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A Solid-phase Microextraction Method for the Detection of Ignitable Liquids in Fire Debris

ABSTRACT: A solid-phase microextraction (SPME) procedure involving direct contact between the SPME fibers and the solid matrix and subsequent gas chromatography/mass spectrometric analysis for the detection of accelerants in fire debris is described. The extraction performances of six fibers (100 μm polydimethylsiloxane, 65 μm polydimethylsiloxane-divinylbenzene, 85 μm polyacrylate, 85 μm carboxen-polydimethylsiloxane, 70 μm Carbowax-divinylbenzene, and 50/30 μm divinylbenzene-Carboxen-polydimethylsiloxane) were investigated by directly immersing the fibers into gasoline, kerosene, and diesel fuel. For simulated fire debris, in the direct contact extraction method, the SPME fiber was kept in contact with the fire debris matrix during extraction by penetrating plastic bags wrapping the sample. This method gave comparable results to the headspace SPME method in the extraction of gasoline and kerosene, and gave an improved recovery of low-volatile components in the extraction of diesel fuel from fire debris. The results demonstrate that this procedure is suitable as a simple and rapid screening method for detecting ignitable liquids in fire debris packed in plastic bags.

KEYWORDS: forensic science, arson analysis, solid-phase microextraction, ignitable liquids, accelerants, fire debris, plastic evidence bag, gas chromatography, mass spectrometry

In Japan, arson has been the primary cause of fire for the past eight consecutive years, and financial losses because of arson and suspected arson were about 17.4 billion yen in 2004, accounting for almost 13% of total damage caused by all fires (1). In most arson cases, an ignitable liquid is used as an accelerant. Gasoline and kerosene are the most common accelerants used in arson cases in Japan because they are easily obtained from gas stations. In Chiba Prefecture, about 80% of arsons involve gasoline or kerosene. At fire scenes, local police investigators retrieve fire debris and seal it in a plastic bag with a fastener. To prevent ignitable liquids from evaporating, the bag containing the fire debris is wrapped in one or two additional plastic bags. The wrapped debris is then taken to a forensic science laboratory and tested for the presence of accelerants. Plastic bags have been much more widely used than metal cans or glass jars as fire debris containers. In Japanese forensic science laboratories, solvent extraction and sampling of headspace (HS) vapor have been the major methods for separation and concentration of ignitable liquids (2). Solvent extraction is time-consuming, and the use of potentially toxic organic solvents is inevitable. Headspace sampling, a simple and efficient procedure, has room for improvement in the extraction of low-volatility components.

Solid-phase microextraction (SPME) was developed in 1989 (3) and has been used as a sampling method for ignitable liquids in arson investigations (4–14). The method has been standardized by the American Society for Testing and Materials (ASTM) since 2002 (15). Solid-phase microextraction is a simple and rapid method of sample preparation. The SPME fiber is usually immersed directly to an aqueous solution or exposed to the HS of a matrix to adsorb the analyte (16). In arson investigations, headspace SPME (HS-SPME) has been mainly used for accelerant detection because fire

debris is usually a solid material with a complex composition, and it usually contains a lot of water. Direct immersion SPME (DI-SPME) was used for the recovery of accelerants from aqueous samples (17). Membrane protected SPME has been applied to recoveries from a complex or a dirty liquid matrix (18). Direct SPME extraction of analytes from an organic aqueous solution was reported (19). For SPME extraction from a solid matrix, a solid–liquid extraction technique such as leaching with solvents has been usually used prior to the direct SPME extraction (20). This method was applied to the determination of petroleum hydrocarbons in soil (21). Multiple HS-SPME extraction is an alternative for the extraction from a solid matrix; it eliminates the solid–liquid extraction step (20,22,23). However, an SPME method in which a fiber comes into a direct contact with a solid matrix, which could be possible because the water in fire debris does not interfere with the extraction of ignitable liquids by SPME, has not been reported so far. As noted before, fire debris is packed in plastic bags in Japan. Although plastic bags have some problems as fire debris containers (24), they are widely used because they are easy to store and transport. Direct contact between an SPME fiber and the fire debris can be achieved readily by piercing the plastic bags with the SPME needle. If such an extraction method is possible, it would become an easy and quick method because no other equipment except an SPME device is needed. An improvement in the recovery of low-volatility components could be expected by direct contact of the SPME fiber with ignitable liquids on the surface of the matrix unless background noise derived from the matrix increases. It would also be suitable as a screening method because the process is completely nondestructive; the evidence is kept intact in plastic bags during the extraction.

In this study, extraction of ignitable liquids by direct contact between the SPME fibers and the fire debris was investigated. In this paper, we called this method direct-contact SPME (DC-SPME). When the SPME fibers are in contact with the fire debris, the extraction behavior of the fibers toward ignitable liquids on the surface of the debris comes into the question; therefore, we

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investigated the extraction performance of SPME with bulk ignitable liquids. And since the distribution of ignitable liquids in the matrix would affect the extraction volume, the influence of sampling position on the extraction volume was examined. The extraction time for DC-SPME was optimized using a matrix containing accelerants. Under the optimized conditions, detection of fire accelerants from fire debris samples was carried out. The results were compared with results obtained by HS-SPME. To the best of our knowledge, this is the first report of direct extraction of ignitable liquids from a bulk matrix using SPME.

Methods

Materials

Gasoline (regular), kerosene, and diesel fuel were purchased from a local JOMO (Japan Energy Co.) station. Soil was purchased from a local gardening shop. Plastic bags with fasteners were purchased from Sei-Nichi (Tokyo, Japan). SPME was performed with 100 μm polydimethylsiloxane (PDMS), 65 μm StableFlex polydimethylsiloxane-divinylbenzene (PDMS/DVB), 85 μm polyacrylate (PA), 85 μm StableFlex Carboxen-polydimethylsiloxane (CAR/PDMS), 70 μm StableFlex Carbowax-divinylbenzene (CW/DVB), and 50/30 μm StableFlex divinylbenzene-Carboxen-polydimethylsiloxane (DVB/CAR/PDMS) fibers housed in a manual holder (Supelco, Bellefonte, PA). All SPME fibers were conditioned with a fiber conditioner (GL Science, Tokyo, Japan) under recommended conditions.

Sample Preparation

A matrix spiked with ignitable liquids was prepared by adding 100, 10, or 0.1 μL of gasoline, kerosene, or diesel fuel to 100 or 10 g of soil. The spiked matrix was then sealed in a plastic bag with a fastener, and the first bag was sealed in a second plastic bag and immediately subjected to the DC-SPME procedure. For HS-SPME, the spiked matrix was sealed in a 1,000 mL stainless steel can with a lid.

Fire debris samples were generated by burning small structures treated with gasoline, kerosene, or diesel fuel (13). The structures were built of alternating layers of wood and newspaper placed on a 1 cm layer of soil foundation. The structures consisted of four layers: a base layer of three equally spaced pieces of 1.8 cm × 1.8 cm × 30 cm cedar planks was topped with a 4 cm layer of wadded newspaper, three more cedar planks, and a second 4 cm layer of wadded newspaper. 50 mL of ignitable liquid was poured on top of the structure, which was immediately lit with a match. The fire was allowed to burn for 5 min and then extinguished with 1,000 mL of water. The fire was set in a fume hood at ambient temperature. After the fire was extinguished, the debris was collected using metal tongs and sealed in doubled plastic bags with a fastener or in a stainless steel can.

Solid-Phase Microextraction

Bulk ignitable liquids were extracted by immersing the SPME fiber directly into bulk gasoline, kerosene, or diesel fuel for 1 sec at ambient temperature. The whole fiber was immersed in the liquid.

For HS-SPME analysis, the fiber assembly was inserted into the HS of the stainless-steel can through a hole in the lid. The can was heated at 80°C on a heating plate (9), and the fiber was exposed to the HS for 15 min.

For DC-SPME analysis, the fiber assembly was inserted through the two layers of plastic bags, and the fiber was kept in a contact with the matrix at ambient temperature. After the extraction, the stainless steel tubing of the SPME fiber assembly was wiped with soft tissue to remove the matrix.

Immediately after the extraction, the fiber was inserted into the GC injection port and held there for 5 min to desorb the analyte.

GC-MS Analysis

All analyses were performed on an Agilent Technologies 5890N GC/5973N MSD GC-MS system equipped with a 7683 Series automatic liquid sampler (Palo Alto, CA). The GC was fitted with an HP-5MS column (30 m, 0.25 mm i.d., 0.25 μm thickness) from Agilent Technologies. Helium was used as the carrier gas at a flow rate of 1.0 mL/min.

For the analysis of gasoline, kerosene and diesel fuel, the column temperature was kept at 40°C for 5 min, ramped to 280°C at 5°C/min, held at 280°C for 3 min, and then ramped to 300°C at 5°C/min. For the evaluation of the optimum extraction time and for the analysis of the effect of sampling position for DC-SPME, the column temperature program was as follows: initial temperature 40°C and then ramp to 300°C at 15°C/min. The injector temperature was 280°C. The interface temperature was 260°C.

The injection was made either in a splitless or a split mode (10:1 or 100:1). The detector scanned in an m/z range of 35–650. The soil used as a matrix contains organic substances such as plant leaves. There exists the possibility of extracting organic compounds derived from these organic substances by the direct contact method. The scan range was expanded for higher mass in order to identify these compounds in case they were extracted.

Results and Discussion

Extraction of Bulk Ignitable Liquids by SPME

The extraction behavior of a fiber toward ignitable liquids in a liquid phase is of concern in the adsorption of ignitable liquids by means of direct contact between the SPME fiber and the solid matrix, because the fiber has a possibility of contacting directly to some of the ignitable liquids in the fire debris which is considered to exist on the surface of the debris in a liquid state. However, the extraction performance of SPME for bulk hydrophobic organic liquids has not been investigated, probably because the manufacturer recommends against soaking SPME fibers in nonpolar organic liquids to avoid deterioration of the fibers (25,26). The assessment of the extraction performance of SPME fibers for bulk nonpolar organic liquids is necessary for determining suitable fibers for DC-SPME. We supposed that short exposure of SPME fibers to bulk ignitable liquids would not damage the fibers. Six fibers were immersed in gasoline, kerosene, or diesel fuel for 1 sec at ambient temperature and were then immediately inserted into the GC-MS for analysis. The injection was made in a split mode (100:1). The total ion chromatograms (TICs) obtained from bulk extraction by SPME were compared with the chromatograms of directly injected ignitable liquids. Direct injection was carried out with an automatic liquid sampler. The injection volume was 0.2 μL, and the injection mode was split (100:1). Figure 1 compares the chromatograms obtained by liquid injection and by direct extraction with the SPME fibers. All the chromatograms are displayed at the same scale, except for those obtained by liquid injection, because the peak intensities of the liquid chromatograms were substantially larger than those of the fibers. The label C9 denotes the peak for
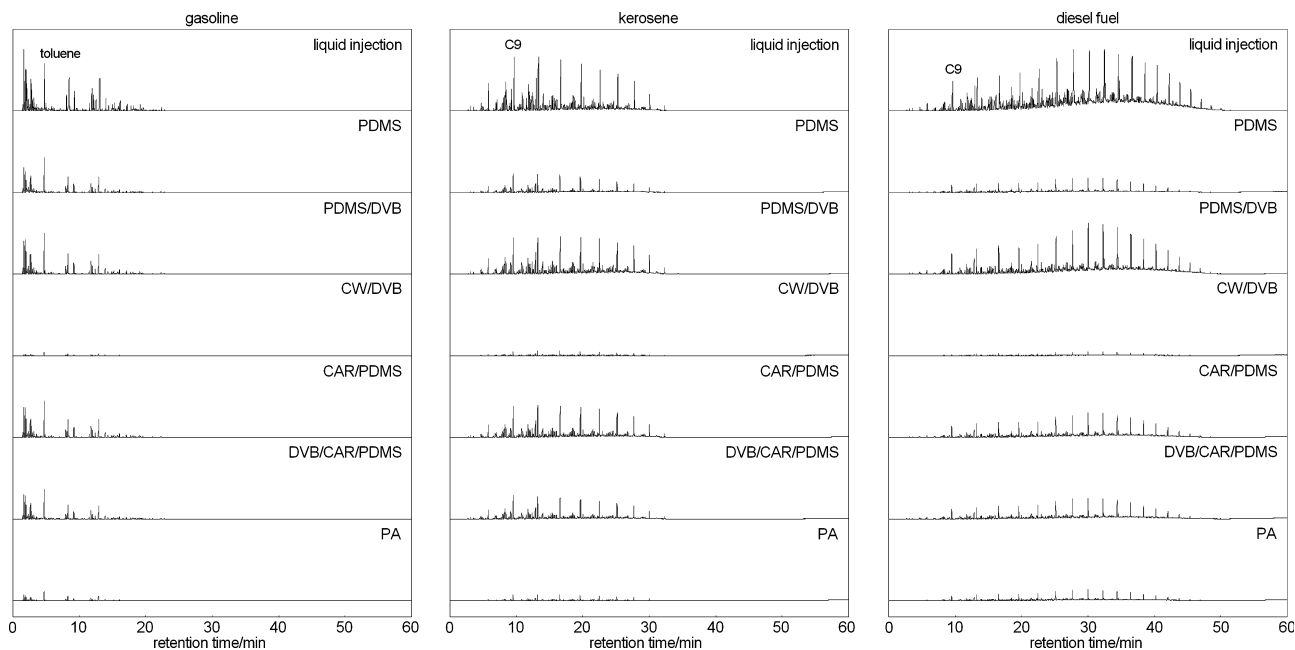
FIG. 1—*Total ion chromatograms for liquid injection and for extraction of ignitable liquids by direct immersion of various SPME fibers.*

TABLE 1—*Comparison of TIC area for direct-immersion extraction by SPME fibers (n = 5).*

	Ignitable liquid					
	Gasoline		Kerosene		Diesel fuel	
SPME fiber	Area*	RSD/%	Area*	RSD/%	Area*	RSD/%
Liquid injection	–	4.65	–	4.79	–	9.20
PDMS	1	5.16	1	3.43	1	5.34
PDMS/DVB	1.51	3.88	2.66	6.80	3.61	2.24
CW/DVB	0.09	3.50	0.17	1.60	0.30	1.29
CAR/PDMS	1.34	1.45	2.07	8.67	1.87	8.75
DVB/CAR/PDMS	0.94	5.16	1.24	5.12	1.52	4.94
PA	0.25	3.08	0.21	7.71	0.80	7.28

PDMS, polydimethylsiloxane; DVB, divinylbenzene; CW, carbowax; CAR, carboxen; PA, polyacrylate.
*Relative value to the TIC area of PDMS extraction was shown.

n-nonane. Table 1 shows the TIC areas and relative standard deviations (RSDs) of direct extraction with the SPME fibers (*n* = 5). The areas are shown as relative values to the area of PDMS extraction. RSD values of liquid injections are also shown. Each fiber showed different peak patterns and intensities. The PDMS/DVB fiber gave the largest responses for all three ignitable liquids. Peak heights of the PDMS, CAR/PDMS, and DVB/CAR/PDMS fibers, which were about the same in extracting gasoline, became smaller than those of the PDMS/DVB fiber in extracting kerosene or diesel fuel. The CW/DVB and polyacrylate fibers exhibited substantially smaller responses than the other fibers. Most of the SPME fibers gave RSD values better than those of liquid injections, and direct extraction offered good repeatability, indicating the SPME fibers withstood a short-time exposure to bulk ignitable liquids. In the case of diesel fuel, direct extraction by SPME fibers gave much better RSD values than liquid injection probably because the high viscosity of diesel fuel causes fluctuation in the ejected volume from the syringe in liquid injection.

To determine the degree of preferential extraction by the fibers, the total area of each chromatogram in Fig. 1 was unified, and divided according to the retention times (gasoline) or the peaks for normal paraffins (kerosene and diesel fuel). Then the area of each division was subtracted from the corresponding area in the chromatogram obtained by liquid injection. The results are shown in Fig. 2 (*n* = 5). The error bar indicates the range between the largest and the smallest values. A positive value indicates preferential extraction; the extraction efficiency of the component was high compared to that of the other components. A negative value indicates relatively low-extraction efficiency. Note that the figure does not indicate absolute quantities of extracted components; the values are relative. The shorter the bar, the smaller the deviation of the chromatogram from the true profile (chromatogram obtained by liquid injection). The figure shows that for the extraction of gasoline, the PDMS fiber preferentially extracted components with retention times shorter than 6 min, whereas the extraction efficiency of the PDMS fiber was lower for components with retention times longer than 8 min. The PDMS/DVB fiber showed preferential extraction at retention times between 0 and 2 min and between 4 and 8 min, and relatively low-extraction efficiency between 2 and 4 min and after 8 min. The CW/DVB fiber showed a random pattern of preferential extraction and inferior extraction. The CAR/PDMS fiber showed a pattern similar to that of the
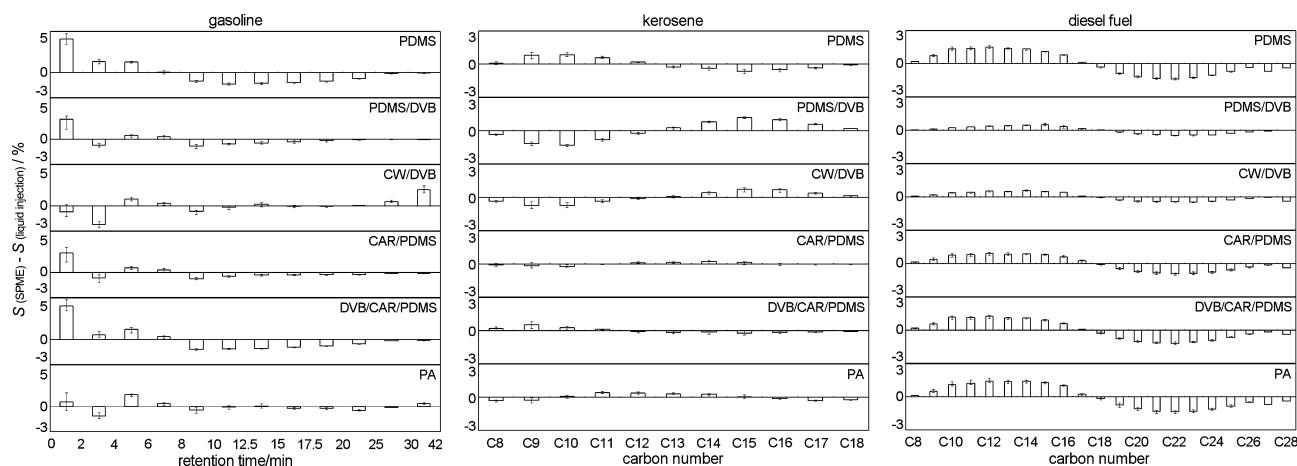
FIG. 2—*Deviation of chromatogram areas for ignitable liquids extracted by direct immersion of SPME fibers (n = 5).*

PDMS/DVB fiber. The DVB/CAR/PDMS fiber gave a similar pattern to that of the PDMS fiber. The polyacrylate fiber also exhibited a random pattern of preferential extraction and inferior extraction, though the deviation was smaller than that of the CW/DVB fiber.

In the extraction of kerosene, the PDMS and DVB/CAR/PDMS fibers showed the same extraction tendency: preferential extraction below C11 or C12, low-extraction efficiency over C12 or C13. The PDMS/DVB and CW/DVB fibers gave a same extraction pattern, and the selectivity was the opposite of that of the PDMS or DVB/CAR/PDMS fiber: low efficiency below C12, high efficiency over C13. The CAR/PDMS and polyacrylate fibers showed a similar pattern: low efficiency under C9 or C10, high efficiency between C10 or C11 to C15, and lower efficiency again over C16.

In the extraction of diesel fuel, all six fibers showed the same extraction pattern: preferential extraction below C17 and low-extraction efficiency over C18.

Deviation values (DVs) for the data shown in Fig. 2 were calculated from the following equation and listed in Table 2 (n = 5):

$$DV = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(S_{i(SPME)} - S_{i(\text{liquid injection})}\right)_i^2}$$

In this equation, n is the number of area divisions in the chromatogram (12, 11, and 21 for gasoline, kerosene, and diesel fuel, respectively), and S_i is the area of the ith chromatogram division; for example, $S_{I(SPME)}$ of gasoline is the area with retention times between 0 and 2 min in the chromatogram obtained by the direct SPME method.

TABLE 2—*Deviation values calculated for direct-immersion extraction by SPME fibers relative to liquid injection (n = 5).*

SPME fiber	Deviation value/%		
	Gasoline	Kerosene	Diesel fuel
PDMS	1.52	0.51	1.03
PDMS/DVB	0.82	0.82	0.32
CW/DVB	0.98	0.50	0.38
CAR/PDMS	0.79	0.16	0.65
DVB/CAR/PDMS	1.41	0.23	0.86
PA	0.66	0.30	1.02

PDMS, polydimethylsiloxane; DVB, divinylbenzene; CW, carbowax; CAR, carboxen; PA, polyacrylate.

For the extraction of gasoline, the polyacrylate fiber gave the smallest DV. The CAR/PDMS fiber was the best in DV for the extraction of kerosene. For the diesel fuel, the PDMS/DVB fiber gave the best DV. Though the DVs varied depending on what fiber to use and what ignitable liquid to extract, they were within the range from 0.23% to 1.52%. The result indicates that, for direct contact extraction of ignitable liquids, deviation from the TIC profile of liquid injection was not significant. In a practical screening test, it would be desirable to find a single fiber that could be used to detect all three ignitable liquids. The durability of the fiber is also important. The coating of the PDMS/DVB fiber immersed in ignitable liquids broke upon insertion in the GC injector even though it was a StableFlex fiber. The other fibers did not suffer damage during direct extraction. The CW/DVB and polyacrylate fibers were not suitable because extraction volume was substantially smaller. The PDMS and DVB/CAR/PDMS fibers exhibited the same extraction profile for gasoline, kerosene and diesel fuel: high efficiency for high-volatile components, low efficiency for low-volatile ones (Fig. 2). The CAR/PDMS fiber showed different patterns for each three ignitable liquids, though the DVs of the fiber were superior. These results of the PDMS fiber are in accordance with the results of HS-SPME extraction of ignitable liquids, producing the lowest distortion of the profile (9). On the basis of these recovery properties and usability such as robustness (13) and rapid desorption of the analyte (7), we considered the PDMS fiber to be the best for direct-contact SPME, and we used that fiber for further investigations.

Effects of the Sampling Position in the Matrix on DC-SPME

Ignitable liquids are supposed not to distribute uniformly in fire debris. This could be problematic when DC-SPME is employed. The SPME fiber comes into a contact with a very limited part of the matrix during direct contact extraction. The extracted amount would differ according to the volume of ignitable liquids that the contact position with the fiber retains. The effect of the sampling position on the extracted amount of ignitable liquids was evaluated. 100 g of soil was spiked with 100 μL of kerosene. Soil is the most common matrix found in fire debris in Japan. The spiked soil was sealed in a 10 × 14 cm plastic bag, which was sealed in another bag and used as a sample. The sample was extracted at five positions by DC-SPME as shown in Fig. 3. Extraction time was 15 min and the temperature was set at ambient, because heating of the matrix in a plastic bag leads to the evaporation of ignitable
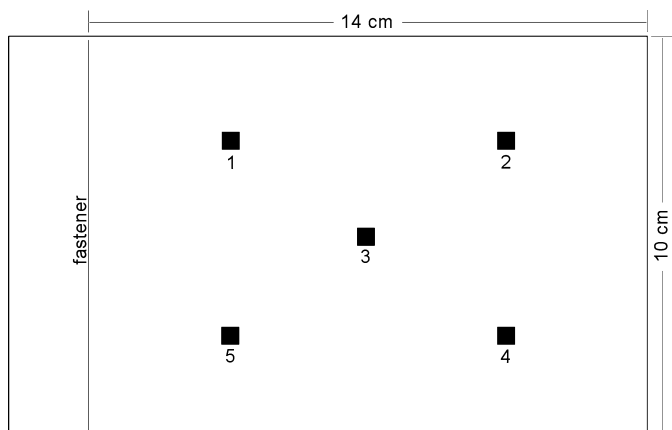
FIG. 3—*Diagram of sampling positions for DC-SPME extraction of kerosene-spiked soil matrix in plastic bag.*

FIG. 5—*Relationship between TIC area and extraction time for DC-SPME extraction of kerosene-spiked soil matrix (n = 3).*
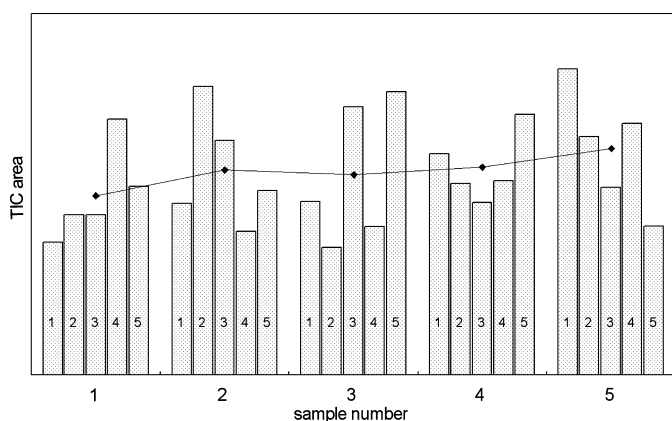

FIG. 4—*Relationship between TIC area and sampling position for DC-SPME extraction of kerosene-spiked soil matrix in plastic bag. The number in bar graph corresponds to the sampling position in Fig. 3. Line graph indicates the average area of 5 sampling positions in a sample.*

liquids. The split mode for the GC injection was 10:1. The extraction was carried out five times. Each time a new sample was prepared and used. The results are shown in Fig. 4. The bar graph indicates the extracted amount at each sampling position. The number in the bar refers to the sampling position in Fig. 3. The line graph indicates the average of extracted amounts at five sampling positions in a sample. Extracted volume was different from sampling position to position. The difference in the extracted volume was as large as twice in a sample. The average area was about the same among five samples. The result indicates that the soil matrix was not homogeneous with respect to the distribution of ignitable liquids. Even though the distribution of ignitable liquids was heterogeneous, false negative result was not encountered at any sampling point. Therefore, the direct contact method can be applied for the detection of ignitable liquids in soil matrix. The direct contact method is not suitable for the quantification of ignitable liquids, though, the concentration can be estimated by a multiple point sampling.

Evaluation of the Extraction Time for DC-SPME

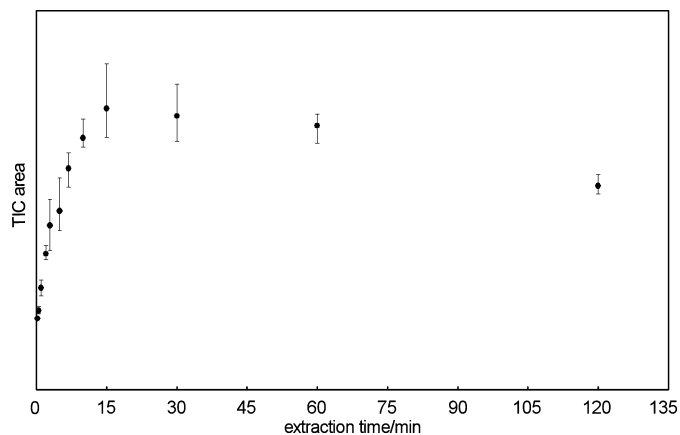The optimal extraction time for DC-SPME was determined. 10 g of soil matrix spiked with 10 µL of kerosene, which was sealed in two plastic bags, was used as a sample. The extraction temperature was set at ambient. The split ratio of GC injection was 10:1. The extraction time was changed from 15 sec to 120 min. The results are shown in Fig. 5 (*n* = 3). The error bar indicates the range between the largest and the smallest values. The total area of the chromatogram increased logarithmically as the extraction time increased and reached the maximum at 15 min. Extraction time longer than 30 min led to a decrease in the adsorption. A longer extraction time also resulted in the substitution of high-volatile compounds with low-volatile ones, and the pattern of the chromatogram changed. When the extraction time was shorter than 10 min, C9 gave the highest peaks. C10 was the highest at extraction times between 15 and 30 min, and C11 was the highest when the extraction time was longer than 60 min. As shown in Fig. 1, bulk kerosene gave C10 as the highest peak. On the basis of these results, we set the optimum extraction time at 15 min for DC-SPME.

Extraction of Ignitable Liquids from Soil Matrix by HS-SPME and DC-SPME

Ten microliters of gasoline, kerosene, and diesel fuel spiked in 10 g of soil were extracted by DC-SPME under the optimized condition (PDMS fiber and an extraction time of 15 min at ambient temperature). The HS inside the bag containing the matrix was also extracted by placing a SPME fiber in the bag without contacting the matrix at ambient temperature. The same sample was also analyzed by HS-SPME, and the results were compared with the DC-SPME results. The split mode for the GC injection was 10:1 for gasoline and kerosene, splitless for diesel fuel. The results are shown in Fig. 6. The chromatograms were displayed on the same scale. DC-SPME and HS-SPME method gave comparable results in extracting three ignitable liquids. On the other hand, very limited recovery was obtained by sampling HS inside bag, and the recovery was getting lower as the volatility of ignitable liquid decreased. The result indicates that the contact between the fiber and the matrix played an important role in increasing the recovery of ignitable liquids. None of the chromatograms obtained from the HS sampling inside bag were identifiable by ASTM criteria (27). The DC-SPME and HS-SPME chromatograms of gasoline and kerosene were identified by the ASTM standard while those of diesel fuel were not identifiable.

Figure 7 illustrates the chromatograms of the extraction of 0.1 µL gasoline, kerosene, and diesel fuel spiked in 10 g of soil by DC-SPME and HS-SPME method. The split mode for the GC
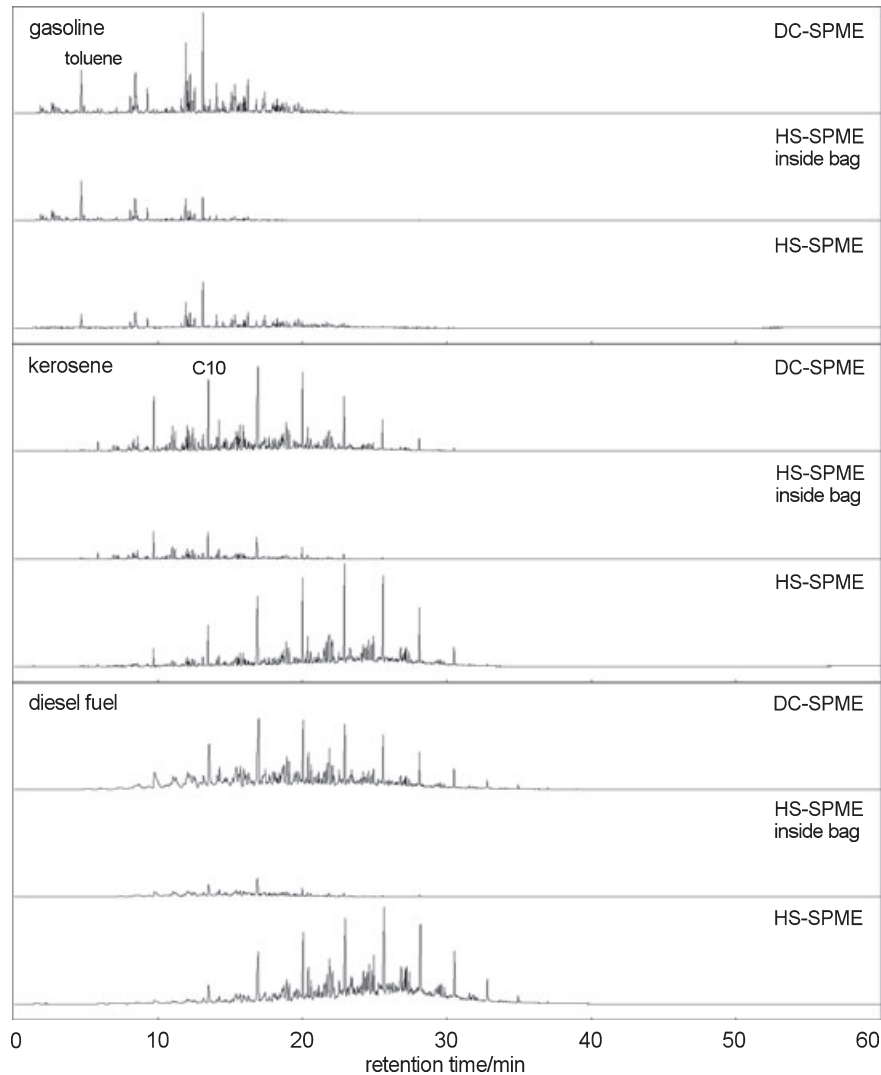
FIG. 6—*Total ion chromatograms for extraction of soil matrix spiked with 10 μL ignitable liquids.*

injection was splitless. The chromatograms were displayed on the same scale. In the chromatograms, some background signals, polydimethylsiloxanes (A1, A2 in Fig. 7) and butylated hydroxytoluene (BHT, B in Fig. 7), appeared. In the extraction of gasoline, DC-SPME gave clearly the signals of gasoline components while almost no signal of gasoline was observed in the HS-SPME chromatogram. The result gave a marked contrast with the fact that a 0.1 μL spike of gasoline on a cellulose wipe inside of a 1-gal can is detectable by HS-SPME method (15). Lighter components of gasoline were missing from the chromatograms probably because of the very limited volume of the spikes, absorption by the matrix, and the property of the PDMS fiber exhibiting relatively poor recoveries for highly volatile compounds (13). Although the DC-SPME chromatogram of gasoline was somewhat poor in resolution, the target compounds described in the ASTM standard (28) were identified in the chromatogram. In the extraction of kerosene and diesel fuel, DC-SPME gave very limited recoveries, especially for diesel fuel, compared with HS-SPME method. When the amount of spiked diesel fuel was increased to 1 μL, the recovery was improved and paraffins were detected up to C20 in the DC-SPME chromatogram. The HS-SPME chromatogram profile of 1 μL diesel fuel did not show much change from that of 0.1 μL diesel fuel. While only the HS-SPME chromatogram of kerosene was

identifiable by ASTM guideline among the chromatograms of kerosene and diesel fuel, some components of kerosene or diesel fuel could be observed in the DC-SPME chromatograms. Background signals were to some extent increased in the DC-SPME chromatogram, but they were found not to interfere the detection of ignitable liquids.

Extraction of Ignitable Liquids from Fire Debris Samples

DC-SPME was used for the extraction of ignitable liquids from fire debris samples. Because most of single-family houses are made of wood and because more than half of the fire cases involve wooden structures in Japan (1,29), we selected structures made of wood and paper for our tests. HS-SPME was also carried out for comparison. The GC injection mode was splitless for DC-SPME and split (10:1) for HS-SPME analysis. The results are shown in Fig. 8. Broadening of peak profiles at short retention times was observed in the DC-SPME chromatograms of gasoline and kerosene. This arises probably as a result of the splitless injection of the extracts. Fire debris contained a lot of water used as an extinguisher. During the extraction some water was transferred to the fiber, and the amount of the water on the fiber exceeded the capacity of splitless injection. It would be necessary to remove the water on the fiber
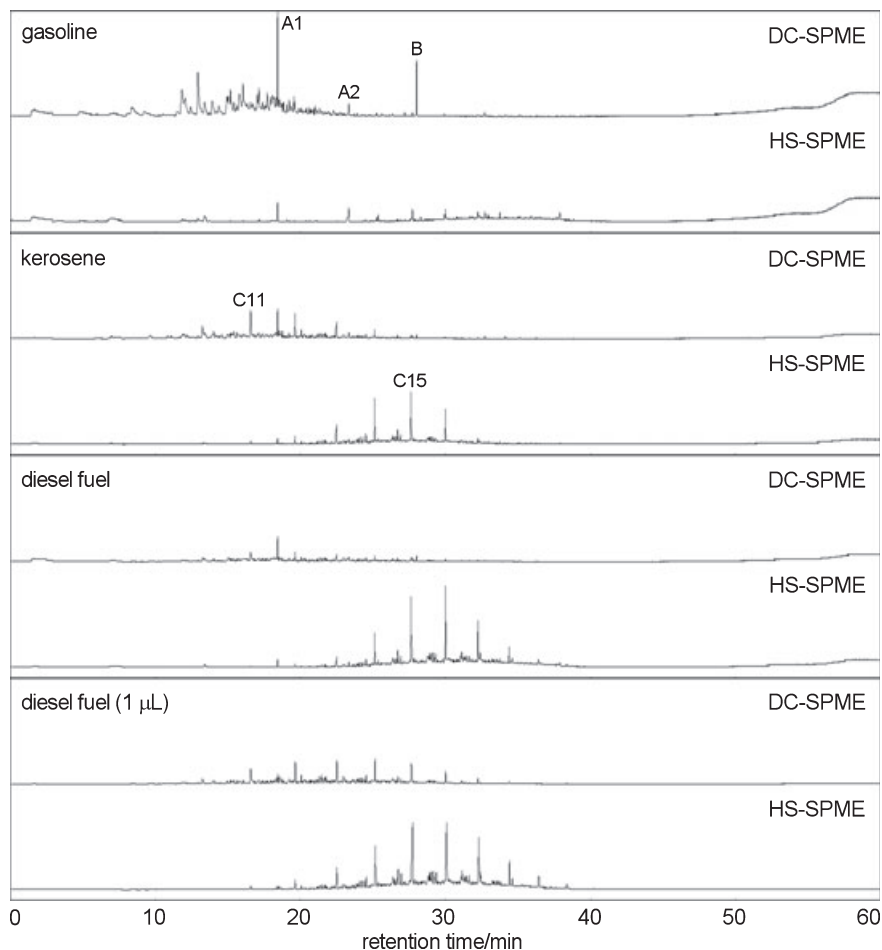
FIG. 7—*Total ion chromatograms for DC-SPME and HS-SPME extraction of soil matrix spiked with 0.1 µL ignitable liquids. A1, A2, polydimethylsiloxane; B, butylated hydroxytoluene.*

by wiping with soft tissue to prevent the phenomenon when split-less mode is used (17). In the extraction of gasoline, DC-SPME gave comparable results to HS-SPME in the abundance of peaks. DC-SPME exhibited high-extraction efficiency for components with long retention times. In the kerosene extraction by DC-SPME, peak intensities were lower, and the overall peak profile was almost the same as that observed with HS-SPME. HS-SPME extraction of gasoline and both HS-SPME and DC-SPME extraction of kerosene were identifiable by ASTM criteria. Part of the DC-SPME chromatogram of gasoline was poor in resolution, although, the target compounds described in the ASTM standard were identified in the chromatogram. In the extraction of diesel fuel, the signals were much smaller for DC-SPME than for HS-SPME, and the peaks of the background signals were significant in the DC-SPME chromatogram. Some of the background peaks were determined as polydimethylsiloxanes and BHT; however, the other peaks were not identifiable. By producing a mass chromatogram of ions 57, the background signals almost disappeared, and the alkane pattern of heavy petroleum distillates became apparent. While the HS-SPME chromatogram of diesel fuel was not identifiable by the ASTM standard, DC-SPME gave an identifiable chromatogram; the C20–C25 *n*-alkane which is diagnostic for diesel fuel was clearly visible in the mass chromatogram. DC-SPME method failed to extract these high-molecular weight alkanes in diesel fuel spiked in the soil matrix (Figs. 6 and 7). The improvement in the recovery of high-molecular weight alkanes in fire debris could be the effect

of water in the matrix. Furton et al. reported that significantly enhanced recoveries for high-molecular-mass compounds yielded by partial HS sampling of wet ignitable liquids (7). The fiber was not dipped in bulk water in DC-SPME, although, an extraction mode similar to partial HS sampling probably took place in DC-SPME extraction of fire debris containing water used for extinguishing the fire.

We were concerned about the durability of the SPME fibers and contamination of the fibers because the fibers were placed in direct contact with the matrix. However, in these experiments, all the DC-SPME extractions (more than 20 extractions) were carried out using a single PDMS fiber, and no noticeable breakage or increases in background peaks were encountered.

Conclusions

An SPME method involving a direct contact between a fiber and a solid matrix in the extraction of ignitable liquids was developed, and the optimal conditions were determined. Of the six SPME fibers tested, the PDMS fiber was found to be the most suitable based on the recovery property and usability for the extraction of bulk gasoline, kerosene, and diesel fuel, and an extraction time of 15 min at ambient temperature was optimal. Compared with HS-SPME, direct contact SPME showed a better recovery for gasoline and a very limited recovery for diesel fuel spiked in soil matrix when the spiked volume was small. On the other hand, recovery of
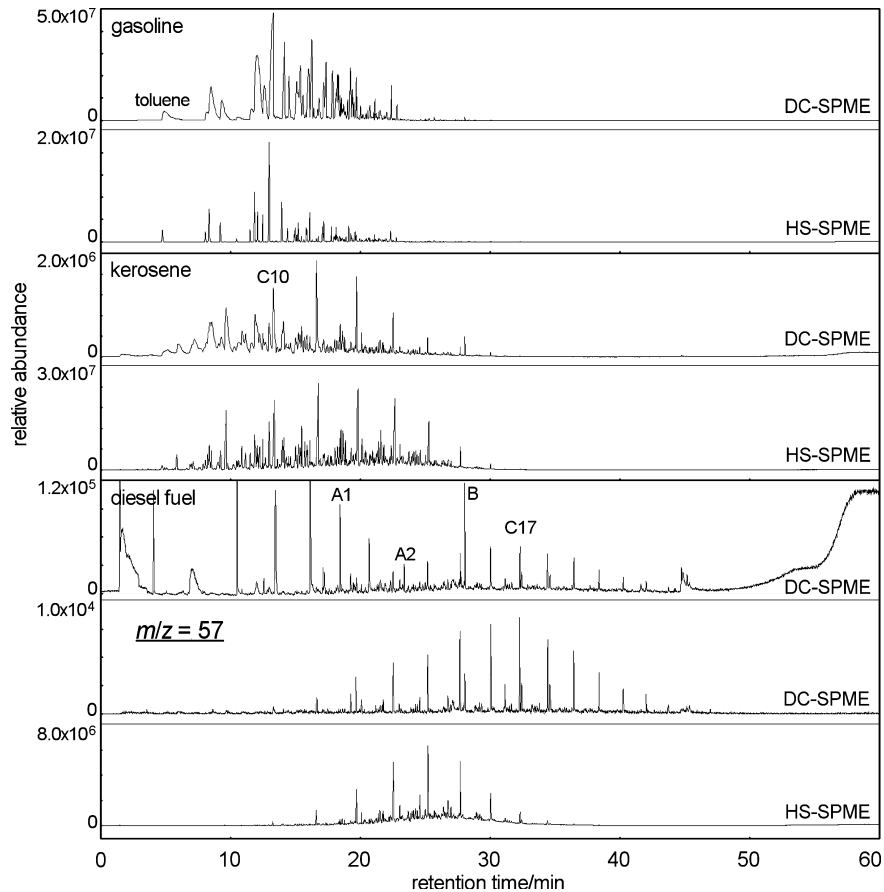
FIG. 8—*Total ion chromatograms for DC-SPME and HS-SPME extraction of ignitable liquids from fire debris samples. For DC-SPME extraction of diesel fuel, both TIC and mass chromatogram (m/z = 57) are shown. A1, A2, polydimethylsiloxane; B, butylated hydroxytoluene.*

low-volatile components in diesel fuel from fire debris was much higher for direct-contact SPME than for HS-SPME, which would be the effect of water in the matrix used as an extinguishing agent. Homogeneity of the sample was concerned in applying the direct contact method. The matrix was found to be heterogeneous with respect to the distribution of ignitable liquids, making the quantification impossible, nonetheless ignitable liquids were successfully detected regardless of the sampling position in the soil matrix. Repeated use of an SPME fiber was possible with this method. Direct-contact SPME could be useful for the extraction of ignitable liquids in fire debris wrapped in plastic bags. This method is also suitable as a screening method for forensic evidence because analysis at ambient temperature protects the evidence from degradation, making the re-analysis of the evidence by other methods possible.

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