

TECHNICAL NOTE**CRIMINALISTICS**

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Evaluation of a Headspace Solid-Phase Microextraction Method for the Analysis of Ignitable Liquids in Fire Debris

ABSTRACT: The chemical analysis of fire debris represents a crucial part in fire investigations to determine the cause of a fire. A headspace solid-phase microextraction (HS-SPME) procedure for the detection of ignitable liquids in fire debris using a fiber coated with a mixture of three different sorbent materials (Divinylbenzene/Carboxen/Polydimethylsiloxane, DVB/CAR/PDMS) is described. Gasoline and diesel fuel were spiked upon a preburnt matrix (wood charcoal), extracted and concentrated with HS-SPME and then analyzed with gas chromatography/mass spectrometry (GC/MS). The experimental conditions—extraction temperature, incubation and exposure time—were optimized. To assess the applicability of the method, fire debris samples were prepared in the smoke density chamber (SDC) and a controlled-atmosphere cone calorimeter. The developed methods were successfully applied to burnt particleboard and carpet samples. The results demonstrate that the procedure that has been developed here is suitable for detecting these ignitable liquids in highly burnt debris.

KEYWORDS: forensic science, arson analysis, fire debris, ignitable liquids, solid-phase microextraction, smoke density chamber, cone calorimeter

The detection and identification of ignitable liquids from fire debris is of primary concern for forensic fire investigations. Ignitable liquids, such as gasoline and diesel fuel, consist of high volatile and combustible organic compounds. Thus, due to the high thermal impact during the fire, samples taken from a fire site may contain only traces of the used ignitable liquid. However, to proof the presence of ignitable substances, the analysis of fire debris requires the volatile components to be extracted from the fire debris. Different extraction methods have been developed to meet this requirement: solid/liquid extraction (1), headspace sampling (2), using passive adsorbent materials like activated charcoal (3,4) or Tenax TA[®] and Carbotrap 300[®] (5) and solid-phase microextraction (SPME) techniques (6,7). The disadvantage of solvent extraction and headspace sampling is its high detection limit. For trace analysis, methods enriching the volatiles by using adsorbent materials, such as dynamic headspace sampling or SPME, are better suited to extracting the flammable substances. The determination of the ignitable liquid is performed by matching visual patterns with those known from ignitable reference liquids (8). Before analyzing the debris after a fire event within a fire investigation, it is impossible to predict the nature of the ignitable liquid applied. The challenges, therefore, are both the detection and the identification

of the substances used with only one analysis of the sample. In this study, we used gasoline and diesel fuel as flammable liquids. A mixture of these substances is commonly used in Germany to prepare a Molotov cocktail utilized to start a fire in terms of petrol bomb. These ignitable liquids contain different substances with a variety of components and different polarities:

- Gasoline: alkanes, alkylbenzenes, indanes, naphthalenes, etc.
- Diesel fuel: alkanes, cycloalkanes, alkylbenzenes, etc.

Because of the different polarities and volatility of these components it is necessary to choose an adsorbent material capable to cope with this requirement. In this study, a mixed polymeric stationary phase (Divinylbenzene/Carboxen/Polydimethylsiloxane, DVB/CAR/PDMS) for the SPME technique was selected to adsorb analytes of different polarities. It was, consequently, possible to investigate all tested ignitable liquids without changing the SPME fiber. For real fire investigations, this would be a main advantage to determine the possible presence of an unknown flammable liquid.

Methods

Materials

The ignitable liquids (gasoline and diesel fuel) were purchased from a local gas station. SPME was performed with a 50/30 μ m DVB/CAR/PDMS coated fiber housed in a manual holder (Supelco, Bellefonte, PA). The fiber was conditioned in a gas chromatography (GC) injection port at 270°C for 1 h prior to use. Particleboard (EUROSPAN[®]) was purchased from Egger (FRITZ EGGER GmbH & Co., Johann in Tirol, Austria) and

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cut into 10 cm × 10 cm × 1.6 cm pieces. Carpet samples (nylon-66) were from Vorwerk & Co. KG (Wuppertal, Germany) and cut into 10 cm × 10 cm × 1.6 cm pieces.

Sample Preparation

For the development of the HS-SPME method, solutions of pure ignitable liquids were prepared by diluting 10 µL of gasoline and diesel fuel in 10 mL acetone. Spiked wood charcoal samples were prepared by adding 10 µL of the gasoline and diesel fuel solution to *c.* 100 mg of the matrix. The spiked charcoal samples were added into a 20-mL vial equipped with a septum cap and were then filled with 2 mL ultra pure water. The addition of 2 mL ultra pure water was used to ensure equal headspace volume in each sample. Fire debris samples (particleboard, carpet) were prepared in the standardized reaction-to-fire setup smoke density chamber (SDC; DIN EN ISO 5659-2) and in an experimentally controlled atmosphere cone calorimeter (9–12) by using gasoline and diesel fuel as ignitable liquids. About 100 mg of the resulting debris was added into a 20-mL vial and provided with 2 mL ultra pure water. The sample to be analyzed was taken from the center of the burnt debris, which equates to the area where the highest thermal impact might have occurred.

Solid-Phase Microextraction

For the HS-SPME analysis, the fiber assembly was inserted into a septum capped 20-mL vial and the DVB/CAR/PDMS fiber was then exposed to the headspace of the spiked charcoal sample. The sample was conditioned in an incubation oven. Thermal desorption of the analytes occurred immediately after extraction by inserting the fiber into the GC injection port for 2 min at 250°C. Duplicate analyses were performed for each parameter. Blanks were run between each sample. No peaks were detected indicating that no carry over had occurred.

Instrumentation

Gas chromatography analysis was performed using a Shimadzu GC-2010 gas chromatograph (Shimadzu Europe GmbH, Duisburg, Germany) equipped with an Agilent DB-5MS (Agilent Technologies GmbH, Böblingen, Germany) capillary column (30 m × 0.25 mm × 0.25 µm) and interfaced with a Shimadzu QP 2010 Plus mass spectrometer. The split/splitless injector temperature was 250°C, and the helium carrier gas flow rate was set to 1.6 mL/min. The samples were injected with a split ratio of 1:10 and alternatively in splitless mode into a low-volume injection port sleeve with a CombiPal automated sampler (CTC Analytics AG, Zwingen, Switzerland). The transfer line between the GC and the MS was maintained at 310°C. The mass spectrometer equipped with an electron ionization source (70 eV), and a quadrupole mass analyzer was operating either in full scan mode (m/z = 50–500) or in SIM mode (m/z = 57, 91, 105, 117). The identification of the detected compounds was carried out by using the NIST 08 mass spectra library and by the comparison of retention times of standard compounds. The oven temperature was held at 50°C initially for 2 min, then increased at a rate of 20°C/min to 110°C, followed by a second temperature ramp of 30°C/min to 310°C and finally held for 1 min. The resulting data were analyzed with LabSolutions GC/MS solution Version 2.53 SU1© (Shimadzu Cooperation). The SDC and the controlled atmosphere cone calorimeter are manufactured by FTT Fire Testing Technology Ltd. (East Grinstead, U.K.).

Results and Discussion

Solid-phase microextraction is based on an equilibrium between the polymer-coated fiber and the sample. The impact of main parameters affecting the process of HS-SPME was evaluated by varying the extraction temperature, incubation and expo-

TABLE 1—Target compounds of the ignitable liquids and associated mass-to-charge ratio.

Ignitable Liquid	Target Compound	m/z
Gasoline	Toluene	91
	<i>m</i> -, <i>p</i> -Xylene	91
	Trimethylbenzene	105
	Indane	117
Diesel fuel	Dodecane	57
	Tetradecane	57
	Heptadecane	57
	Octadecane	57
	Eicosane	57

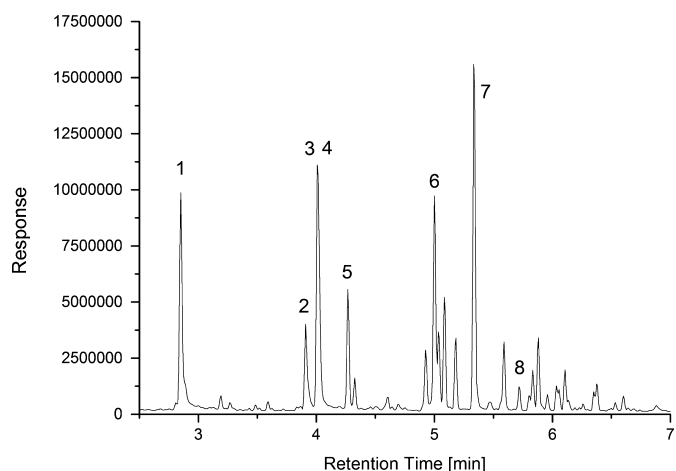


FIG. 1—Chromatogram (m/z 50–500) of a pure gasoline solution; labeled components: (1) toluene, (2) ethylbenzene, (3, 4) *m*-, *p*-xylene, (5) *o*-xylene, (6) ethylmethylbenzene, (7) trimethylbenzene, (8) indane (incubation time 5 min, exposure time 10 min, temperature 50°C).

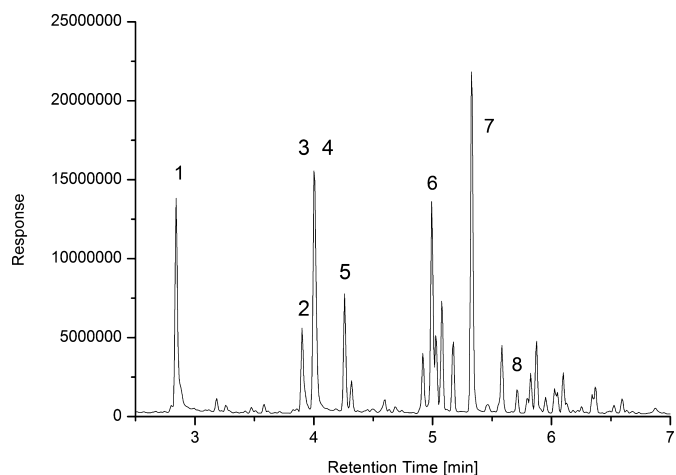


FIG. 2—Chromatogram (m/z 50–500) of a pure gasoline solution in 2 mL ultra pure water; labeled components: (1) toluene, (2) ethylbenzene, (3, 4) *m*-, *p*-xylene, (5) *o*-xylene, (6) ethylmethylbenzene, (7) trimethylbenzene, (8) indane (incubation time 5 min, exposure time 10 min, temperature 50°C).

sure time and subsequent GC/MS analysis. The variation of the main extraction parameters generates a compromise maximizing the success in detecting the selected target compounds. Target compounds for each ignitable liquid were selected to investigate the effect of different parameters by comparing the peak area of the respective extracted ion profiles (EIP) of the selected compounds. The selected compounds for the peak area evaluation and the associated mass-to-charge ratio for the ignitable liquids being tested are shown in Table 1. Figure 1 shows the HS-SPME chromatogram of the analyzed neat gasoline solution. The addition of ultra pure water does not change the recovery

rates of the target substances (see Fig. 2). Comparisons of ignitable substance chromatograms in water with chromatograms of spiked charcoal samples in water do not show significant differences that indicate that no partition of the initial ignitable liquids occurs.

Effect of Temperature

The rate of which analytes diffuse toward the fiber coating to be adsorbed is affected by the extraction temperature. With an enhanced extraction temperature, the extraction rate increases.

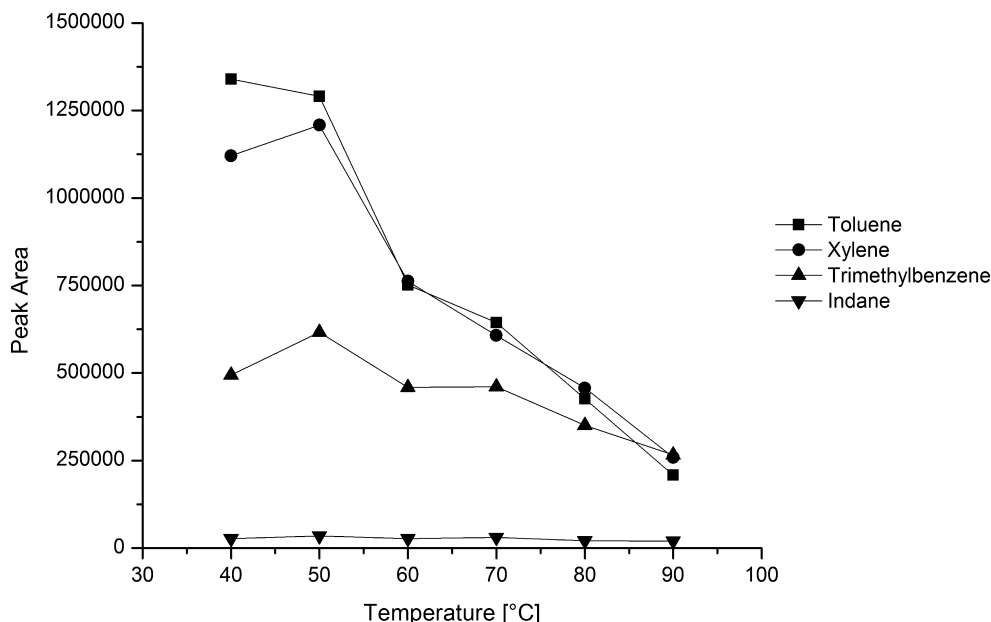


FIG. 3—Influence of temperature on the response of the selected target compounds of gasoline and HS-SPME (spiked wood charcoal samples, incubation time 5 min, exposure time 10 min). The decrease with increasing temperature is due to molecular weight, respectively, vapor pressure of the compounds. HS-SPME, headspace solid-phase microextraction.

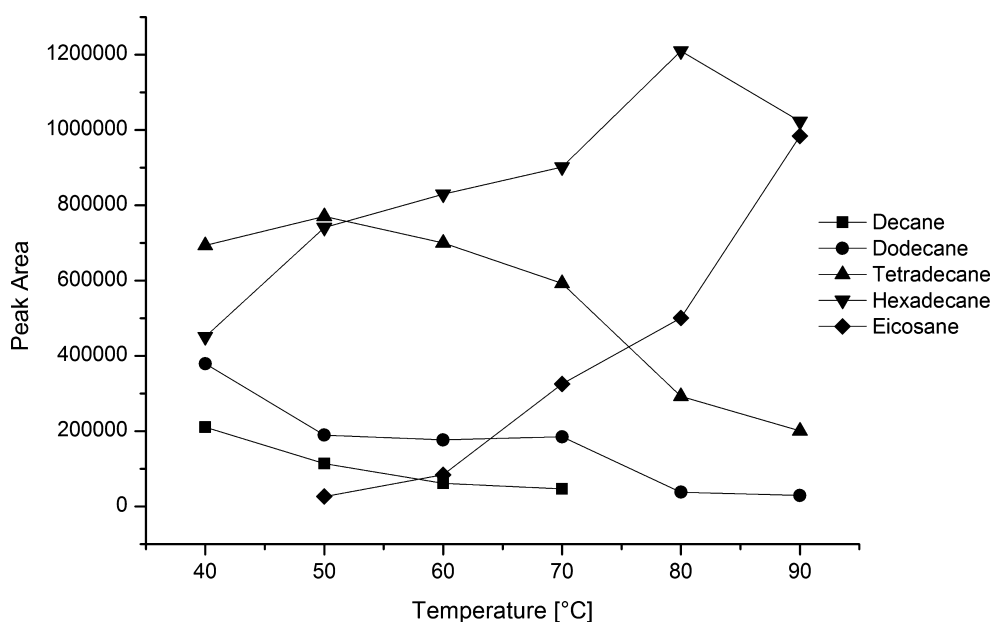


FIG. 4—Influence of temperature on the response of the selected target compounds of diesel fuel and HS-SPME (spiked wood charcoal samples, incubation time 5 min, exposure time 10 min, octadecane co-eluting with phytane). The increased recovery with increased temperature is due to the approaching equilibrium of the heavier compounds. HS-SPME, headspace solid-phase microextraction.

However, the distribution constant decreases with an increasing diffusion coefficient. By varying the extraction temperature between 40°C and 90°C while keeping the incubation and exposure time constant, the effect of the extraction temperature was investigated. Figures 3 and 4 demonstrate that the relationship between the temperature and the peak area of the selected target compounds. For gasoline, 50°C was found to be a good extraction temperature. A temperature of 70°C was chosen to analyze diesel fuel that consists of components with a wider boiling range (170–390°C). Here, at 50°C, the more volatile compounds like decane are detected in an acceptable yield, whereas the extraction rate of eicosane is very poor.

Effect of Incubation Time

The incubation time is the time to which the sample is conditioned in the incubation oven before the fiber is exposed to the headspace of the sample. The incubation time was varied between 10 sec and 10 min. The detected peak areas for the ignitable liquids differ only in a small range within the incubation times of 5 and 10 min (Figs 5 and 6). Five minute was selected as the incubation time for further experiments. Ten seconds seemed to be too short to produce reproducible results. The risk of a rupturing sample container and the subsequential loss of volatile compounds with an incubation time of ten minutes,

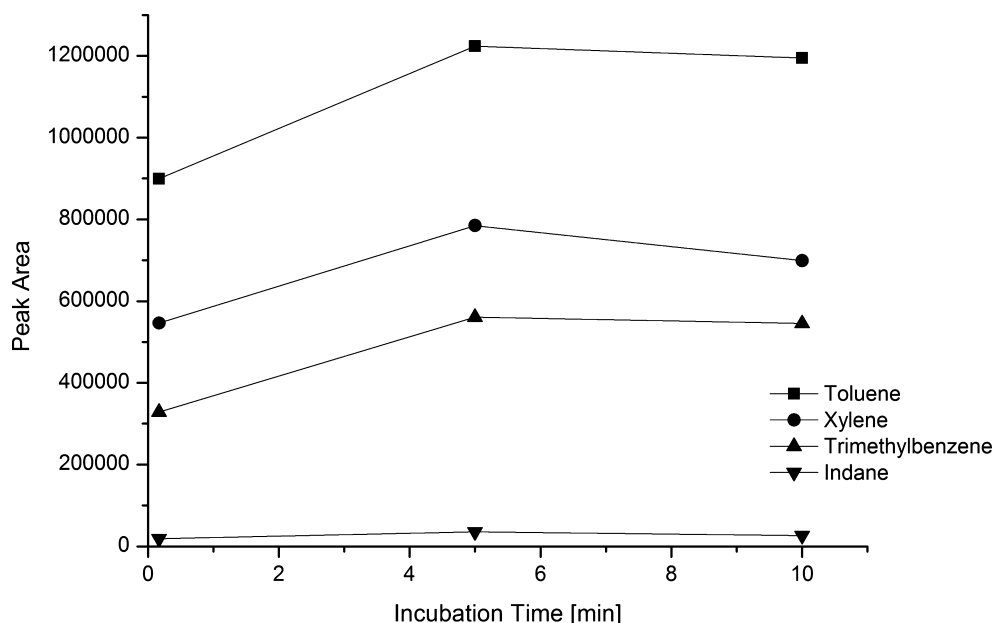


FIG. 5—Influence of incubation time on the response of the selected target compounds of gasoline and HS-SPME (spiked wood charcoal samples, exposure time 30 min, temperature 50°C). HS-SPME, headspace solid-phase microextraction.

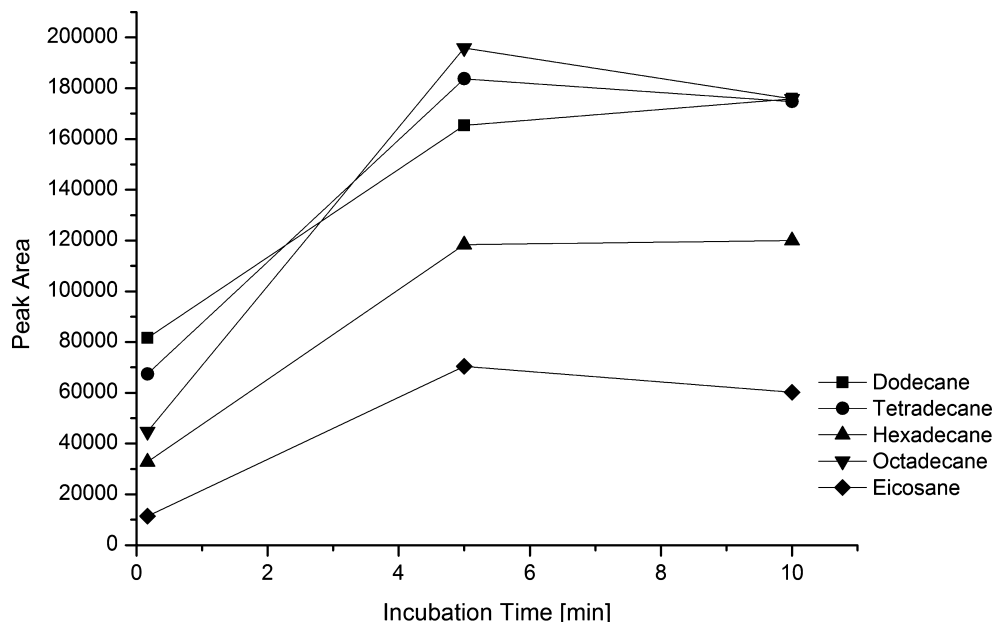


FIG. 6—Influence of incubation time on the response of the selected target compounds of diesel fuel and HS-SPME (spiked wood charcoal samples, exposure time 30 min, temperature 70°C, octadecane co-eluting with phytane). HS-SPME, headspace solid-phase microextraction.

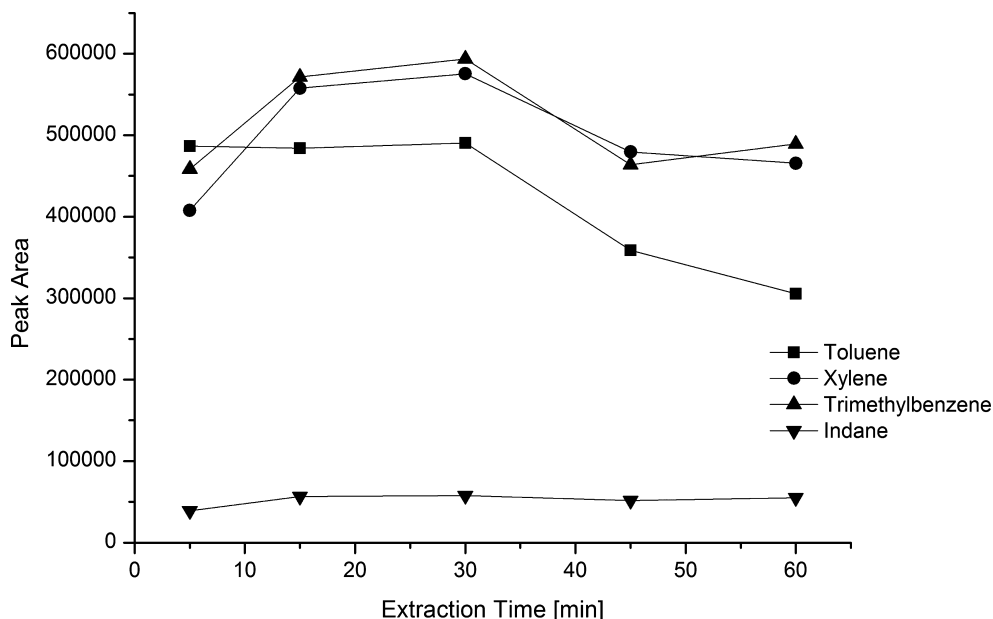


FIG. 7—Extraction time and corresponding peak area for the target compounds of gasoline (spiked wood charcoal samples, incubation time 5 min, temperature 50°C).

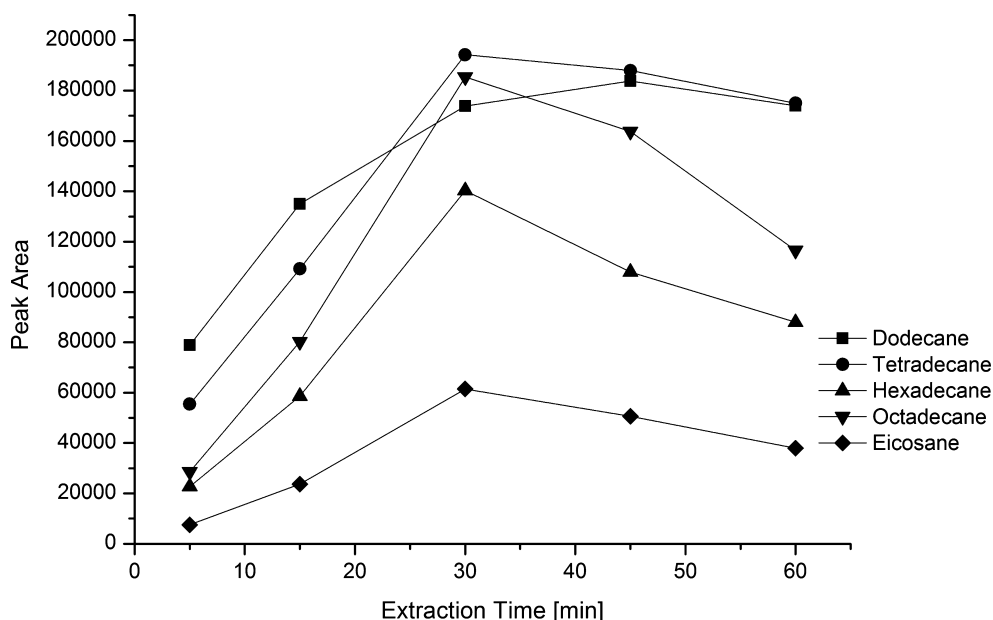


FIG. 8—Extraction time and corresponding peak area for the target compounds of diesel fuel (spiked wood charcoal samples, incubation time 5 min, temperature 70°C, octadecane co-eluting with phytane).

however, seemed to be preventable by choosing the shorter incubation time of 5 min.

Effect of Extraction Time

The SPME fiber's exposure time also affects the extraction rate. Detection can be difficult if the extraction time is too short. As soon as the fiber/headspace/sample system reaches equilibrium, it becomes static. However, the accomplishment of the equilibrium is sometimes inconsistent for an acceptable analysis time, and for SPME analysis, it is not necessarily required to

reach that equilibrium. To study the extraction time effect, the period of exposing the fiber to the headspace was varied between 5 and 60 min (Figs 7 and 8). For the ignitable liquids being tested here, 30 min of exposure time was determined to yield satisfying results.

Extraction of Ignitable Liquids from Fire Debris Samples

The developed HS-SPME methods were applied to fire debris samples. Particleboard and carpet samples—spiked with ignitable liquid—were exposed to horizontal thermal irradiation for

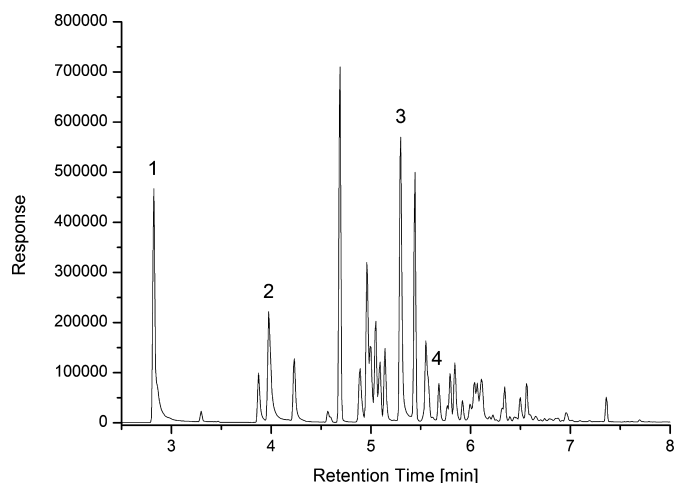


FIG. 9—Chromatogram (m/z 91, 105, 117) of a burnt carpet sample, spiked with gasoline (1 mL) and thermally exposed (SDC, 5 min, 25 kW/m^2); labeled components: (1) toluene, (2) *m*-, *p*-xylene, (3) trimethylbenzene, (4) indane. SDC, smoke density chamber.

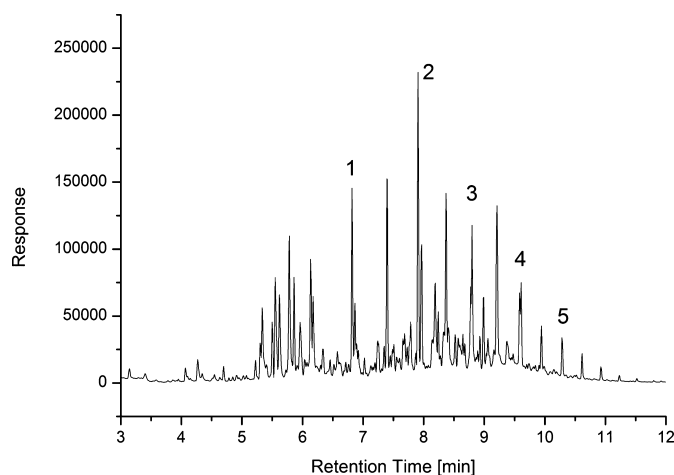


FIG. 10—Chromatogram (m/z 57, 71) of a burnt particleboard sample spiked with diesel fuel (1 mL) and thermally exposed (SDC, 20 min, 25 kW/m^2); labeled components: (1) dodecane, (2) tetradecane, (3) hexadecane (4) octadecane co-eluting with phytane, (5) eicosane. SDC, smoke density chamber.

5–20 min (at 25–50 kW/m^2) in the SDC and the controlled atmosphere cone calorimeter. Hundred milligram of the debris was analyzed with HS-SPME–GC/MS. The analyzed sample was taken from the center of the debris, which equates to the area where the highest thermal impact might have occurred. Figures 9–11 show the MIC-chromatograms of some burnt specimens that were spiked with ignitable liquid before thermal irradiation. Beside components of combustion products of the samples, ignitable substances could be detected with the developed HS-SPME–GC/MS-method. Visual pattern matching justifies the evidence of the used flammable liquids. When a mixture of gasoline and diesel fuel was used as ignitable liquid, the HS-SPME method parameters for gasoline were applied as a compromise to detect both ignitable liquids. To ensure that no semivolatile substances are missed, we recommend to analyze an additional part of the sample with an extraction temperature of 70°C.

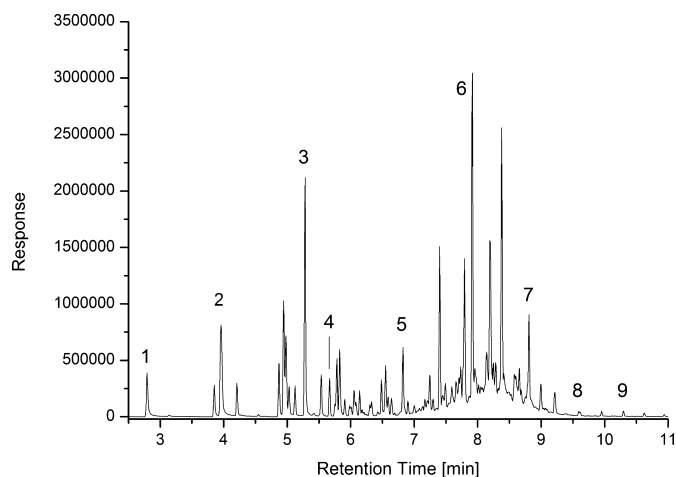


FIG. 11—Chromatogram (m/z 57, 71, 91, 105, 117) of a burnt particleboard sample, spiked with gasoline and diesel fuel (respectively, 2.5 mL) and thermally exposed (controlled atmosphere cone calorimeter, 5 min, 25 kW/m^2 with additional spark igniter); labeled components: (1) toluene, (2) *m*-, *p*-xylene, (3) trimethylbenzene, (4) indane, (5) dodecane, (6) tetradecane, (7) hexadecane (8) octadecane co-eluting with phytane, (9) eicosane.

Conclusions

For the volatile compounds of the investigated ignitable liquids (gasoline and diesel fuel), HS-SPME methods were developed using a mixed SPME fiber (DVB/CAR/PDMS). The feasibility of the recovery of ignitable liquids in residues from burnt particleboard and carpet samples were demonstrated. The best SPME conditions for gasoline detection were determined to be 50°C with an incubation time of 5 min and an exposure time of 30 min. For diesel fuel, the temperature should be adjusted at a higher level (70°C), with other parameters kept similar. The method developed here was verified by analyzing burnt specimens prepared in the SDC and the controlled atmosphere cone calorimeter. The ignitable liquid applied prior to the burning could be detected and identified in all samples. This applies even though the thermal exposure rate and exposure time were high and the samples were taken from the center of the burnt specimen, where the heat exposure might have reached highest levels. In experiments using a mixture of gasoline and diesel fuel before burning, it was possible to extract both ignitable liquids side by side and to identify each by GC/MS. Further investigations are due to elucidate the applicability of the procedure to detect a wider range of different ignitable liquids like lamp oil, paint or lacquer thinners. First experiments show promising results for the detection of denaturated spirits (containing mainly ketones as denaturing agents) with the presented procedure.

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