method. When comparing the results of overnight extraction of wet sample and dry sample by ASTM method, the addition of water also increased the recovery of long chain components and decreased the recovery of low-molecular-mass ignitable liquids consistent with the results of headspace SPME. It is therefore important to consider the influence of water present in a sample regardless of the extraction method being employed. It is important to note that most of these comparisons were conducted at lower temperatures to demonstrate the relative effects of major controllable variables other than temperature but that optimal recoveries

are achieved at elevated temperatures and SPME has repeatedly been shown to be more sensitive than the standard ASTM method [5,10,17].

A comparison of SPME and direct injection of a standard EPA explosive mixture with GC–ECD and HPLC–UV analysis is shown in Table 6 for 30 min extractions using CW–DVB for GC and CW–TPR for HPLC. For the direct injection method, standards were in acetonitrile and diluted with the mobile phase. For the SPME method, all samples were in the 25% NaCl aqueous solution and the acetonitrile–water ratio was 1:199. SPME–GC–ECD generally yielded the best separations and highest sensitivity; however the GC method proved unsuitable for quantitation of the thermally unstable HMX. Addi-

Table 6  
Comparison of the detection limits of explosives by SPME–GC–ECD and SPME–HPLC–UV

Explosives	Detection limits in ng/ml (%RSD for 5 replicates) at $S/N > 3$			
	GC–ECD		LC–UV (254 nm and 220 nm)	
	Direct injection	SPME–GC	Direct injection	SPME–HPLC
NB	53 (3.3)	0.24 (3.5)	3.9 (2.7)	1.2 (2.7)
1,3-DNB	44 (2.7)	0.22 (2.7)	2.3 (1.2)	0.8 (1.2)
1,3,5-TNB	39 (3.7)	0.18 (2.1)	2.6 (1.1)	0.6 (1.2)
2-NT	55 (3.2)	0.24 (3.4)	8.0 (3.7)	1.8 (3.8)
4-NT	47 (2.7)	0.24 (2.8)	7.4 (4.1)	1.9 (4.2)
3-NT	64 (2.7)	0.24 (2.9)	7.3 (4.0)	1.7 (4.0)
4-A-2,6-DNT	30 (1.7)	0.10 (1.6)	2.9 (1.6)	1.2 (1.6)
2-A-4,6-DNT	29 (1.4)	0.090 (1.4)	3.4 (2.1)	1.2 (1.9)
2,6-DNT	27 (1.9)	0.09 (1.5)	4.4 (3.0)	1.3 (2.9)
2,4-DNT	29 (1.5)	0.10 (1.7)	3.4 (1.9)	1.2 (1.7)
TNT	22 (1.7)	0.090 (1.7)	2.9 (1.2)	1.1 (1.3)
HMX	N/A	N/A	3.8 (2.6)	1.2 (2.7)
RDX	130 (5.0)	0.61 (5.2)	2.9 (2.3)	1.1 (2.5)
Tetryl	43 (4.0)	0.25 (4.2)	3.2 (2.8)	1.3 (2.9)
EGDN	51 (3.7)	0.22 (3.8)	550 (5.4)*	120 (4.6) <sup>a</sup>
NG	89 (2.8)	0.58 (2.9)	500 (5.5)*	110 (4.8) <sup>a</sup>
PETN	94 (3.7)	0.61 (3.8)	380 (5.1)*	80 (4.3) <sup>a</sup>

<sup>a</sup> Detected at 220 nm.

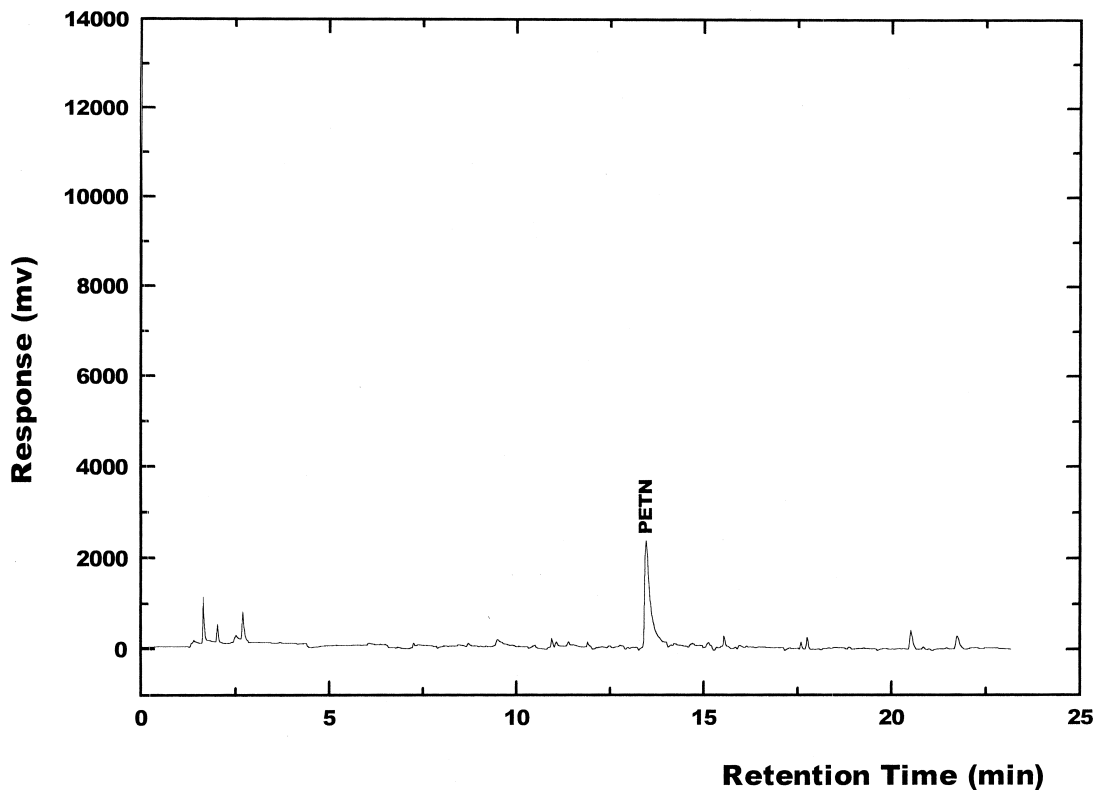


Fig. 6. SPME–GC–ECD of PETN from an actual post-explosion soil sample.

tional details are presented elsewhere [25,28]. An example of the application of SPME–GC–ECD to recover explosive residues from actual post-blast debris is shown in Fig. 6 for PETN. One of the major advantages of the direct SPME technique for explosives from acetonitrile–water solutions is the obvious simple chromatogram obtained, devoid of interferences from endogenous compounds present in the matrix. No explosives were detected in the soil control samples. Overall, SPME methods have proven to be superior to existing extraction methods for ignitable liquids and explosives 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 in the application of SPME to the analysis of ignitable liquids and explosive traces from forensic specimens will likely include development and increased use of field sampling and analysis including fast GC, portable GC–MS and HPLC methods providing rapid on-site confirmation. Hurdles to widespread acceptance include the need for additional optimization particularly for SPME–HPLC methods and the establishment of standard methods (i.e. ASTM) for flammable or combustible liquid residues from fire debris samples and for organic high explosives from explosive debris, soils, sediments and aqueous solutions.

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