Kenneth Paul Kirkbride,[1] Ph.D.; Gunter Klass,[2] Ph.D.; and Paul Edwin Pigou,[1] Ph.D.

Application of Solid-Phase Microextraction to the Recovery of Organic Explosives*

ABSTRACT: The application of solid-phase microextraction to the recovery of residues of organic explosives by headspace sampling is discussed. It was found that the technique was rapid and simple. Polydimethylsiloxane and polyacrylate resin were examined as adsorption phases and the latter was found to be more effective. It was found that non-volatile explosives (PETN, RDX, and TNT) should be extracted at about 100°. Acceptable limits of detection were achieved using bench top quadrupole mass spectrometry and short extraction times (about 30 min). Increasing the extraction times to many hours resulted in significantly enhanced detection. Desorption of PETN from the solid phase was found to induce some decomposition of the explosive, but the technique was still valuable for the analysis of this compound.

This article describes a preliminary investigation into the application of solid-phase microextraction (SPME) to the recovery of residues of organic explosives from explosion debris. SPME has been shown to be an efficient and universal technique for solventless extraction of a wide variety of trace organic compounds including contaminants in water and food (1–4), fuels in fire scene debris (5), and drugs in blood and urine (6,7). The basis of the technique is an extraction device, which is a thin fiber of fused silica coated with an adsorbent film (8); films are available in various thicknesses and polarity. The sampling fiber is captive within a syringe arrangement complete with a stainless steel needle into which it can be retracted. To load the fiber with sample the plunger of the syringe is depressed, exposing the fiber. In this configuration organic compounds can be adsorbed from headspace or aqueous matrices. Once adsorption is complete the fiber is retracted into the needle. Analysis is performed by inserting the needle into the injector of a gas chromatograph *via* the standard rubber septum in the manner of a conventional liquid injection. When the plunger is depressed the fiber becomes exposed to the

hot injection zone of the chromatograph. Any adsorbed compounds will be thermally desorbed, and chromatographed in the usual fashion.

In theory, explosion debris could be extracted in two ways using SPME. Using a condensed phase approach the fiber could be placed in contact with any water that might be present in the sample (or that has been purposely added to it). Alternatively, SPME could be used to extract explosives residues from the headspace above debris. Both of these techniques have been discussed in detail elsewhere (9,10). Successful recovery of explosives from headspace using other techniques has been described (11,12). Due to the simplicity of the headspace extraction technique, and its selectivity towards volatile substances, it was decided to pursue SPME recovery of explosives from headspace and not the condensed phase.

Most organic explosives have a very low vapor pressure at room temperature (Table 1) and so their concentration in the headspace can be expected to be low. Therefore, any technique for identification of explosives residues based on headspace extraction is potentially fraught with problems, and SPME brings with it some additional features that must be considered. Firstly, the selectivity of the fiber might play a part; from the literature (13) one can expect polar adsorbent films such as polyacrylate (PA) resin to exhibit high selectivity for polar analytes. The thermodynamics of adsorption and desorption might be critical. Although the vapor pressure of explosives increases at higher temperature (Table 1), it might not necessarily follow that partition into the SPME phase increases at higher temperature. The kinetics of adsorption might be important. How quickly, and to what extent, does the fiber deplete the headspace, and how quickly can be headspace concentration reestablish? Finally, the desorption temperature might also be important; explosives are not thermally stable. Table 1 also lists the

TABLE 1—*Organic explosives and their vapor pressure.*

Explosive	Explosive Temperature (°C)	Vapor Pressure (millibar)*	Deflagration Temperature (°C)*
EGDN	20	0.05	217
	100	29	
NG	50	0.0097	224
	90	0.31	
PETN	97	0.0011	202
	110.6	0.0042	
TNT	81	0.057	300
	100	0.014	
RDX	110	0.00054	230
	121	0.0014	

*Data from Meyer (15).

deflagration temperatures for the explosives used in this study, these are the temperatures at which the explosives undergo subsonic decomposition without the assistance of oxygen. Deflagration could occur upon thermal desorption, therefore detection of intact explosive after desorption above the deflagration temperature might not be possible. On the other hand, desorption must take place as rapidly as possible to ensure narrow chromatographic peaks, therefore, a high temperature is desirable. Each of these features will be discussed in the following sections.

Experimental

Explosive standards, ethyleneglycol dinitrate (EGDN), nitroglycerine (NG), pentaerythritoltetranitrate (PETN), 2,4,6-trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX) were obtained from Radian Corporation at concentrations of either 100 μg/mL or 1000 μg/mL in acetonitrile as 1 mL aliquots sealed in glass ampoules.

SPME fibers: 100 μm thick polydimethylsiloxane (PDMS) and 85 μm thick polyacrylate (PA) resin coated fibers were obtained from Supelco (Bellefonte, PA) and conditioned according to the suppliers instructions before use.

Explosives samples for extraction were prepared on the day of the experiment by placing a known volume (1–5 μL) of the explosives standard solution onto a small square of tissue paper placed in a glass bottle (700 ± 10 mL capacity). The solvent was then allowed to evaporate for the appropriate time, 5 min for EGDN and 10 min for the other explosives. Such volatile solvents are not normally present in explosives residues. As it was felt that solvent might decrease the concentration of the less volatile analytes in the headspace and might compete with the analyte during adsorption into the fiber coating, it was considered prudent to allow the solvent to evaporate. Sample bottles were then sealed with a plastic cap until the sample was ready for extraction.

To extract a sample a special cap with a small hole (1 mm) was fitted to the sample bottle, the fiber (protected by the needle) was inserted through the hole, and then exposed for the prescribed time.

Extractions at elevated temperature were performed in a thermostated oven (quoted temperatures varied by ± 5°C) which held the entire extraction device and sample bottle. For the adsorption temperature and adsorption time profiles at elevated temperatures, the sample bottles were preheated at the adsorption temperature for 10 min.

Desorption was carried out by exposing the fiber in the injection zone for 1 min at the temperatures specified. Such desorption times have been shown to be adequate for PA coated fibers in previous studies (13).

In general, each of the graphical data points presented in the Results and Discussion section was the average of three experimental points determined under identical conditions. No internal standards were used in any of the experiments, hence the precision of each determination is relatively low. The important aspects of the results, therefore, are the trends found, as opposed to the individual values.

Only one PA fiber was used for the whole study. During the course of the study it became darker, eventually ending up nearly black, without any apparent change in its adsorptive properties. This finding is in agreement the product information supplied with the Supelco SPME kit. Gas Chromatograph: Hewlett-Packard 5890A, Column: 15 m × 0.257 mm × 0.25 μm DB-1 fused silica, Carrier Gas: Helium at 3 psig, Flow Rate: 58 cm/sec at 70°, Split Ratio: spitless, Mass Spectrometer Transfer Line: 200°, Injector

block 200°, Oven program: Initial Temp 70°; Initial Time 1 min; then 30°/min to 120°, 10°/min to 170°, 60°/min to 280°; Final Temp 280°; Final Time 2 min. Mass Spectrometer: Hewlett-Packard 5971 Mass Selective Detector, Scan Range, TIC Mode: 40–220 Daltons (scan rate 3.6 scans/s) Vacuum: 60–70 mTorr. The mass spectrometer was tuned (Maximum Sensitivity Autotune) and a background fiber chromatogram run each day prior to use.

Results and Discussion

Adsorption Parameters

EGDN, the most volatile organic explosive studied, was used to investigate the comparative adsorptive abilities of the non-polar PDMS fiber and the polar PA fiber. As expected, compared to PDMS the PA fiber adsorbed more EGDN from the headspace per unit time (see Fig. 1); therefore a lower limit of detection (LOD) was possible with this fiber. However, equilibration between the vapor phase and the fiber was established more rapidly with the PDMS phase. It was found that with the PDMS fiber equilibrium was reached within 5 min, while for the PA fiber it was not reached even after 40 min. This is in agreement with the results of previous studies (13), where the difference in equilibration times was attributed to the fact that PA is a solid, while PDMS is a viscous liquid. It was felt that EGDN was a good model for the adsorption characteristics of other explosives, so given the enhancement in detection offered by the PA fiber it was used for the remainder of this study.

Figure 2 shows adsorption kinetics for NG and EGDN with the polyacrylate fiber at room temperature. Not surprisingly, the amount of explosive adsorbed increased with time, but unlike the case with EGDN the amount of NG adsorbed increased sharply and did not level out within 40 min. In this respect RDX and TNT behaved in a manner similar to NG but required a higher adsorption temperature. This indicated that longer adsorption times, up to several hours, are likely to increase significantly the response from these explosives.

For those explosives with a lower vapor pressure than NG, it was necessary to sample the headspace at high temperature. Figure 3 shows that even though NG provided a reasonable response at room temperature this increased significantly on raising the adsorption temperature to 60°. Its response then gradually decreased with further increase in temperature. However, no appreciable amount of the less volatile TNT was detected at room temperature. For
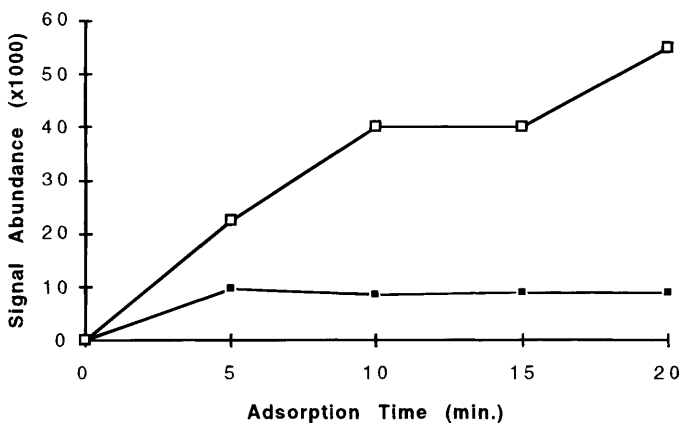

FIG. 1—*TIC response from separate samples of 0.5 μg EGDN extracted from standard sample bottles for increasing adsorption time at room temperature using PDMS fiber (■) and PA fiber (□).*
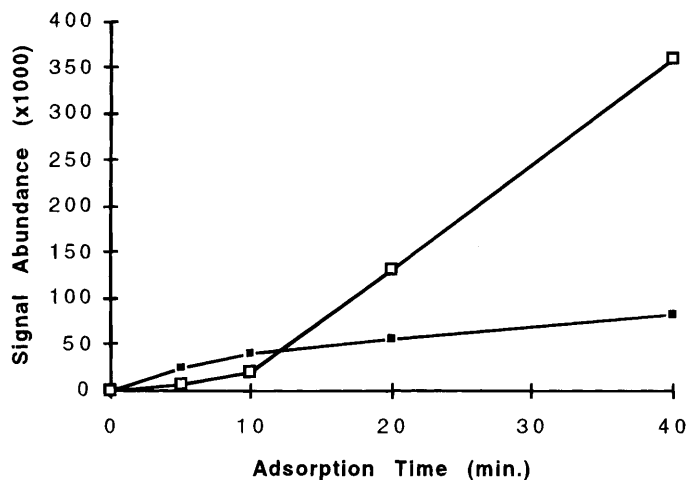
FIG. 2—*TIC response from separate samples of 0.5 μg EGDN (■) and 5.0 μg NG (□) extracted from standard sample bottles for increasing adsorption time at room temperature.*

FIG. 4—*Response from a single sample containing equimolar amounts of NG (■), TNT (□), RDX (◆) extracted from a standard sample bottle for increasing adsorption time at constant adsorption temperature (100°).*

this explosive it was found that an adsorption temperature of at least 60° was required, response then increased sharply up to the highest temperature used (110°). A minimum headspace temperature of 80° was required for the adsorption of RDX, the least volatile explosive studied. These results indicate that if SPME is to be used as a universal technique for the extraction of organic explosives residues from debris an adsorption temperature of at least 80° and less than 110° should be used.

The adsorption kinetics for NG, TNT and RDX at a temperature of 100° are displayed in Fig. 4. Interestingly, under these conditions NG reached equilibrium in less than 5 min, as indicated by the fact that its response was essentially constant for adsorption times from 5 to 40 min. The response of TNT increases significantly with increasing time, while RDX required an adsorption time of at least 10 min before a significant response was obtained. Its response then also increased with time up to 40 min, the maximum adsorption time used. These results indicate that a minimum adsorption time of 30 min at 100° should be used for the analysis of these explosives. Clearly, from the slopes of the graphs obtained, longer adsorption times (over 40 min) would increase the response from TNT and RDX significantly, but not NG, since it has already reached equilibrium under the conditions used.
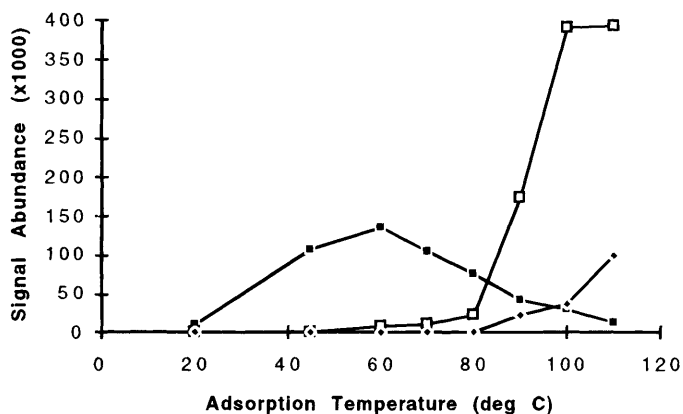

FIG. 3—*Response from a single sample containing equimolar amounts of NG (■), TNT (□), RDX (◆) extracted from a standard sample bottle for increasing adsorption temperature at constant adsorption time (30 min).*
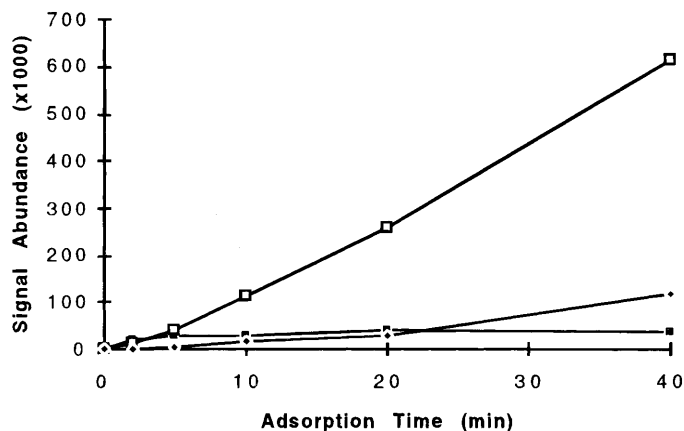
Extraction and Analysis of PETN

Due to its thermal instability, the extraction and chromatography of PETN was not straightforward. Not only did PETN degrade upon high temperature desorption, it would appear that it also degraded upon chromatography. In our instrument, when PETN was injected at 240° as a solution in acetonitrile and subjected to an oven program starting at 70° for 1 min then rising to 280° at a rate of 30°/min, three major features were observed in the chromatogram (see Fig. 5). An early eluting peak, possibly pentaerythritolmononitrate, was detected at 2.8 min, a broad hump was observed between 5 and 6 min, and a sharp peak was detected at 6.0 min. Each peak and the hump gave similar mass spectra with a base peak of 46 Daltons and another major peak at 76 Daltons. The early peak appeared to be due to decomposition of PETN in the injector; when the injector temperature was dropped to 200° this peak disappeared. The broad hump appeared to arise from decomposition during chromatography. When the temperature program of the chromatograph was adjusted so that PETN did not experience a temperature greater than 180°, this feature disappeared. Chromatography of PETN injected as a solution in acetonitrile using the oven program described in the Experimental section provided the chromatogram shown in the middle trace of Fig. 5, showing essentially one peak at retention time 7.80 min for PETN.

Experiments with PETN using SPME fiber extraction yielded further problems. When the optimized injector and column conditions described above were used, PETN gave two peaks at 7.80 min and 7.95 min as illustrated in the lower trace of Fig. 5, both peaks were sharp and gave essentially the same mass spectrum. It appeared therefore that PETN was still undergoing thermal decomposition, probably in the injection port, under the SPME desorption conditions. This was confirmed by experiments performed at decreasing injection port temperatures (Fig. 6) which indicated that the peak at 7.95 decreased with decreasing injector temperature. The peak at 7.95 min almost disappeared at an injector temperature of 140°. Unfortunately, at this temperature total response from PETN decreased significantly (Fig. 6). At injection port temperatures greater than 200°, PETN decomposed further to yield another peak at 3.20 min. This became the major peak from PETN when an injection port temperature of 240° was used. The appearance of this peak was accompanied by a sharp decrease in response for the two peaks at 7.80 min and 7.95 min.

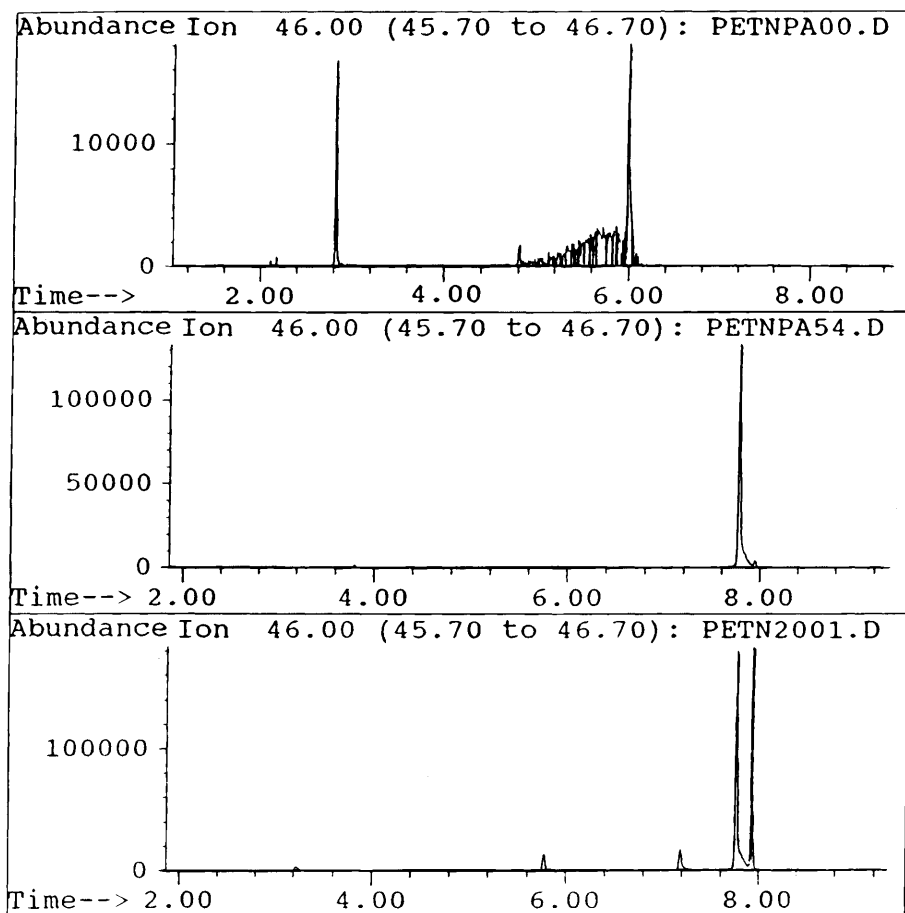Adsorption temperature studies using PETN indicated that its

FIG. 5—*Chromatographic analysis of PETN. Upper trace; Reconstructed ion chromatographic (RIC) response from direct injection of PETN solution, injection port temperature 240°, temperature program 70° for 1 min, then 30°/min to 280°. Middle trace; RIC response from direct injection of PETN solution, injection port temperature 200°, temperature program 70° for 1 min, then 30°/min to 120°, 10°/min to 170°, 60°/min to 280°, direct liquid injection of PETN in acetonitrile. Lower trace; RIC response from SPME of 5.0 μg PETN from standard sample bottle, adsorption time 30 min, adsorption temperature 100°, chromatographic conditions as for middle trace.*

response increased with temperature up to 100°, the maximum temperature investigated. Hence the ideal injection port temperature for PETN appeared to be about 180–200° and the ideal adsorption temperature about 100°. Even though two peaks were produced for PETN under these conditions, a maximum response was
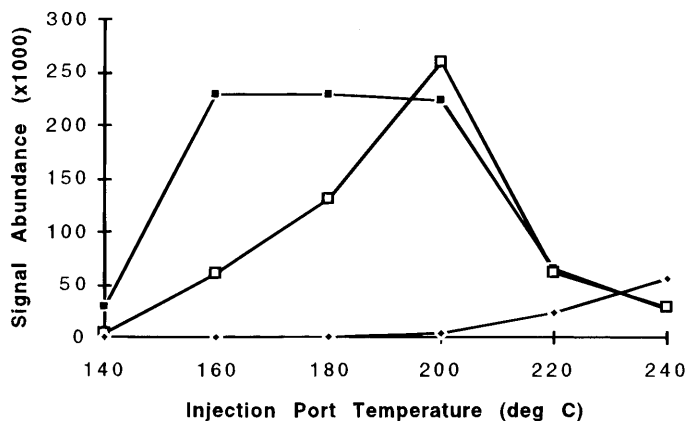
achieved. These temperatures were also found to be suitable for the other less volatile organic explosives used in this study.

Limits of Detection

As outlined above, the absolute quantity of material adsorbed by the fiber depended upon the temperature and length of time over which the adsorption took place. Given these variables, Table 2 shows limits of detection (LOD) achieved with representative

FIG. 6—*TIC response from 5.0 μg PETN in a standard sample bottle adsorbed onto PA fiber with increasing injection port temperature, (■) peak at 7.80 min, (□) peak at 7.95 min, (◆) peak at 3.20 min.*

TABLE 2—*Limits of detection achieved with representative explosives.*

Explosive	Limits of Detection*	SNR†	Adsorption Temperature	Time
EGDN	0.5 ng	10:1	25°C	20 min
NG	10 ng	15:1	25°C	30 min
PETN	0.5 ng	8:1	105°C	30 min
TNT	10 ng	2:1	70°C	20 min
RDX	10 ng	20:1	100°C	30 min

*Amount present in 700 mL of headspace, detected with the signal to noise ratio shown in single ion mode, 46 Daltons for EGDN, NG, PETN and RDX, 210 Daltons for TNT.

†Signal to noise ratio after Skoog and Leary (12) noise equivalent to peak to peak noise in the region of the analyte divided by 5.

explosives. Much lower LOD are to be expected if the sampling times are increased to the order of hours instead of minutes, especially for those explosives which fail to reach equilibrium in the adsorption time used. For example, Fig. 7 illustrates the increase in response for NG (about thirty-fold) obtained by increasing the adsorption time from 30 min to overnight.

Collaborative Study

Fortuitously, this investigation coincided with an Australia-wide blind collaborative study. One item examined was the remains of an exploded cardboard box. The debris, and the plastic bag in which it had arrived, were placed into a 1L paint tin. A small hole was made in the lid through which the SPME needle was inserted. The contents of the can were exposed to the fiber at 100° for 60 min. The resultant total ion chromatogram (TIC) appears in Fig. 8. It is dominated by a large peak at 9.1 min due to a phthalate plasticizer, which probably originated from the plastic bag, and a series of peaks characteristic of high boiling point hydrocarbons, probably due to waxes from the cardboard. The region between 0 and 7.0 min was essentially clean, therefore the presence of EGDN, NG and TNT was eliminated. An expansion of the region from 7.0 to 8.0 min, where peaks due to RDX and PETN are found, appears in Fig. 8. The region is quite complicated, and contains peaks whose retention times correspond to both PETN and RDX. To confirm the presence of either of these explosives a reconstructed ion chromatogram (RIC) was extracted from the TIC using ion abundance at 46 Daltons (an ion common to both RDX and PETN); see Fig. 8. This chromatogram clearly indicates

the presence of PETN by the two peaks at 7.80 and 7.95 min. Mass spectra of the peaks at 7.80 and 7.95 min were consistent with PETN. According to the suppliers of the trial this sample was a small cardboard box which had been destroyed by a small charge of Semtex 10SE and an electrical detonator; both the detonator and the explosive charge contained only PETN, as confirmed in our tests.

Conclusions

SPME has been shown to be applicable to the recovery of organic explosives from headspace. Although this study was restricted to analysis of recovered explosives using a modest mass spectrometer, SPME is a universal sampling technique that can be used with a variety of detection mechanisms. Use of electron capture, thermal energy analyzer, or high performance mass spectrometric detectors should significantly improve the limits of detection reported in this study. No modification of chromatographic hardware, other than the installation of a special narrow bore injector liner, is required, and the sampling device itself is quite inexpensive. The extraction technique is elegantly simple, quite rapid, and does not use solvent. Even though many minutes are required for extraction, the analyst needs not be present for that period; the amount of time an analyst must spend on the entire procedure is only about a minute to place the fiber in contact with the headspace, and about a minute to desorb it and start the chromatography. Liquid phase extracts of explosion debris often contain fats, waxes, and oils, which can seriously effect the reliability of gas chromatographic analysis of explosives through contamination of the col-
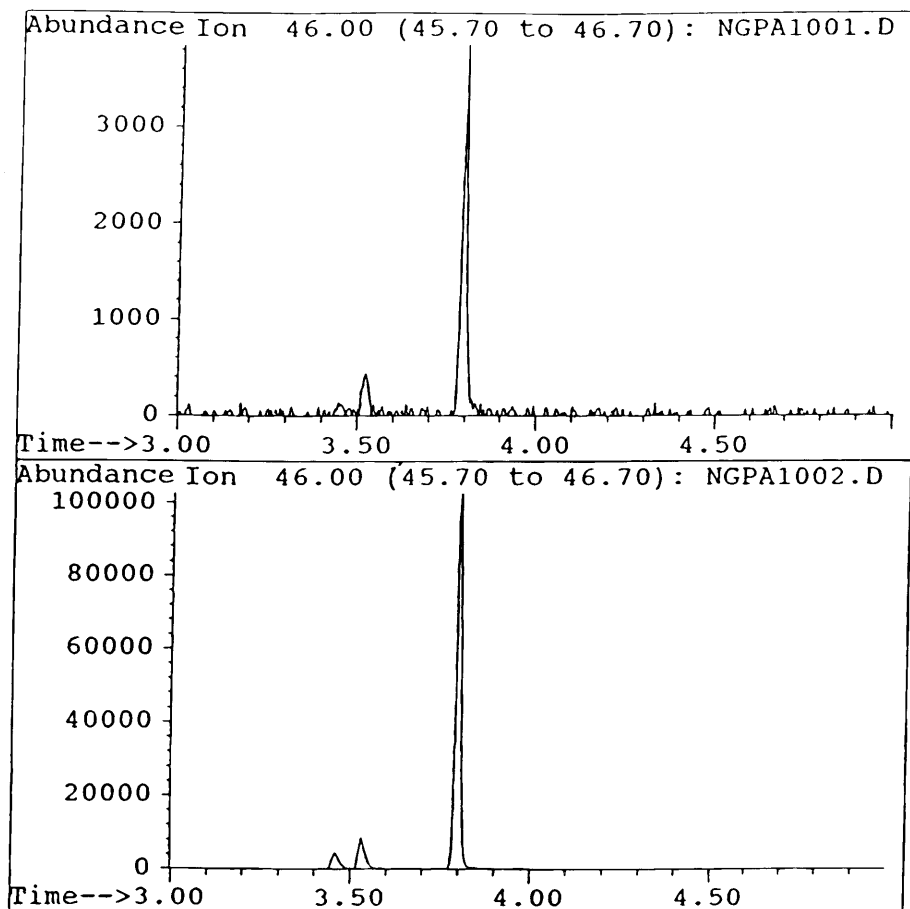

FIG. 7—*RIC response from 0.5 μg NG for 30 min adsorption time (upper trace), and 18 h adsorption time (lower trace).*
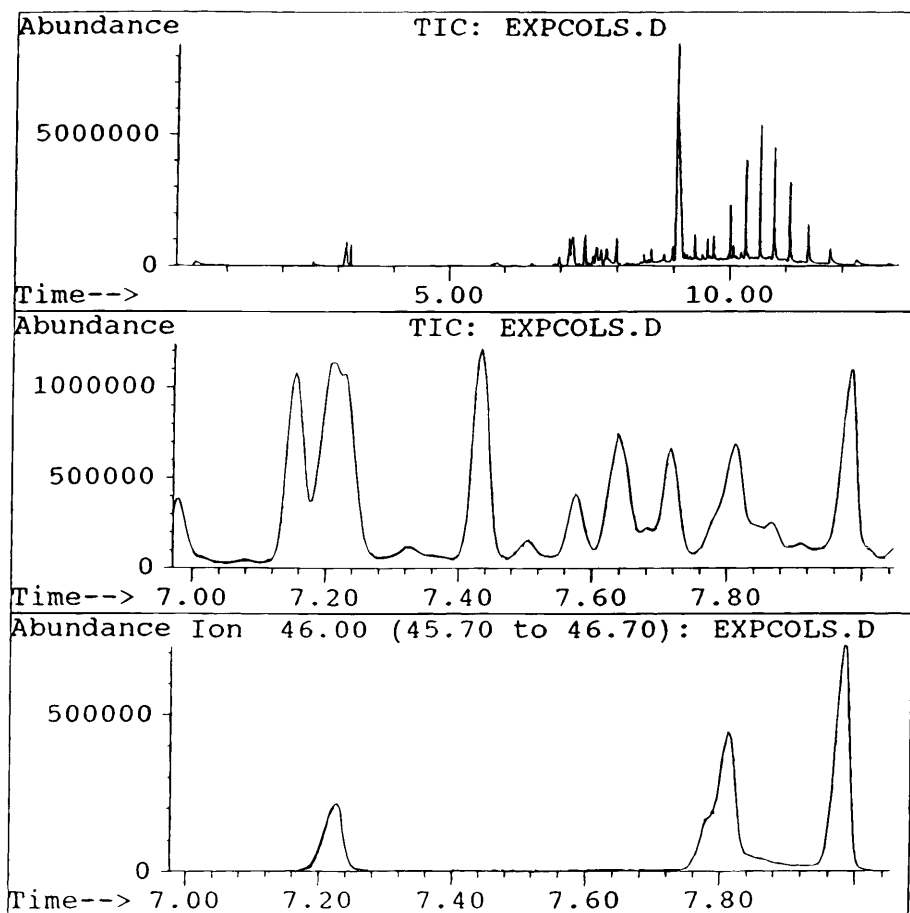
FIG. 8—*SPME GC-MS of explosives collaborative study, adsorption time 60 min, adsorption temperature 100°, chromatographic conditions as in Experimental section. Upper trace; TIC response from 0 to 12 min. Middle trace; TIC response of expanded region from 7.0 to 8.0 min. Lower trace; RIC using ion 46 Daltons of the expanded region from 7.0 to 8.0 min.*

umn and injector liner. SPME can be expected to provide clean extracts that should ensure reliable chromatographic performance.

Headspace extraction at about 100° for at least 30 min, followed by desorption at 200° gave good limits of detection for the organic explosives investigated. Significantly enhanced detection can be expected if the extraction period is increased to several hours.

References

1. Boyde-Boland AA, Pawliszyn J. Solid-phase microextraction coupled with high-performance liquid chromatography for the determination of alkylphenol ethoxylate surfactants in water. Anal Chem 1996;68:1521–29.
2. Gorecki T, Pawliszyn J. Determination of tetra ethyllead and inorganic lead in water by solid-phase microextraction/gas chromatography. Anal Chem 1996;68:3008–14.
3. Yang X, Peppard T. Solid-phase microextraction of flavor compounds—a comparison of two fiber coatings and a discussion of the rules of thumb for adsorption. LC-GC 1995;13:882–5.
4. Coleman WM. A study of the behavior of Maillard reaction products analyzed by solid-phase microextraction-gas chromatography-mass selective detection. J Chromatog Sci 1996;34:213–8.
5. Furton KG, Almirall JR, Bruna JC. A novel method for the analysis of gasoline from fire debris using headspace solid-phase microextraction. J Forensic Sci 1996;41:12–22.
6. Nagasawa N, Yashiki M, Iwasaki Y, Hara K, Kojima T. Rapid analysis of amphetamines in blood using head space-solid phase microextraction and selected ion monitoring. Forensic Sci Int 1996; 78:95–201.
7. Yashiki M, Kojima T, Miyazaki T, Nagasawa N, Iwasaki Y, Hara K. Detection of amphetamines in urine using head space-solid phase microextraction and chemical ionization selected ion monitoring. Forensic Sci Int 1995;76:169–77.
8. Arthur CL, Pawliszyn J. Solid-phase microextraction with thermal desorption using fused silica optical fibers. Anal Chem 1990; 62:2145–8.
9. Louch DL, Motlagh S, Pawliszyn J. Dynamics of organic compound extraction from water using liquid-coated fused silica fibers. Anal Chem 1992;64:1187–99.
10. Zhang Z, Pawliszyn J. Headspace solid-phase microextraction. Anal Chem 1993;65:1843–52.
11. Chrostowski JE, Holmes RN, Rehn BS. Collection and determination of ethylene glycol dinitrate, nitroglycerine and trinitrotoluene explosive vapors. J Forensic Sci 1976;21:611–5.
12. Prime RJ, Krebs J. Can Soc Forensic Sci J 1980;13:27–33.
13. Buchholz KD, Pawliszyn J. Optimization of solid-phase microextraction conditions for the determination of phenols. Anal Chem 1994;66:160–7.
14. Skoog DA, Leary JJ. Principles of instrumental analysis. 4th Edition. Fort Worth: Harcourt Brace College Publishers, 1992;47.
15. Meyer R. Explosives. Weinheim: Verlag Chemie, 1997.

Additional information and reprint requests:
Dr. K. Paul Kirkbride
Assistant Chief Scientist, Chemistry
Forensic Science Center
21 Divett Place
Adelaide
South Australia, 5000