J Forensic Sci, Jan. 2003, Vol. 48, No. 1
Paper ID JFS2002223_481
Available online at: www.astm.org

TECHNICAL NOTE

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Preferential Extraction of Hydrocarbons from Fire Debris Samples by Solid Phase Microextraction*

ABSTRACT: Headspace analysis by extraction/GC-MS is a common method of detecting volatile hydrocarbon accelerants in fire debris samples. Solid-phase microextraction was tested to determine if there is selective extraction of chemically distinct compounds. It was found that both the polydimethylsiloxane (PDMS) and Carboxen/PDMS solid phase microextraction fibers show preferential extraction of aliphatic or aromatic compounds from the headspace depending on fiber type and temperature. The Carboxen/PDMS fiber type showed particular (although not exclusive) selectivity for extraction of aromatic hydrocarbons. Other experimental considerations of SPME are noted.

KEYWORDS: forensic science, arson, fire debris, accelerant detection, solid-phase microextraction, gas chromatography, mass spectrometry

Detection of ignitable liquid residue from solid fire debris is a widely used approach to help investigators assess if the cause of a particular fire was possibly arson (1,2). A variety of methods to isolate volatile residues from samples have been used including solvent extraction (3), direct headspace analysis (4), and enrichment by dynamic (5), or static (6) adsorbent-based methods. Several of these methods have been well established and have been standardized by ASTM International (7–10). More recently, solid-phase microextraction (SPME) has been investigated as a sampling method for volatile residues for forensic investigations (11–19). SPME has been found to be advantageous for many applications because it is faster and easier to use than other methods, and can provide lower detection limits for many analytes. In addition, SPME eliminates the use of solvents which prevents potential exposure to toxic chemicals such as carbon disulfide. Desorption and analysis of volatile samples collected by SPME is most often performed using gas chromatography with either FID or MS detection.

An overview of SPME and the theoretical aspects of sampling have been reviewed (20–21). Many experimental variables associated with the use of SPME to study forensic samples have been studied to optimize sample collection efficiency. These parameters include fiber type (16–18,22), sampling temperature (16,17), extraction time (16,18), and matrix effects (16,18). Use of SPME for field sampling applications has also been investigated (23).

It is important that a representative sample be obtained by the extraction process in order to determine the presence and potentially the identity of an accelerant from fire debris. In this study, we tested the extraction selectivity of the two most common types of SPME fibers used for the extraction of volatile accelerant hydrocarbon vapors from fire debris samples. Selectivity was evaluated as a function of temperature and fiber type.

Experimental

Materials

Unleaded 87 octane gasoline was obtained from a local Shell station. Carboxen/polydimethylsiloxane (Carboxen/PDMS) and nonbonded polydimethysiloxane (PDMS) SPME fibers (Supelco, Bellefonte, PA) with film thicknesses of 75 μm and 100 μm, respectively, were used with their associated holders. A Teflon test tube (Cole Parmer) was fitted over the end of the holder preventing the fiber from being exposed to the atmosphere while not in use. Nonane, heptane, ethylbenzene, and 1,4-dimethylbenzene, were obtained from Sigma-Aldrich (St. Louis, MO).

Sample Preparation

Test mixtures containing equal volumes of heptane, 1,4-dimethylebenzene, ethylbenzene, and nonane were prepared and sealed in glass vials prior to use. Direct headspace analysis over test mixtures or gasoline was carried out by sealing 50 μL of the liquid sample in a vial with a septum. After equilibration at a specific temperature, 5 μL of the headspace gas was removed by an airtight syringe and immediately injected to the chromatograph.

Fire debris samples were generated by burning small structures with and without added gasoline. The structures consisted of a base built with alternating layers of wood and newspaper placed upon a concrete foundation. The first layer of the base consisted of three equally spaced pieces of 1 × 3 × 36 cm cedar planks (Sovebec, Inc., Charny, Quebec), topped by a 4 cm layer of wadded newspaper, topped by three more cedar planks which was covered by another 4 cm layer of wadded newspaper (four total layers). A 15 × 15 cm piece of Dupont Stainmaster® nylon carpet was then centered upon this layered base structure.

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* This work was supported by the National Science Foundation CCLI grant #9952294 (P.L.E.).

Received 29 June 2002; and in revised form 20 Sept. 2002; accepted 20 Sept. 2002; published 11 Dec. 2002.

Two exact structures were constructed at the same time with a considerable distance between each other ensuring that there would be no cross-contamination of the fire sites. During construction, 50 mL of gasoline was added to the carpet of one set-up. Immediately after construction, both structures were set afire by match, allowed to burn for 10 min, and then extinguished using 800 mL of water. The fires were set outdoors under conditions where the ambient temperature was between 18–26°C, winds less than 10 km/h, and in dry weather. Immediately after the fires were extinguished, the debris was collected using metal tweezers and sealed in half-gallon metal cans.

SPME Headspace Sampling

Before each use fibers were thermally cleaned for at least 30 min by insertion into the injection port of the GC set at 280°C. The headspace above test mixtures or neat gasoline was sampled by placing 100 μL of liquid sample into a glass vial which was sealed with Teflon film. The SPME fiber was inserted through the film and remained in contact with the headspace at a given temperature for 3 min prior to insertion into the GC-MS. A vial containing no gasoline was sampled in the same manner to serve as a blank.

The headspace of carpet coated with neat gasoline was sampled by first dispersing 500 μL of gasoline dropwise across a 15 × 15 cm piece of carpet. A 10 cm diameter steel can was placed over the carpet to generate a sealed sampling chamber for 8 min. A small hole was drilled in the closed end of the can into which the SPME fiber was inserted for 30 s at room temperature. After this time, the fiber was withdrawn and immediately inserted into the inlet of the GC-MS. Carpet with no added gasoline was sampled using the identical procedure.

To sample the headspace of the fire debris, a small hole was drilled into the top of the metal can containing the collected debris material. The hole was sealed with tape and the can was then placed in an oven to equilibrate to temperature. The tape was removed and the SPME fiber was inserted into the can. After exposure to the sample headspace, the fiber was immediately inserted into the inlet of the GC-MS.

For all the sampling procedures described above, the SPME fiber was allowed to desorb for 5 min following insertion into the GC-MS inlet. During the desorption time, the oven was held at 30°C with the purge vent set at 1.9 mL/min.

Gas Chromatography Mass Spectrometry

An Agilent Technologies (Wilmington, DE) 6890 gas chromatograph equipped with a 5973 mass spectrometer was used for all measurements. Liquid injections were made using a 7673 autoinjector. The sample inlet used a Merlin Microseal™ port (Merlin Instrument Company, Half Moon Bay, CA) and SPME liner (Supelco, Bellefonte, PA). All samples were separated on an Agilent HP-5MS 5%-diphenyl-95%dimethylsiloxane capillary column. Data analysis was performed using Agilent MSD ChemStation™ software which was coupled to the NIST 98 mass spectrum library. The operating conditions are listed in Table 1.

TABLE 1—*GC-MS parameters.*

GC	
Inlet temperature	280°C
Inlet	Liquid injections: 0.1 μL, split mode, 1:200 split ratio Direct sampling of headspace: 5.0 μL, splitless SPME, headspace over neat gasoline: split mode, 1:50 ratio SPME, fire debris samples: splitless
Oven program	Initial 30°C for 1 min, ramp 7.5°C/min to 110°C, ramp 35°C/min to 280°C, hold 280°C for 2 min
Column	Agilent HP-5MS, 30 m × 250 μm × 0.25 μm
Column flow	He, 1.0 mL/min
Transfer line temperature	300°C
MS	
Mass range	40–400 m/z
Sampling rate	2.08 scans/s
Threshold	150 counts

Results and Discussion

There are several varieties of SPME fibers that are commercially available (26). Each possess a separate chemical composition with variable recovery efficiencies for different compounds. Several types of fibers have been tested for use in the headspace enrichment of volatile residues involving typical accelerants (17). Although most SPME fibers that were tested exhibited relatively poor recoveries for highly volatile compounds, a Carboxen/PDMS fiber was found to be the exception. Since gasoline is composed of more volatile components, the Carboxen/PDMS fiber was used for most experiments. A pure PDMS fiber, which is also useful in extracting volatile compounds, was also used in this study.

Recovery of volatile gasoline components by Carboxen/PDMS fibers was verified by comparing the chromatograms of a standard liquid injection of gasoline to samples extracted from the headspace over neat gasoline and gasoline placed on carpet (Fig. 1). These samples were chosen to give a representation of the actual composition of the gasoline (direct injection), the recovery gasoline components from the headspace over liquid gasoline (headspace extraction over neat gasoline), and the difference in recovery if the gasoline was found on a common building substrate (headspace sampling of gasoline on carpet). One of the outcomes of this initial comparison was that compounds separated after desorption from SPME fibers (Fig. 1, middle & bottom) eluted earlier than the compounds separated after direct injection (Fig. 1, top). In addition, the magnitude of the difference between corresponding peaks was inversely proportional with retention time. This chromatographic behavior strongly suggests that the components have some mobility through the GC column during the desorption time which is relative to their boiling point. Such a result is not surprising since the column temperature was 35°C throughout the 5 min desorption time and may explain why the most volatile components are absent from the SPME chromatograms. A desorption time of 5 min has been used in prior SPME investigations (14) and was used in this study to ensure complete desorption of volatile residues from the fibers so as to accurately assess the selectively of the absorption process. Desorption times of ca. 10 s or less are also routinely performed (12,13), and the results found here indicate that if retention times are to be used to draw conclusions, precise control of this variable may be important for reproducible chromatographic behavior unless the column temperature can be significantly lowered during desorption.

The comparison of SPME to direct injection (Fig. 1) also indicates that *significantly* fewer components are detected by microextraction than actually are found in the gasoline. Compounds having higher boiling points are extracted to a lesser degree which is consistent with previous data (17). Low boiling compounds are also not detected by microextraction. As noted above, these components most likely eluted from the column during thermal desorp-

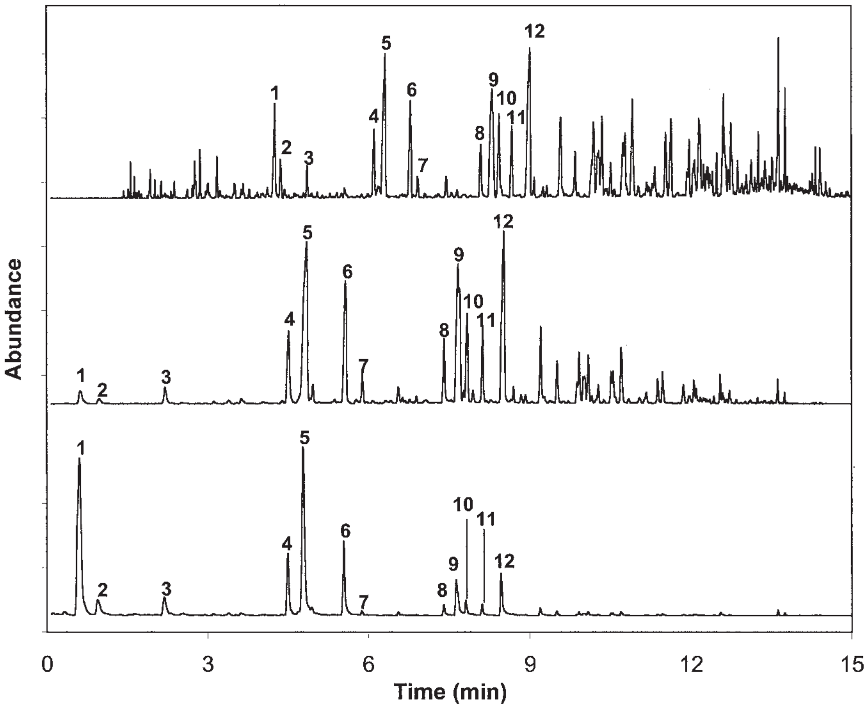

FIG. 1—*Comparison of gasoline component recovery by headspace SPME using a Carboxen/PDMS fiber.* Top: *Results obtained by direct injection of gasoline.* Middle: *Headspace sampling by SPME over neat gasoline.* Bottom: *Headspace sampling by SPME of gasoline on carpet. Peaks in the chromatograms correspond to: 1, toluene; 2, 3-methylheptane; 3, octane; 4, ethylbenzene; 5, 1,3- and 1,4-dimethyl benzene; 6, 1,2-dimethylbenzene; 7, nonane; 8, propylbenzene; 9, 1-ethyl-(2 or 3)-methylbenzene; 10, 1,3,5-trimethylbenzene; 11, 1-ethyl-2-methylbenzene; 12, 1,2,4-trimethylbenzene. All chromatograms are on the same scale.*

tion. If such were the case, cryogenic cooling of the column could allow these compounds to be detected. For compounds in the mid-boiling point range there appears to be some amount of preferential extraction. Mass spectral analysis indicates that the compounds extracted in greatest relative abundance by the Carboxen/PDMS fibers are aromatic hydrocarbons. Interestingly, the preferential extraction is more apparent in the chromatogram measured from headspace extraction above gasoline placed on carpet (Fig. 1, bottom). For instance, the nonane peak at 5.9 min almost disappears from the chromatogram. All but one of the major peaks in the chromatogram of the carpet headspace extraction at room temperature are single ring aromatic compounds. Although gasoline is primarily composed of aromatic hydrocarbons, the apparent selectivity in extracting aromatics would make a comparison of gasoline samples significantly more difficult, and in some cases impossible.

Preferential extraction was confirmed in further experiments by comparing the integrated peak areas obtained by SPME of the headspace at room temperature over an equal-molar mixture of 1,4-dimethylbenzene and nonane to results obtained by direct injection of the same headspace gas into the GC-MS. (These two compounds were chosen since they are both in the gasoline sample and have similar boiling points: 1,4-dimethylbenzene, 138°C; nonane, 151°C.) The ratio of the 1,4-dimethylbenzene:nonane peak areas was 1.4:1 by direct sampling, but was 2.5:1 using SPME. These results directly demonstrate that there is selectivity in the extraction of compounds from the headspace by the Carboxen/PDMS fibers.

The preferential extraction of aromatic species was further studied using a four component mixture of heptane, ethylbenzene, 1,4-dimethylbenzene, and nonane (boiling points of 98°C, 136°C, 138°C, and 151°C, respectively). A mixture of these compounds was chosen because they are: 1) common components in hydrocarbon fuels, 2) have similar boiling points and are present in the headspace in relatively similar amounts, and 3) can be resolved chromatographically. The extraction of these compounds was studied at different temperatures and with different fiber types (Table 2). In all experiments using SPME heptane was not detected although it was present in the headspace gas. This result clearly indicates that heptane elutes from the column during the thermal desorption step used in SPME analyses. Both the PDMS and Carboxen PDMS fibers show preferential extraction of the sample compounds from the headspace. The degree of the selectivity in the extraction of different compounds (aromatic vs. aliphatic) is dependent on temperature. The selectivity to extract aromatic compounds was calculated using the data for 1,4-dimethylbenzene by dividing the relative amount of 1,4-dimethylbenzene extracted using SPME by the relative amount found in the headspace. As shown in Table 2, Carboxen/PDMS fibers extract a greater amount of aromatic compounds compared to aliphatic species regardless of temperature, although the preferential extraction is greater at lower temperatures. The pure PDMS fiber type shows variable selectivity dependent on temperature. At 4°C the PDMS shows a slight preferential extraction of aromatics, while at 45°C the same material extracts nonane 2.4 times more efficiently than 1,4-dimethylbenzene from the headspace. Thus, careful control of temperature is critical if comparisons of relative or absolute abundance are to made between fire debris samples and accelerant standards.

Solid-phase microextraction of the fire debris at 80°C using Carboxen/PDMS fibers followed by GC-MS analysis generated complex chromatograms consisting of peaks corresponding to compounds produced by the combustion of the wood, paper, and carpet material in addition to residual accelerant if present (Fig. 2). The chromatogram of the control fire yielded a very similar chromatographic signature, although a lesser amount of low molecular weight aromatic hydrocarbons characteristic of gasoline were de-

TABLE 2—*Relative abundance values from a four component sample as detected by direct headspace/GC-MS compared to SPME/GC-MS. Selectivity for the extraction of aromatic compounds by SPME is listed.*

	Relative Abundance*				
Temp.	Heptane	Ethylbenzene	1,4-dimethylbenzene	Nonane	Selectivity for Aromatics†
Liquid injection					
25°C	0.51	1.33	1.35	1.00	
Direct headspace injection					
4°C	10.52	2.54	2.84	1.00	
25°C	7.96	3.13	3.70	1.00	
45°C	8.79	3.27	3.13	1.00	
SPME, fiber PDMS					
4°C	n/d‡	3.57	3.45	1.00	1.21
25°C	n/d	2.53	2.51	1.00	0.81
45°C	n/d	1.24	1.31	1.00	0.41
SPME, Carboxen/PDMS fiber					
4°C	n/d	4.02	4.77	1.00	1.67
25°C	n/d	3.15	3.93	1.00	1.28
45°C	n/d	2.89	3.42	1.00	1.09

* Relative abundance as compared to nonane measured by GC-MS and calculated using integrated peak areas. Precision is ±5% (relative standard deviation).

† Selectivity to aromatics is calculated as (relative abundance of 1,4-dimethylbenzene as detected by SPME)/(relative abundance of 1,4-dimethylbenzene in headspace) at each given temperature.

‡ n/d: not detected.

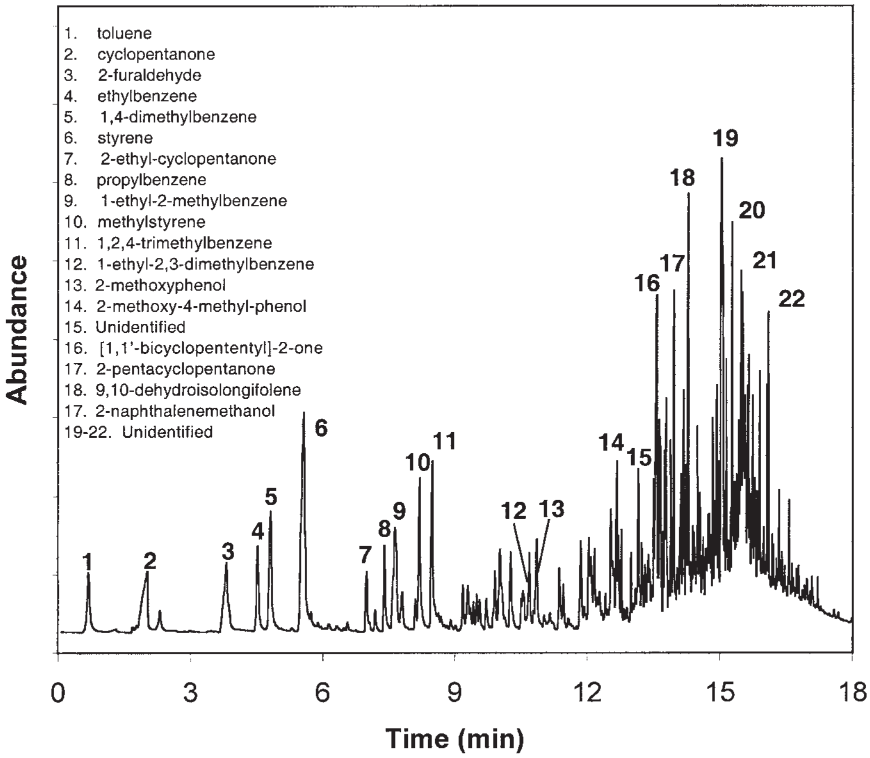

FIG. 2—*Chromatogram obtained from gasoline accelerated fire debris sampled by headspace solid phase microextraction using a Carboxen/PDMS fiber sample at 80°C. Listed are the compounds identified using mass spectrometry for the peaks indicated.*

tected by selected ion monitoring (results not shown). Mass spectral identification of the compounds in highest abundance in Fig. 2 determined that most are aromatic. The preferential extraction of aromatic compounds by the Carboxen/PDMS SPME fibers is apparently occurring, but without sufficient standards, quantitative or definitive claims cannot be made from this observation.

SPME is a simple and sensitive method for sampling the headspace of the fire debris samples. However, we encountered two experimental problems when using the fibers. First, the fibers are quite fragile and are prone to break if accidentally touched against fire debris. This was particularly true for the Carboxen/PDMS fiber. A more significant problem was the presence of background peaks that could not be eliminated by thermal cleaning. Before each measurement fibers were cleaned followed by a blank run to ensure that a good chromatographic baseline had been achieved. In some cases, the fibers could not be cleaned and showed extraneous and unusually shaped peaks in blank chromatograms. Mass spectral analysis identified several of these peaks as polysiloxane compounds which may indicate the decomposition of the fibers over time. These background peaks were never observed in new fibers and became problematic only after 10–20 repeat uses. Before this time the fibers showed no memory effects to measurement of a prior sample after thermal cleaning. The appearance of irreversibly poor backgrounds necessitated that a fiber be discarded. Storage of the fibers in Teflon sleeves did not prevent the eventual manifestation of this problem.

Conclusion

The results of this study indicate that while SPME is sensitive and easy to perform, there are some considerations that must be made when using the technique. The first is the selectivity of some fiber types to certain chemical species. The selectivity in the recovery of aromatic species through headspace microextraction using Carboxen/PDMS fibers may allow investigators to eliminate interferences that may be found in fire debris although it may hinder some analyses where recovery of aliphatic hydrocarbons is desired. The amount of enrichment of aromatic and aliphatic compounds from the headspace by PDMS fibers was particularly sensitive to temperature. Problems associated with the fragility of the fibers and irreproducible backgrounds are minor, but should be realized before using SPME.

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