

## A Novel Method for the Analysis of Gasoline from Fire Debris Using Headspace Solid-Phase Microextraction

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**ABSTRACT:** Solid-phase microextraction (SPME) has been adapted for the analysis of gasoline in fire debris. Compared to traditional passive headspace concentration (activated charcoal strip), the SPME method presented here was found to be faster, simpler and have a higher sensitivity. This method also eliminates the need for the highly flammable and toxic solvent carbon disulfide.

**KEYWORDS:** criminalistics, solid-phase microextraction, SPME, fire debris analysis, arson, gasoline

Solid-phase microextraction (SPME) is a fast, simple and sensitive technique which does not require the use of solvents and is readily automated (1,2). SPME involves the extraction of organic compounds from aqueous or gaseous samples into sorbent-coated silica fibers which can be transferred directly to the injector of a gas chromatograph. SPME has primarily been applied to the analysis of environmentally important organic contaminants, either directly from water or from the headspace above aqueous solutions (3,4). To the authors' knowledge, the use of SPME for the detection of accelerants from fire debris has not been attempted until now.

Established methods for sampling flammable or combustible liquid residues from fire debris samples include: screening methods such as static headspace sampling which is capable of detecting ca. 10  $\mu\text{L}$  of petroleum product (5) and concentration methods, including solvent extraction (6), dynamic headspace (7) and passive headspace (8) concentration which are capable of detecting ca. 0.1  $\mu\text{L}$  of liquid residues. The concentration methods all involve the desorption of residues with a volatile solvent, typically carbon disulfide, followed by analysis by gas chromatography (9). The concentration methods are somewhat cumbersome, time consuming, and use the highly flammable and toxic solvent, carbon disulfide.

One recently described solventless technique involves the use of a dynamic heated headspace procedure followed by on-line thermal desorption of the Tenax trap onto dual cryogenic units

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cooled with liquid nitrogen (10). Although this on-line thermal desorption method eliminated the need for  $\text{CS}_2$  it involved a somewhat elaborate experimental apparatus, a lengthy analysis time, and, due to the risk of overloading the column, required preliminary static headspace analysis in order to set the proper trap loading time. The goals of the present study were to develop a simple, rapid, solventless concentration method with sensitivity comparable to conventional concentration methods. Presently, we report a comparison of the developed SPME method to the activated charcoal strip (ACS) passive headspace concentration method (8).

### Experimental

Standard fixed volumes of Fina 87 octane gasoline were spiked on Kimwipes (Kimberly-Clark, Roswell, Georgia) and placed into aluminum quart cans (American International, Miami, Florida) and analyzed by the two methods described below. Gasoline spiked samples of burned pine and plastic were also analyzed to provide preliminary data on the utility of the SPME method in the presence of pyrolysis products.

#### ACS Procedure

An activated charcoal strip (ACS), 6.7-cm long by 0.9-cm wide (Pro-Tek, Portland, Connecticut) was cut into eight equal parts. Each piece was placed on a safety pin and suspended by a string inside a one quart aluminum can containing a fixed volume sample of Fina 87 octane gasoline on a Kimwipe. The can was heated in an oven at 80°C overnight (ca. 16 hours) and then allowed to cool to room temperature. The ACS was removed from the can and placed in a vial with 50  $\mu\text{L}$  of carbon disulfide (Fisher Scientific, Fair Lawn, New Jersey). The vial was centrifuged for one minute and 1  $\mu\text{L}$  of the extract was injected in the split mode into a Perkin Elmer 8420 gas chromatograph interfaced to a Perkin Elmer 7700 Data System (Norwalk, Connecticut).

#### SPME Procedure

The can containing the gasoline standard on a Kimwipe was sealed with a lid having a 6 mm septum (Fisher Scientific) and heated in an oven at 40°C for 30 minutes. The can was removed from the oven and a 100  $\mu\text{m}$  film thickness polydimethylsiloxane coated fiber which was previously retracted into the needle of the SPME holder (Supelco, Bellefonte, Pennsylvania) was inserted into the can through the septum. A photograph of the actual SPME assembly with the fiber used is shown in Fig. 1 (total length of holder and fiber = 21 cm). The plunger was then depressed, exposing the fiber to the headspace for ca. 20 minutes. The complete SPME experimental setup is illustrated in Fig. 2. The fiber



FIG. 1—Photograph of the SPME fiber and assembly used in this work.

was then retracted into the SPME needle and the assembly was removed from the can. The needle was inserted directly into the injection port of the Perkin Elmer 8420 gas chromatograph (Norwalk, Connecticut) and the plunger was depressed for ten seconds to desorb the analytes into the GC column (Hewlett Packard, Wilmington, Delaware). Injection was performed in the splitless mode with the split turned on 6 seconds after injection. Complete chromatographic conditions are listed in Table 1. The fiber assembly was cleaned between injections by allowing the fiber to remain in the heated injector of the GC for ca. 5 minutes after the splitter was turned on.

### Results and Discussion

The amount of liquid residues extracted by SPME is governed by the equilibrium which is established between the polydimethylsiloxane phase on the microextractor fiber and the heated headspace

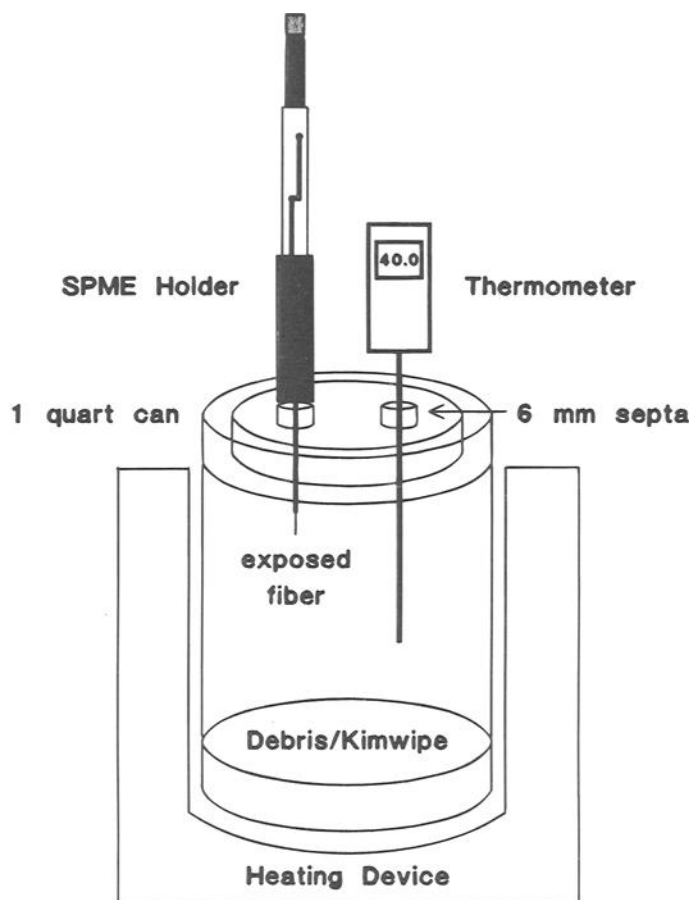


FIG. 2—Schematic diagram of the experimental setup for this work.

TABLE 1—Gas chromatographic conditions used in this study.

Column	HP-1, 30 Meter, 0.25 mm ID, 0.25 $\mu$ m film thickness
Injection Port Temperature	220°C
Oven Program	Initial 35°C, 2 min, Ramp <sub>1</sub> 10°C/min to 220°C, hold 2 min, Ramp <sub>2</sub> 30°C/min to 300°C, 5.0 min
Detector Temperature	300°C
Splitless Mode (SPME), (ACS injections were Split)	Split was turned on 6 sec after injection and holder was removed from the injection port 4 sec later
Gas Flows	1 mL/min, 50:1 split ratio
Injection Port Sleeve Size (SPME)	Low Volume, (2 mm)

above the fire debris. Previous workers (3) have shown that, for similar compounds, the equilibration time is very rapid (40 seconds to 2 minutes for benzene, ethylbenzene, toluene and xylene). The sample amount is limited by the adsorptive capacity of the polydimethylsiloxane coated fibers allowing for some concentration of the headspace compounds while reducing the potential problem of column overloading, which can be a problem with other concentration methods. The limited amount of analytes extracted with each sampling step also allows for multiple analysis of fire debris samples, such as that reported recently for the ACS method using an unknown concentration of flammable or combustible liquids

found in actual cases (11). Although the amount of analytes recovered by SPME may be relatively small compared to conventional methods, the entire extract is desorbed into the injection port of the GC for analysis, thus yielding high sensitivity as there is no analyte lost due to sample transfer or handling.

For the present study, a series of n-alkanes (C-7 to C-14) were used for "mapping" chromatograms with respect to retention times for these alkanes and the resulting carbon "map" was superimposed below the retention times to facilitate identification of the individual gasoline components. The chromatogram for the standard aromatic mixture used in this study and a chromatogram for a 1  $\mu$ L injection of a 5% v/v mixture of gasoline in carbon disulfide are compared in Fig. 3. Table 2 lists the aromatic compounds used as standards in this study and also serves as a key to the peaks labeled in Figs. 3-6. A blank was run between all samples for both ACS and SPME extractions and no peaks were detected, indicating no carryover was occurring using either method.

Figure 4 compares the chromatograms obtained via the standard ASTM ACS extraction method to that observed with the SPME method described for a 5  $\mu$ L sample of gasoline in a one quart can using the same GC and conditions to analyze the extracts. It is apparent that all of the same components are recovered by SPME (the solvent CS<sub>2</sub> is missing since no solvent is required for SPME) although the relative amounts are different and the total amount is greater for SPME compared to the ACS method. When the chromatograms are scaled to include the majority of the peaks of interest, the voltage scale (using the FID electrometer at attenuation of 16 for all readings) for the SPME extract is ca. 40% larger than that for the ACS extract illustrating the greater sensitivity of the SPME method under the conditions employed. Similarly, Figures 5 and 6 compare ACS and SPME extractions for cans spiked with a 1  $\mu$ L and 0.1  $\mu$ L gasoline, respectively. Again, the SPME extracts generally showed a significantly greater FID response when compared to the ACS extracts, and a corresponding increase in sensitivity.

The magnitude of the increase in FID response, for the SPME extracts relative to the ACS extracts was dependent on the boiling point range of the analytes, increasing with increasing boiling point (corresponding to an increase in retention time using a non-polar gas chromatographic stationary phase) as seen in Table 3. For example, comparing the relative response for the two methods (SPME FID volts/ACS FID volts) for ethyl benzene (peak 3), n-butylbenzene (peak 9) and 2-methyl naphthalene (peak 11) yield average relative responses of 1.1, 7.7 and 44.7 respectively, for an overall average increase in response of over an order of magnitude for SPME relative to ACS. The net result observed was an increase in sensitivity by SPME for the higher boiling components which are typically more difficult to detect at low concentrations by ACS. The SPME method produced acceptable and identifiable chromatograms from cans spiked with as little as 0.04  $\mu$ L of gasoline. This amount was significantly less than the 0.1  $\mu$ L of gasoline which is the normal lower limit employing the ACS technique. It is important to note that the SPME results are compared to the current ACS method in use at the Metro-Dade Police Department and in common use around the country employing split injection. It is possible that the sensitivity of the current ACS method could be improved by concentration of the CS<sub>2</sub> extract, cold on-column injection, etc., although this is beyond the scope of our study.

The increased average relative response for the higher boiling compounds analyzed by SPME is due in part to the fact that the SPME method produces patterns that are skewed to the high boiling end of the chromatogram under the conditions employed. This

skewing towards the high boilers could be due to a 'replacement' effect similar to that observed for the ACS method when sampling is occurring over too long a period of time and heavier hydrocarbons replace the lighter ones already adsorbed. Alternatively, the equilibrium established between the polydimethylsiloxane phase on the microextractor fiber and the heated headspace above the fire debris may simply favor the higher boiling components under the experimental conditions employed. It is possible that the sensitivity of the proposed SPME method can be improved and distortion of the chromatograms towards the high end minimized by adjustments in experimental variables, including decreasing fiber exposure time, changing the fiber film type, film thickness, employing cryogenic focusing, etc. and research is ongoing to investigate these and other experimental variables.

In addition to the improved sensitivity, the analysis time is significantly reduced using the SPME method compared to the ACS technique. Our sample throughput was limited by the equilibration time of the GC instrument, hence a sampling time of 20 minutes was used, although previous studies indicate that much shorter sampling times may be used (3). This is a significant improvement in the sampling time compared to the ACS method which typically employs overnight (such as, 16 hours) heating/sampling. The SPME method is also very inexpensive. After the initial investment for the purchase of the SPME sample holder for ca. \$160.00, fiber assemblies can be purchased at a cost of ca. \$40.00 each and, with care, can be reused for over 80 injections yielding an average cost of less than \$0.50 per injection. This makes the SPME technique cost effective with the ACS method which uses charcoal strips costing ca. \$4.00 each, cut into eight pieces bringing the cost to \$0.50 per strip and also requires the purchase and disposal of the CS<sub>2</sub> solvent used.

The fact that the SPME technique is solventless is one of its greatest advantages, not only eliminating solvent and disposal costs but also eliminating the exposure of workers to toxic solvents. Although other solventless techniques such as the automated on-line thermal desorption technique (10) have been reported, the SPME concentration method precludes the possibility of GC column overload when high levels of accelerants are present since sampling by SPME is an equilibrium condition with a thin sorbent film. We have also found that multiple analysis from the same spiked can were possible similar to that reported recently for the ACS technique (11). The fact that only the amount of accelerants required for a single GC run is sampled by the SPME method makes this method ideally suited for multiple sampling while maintaining the integrity of the specimen.

Finally, we have not observed any significant SPME equilibrium effects when pyrolysis products of wood and synthetic materials commonly present in fire debris are included as a background. We have had no problem in performing multiple SPME analyses of gasoline spiked on pyrolyzed backgrounds, including burnt pine and burnt polyethylene plastic. The chromatograms of two successive SPME analyses of gasoline spiked on burnt polyethylene are compared in Fig. 7. The chromatograms of two successive SPME analyses of gasoline spiked on burnt wood are compared in Fig. 8. Figures 7 and 8 clearly demonstrate the ability of the SPME method to provide reproducible multiple analyses and the lack of any significant interfering equilibrium effects when volatile pyrolysis products are present in the sample.

## Conclusions

Compared to the established ACS passive headspace concentration technique, the headspace SPME technique described here has

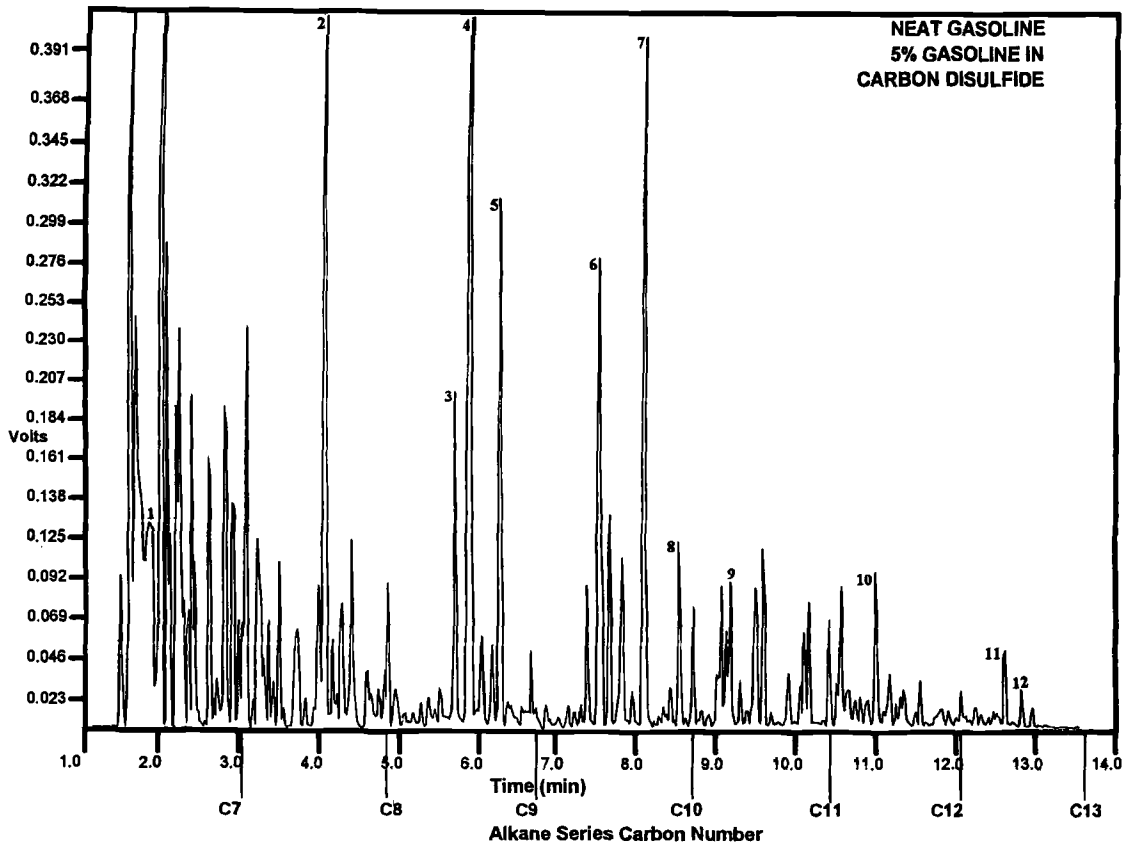
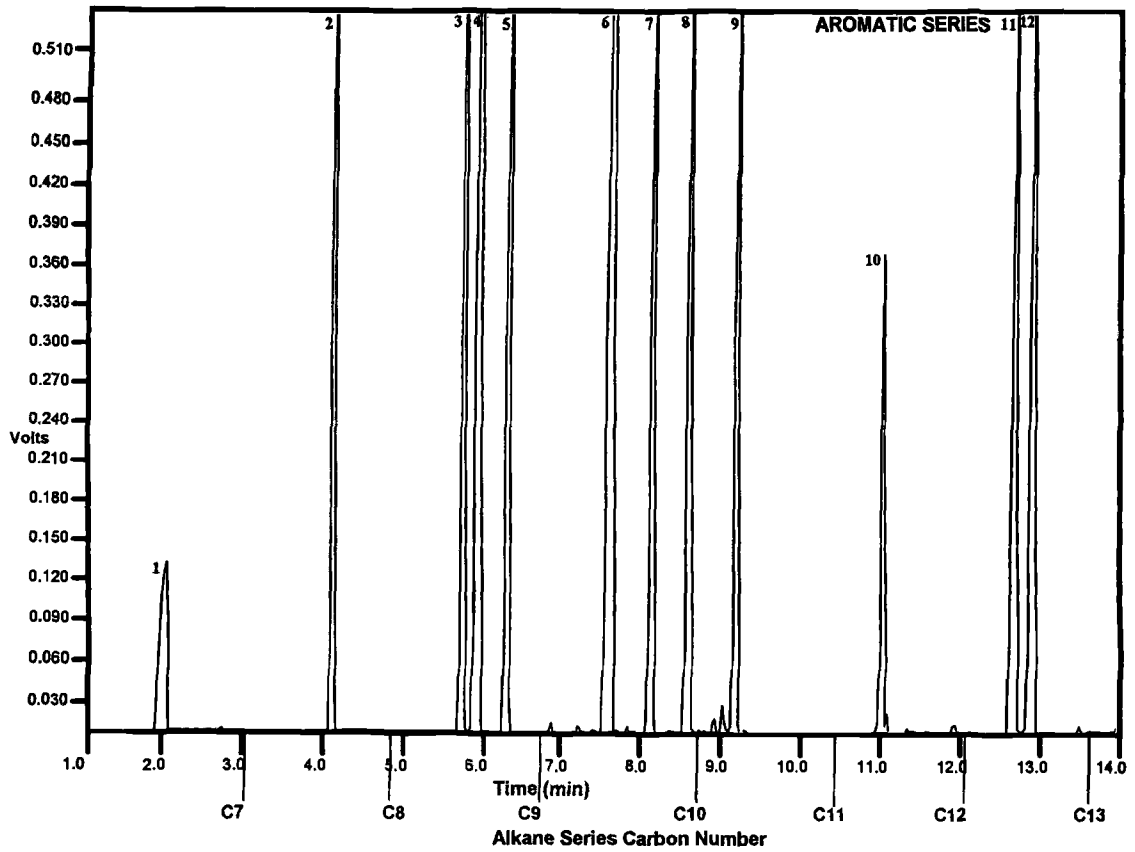
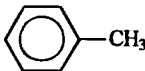
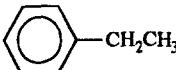
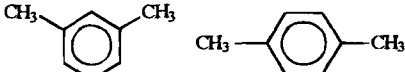
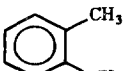
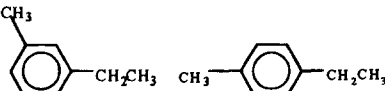
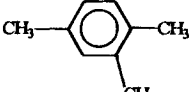
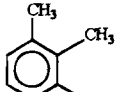
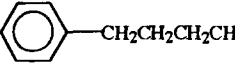

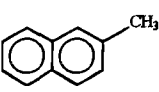
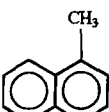


FIG. 3—Chromatograms of the aromatic series of compounds (TOP) and 5% v/v gasoline in CS<sub>2</sub> (BOTTOM) with n-alkane series labeled along with retention times. (Peak identity in Table 2.)

TABLE 2—Key to the peak identification of aromatic compounds used in this study.

Peak Number	Name of Compound	Chemical Structure
1	Carbon disulfide	S=C=S
2	Toluene	
3	Ethylbenzene	
4	m & p-Xylene	
5	o-Xylene	
6	m & p-Ethyltoluene	
7	1,2,4 Trimethylbenzene	
8	1,2,3 Trimethylbenzene	
9	n-Butylbenzene	
10	Naphthalene	
11	2-Methylnaphthalene	
12	1-Methylnaphthalene	

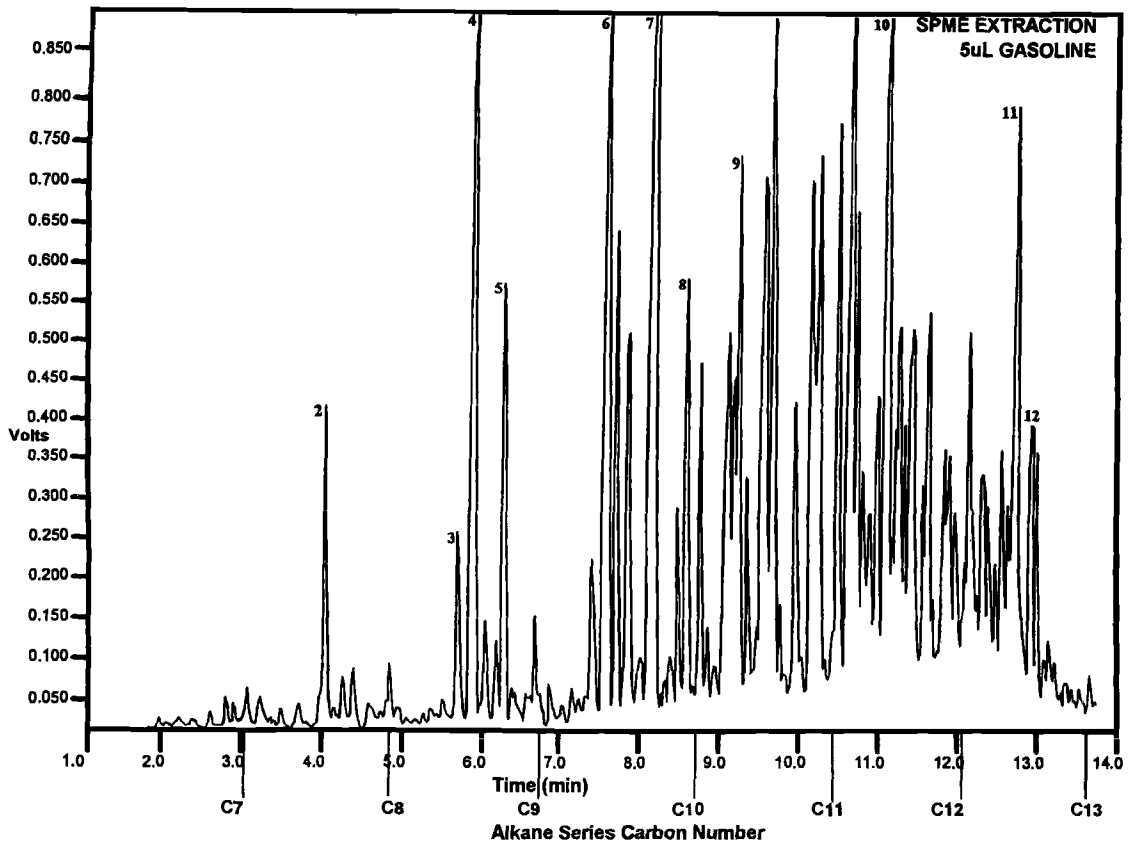
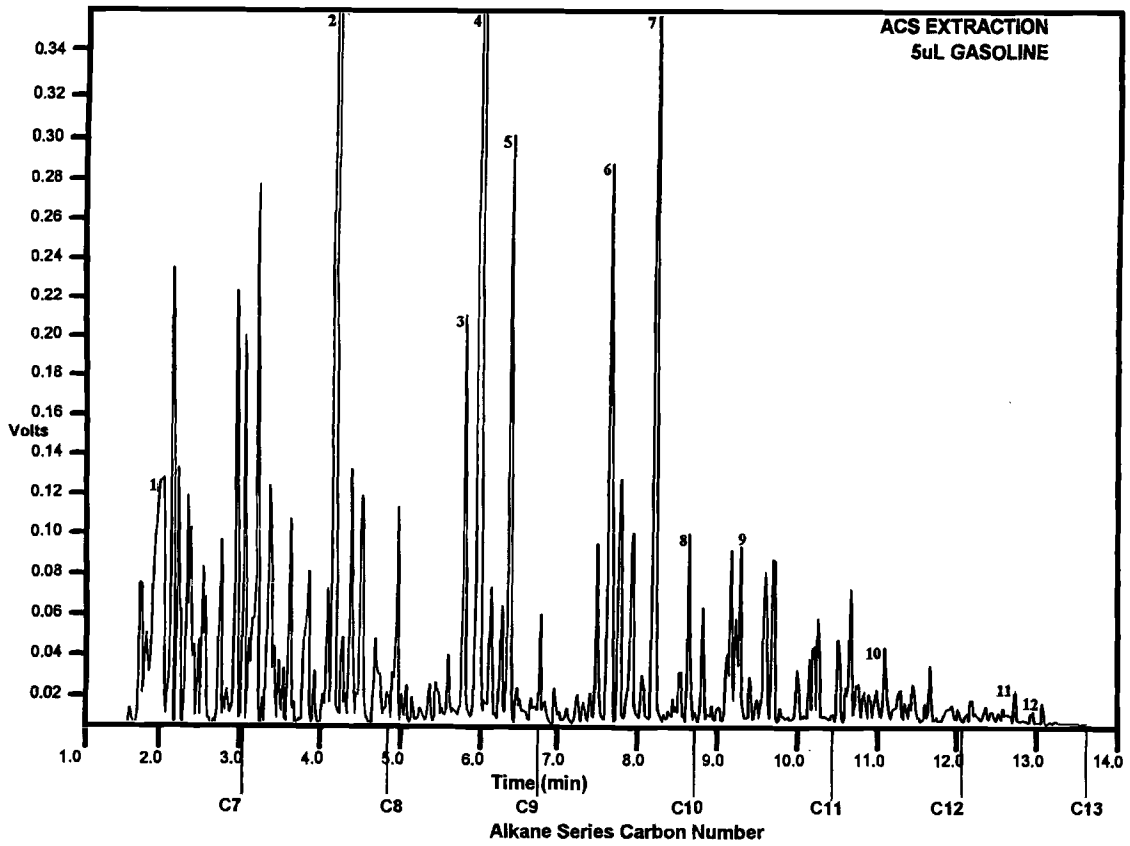


FIG. 4—Chromatogram of the ACS extraction (TOP) and SPME extraction (BOTTOM) of a can spiked with 5 μL of gasoline. (Peak identity in Table 2.)

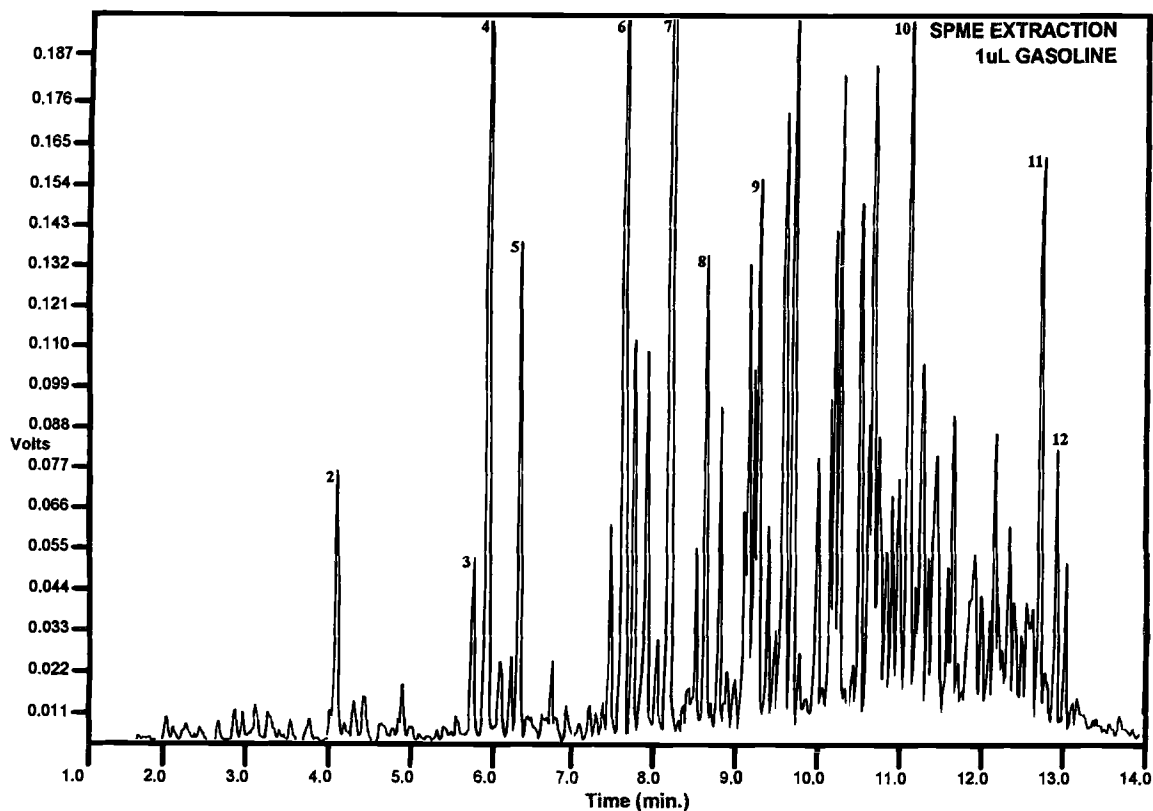
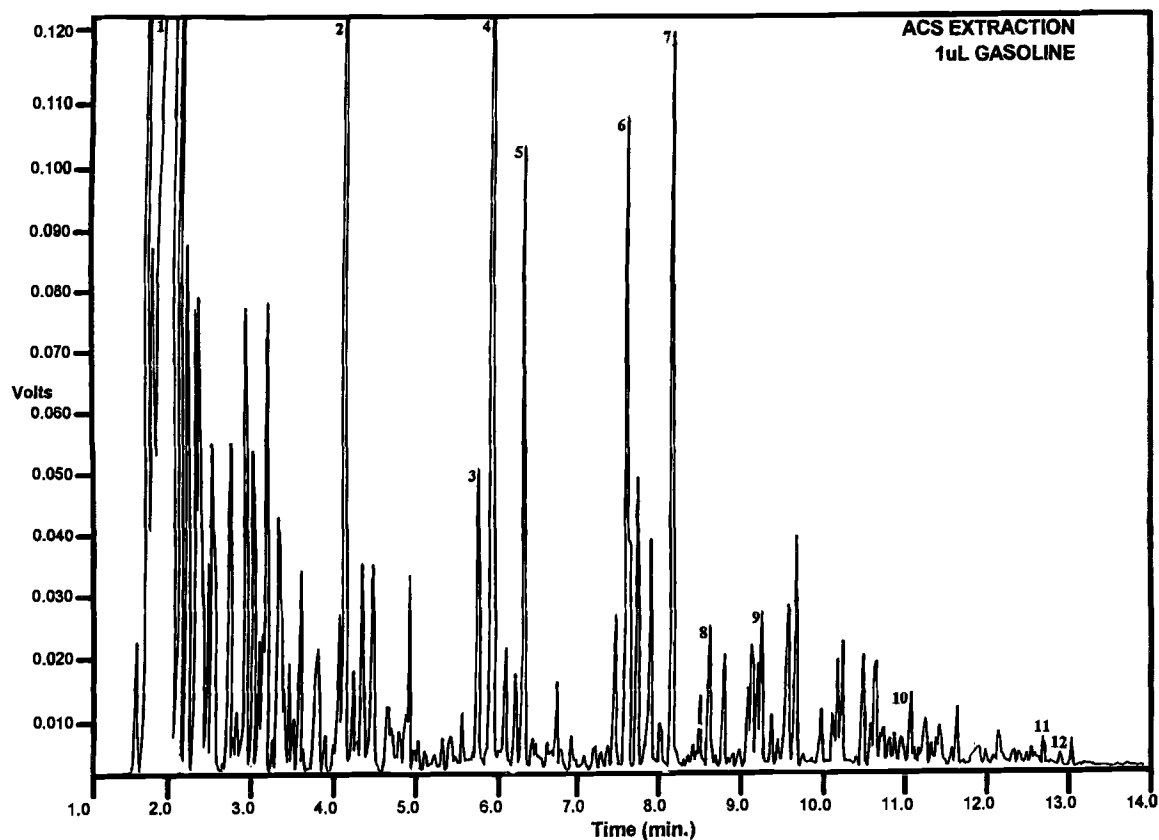


FIG. 5—Chromatogram of the ACS extraction (TOP) and SPME extraction (BOTTOM) of a can spiked with 1  $\mu$ L of gasoline. (Peak identity in Table 2.)

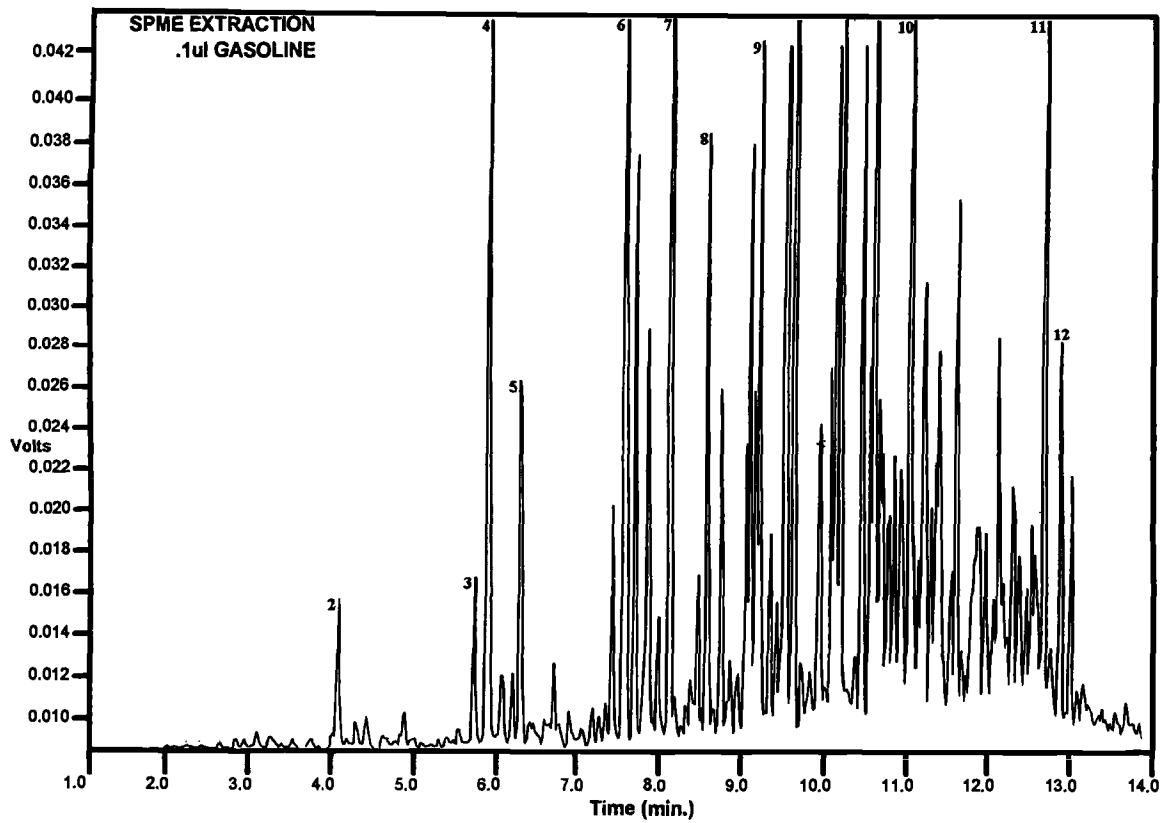
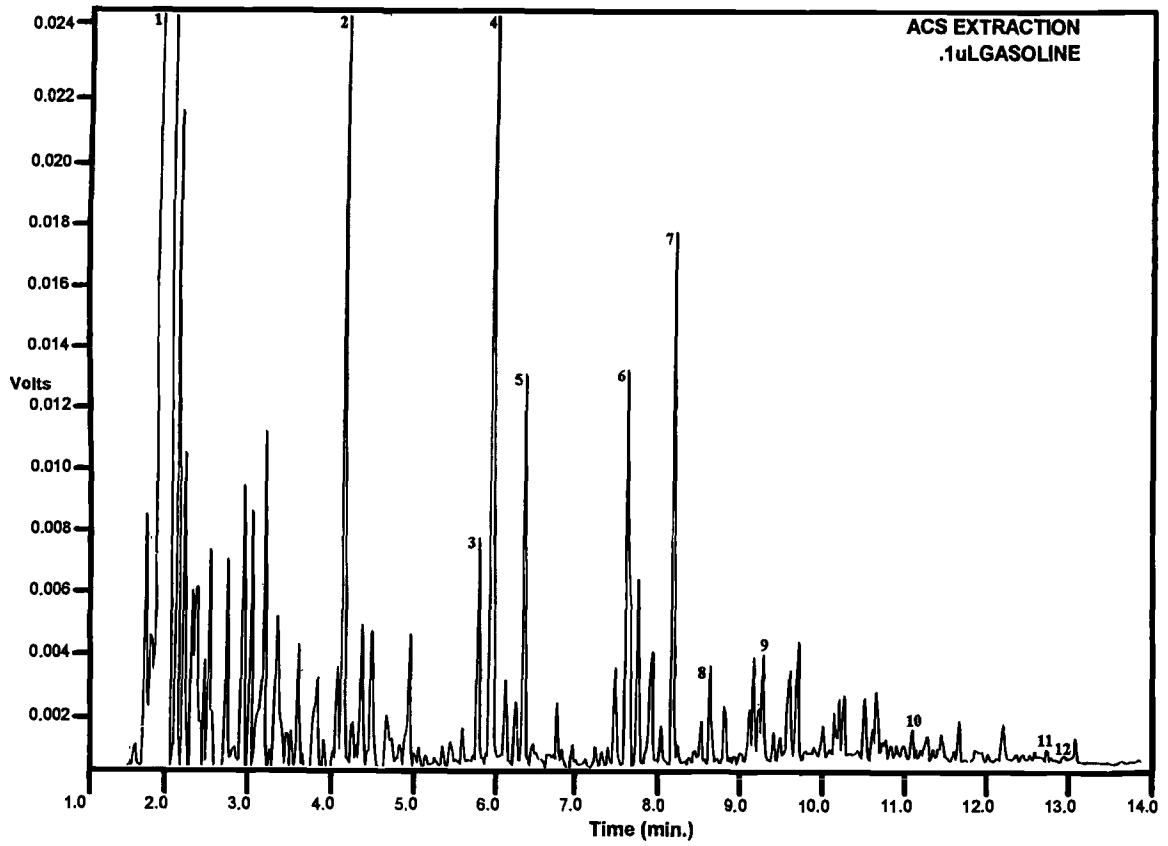


FIG. 6—Chromatogram of the ACS extraction (TOP) and SPME extraction (BOTTOM) of a can spiked with 0.1 µL of gasoline. (Peak identity in Table 2.)



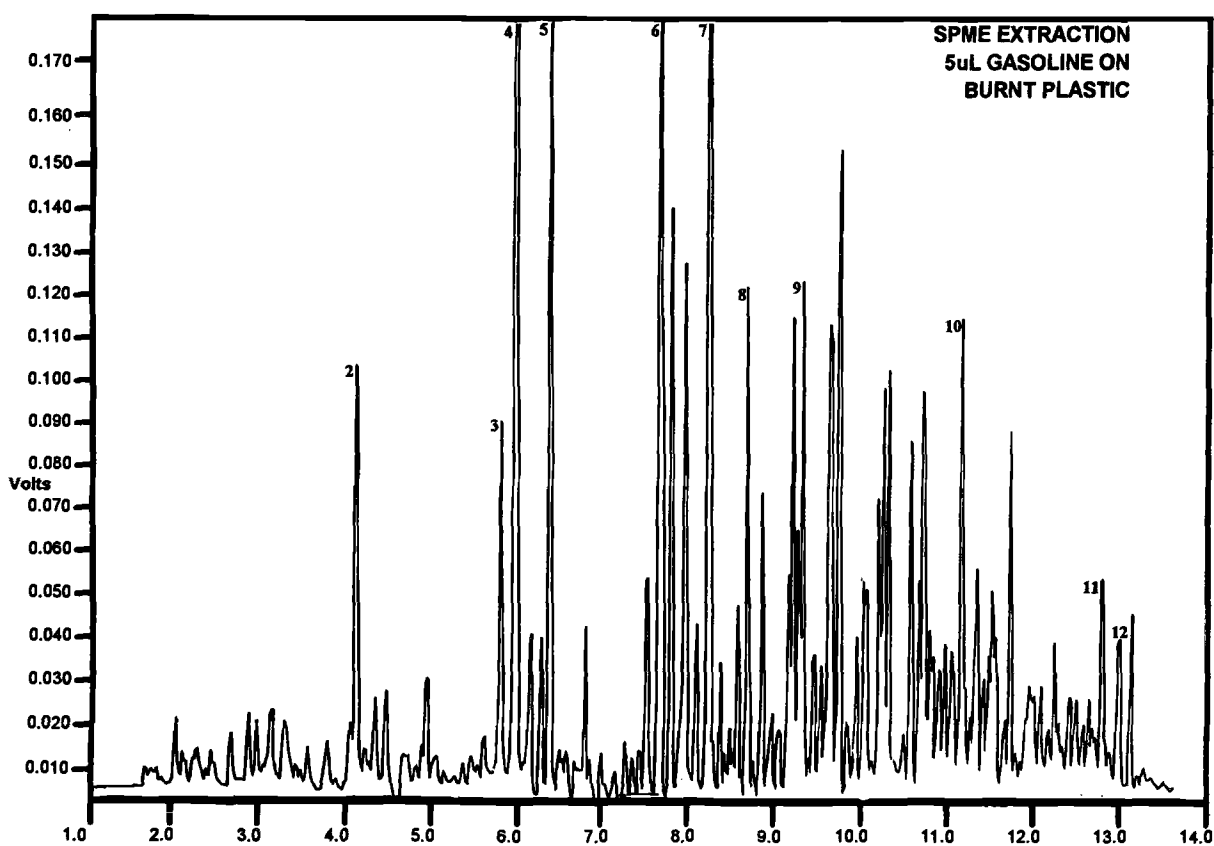
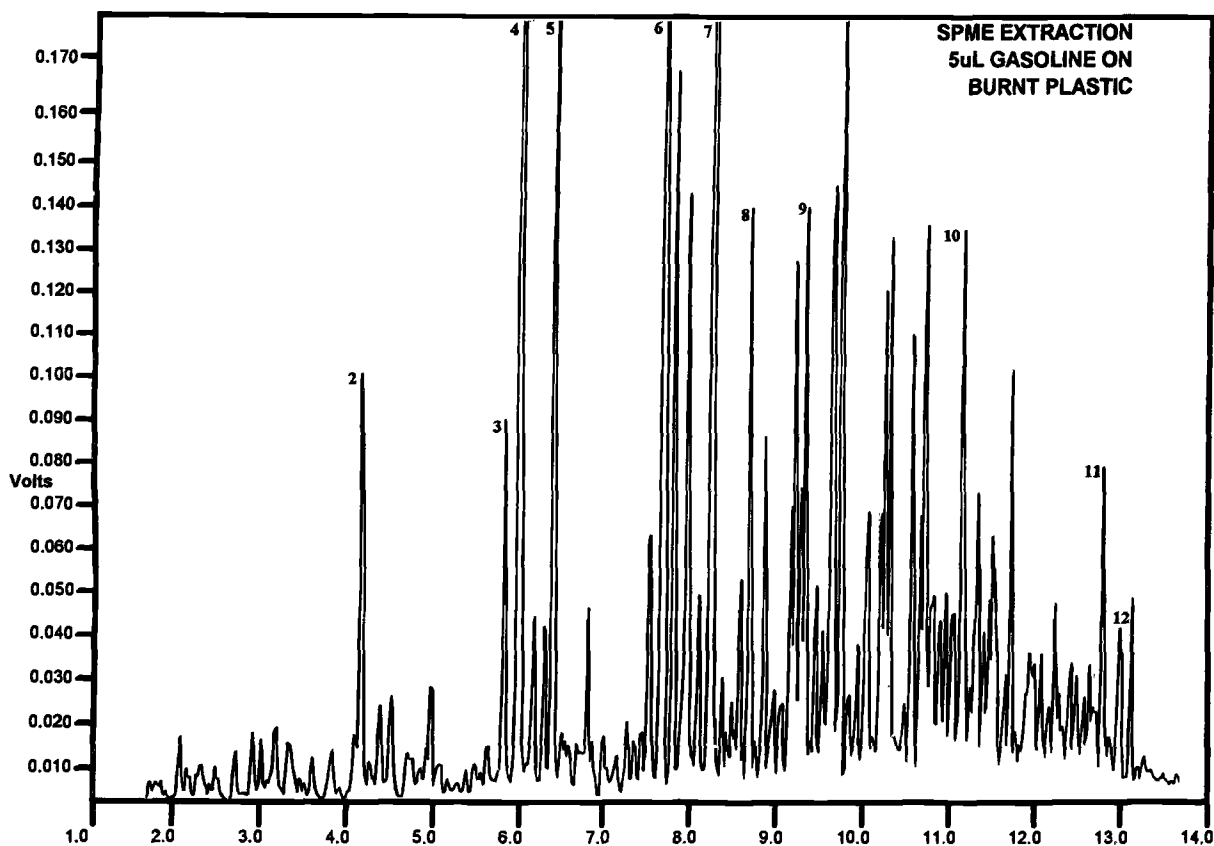


FIG. 7—Chromatogram of the first SPME extraction (TOP) and a duplicate SPME extraction (BOTTOM) of a can spiked with 5.0  $\mu$ L of gasoline on a matrix of burnt plastic. (Peak identity in Table 2.)

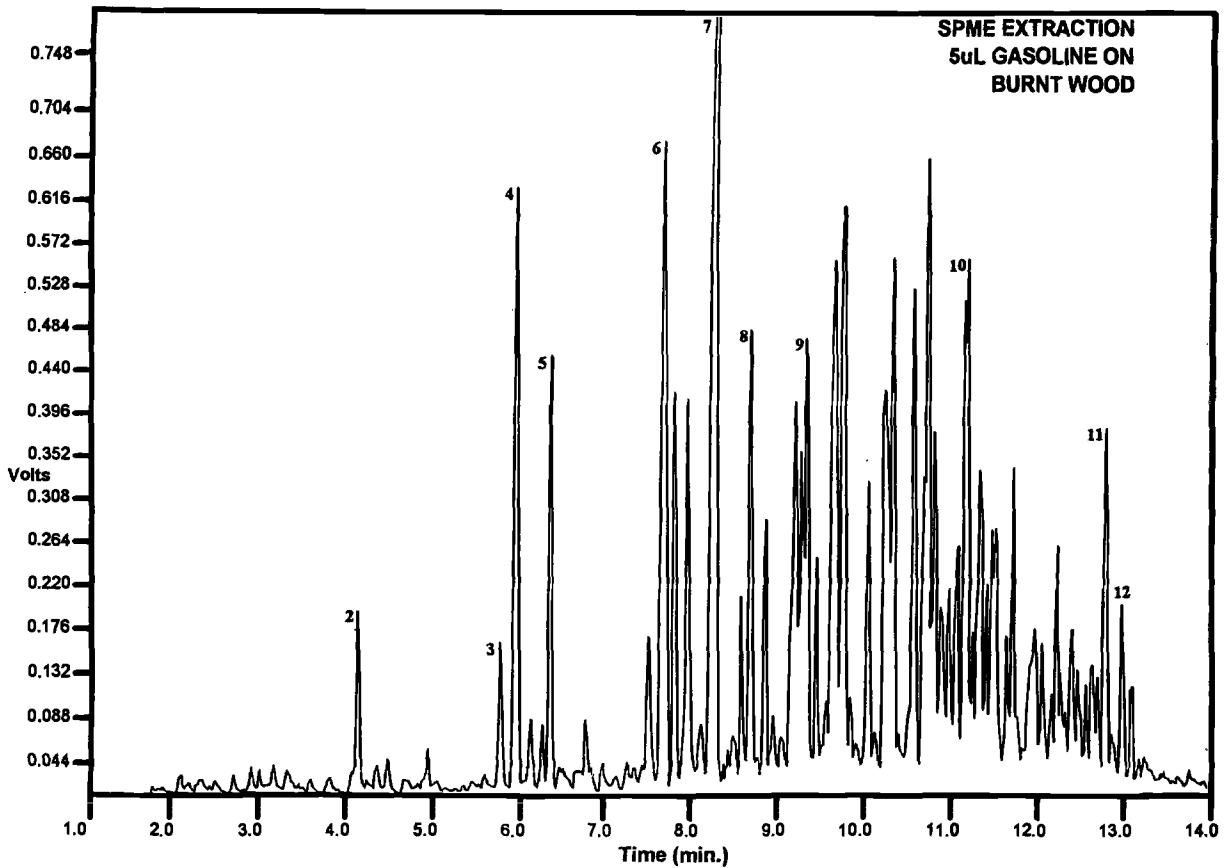
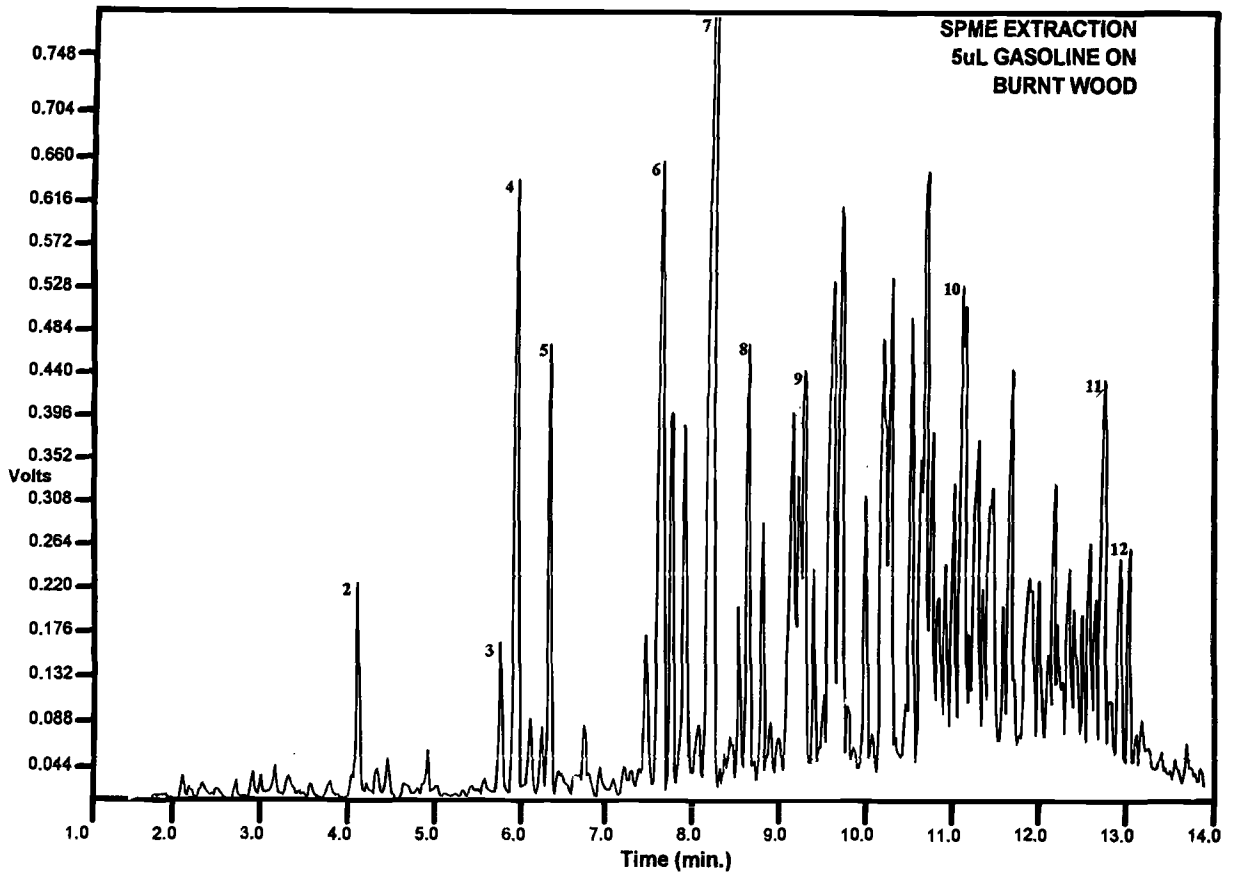


FIG. 8—Chromatogram of the first SPME extraction (TOP) and a duplicate SPME extraction (BOTTOM) of a can spiked with 5.0  $\mu$ L of gasoline. on a matrix of burnt wood. (Peak identity in Table 2.)

TABLE 3—Comparison of FID response<sup>a</sup> for SPME extracts versus ACS extracts.

Compound (Peak number)	Amount (μL)	FID Response (volts) using ACS	FID Response (volts) using SMPE	SPME Response/ ACS Response
Ethyl Benzene (3)	5	0.1992	0.2315	1.2
	1	0.0461	0.0479	1.0
	0.1	0.0070	0.0079	1.1
			<b>Average</b>	<b>1.1</b>
n-Butyl Benzene (9)	5	0.0849	0.6489	7.6
	1	0.0238	0.1424	6.0
	0.1	0.0034	0.0324	9.5
			<b>Average</b>	<b>7.7</b>
2-Methyl Naphthalene (11)	5	0.0159	0.6273	39.5
	1	0.0044	0.1424	32.4
	0.1	0.0005	0.0311	62.2
			<b>Average</b>	<b>44.7</b>
			<b>Overall</b>	<b>17.8</b>

<sup>a</sup>FID response in volts corrected for baseline (total voltage – background voltage).

a comparable cost, yet is more sensitive, simpler, faster, and does not require the use of any solvents. Optimization of the injection parameters, including cryogenic focusing, and other variables, including the SPME fiber film thickness and type as well as the extraction temperature are currently being investigated in an attempt to further improve this method. Other liquid residues ranging from alcohols to diesel fuel have been successfully sampled by this SPME method and the results of these ongoing investigations will be published soon.

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