

# Detection of Gasoline Residues Present in Household Materials via Headspace-Solid Phase Microextraction and Gas Chromatography–Mass Spectrometry

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**Abstract**—This paper describes the detection and persistence of gasoline residues present in household materials, cotton fabric, cardboard, and carpet. These samples were spiked with 50  $\mu\text{L}$  of gasoline and dried for a controlled period of time at room temperature prior to chemical analysis. The extraction and chemical analysis of gasoline residues were conducted via headspace-solid phase microextraction and gas chromatography–mass spectrometry, respectively. Our data showed that gasoline residues were detected in the cotton fabric samples after up to 7 days of drying, while both the cardboard and carpet samples could retain gasoline residues for longer than 3 weeks. The adoption of small-sized vials for headspace analysis improved the detection limit of gasoline residues in the samples. The physical features of the samples, such as porosity, thickness, and number of layers, were found to be more important than chemical compositions for the increased persistence of gasoline residues.

**Keywords:** gasoline residues, persistence, gas chromatography, mass spectrometry, headspace, solid phase microextraction

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The detection and identification of ignitable liquids present on solid substrates is an important issue in fire investigations [1–3]. If the fire investigator suspects that a fire was deliberately started by ignitable liquids, any physical evidence potentially containing these liquids will be collected at the fire scene, as well as from the arson suspects, for further investigation. Gas chromatography–mass spectrometry (GC–MS) is the standard analytical method in forensic laboratories to identify the presence of ignitable liquids [1–3].

Prior to instrumental analysis, any ignitable liquid present in the collected samples can be recovered by several techniques, including solvent extraction, headspace vapor sampling, passive headspace concentration with activated carbon, and headspace concentration–solid phase microextraction (HS–SPME) [3–12]. One or multiple techniques can be used to optimize the collection process for the given samples. Muller et al. reported that passive headspace concentration with activated carbon and subsequent solvent extraction using dichloromethane was an effective method for recovering gasoline residues on an arson suspect's hands [5]. Almirall et al. demonstrated [6] that HS–SPME was an effective technique for extracting various types of ignitable liquids at extremely low quantities from human skin.

We note that HS–SPME provides an easy and convenient sampling method for detecting gasoline residues in various types of solid samples [13–15]. Headspace concentration is a sampling technique that collects volatile organic compounds associated with non-volatile solid samples without the use of direct solvent extraction. In static headspace mode, a sample containing target volatile compounds is tightly sealed into a container and heated. Volatile compounds present in the sample diffuse into the gas phase, and their concentrations in the headspace reach a state of equilibrium. Then, the solid phase microextraction technique selectively extracts volatile compounds from the headspace and injects them into the injection port of the gas chromatograph for chemical analysis. The amount of the compounds extracted by the SPME fiber is critical to enhance the detection limit of the target compounds. Several factors are known to affect the amount extracted by the SPME fiber, including the size and composition of the fiber, the chemical and physical properties of the extracted compounds, and the headspace volume [6, 16].

Until recently, a majority of previous studies focused on the detection of ignitable liquids from either burnt samples or human skin to reconstruct fire scene investigation [6–11]. In addition, the presence

and persistence of ignitable liquids in unburnt materials encountered in our daily lives such as clothes, shoes, carpets, and household products were extensively investigated [17–22]. These studies have shown that ignitable liquids could be unintentionally transferred to clothes and shoes [17–19]. However, it was also found that these samples may contain inherent ignitable components which originated from the manufacturing process [21, 22]. Because of the size and nature of samples used in these studies, large-sized nylon bags or cans were used for headspace analysis which, in turn, may limit the detection capability of ignitable liquid residues present in these samples.

In this study, we investigated the presence and persistence of ignitable liquids from unburnt household samples via HS-SPME and GC–MS. In particular, small-sized headspace vials were used to improve the detection capability of trace amounts of ignitable liquids present in our samples. We chose to examine cotton fabric, cardboard, and carpet samples, which are materials commonly encountered in living spaces. We assumed that these samples likely contained gasoline residues if they were in contact with gasoline and/or persons carrying gasoline. A small quantity (50  $\mu\text{L}$ ) of gasoline was added to the samples, which were then dried over a controlled period of time at room temperature and placed into a small-sized headspace vial (10 mL). The headspace vapors were collected and extracted by SPME and finally analyzed by GC–MS. Herein, our GC–MS data from samples dried for different periods are presented for the detection and persistence determination of gasoline residues.

## EXPERIMENTAL

**Materials and sample preparation.** Household samples used in this study were purchased from local stores. The bulk samples were cut into pieces with the size of ca.  $2.5 \times 2.5 \text{ cm}^2$  for the carpet and cardboard samples and ca.  $3.5 \times 3.5 \text{ cm}^2$  for cotton fabric samples. These samples were stored in airtight fire debris evidence collection nylon bags (Sirchie, Youngsville, NC) to prevent any potential contamination before use. The gasoline used in this study was 87 octane grade which was purchased from a local gas station and stored in an airtight container. Selected components in gasoline, *p*-xylene (>99%, Sigma-Aldrich), 1,2,4-trimethylbenzene (>98%, Sigma-Aldrich), 1,2,3-trimethylbenzene (>90%, Sigma-Aldrich), 1,2,4,5-tetramethylbenzene (>97%, Acros), 2-methylnaphthalene (>97%, Sigma-Aldrich), *n*-octane (>99%, Acros), *n*-nonane (>99%, Acros), *n*-decane (>99%, Acros), *n*-undecane (>99%, Acros), *n*-dodecane (>99%, Acros), and *n*-tridecane (>99%, Acros) were purchased and used as received without further purification as reference materials.

A 50  $\mu\text{L}$  portion of gasoline was precisely taken by micropipette and spiked onto household samples. The

samples were then dried in a vented cabinet for a controlled period of time up to 21 days (e.g., 1, 2, 4 h, 1, 2, 3, 4 days, etc.) at 25°C. To prevent potential cross-contamination between the samples, household samples of the same type were dried together for the same controlled period of time. In addition, samples in the cabinet were separated by at least 4 inches while drying. After the given drying period, each sample was placed into a 10 mL headspace vial (Restek, Bellefonte, PA) using clean forceps and then tightly sealed before chemical analysis. For each type of household material, at least four samples were prepared for a given drying time. Samples that were not spiked with gasoline (negative control or blank samples) were also prepared and placed in headspace vials for analysis.

**Extraction and chemical analysis.** An Agilent GC Sampler 80 was used to heat the headspace vials, followed by SPME extraction and injection into a gas chromatograph. The SPME fibers used in this study were made of polydimethylsiloxane with a 100  $\mu\text{m}$  diameter and were purchased from Sigma-Aldrich (St. Louis, MO). The SPME fibers were conditioned in the GC injection port at 250°C for 1 h before use. Although standard experimental procedures for separation and concentration of gasoline residues from solid substrates via HS-SPME are described in ASTM standard E2154-15a [23], experimental parameters such as headspace vial heating temperature and time, SPME sampling time, and desorption time, were optimized using gasoline-spiked carpet samples prior to data collection. Headspace vials containing household samples were heated at 100°C for 3 min to transfer volatile components from the solid sample matrices to the headspace. Then, SPME sampling was conducted for 3 min at 100°C in a headspace vial. Our preliminary experiments showed that both heating and sampling times longer than 3 min did not make any noticeable difference in the data. The results indicate that volatile components are equilibrated between headspace, SPME fiber, and solid sample matrices in 3 min at 100°C under our experimental condition. Finally, an SPME fiber was injected into the GC, and desorption was conducted for 20 s.

Chemical analysis was conducted via an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass selective detector. The GC–MS experimental parameters were adopted from previously published articles with slight modification [5, 7, 10, 11]. Details of the GC–MS experimental parameters for this study are listed in Table 1. The mass selective detector was frequently optimized before data collection using a tuning agent, perfluorotributylamine. The control of GC–MS, data collection, determination of the retention time, and structural analysis were conducted using the Enhanced GC/MSD ChemStation Software (ver. E.02.02.1431, Agilent Technologies). The retention times of several isomeric compounds in the total ion chromatograms (TICs) and extracted ion chromatograms (EICs) were confirmed using the ref-

**Table 1.** Experimental parameters of gas chromatography and mass spectrometry (GC–MS)

Parameter	Value
Column	Agilent HP-5MS, 30 m (L) × 250 μm (ID) × 0.25 μm (film thickness)
Carrier gas and flow rate	Helium, 1.5 mL/min
Inlet temperature	270°C
Oven parameters	
initial temperature	50°C
initial hold time	1 min
ramp rate	10 grad/min
final temperature	250°C
final hold time	3 min
MSD transfer line temperature	250°C
Source temperature	230°C
Quadrupole temperature	150°C
Scan range and speed	50–550 amu, 2.91 scans/s

erence compounds, *p*-xylene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, 2-methylnaphthalene, and selected normal alkanes (C8–C13).

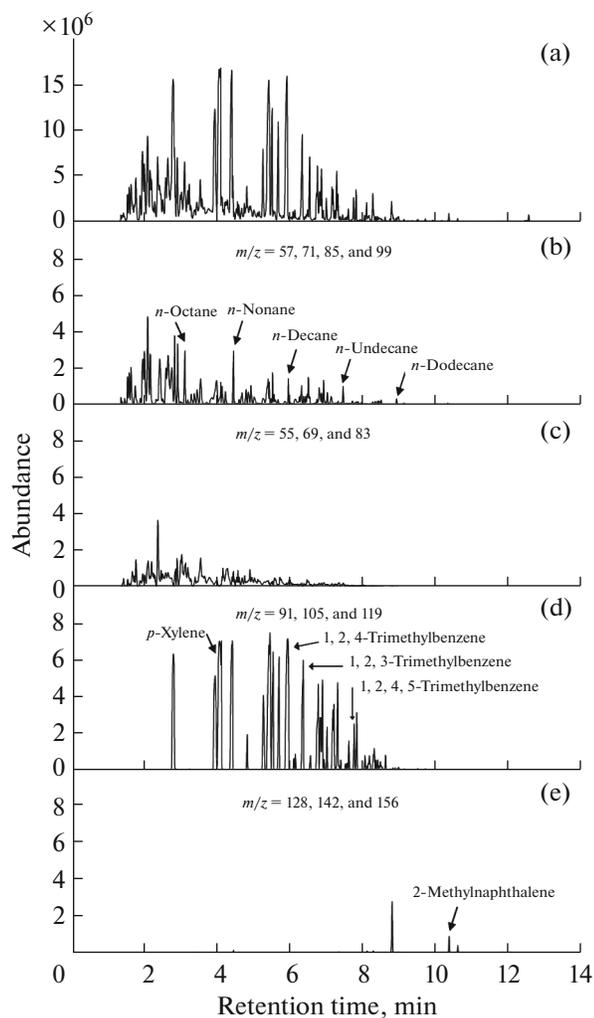
**Identification criteria of gasoline.** According to the ASTM standard E1618, the presence of aromatics such as C3- and C4-alkylbenzenes, as well as alkanes, is required, but quantification of these compounds is not needed for the identification of gasoline [24]. In this study, the presence or absence of gasoline residues in samples was determined by the detection of all markers; 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and one of normal alkanes (C8–C13). For the identification of these compounds, both the TICs and EICs of the samples were evaluated. The major ions used for the construction of EICs for the target compounds are listed in Table 2. One or more ions with signal-to-noise ratio (*S/N*) greater than 10 were used to determine the retention times and mass spectra of the peaks in both the TICs and EICs taken from the samples. The presence of the target compounds in the samples was positively confirmed if the retention times and mass spectra of these compounds were comparable to those obtained from a standard gasoline sample. In addition, peak areas from selected ions of 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and 2-methylnaphthalene in EICs were used to find relative compositions of gasoline residues in the sample over the controlled drying period.

## RESULTS AND DISCUSSION

**Comparison of chromatographs of gasoline via direct injection and headspace-solid phase microextraction.** In the first set of experiments, the quality of the total ion chromatogram and extracted ion chromatograms for the selected ions, listed in Table 2, from gasoline via HS-SPME injection was evaluated through comparison with data obtained via direct injection. A TIC via HS-SPME was produced from a carpet sample immediately after spiking with 50 μL of gasoline using the extraction and desorption conditions described in the experimental section. A TIC via direct injection was obtained by manual injection of 1 μL of undiluted gasoline into GC–MS under the same experimental parameters. The results are presented in Figs. 1 and 2. These TICs and EICs were also used as references for the identification of target compounds from gasoline-spiked samples.

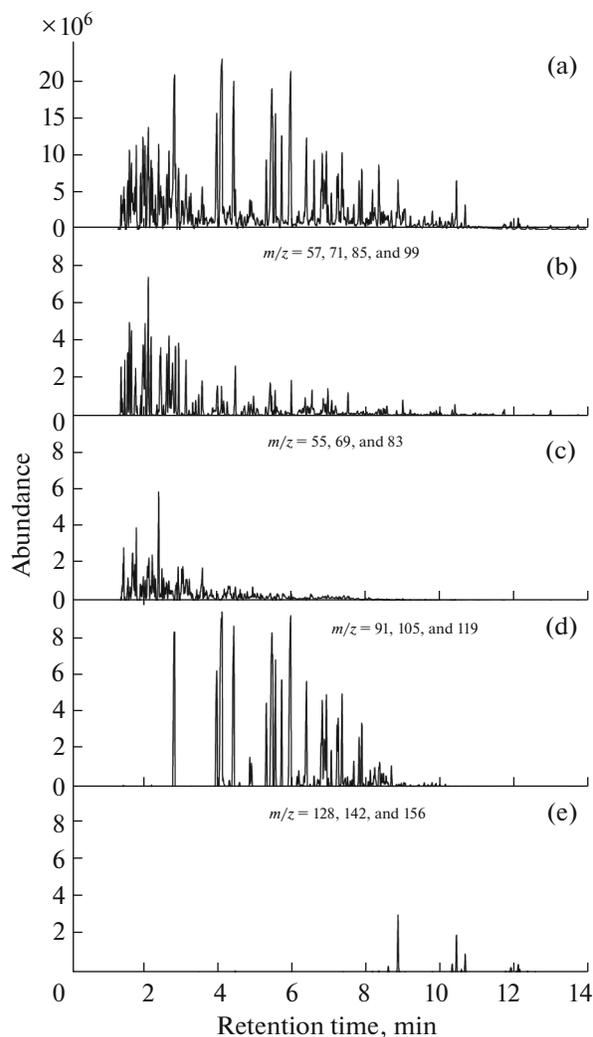
**Table 2.** Major ions used for identification of each class of compounds in gasoline

Class of compounds	<i>m/z</i>
Alkanes	57, 71, 85, 99
Cycloalkanes	55, 69, 83
Aromatics	91, 105, 119
Naphthalenes	128, 142, 156



**Fig. 1.** The total ion chromatogram for gasoline via HS-SPME injection (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 1a. Note that the abundance scale of all EICs is the same.

The TICs and EICs in Figs. 1 and 2 showed that gasoline contains numerous volatile components that eluted during the first 14 min under our experimental conditions. Using both TICs and EICs from gasoline and reference compounds, the presence of several major classes of compounds including reference compounds (*p*-xylene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, 2-methylnaphthalene, and selected normal alkanes) in gasoline and their retention times were confirmed. These compounds include short-chained alkanes and cycloalkanes (C5–C6, retention time,  $R_t < 1.8$  min), toluene ( $R_t \approx 2.8$  min), *n*-octane ( $R_t \approx 3.1$  min), xylenes ( $R_t \approx 3.8$ – $4.5$  min,  $R_t \approx 4.0$  min for *p*-xylene), *n*-nonane ( $R_t \approx 4.4$  min), *n*-decane ( $R_t \approx 5.9$  min), C3-alkylbenzenes ( $R_t \approx 4.5$ – $6.5$  min,  $R_t \approx 5.9$  min for



**Fig. 2.** The total ion chromatogram for gasoline via direct injection (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 2a. Note that the abundance scale of all EICs is the same.

1,2,4-trimethylbenzene,  $R_t \approx 6.3$  min for 1,2,3-trimethylbenzene), C4-alkylbenzenes ( $R_t \approx 6.0$ – $8.4$  min,  $R_t \approx 7.8$  min for 1,2,4,5-tetramethylbenzene), *n*-undecane ( $R_t \approx 7.5$  min), *n*-dodecane ( $R_t \approx 8.9$  min), and *n*-tridecane ( $R_t \approx 10.4$  min). Although they are not major components in gasoline, naphthalene ( $R_t \approx 8.8$  min), C1-alkylnaphthalenes ( $R_t \approx 10.4$ – $10.7$  min,  $R_t \approx 10.4$  min for 2-methylnaphthalene), and C2-alkylnaphthalenes ( $R_t \approx 11.6$ – $12.7$  min) were also identified. Some compounds including markers for gasoline residues were labeled in EICs in Fig. 1.

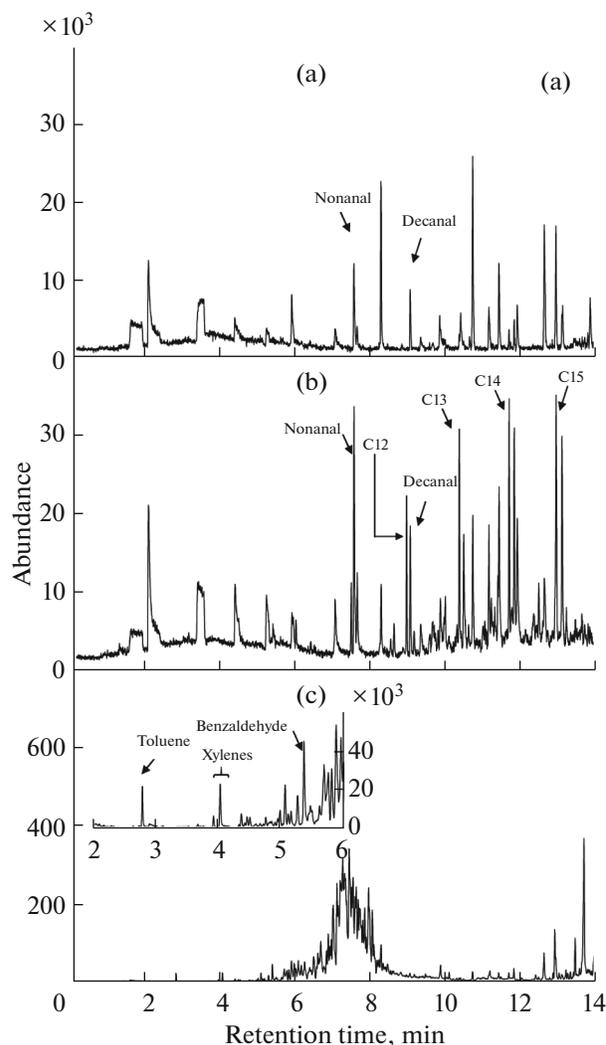
The TICs and EICs in Figs. 1 and 2 were comparable, but a slight difference was found in the intensities of peaks at retention time of less than  $\sim 2.0$  min. The TIC obtained via HS-SPME (Fig. 1a) exhibited lower relative abundances of highly volatile compounds

compared with that obtained via direct injection (Fig. 2a). This observation indicated that a relatively less amount of the lighter compounds was extracted by the HS-SPME sampling technique. Previous studies have shown that the relative concentrations of volatile compounds extracted by SPME fibers are different from their headspace vapor compositions [25–27]. The partition coefficient  $K$  (the ratio of analyte concentrations in the SPME fiber and the headspace) depends on many factors, such as the extraction temperature and time, the structure and polarity of the extracting compounds, and the chemical composition of the SPME fiber. Once all the adsorption sites on an SPME fiber are occupied, compounds with a higher adsorption affinity can replace compounds with a lower adsorption affinity. Thus, the adsorption of analytes on an SPME fiber is competitive, and the composition of analytes extracted by the SPME fiber is different from that in the headspace [26]. This difference is presumably responsible for attenuated relative peak intensities of the lighter components in the TIC and EICs via HS-SPME injection (Fig. 1) compared with those in the TIC and EICs via direct injection (Fig. 2).

**Evaluation of background matrices.** Since all household materials used in this study are man-made, it is possible that these materials contain inherent ignitable liquid or ignitable liquid components, as reported previously [22]. The background matrices were evaluated using the identical HS-SPME sampling and GC–MS conditions described in the “Experimental” to determine the structures of present compounds. Total ion chromatograms from three background matrices are presented in Fig. 3.

All the background matrices released volatile compounds, but their structures and compositions varied. Because of the extremely low relative abundance of peaks in the TICs, it was not feasible to identify all detected compounds. The largest peak found in the TICs from the background matrices had a relative abundance of  $\sim 10^5$  (see Fig. 3c), which is smaller than the largest peak in the TICs from gasoline, shown in Figs. 1 and 2, by an order of  $\sim 10^2$ . Some of the compounds identified in the background matrices are listed in Table 3.

Although the cotton fabric matrix produced a TIC that contained peaks of relatively low abundance, two compounds, nonanal and decanal, were identified (Fig. 3a). These compounds were commonly detected in clean and sterilized cotton products, but their origin in cotton fabric matrix is not clear [28]. One proposed possibility is that they are byproducts of ozone with the cotton fabric [29]. Our data also showed that both the cardboard and carpet matrices contained a larger number of compounds with a higher relative abundance. Alkyl aldehydes and long-chain alkanes (C11–C15) were detected in the cardboard samples, presumably due to the adhesives used in the manufacturing process [30, 31]. Many volatile organic compounds,



**Fig. 3.** Total ion chromatograms from the background matrices via HS-SPME injection for cotton fabric (a), cardboard (b), and carpet (c). Note that the abundance scales of the three TICs are different. For clarity, the inset in Fig. 3c shows the enlarged area of the retention times between 2 and 6 min. Some of the identified compounds are labeled in the TICs. These compounds are also listed in Table 3.

including toluene, xylenes, and benzaldehyde, were detected in the carpet matrix (Fig. 3c). Our data are consistent with previous reports in which new carpet was found to be an adsorptive reservoir for volatile organic compounds [32–34]. Although some components of ignitable liquids have been identified in both the carpet and cardboard matrices, it should be noted that neither contained enough components to identify any ignitable liquid – as per ASTM Standard E1618 [24].

**Chemical analysis of gasoline-spiked samples.** Figures 4–6 show the TICs and EICs for selected ions in Table 2 from gasoline-spiked cotton fabric samples dried at room temperature for 1 h, 1, and 7 days,

**Table 3.** Compounds found in three background matrices and their retention times (min) in the total ion chromatograms shown in Fig. 3

Compound	Retention time
Cotton fabric	
<i>n</i> -Nonanal	7.54
<i>n</i> -Decanal	9.05
Carpet	
Toluene	2.76
<i>m</i> -Xylene	3.91
<i>o</i> -Xylene	4.34
Benzaldehyde	5.34
<i>n</i> -Dodecanoic acid	13.96
Cardboard	
<i>n</i> -Undecane	7.45
<i>n</i> -Nonanal	7.54
<i>n</i> -Dodecane	8.93
<i>n</i> -Decanal	9.05
<i>n</i> -Tridecane	10.35
<i>n</i> -Undecanal	10.50
<i>n</i> -Tetradecane	11.70
<i>n</i> -Dodecanal	11.81
<i>n</i> -Pentadecane	12.96
<i>n</i> -Tridecanal	13.12

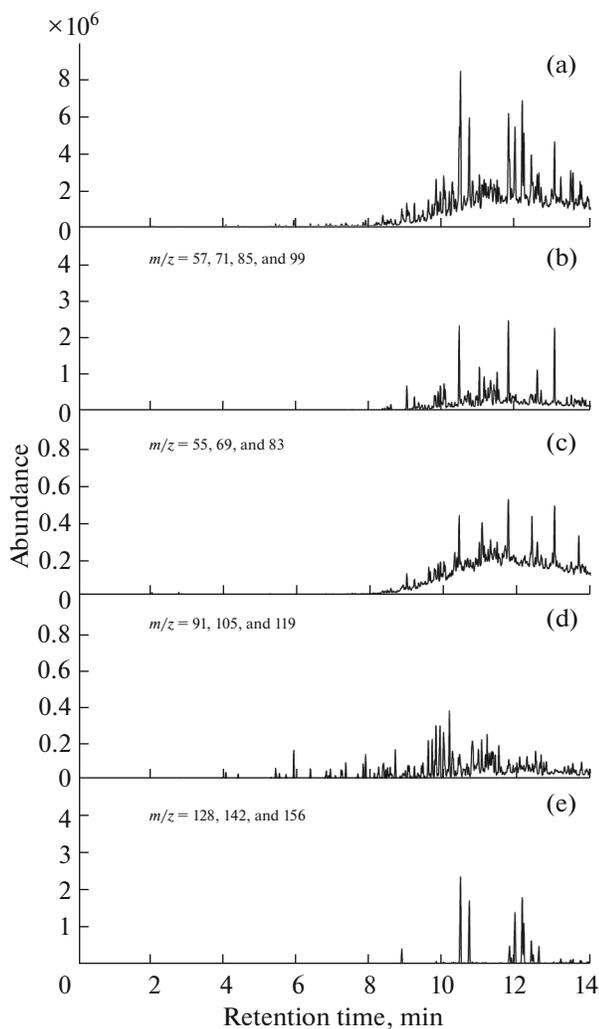
respectively. In the TICs and EICs in Fig. 4, a major portion of the highly volatile components in gasoline (e.g., short-chained alkanes, cycloalkanes, and light aromatics) rapidly evaporated from the cotton fabric samples within 1 h. However, heavier aromatics including 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, long-chain alkanes (e.g., *n*-undecane and *n*-dodecane), and naphthalenes were found in our cotton fabric samples dried for 1 h and 1 day (Figs. 4 and 5). When the cotton fabric samples were dried for 7 days, the presence of some aromatics (e.g., 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, and 1,2,4,5-tetramethylbenzene) was confirmed despite the low abundance of ions from

these compounds and the presence of numerous unidentified ions in the EIC (Fig. 6d).

In addition, the presence of long-chain alkanes (e.g., *n*-tridecane and *n*-pentadecane) and naphthalenes was confirmed, indicating the presence of gasoline residues (Figs. 6b, 6e). Both *n*-tridecane and *n*-pentadecane are also found in both kerosene and diesel residues, but these compounds are detected as major components along with a series of long-chain hydrocarbons (e.g. C13–C17) in the case of kerosene and diesel residues [6, 11, 12, 35]. Therefore, gasoline residues are easily distinguishable from both kerosene and diesel residues. When the cotton fabric samples were dried for 14 days, some aromatics including 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and naphthalenes were clearly detected, but none of long-chain alkanes was detected. Similar results were obtained from cotton fabric samples of drying for 21 days.

The TICs and EICs from cardboard samples dried for 1 h, 1, and 21 days are presented in Figs. 7–9, respectively. As with the cotton fabric samples, the presence of short-chained alkanes and cycloalkanes was not confirmed, regardless of the drying time. However, long-chain alkanes, many C3- and C4-alkylbenzenes including 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and naphthalenes were detected in the cardboard samples even after 3 weeks of drying (Fig. 9). It should be noted that the presence of long-chain alkanes (e.g., undecane, dodecane, and tridecane) was already confirmed in the background matrix (Fig. 3b). However, the relative abundance of these compounds in the TICs and EICs of the gasoline-spiked cardboard samples dried for 21 days was enhanced by ~2.4–2.8 times. This fact indicates that some of these compounds originated from gasoline residues present in the cardboard samples.

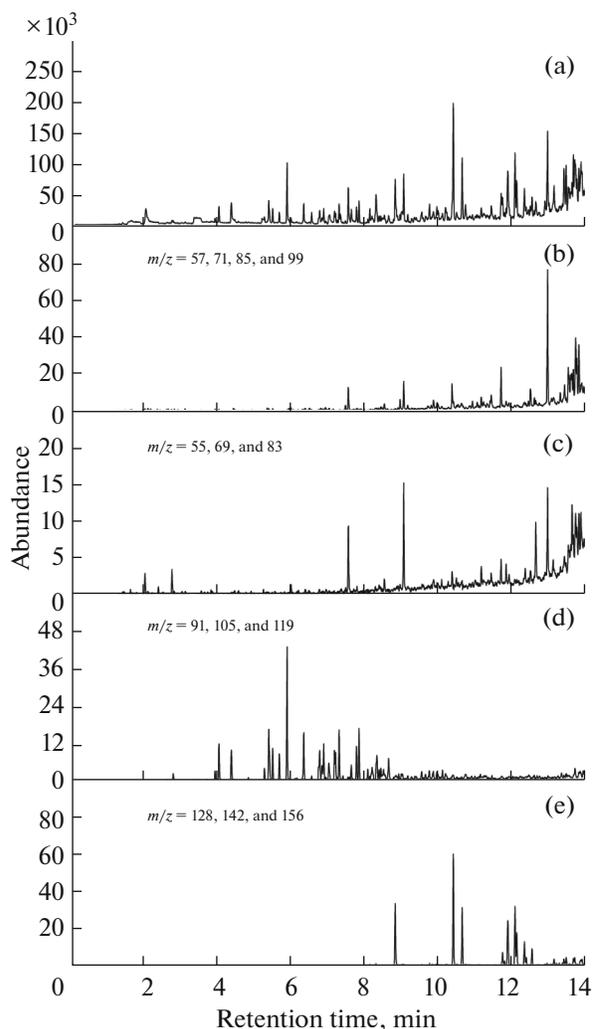
The TICs and EICs of carpet samples dried for 1 h, 1, and 21 days are presented in Figs. 10–12, respectively. More amounts of volatile components were detected than both cotton fabric and cardboard samples over longer drying periods. Unlike both cotton fabric and cardboard samples, the presence of *n*-octane, *n*-decane, and some cycloalkanes were positively confirmed in carpet samples dried for 1 h and 1 day. However, these compounds were no longer found when the drying period was over 7 days (data not shown). Xylenes, C3- and C4-alkylbenzenes including 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, long-chain alkanes, and naphthalenes were detected even after 3 weeks of drying (Fig. 12). The presence of these compounds in the carpet samples was enough to confirm the presence of gasoline residues, according to ASTM Standard E1618 [24]. From our data, both the cardboard and carpet samples could retain gasoline residues for 3 weeks, the cotton fabric samples could



**Fig. 4.** The total ion chromatogram for a gasoline-spiked cotton fabric sample dried for 1 h (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 4a. Note that the abundance scale of the four EICs was adjusted for clarity.

retain gasoline residues up to 7 days of drying. When drying period is longer than 7 days, C3- and C4-aromatics were detected, but the presence of long-chain alkanes (C8–C13) was not positively identified from cotton fabric samples.

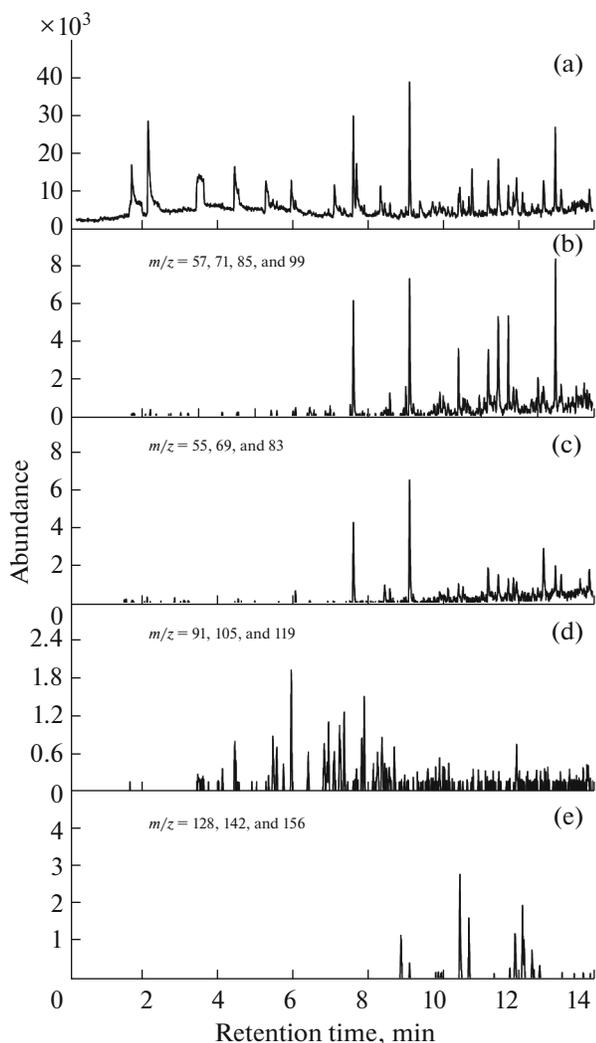
The relative concentrations of selected markers (1,2,3-trimethylbenzene and 1,2,4,5-tetramethylbenzene) with respect to the concentration of 2-methylnaphthalene in samples as a function of drying period were also investigated from our GC–MS data. The concentrations of 1,2,3-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and 2-methylnaphthalene in samples were obtained using calibration curves of each compound. Results are shown in Fig. 13. The relative concentrations 1,2,3-trimethylbenzene and 1,2,4,5-tetramethylbenzene in gasoline residues depend on



**Fig. 5.** The total ion chromatogram for a gasoline-spiked cotton fabric sample dried for 1 day (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 5a. Note that the abundance scale of the four EICs was adjusted for clarity.

the choice of samples. In Fig. 13, the relative concentrations of 1,2,3-trimethylbenzene and 1,2,4,5-tetramethylbenzene are very small in the case of cotton fabric (Fig. 13a) and cardboard (Fig. 13b) samples, but their relative concentrations are much larger for carpet samples (Fig. 13c). In addition, the relative concentrations of 1,2,3-trimethylbenzene and 1,2,4,5-tetramethylbenzene in both cotton fabric samples and cardboard samples are increased until drying periods were less than 4 days (96 h), but they were nearly constant when these samples were dried longer than 4 days. However, the relative concentrations of 1,2,3-trimethylbenzene and 1,2,4,5-tetramethylbenzene in carpet samples were increased over 21 days.

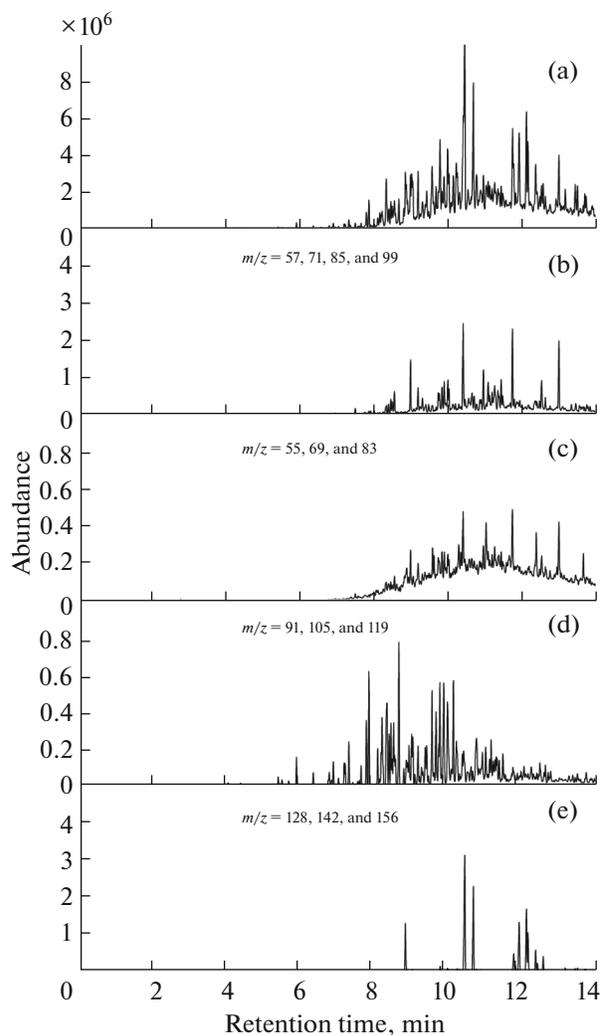
Although we did not investigate samples dried for longer than 3 weeks, our data demonstrate that gaso-



**Fig. 6.** The total ion chromatogram for a gasoline-spiked cotton fabric sample dried for 7 days (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 6a. Note that the abundance scale of the four EICs was adjusted for clarity.

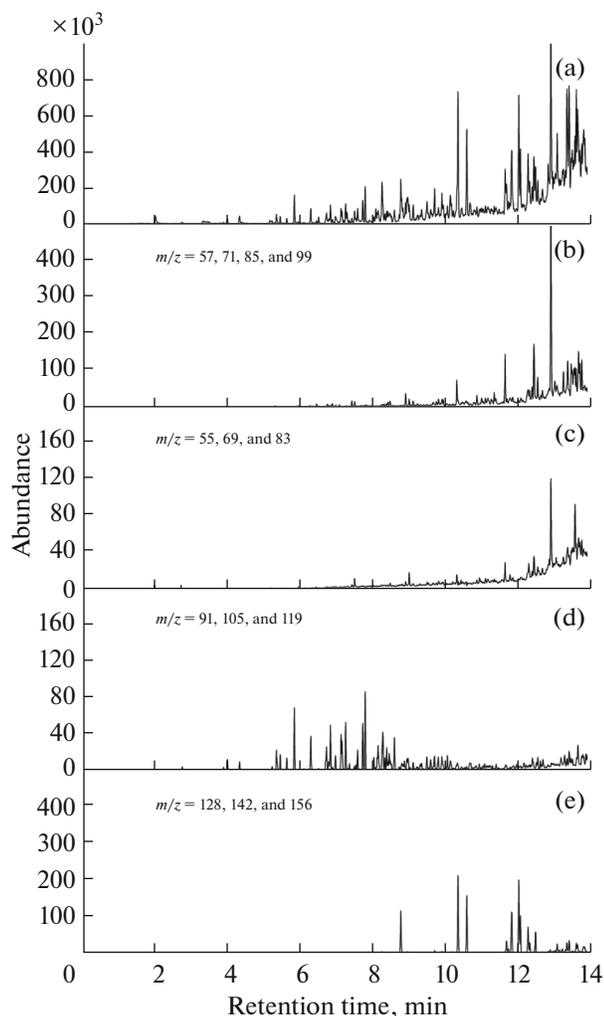
line residues can be detected in cardboard and carpet samples for longer than we expected due to the improved detection sensitivity. Previous studies by Folkman et al. have shown that gasoline residues could be recovered from carpet samples after one week [20]. Considering that nearly the same amount of gasoline was spiked to a given size of carpet ( $50 \mu\text{L}$  of gasoline per  $2.5 \times 2.5 \text{ cm}^2$  of carpet), our method presented here exhibited an enhanced detection capability of gasoline residues presumably because of the employment of small-sized headspace vials, as noted previously [6, 16].

In addition, our experimental results showed that the persistence of volatile components in gasoline-spiked samples primarily depended on the selection of



**Fig. 7.** The total ion chromatogram for a gasoline-spiked cardboard sample dried for 1 h (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 7a. Note that the abundance scale of the four EICs was adjusted for clarity.

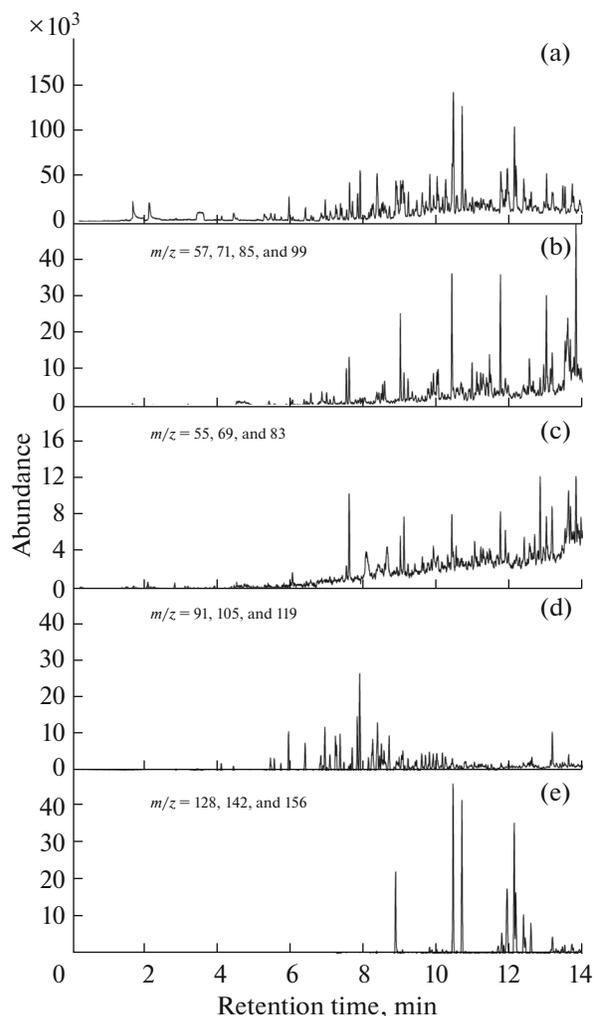
household materials. From our GC–MS data, it was not clear whether the increased persistence of gasoline in the carpet and cardboard samples was due to differences in the chemical properties (e.g., chemical structures) or the physical properties (e.g., thickness and porosity) of the household materials. The samples investigated in our studies were different in terms of physical features and chemical compositions. The cotton fabric samples used in our work consisted of a single layer with a thickness of  $\sim 0.07 \text{ mm}$ . However, the thickness of the carpet and cardboard samples was measured to be  $\sim 5.5$  and  $\sim 6.3 \text{ mm}$ , respectively. In addition, the cardboard and carpet samples had multiple layers. The major chemical composition of the cotton fabric samples was cellulose, but the carpet used in our study consisted of polyethylene-based face



**Fig. 8.** The total ion chromatogram for a gasoline-spiked cardboard sample dried for 1 day (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 8a. Note that the abundance scale of the four EICs was adjusted for clarity.

yarn and one or two polyethylene backing layers. The cardboard was highly porous and contained cellulose as a major component and varying amounts of minerals such as kaolin, talc, and calcium carbonate [36]. The compositions of these samples were obtained from the manufacturers (or vendors) and were confirmed by Fourier-transform infrared spectroscopy experiments at Buffalo State College.

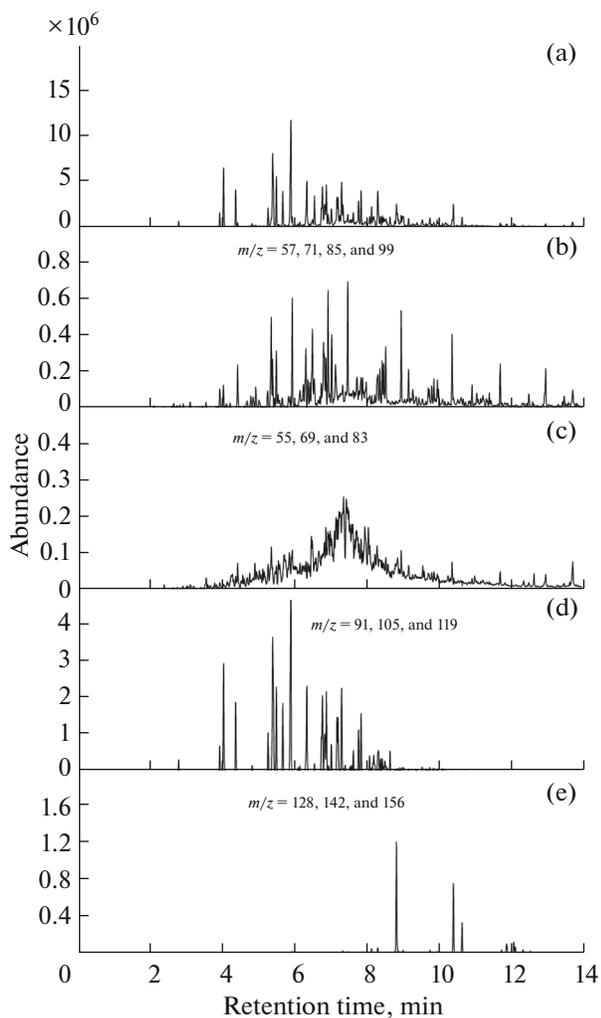
Although it is well known that the increased persistence of gasoline residues is related to the thickness and porosity of the samples, we conducted further investigations to determine the effect of the chemical composition of the samples on the persistence of gasoline residues [20]. For this investigation, four different types of fabric samples (cotton, polyester, silk, and nylon) were chosen. All the fabric samples had differ-



**Fig. 9.** The total ion chromatogram for a gasoline-spiked cardboard sample dried for 21 days (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 9a. Note that the abundance scale of the four EICs was adjusted for clarity.

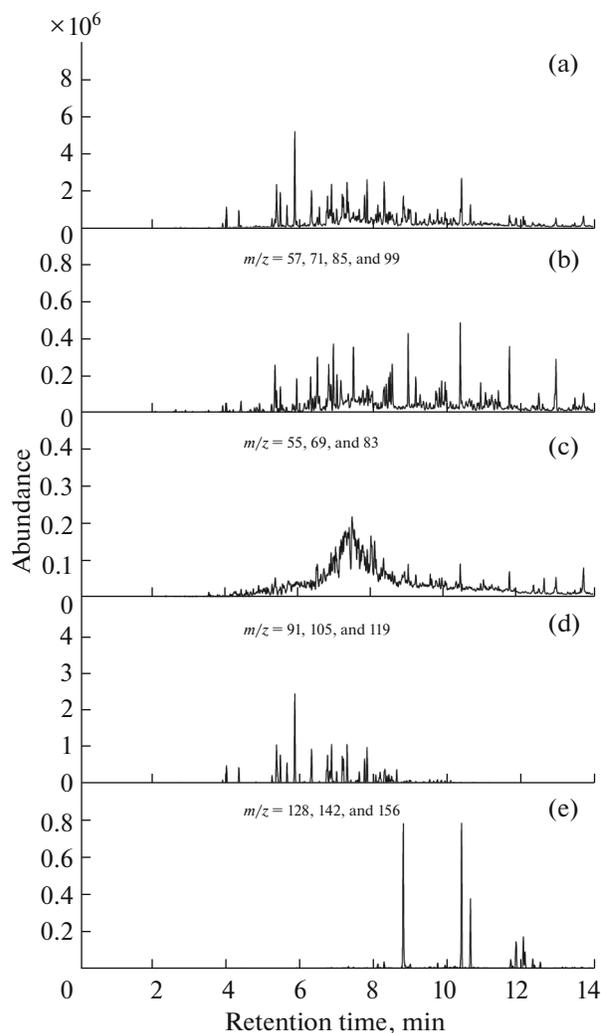
ent chemical compositions but similar thicknesses. The samples were cut into pieces of the same size ( $3.5 \times 3.5 \text{ cm}^2$ ), spiked with the same amount of gasoline ( $50 \mu\text{L}$ ), and dried for the same controlled time prior to chemical analysis via GC–MS. The TICs and EICs of these gasoline-spiked fabric samples were nearly comparable, regardless of the type of fabric (data not shown). However, it was reported that gasoline residues persisted longer on silk than cotton and polyester when these fabric samples containing gasoline were burnt [11].

From our study, we noted that the persistence of gasoline residues in our household samples was mainly governed by the porosity and thickness of the samples, rather than their chemical composition. Once spiked, gasoline quickly soaked into the porous



**Fig. 10.** The total ion chromatogram for a gasoline-spiked carpet sample dried for 1 h (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 10a. Note that the abundance scale of the four EICs was adjusted for clarity.

samples. Although more volatile fractions, such as short-chained alkanes, cycloalkanes, and toluene, quickly evaporated, less volatile (heavier) components, such as long-chain alkanes (e.g., *n*-tridecane), and C3- and C4-alkylbenzenes, persistently remained in some types of household materials, such as carpet and cardboard, for longer than three weeks. In addition, relative compositions of C3- and C4-alkylbenzenes with respect to 2-methylnaphthalene depends on the choice of samples. Therefore, the detection of C3- and C4-alkylbenzenes, and long-chain *n*-alkanes from unburnt household materials strongly indicates the presence of gasoline residues. However, special attention should be given to burnt samples because some components of gasoline such as alkylbenzenes

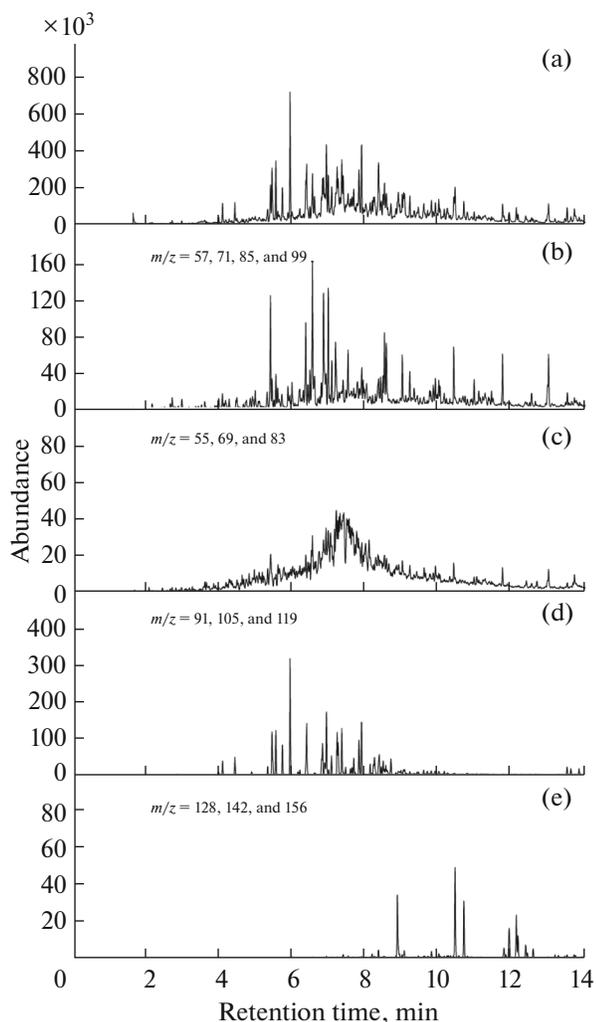


**Fig. 11.** The total ion chromatogram for a gasoline-spiked carpet sample dried for 1 day (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 11a. Note that the abundance scale of the four EICs was adjusted for clarity.

and naphthalenes could be produced by either the pyrolysis or combustion of household products and data analysis will be more complicated [37–40].

## CONCLUSIONS

Our study showed that the extraction of gasoline residues via HS-SPME using small-sized headspace vials is a powerful sampling technique to detect gasoline residues buried in household samples. The persistence of gasoline residues was mainly governed by the physical features of the samples, such as the thickness and porosity, rather than the chemical composition. The thicker and multilayered cardboard and car-

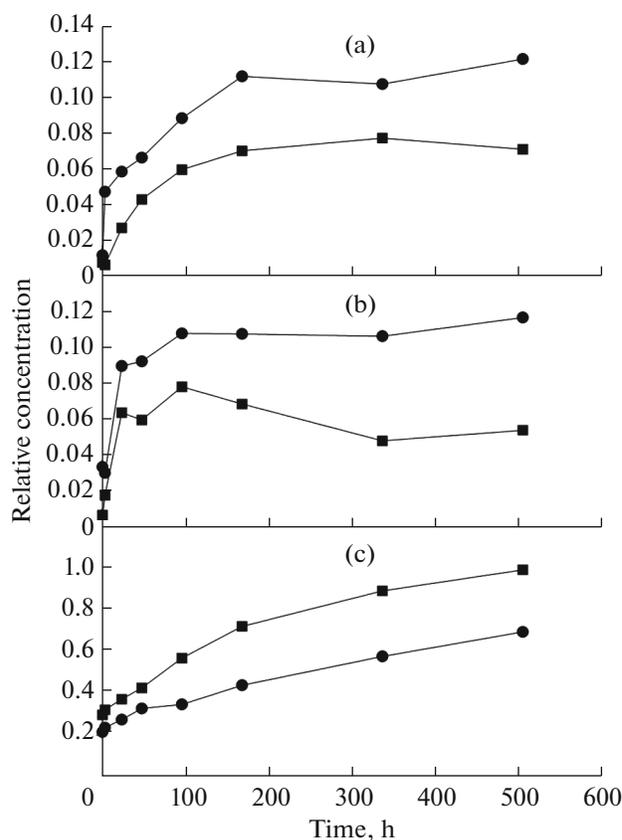


**Fig. 12.** The total ion chromatogram for a gasoline-spiked carpet sample dried for 21 days (a) and extracted ion chromatograms for selected ions of alkanes (b), cycloalkanes (c), aromatics (d), and naphthalenes (e) from the TIC shown in Fig. 12a. Note that the abundance scale of the four EICs was adjusted for clarity.

pet samples retained gasoline residues longer than the single-layered cotton fabric samples. Some components, such as C3- and C4-alkylbenzenes, long-chain alkanes, and naphthalenes, were detected in the gasoline-spiked cardboard and carpet samples even after three weeks of drying. The enhanced detection capability of gasoline residues presented in this work partly resulted from the use of small-sized vials for headspace concentration.

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**Fig. 13.** The relative compositions of 1,2,3-trimethylbenzene (■) and 1,2,4,5-tetramethylbenzene (●) with respect to the concentration of 2-methylnaphthalene in gasoline residues in cotton fabric samples (a), cardboard samples (b), and carpet samples (c) over 21 days of drying.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

#### REFERENCES

1. Almirall, J.R. and Furton, K.G., *Analysis and Interpretation of Fire Scene Evidence*, Boca Raton, FL: CRC, 2004.
2. Hendrikse, J., Grutters, M., and Schafer, F., *Identifying Ignitable Liquids in Fire Debris: A Guideline for Forensic Experts*, Waltham, MA: Academic, 2016.
3. Sandercock, P.M.L., *Forensic Sci. Int.*, 2008, vol. 176, nos. 2–3, p. 93.
4. Frontela, L., Pozas, J.A., and Picabea, L., *Forensic Sci. Int.*, 1995, vol. 75, no. 1, p. 11.
5. Muller, D., Levy, A., and Shelef, R., *Forensic Sci. Int.*, 2011, vol. 206, nos. 1–3, p. 150.
6. Almirall, J.R., Wang, J., Lothridge, K., and Furton, K.G., *J. Forensic Sci.*, 2000, vol. 45, no. 2, p. 453.
7. Montani, I., Comment, S., and Delemont, O., *Forensic Sci. Int.*, 2010, vol. 194, nos. 1–3, p. 115.
8. Darrer, M., Jacquemet-Papilloud, J., and Delemont, O., *Forensic Sci. Int.*, 2008, vol. 175, nos. 2–3, p. 171.

9. Furton, K.G., Almirall, J.R., Bi, M., Wang, J., and Wu, L., *J. Chromatogr. A*, 2000, vol. 885, nos. 1–2, p. 419.
10. Dhabbah, A.M., Al-Jaber, S.S., Al-Ghamdi, A.H., and Aqel, A., *Arab. J. Sci. Eng.*, 2014, vol. 39, no. 9, p. 6749.
11. Aqel, A., Dhabbah, A.M., Yusuf, K., Al-Harbi, N.M., Al Othman, Z.A., and Badjah-Hadj-Ahmed, A.Y., *J. Anal. Chem.*, 2016, vol. 71, no. 7, p. 730.
12. Cacho, J.I., Campillo, N., Aliste, M., Viñas, P., and Hernández-Córdoba, M., *Forensic Sci. Int.*, 2014, vol. 238, p. 26.
13. Kolb, B. and Ettre, L.S., *Static Headspace-Gas Chromatography, Theory and Practice*, New York: Wiley, 2006, 2nd ed.
14. Pawliszyn, J., *Solid Phase Microextraction: Theory and Practice*, New York: Wiley, 1997.
15. Wercinski, S.A., *Solid Phase Microextraction: A Practical Guide*, New York: CRC, 1999.
16. Górecki, T. and Pawliszyn, J., *Analyst*, 1997, vol. 122, no. 10, p. 1079.
17. Pasquier, E., Roux, C., and Lennard, C., *Forensic Sci. Int.*, 2005, vol. 147, no. 1, p. 71.
18. Coulson, S., Morgan-Smith, R., Mitchell, S., and McBriar, T., *Forensic Sci. Int.*, 2008, vol. 175, no. 1, p. 44.
19. Coulson, S.A. and Morgan-Smith, R.K., *Forensic Sci. Int.*, 2000, vol. 112, nos. 2–3, p. 135.
20. Folkman, T.E., Kuehl, A.M., Groves, R.J., and Beveridge, A.D., *J.—Can. Soc. Forensic Sci.*, 1990, vol. 23, nos. 2–3, p. 49.
21. Lentini, J.J., *J. Forensic Sci.*, 2001, vol. 46, no. 6, p. 1470.
22. Lentini, J.J., Dolan, J.A., and Cherry, C., *J. Forensic Sci.*, 2000, vol. 45, no. 5, p. 968.
23. *ASTM E2154-15a: Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME)*, West Conshohocken, PA: ASTM Int., 2015.
24. *ASTM E1618: Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry*, West Conshohocken, PA: ASTM Int., 2011.
25. Bartelt, R.J., *Anal. Chem.*, 1997, vol. 69, no. 3, p. 364.
26. Martos, P.A. and Pawliszyn, J., *Anal. Chem.*, 1997, vol. 69, no. 2, p. 206.
27. Tuduri, L., Desauziers, V., and Fanlo, J.L., *J. Chromatogr. Sci.*, 2001, vol. 39, no. 12, p. 521.
28. Prada, P.A., Curran, A.M., and Furton, K.G., *Anal. Methods*, 2010, vol. 2, no. 5, p. 470.
29. Rai, A.C., Guo, B., Lin, C.H., Zhang, J., Pei, J., and Chen, Q., *Indoor Air*, 2014, vol. 24, no. 1, p. 49.
30. Ziegleder, G., *Packag. Technol. Sci.*, 2001, vol. 14, no. 4, p. 131.
31. Czerny, M., Odors in paper and cardboard packaging, in: *Handbook of Odor*, Buettner, A., New York: Springer, 2017, p. 329.
32. Katsoyiannis, A., Leva, P., and Kotzias, D., *Fresenius Environ. Bull.*, 2006, vol. 15, no. 8, p. 943.
33. Elkilani, A.S., Baker, C.G.J., Al-Shammari, Q.H., and Bouhamra, W.S., *Environ. Int.*, 2003, vol. 29, no. 5, p. 575.
34. Won, D.Y., Corsi, R.L., and Rynes, M., *Environ. Sci. Technol.*, 2000, vol. 34, no. 19, p. 4193.
35. Zadora, G., Borusiewicz, R., and Zieba-Palus, J., *J. Sep. Sci.*, 2005, vol. 28, no. 13, p. 1467.
36. Roberts, J.C., *Paper Chemistry*, New York: R. Soc. Chem., 1996.
37. Almirall, J.R. and Furton, K.G., *J. Anal. Appl. Pyrolysis*, 2004, vol. 71, no. 1, p. 51.
38. Stauffer, E., *Sci. Justice*, 2003, vol. 43, no. 1, p. 29.
39. Prather, K.R., McGuffin, V.L., and Smith, R.W., *Forensic Sci. Int.*, 2012, vol. 222, nos. 1–3, p. 242.
40. Prather, K.R., Towner, S.E., McGuffin, V.L., and Smith, R.W., *J. Forensic Sci.*, 2014, vol. 59, no. 1, p. 52.