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Determination of Gasoline and Diesel Residues on Wool, Silk, Polyester and Cotton Materials by SPME−GC−MS[1]

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Abstract—The identification of ignitable liquids is very important and challenging aspect in arson crime investigations. The detection of gasoline and diesel fuel components using solid phase micro-extraction prior to gas chromatography−mass spectrometry for the forensic analysis of fire debris has been carried out. Previous works show that the absorption characteristics of the substrate are one of the most important factors in determining the evaporation rate of the accelerants. In order to determine the presence of the fuel residues, four of the most common substrate materials were tested in this work; wool, cotton, silk and polyester. The obtained results indicate that both gasoline and diesel fuel accelerants persisted longer on wool and silk than on the other selected substrates. Such information illustrates the influence of fuel persistence times after extinguishing and the best materials to be scanned for ignitable liquids at the fire scene.

Arson is a dangerous crime; even a small amount of an ignitable liquid can cause considerable losses in property and even human life. According to the National Fire Protection Association, more than 280000 intentionally set fires per year were reported to local fire departments in the U.S. between 2007 and 2011. These fires are associated with about 420 annual deaths, 1360 injuries, and $1.3 billion in direct property damage [1]. Usually, an arson is started by using one of the famous ignitable liquid accelerants such as gasoline, diesel fuel and kerosene. These accelerants represent the main choice by many arsonists because of their low cost and availability [2, 3].

The identification of the arson source is a significant forensic aspect of the criminal investigation. However, it is not always straightforward, as fire will often destroy the evidence of arson. In addition to the complex nature of the accelerants and the fire itself, the water, dry chemicals and foams that are most commonly used to extinguish the fires may also destroy the evidence. As a result, no or just trace amount of the substances could be detected at the crime scene [4, 5].

In order to effectively examine and evaluate the fire scene, the investigations should analyze the debris chemicals resulting from the fire, including the presence of such targeted components as hydrocarbons suggesting the presence of ignitable liquid residues. Chemist's job will then consist in extraction, isolation, preconcentration, identification and determination of these target compounds that could be used to accelerate a fire.

Gas chromatography coupled with flame ionization detection or mass spectrometry (GC−MS) are commonly used for identification and determination of ignitable liquids. Both detection techniques are capable of detecting almost all hydrocarbon components of the ignitable liquids [6−9]. Unfortunately, the analysis of ignitable liquid residues is not an easy task. However, extraction techniques have to be carried out prior to any detection method in order to preconcentrate the analytes and remove the matrix interferences.

Several methods have been developed as sample preparation techniques of ignitable liquids. The most

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Analytical parameters

Parameter	Accelerant	
	gasoline	diesel fuel
Carrier gas	Helium, 2 mL/min	Helium, 1 mL/min
Injector temperature, °C	250	220
Temperature program:		
initial temperature	50°C (held 3 min)	80°C (held 5 min)
ramp rate	5 grad/min	15 grad/min
final temperature	250°C (held 15 min)	300°C (held 2 min)
Split ratio	1 : 50	1 : 250
Sample injection volume, μL	0.5	0.5
MS interphase temperature, °C	250	250
MS ion source temperature, °C	200	200

common methods of extraction used for fire debris samples are solvent extraction, headspace extraction with passive or dynamic analysis and steam distillation [2, 10–16]. In early 1990's, Janusz Pawliszyn introduced solid phase microextraction (SPME) as a fast, uncomplicated and efficient extraction tool [17, 18]. Since that time, SPME has been rapidly developing and gaining great interest for sampling and pre-concentration of various analytes in a single and simple step prior to GC determination of the target compounds, particularly for the extraction of volatile organic compounds from fire debris [19–28].

An SPME sorbent contains fused silica fiber coated with various extracting phases that can be solid, liquid or a combination of both [29]. This technique enables rapid sample preparation in the laboratory and even on-site for both volatile and nonvolatile compounds [18]. SPME requires little or no solvents in which the fiber is immersed in case of a liquid sample or exposed to the headspace above a solid or liquid sample [30, 31]. The SPME fiber is then inserted into the injection port of a gas or liquid chromatograph, where the extracted analytes are desorbed and then determined [32, 33].

In this study, a polydimethylsiloxane SPME fiber was used for extraction of gasoline and diesel accelerants prior to their GC–MS separation and determination. Four different substrate materials were tested including wool, cotton, silk and polyester. The main purpose for this work was to determine the evaporation and persistence of the accelerants on each substrate. This kind of studies could provide very useful information for the fire investigators in sampling process at the crime scene and help explaining the real reason behind the fire.

EXPERIMENTAL

Chemicals and materials. Diesel and gasoline (91 octane) samples were regular grade and obtained from local petrol station in Riyadh, Saudi Arabia. The chosen substrate samples: wool, cotton, silk and polyester samples (10 × 10 cm square-shaped pieces) were donated from local markets (Riyadh, Saudi Arabia). SPME fiber (100 μm polydimethylsiloxane, PDMS-100) was purchased from Supelco (Bellefonte, PA, USA). Before being used for the extraction of the accelerant samples studied, the fibers were conditioned according to the suppliers' instructions in the GC injector at 250°C for 1 h.

GC–MS analysis. All determinations were performed using GC–MS system constituted by Thermo Trace GC Ultra gas chromatograph equipped with AI 3000 injector and linked to a Thermo TSQ Quantum mass spectrometer. Peaks were scanned in the m/z range from 40 to 300. For the separation of the target compounds, a TR-5 MS-SQC capillary column (15 m × 0.25 mm i.d., phase thickness 0.25 μm) was used. The GC–MS parameters used for the present study are given in the table. The injections were carried out in a splitless mode for the SPME method while reference samples were injected in a split mode.

Extraction and samples collection. The first part of the study was designed to evaluate gasoline as a reference ignitable liquid. SPME was performed by saturation of the substrate materials (wool, cotton, silk and polyester) with 200 μL accelerant, left to burn for 2 min and extinguished. The burning samples were extinguished by placing under an inverted 1000-mL beaker.

Nylon bags sized 12" × 18" (Tritech Forensics, Executive Park Blvd, Southport, NC, USA) were used for the collection of the fire debris samples after burning. The bags containing the fire debris retrieved from
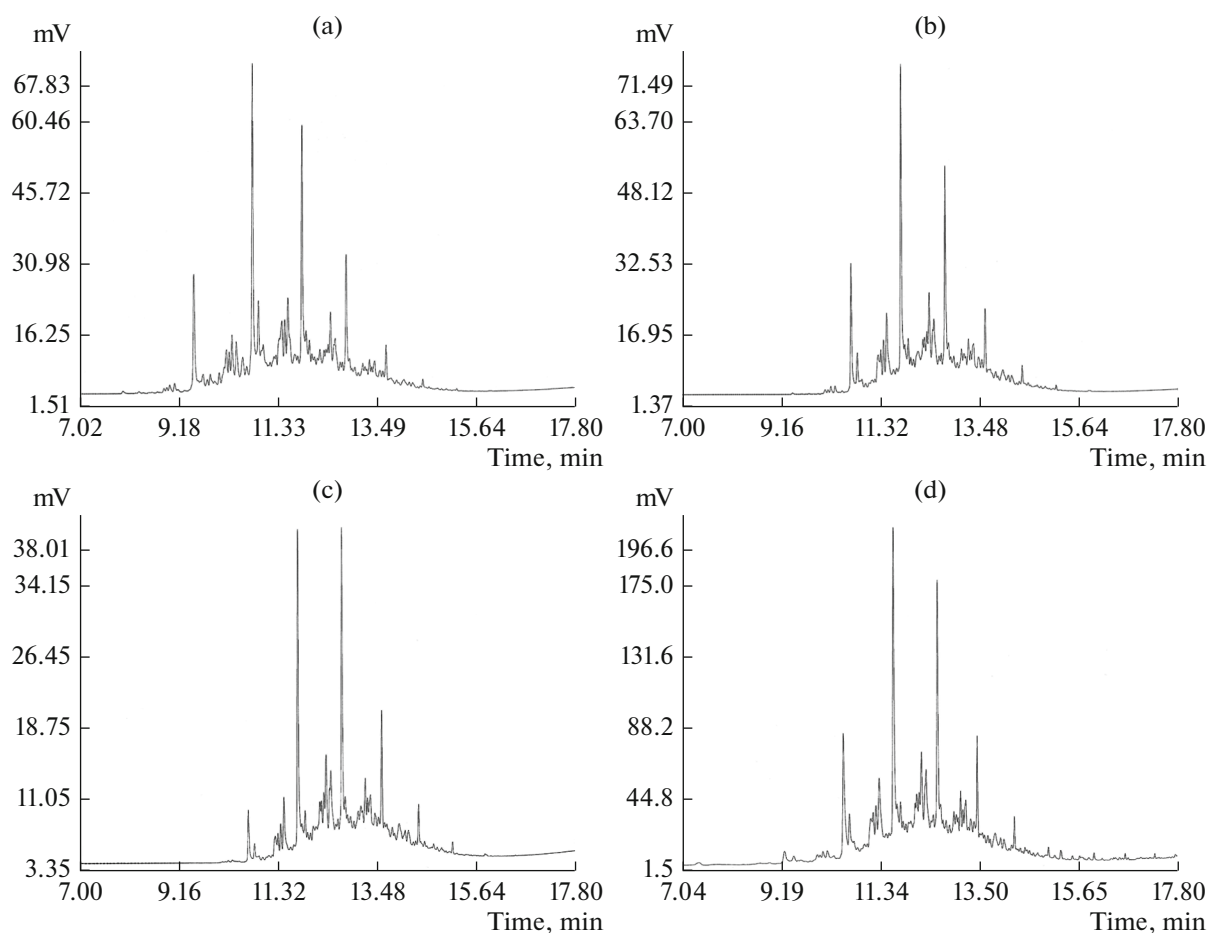
Fig. 1. Total ion chromatograms of the SPME extract after burning with diesel fuel: wool (a), silk (b), polyester (c), and cotton (d) samples collected 3 h from extinguishing.

an arson scene were pierced and an SPME fiber portion was placed into a direct contact with the fire debris for 1 min to extract accelerants and then placed in the GC−MS injection port for 100 s. The extracted compounds were then directly injected into the GC−MS column.

In order to provide information on the effect of delays to the measurements, some of the burnt samples with diesel fuel were collected for analysis after varying times ranged between 1 and 15 h. In all parts of the study, substrate materials were directly transferred separately to the nylon bags. A passive headspace extraction of the volatile compounds was carried out in an oven at 40°C for 30 min. In all cases, each accelerant was drawn along the substrate samples in a circular shape, each sample was then ignited with lighter and allowed to burn about 2 min in a fume hood with controlled ventilation, and then extinguished by smothering. Three replicates were collected for each analysis and the average values were considered.

Identification criteria. A number of target compounds were chosen to determine the presence or absence of gasoline and diesel accelerants (summarized below):

Gasoline	Diesel
Toluene	n-Tridecane
Ethylbenzene	n-Tetradecane
p-Xylene	Pentadecane, branched
n-Propylbenzene	n-Pentadecane
1,3,5-Trimethylbenzene	Hexadecane, branched
1,2,4-Trimethylbenzene	n-Hexadecane
1,2,3-Trimethylbenzene	n-Heptadecane

Total ion chromatograms were obtained and evaluated by visual pattern matching against known standards. All major peaks were identified using mass spectral data and recorded for each sample chromatogram. The identity of each target compound was then confirmed by searching its mass spectra against a reference library. In order to obtain the background signals, mass spectra of both accelerants and substrate materi-
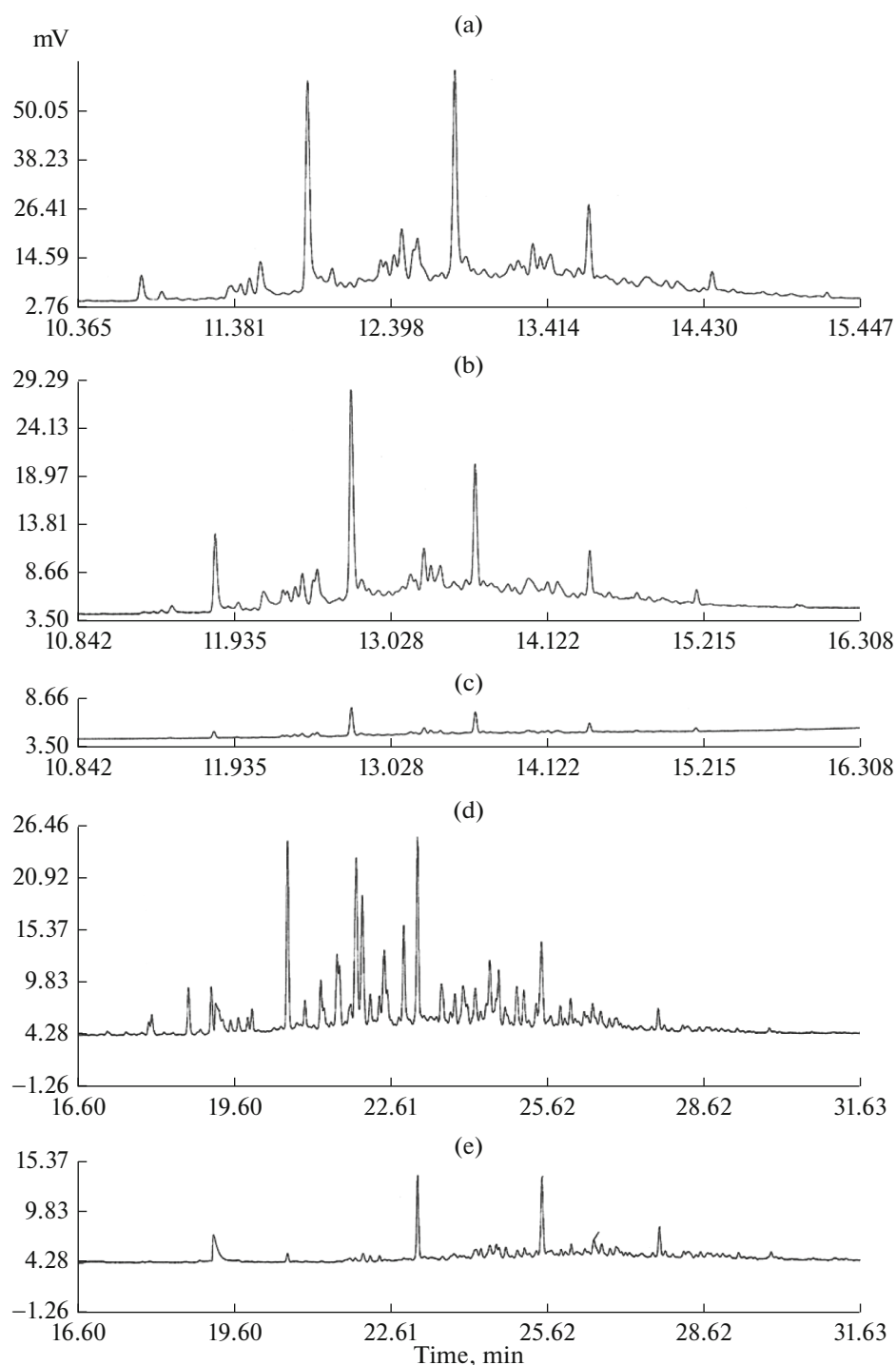
Fig. 2. Total ion chromatograms of the SPME extract after burning with diesel fuel: wool (a), silk (b) and cotton (c) samples after 12 h from extinguishing; burning with gasoline: wool (d) and silk (e) samples collected 3 h from extinguishing.

als were recorded simultaneously as references along all analyses. As the substrates might contribute to the detected accelerants residues, each substrate containing no accelerant was also burned and subjected to the same procedure.

RESULTS AND DISCUSSION

Reference data. Reference spectra for gasoline and diesel accelerants were recorded, both accelerants contain many highly volatile components that elute during the first 8 min for gasoline and 10 min for diesel
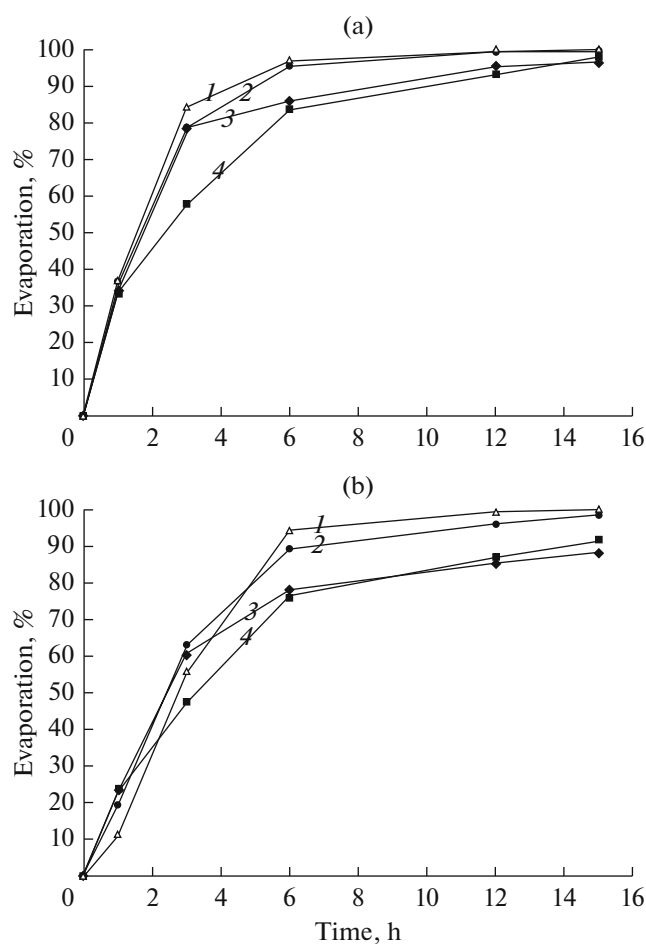
Fig. 3. Evaporation curves for polyester (*1*), cotton (*2*), silk (*3*) and wool (*4*) using 1,3,5-trimethylbenzene (a) and *n*-pentadecane (b) as target compounds over a 15 h period.

yielding intense peaks. Our strategy consists in the detection of greater masses because the burning process always removes more of the lighter compounds. The chromatographic peaks of the compounds listed above were considered as identifiable fingerprints to check the presence of the accelerator. Gasoline and diesel fuel can easily be differentiated from their GC profiles via the presence of characteristic components as their constituents.

Persistence of accelerants on substrate materials. The main target for this study was to measure the persistence of gasoline and diesel residues on various substrate materials. Some of the most common materials normally encountered in homes and workplaces were selected: wool, cotton, silk and polyester. For comparison purposes, all the mentioned materials with the same dimension (10 × 10 cm) were passed through the same burning procedure.

The total ion chromatograms of the SPME extract from burnt substrates after 3 and 12 h from extinguishing are shown in Figs. 1 and 2. It is axiomatic that diesel fuel persisted longer than gasoline on any given

substrate; the rate of evaporation of the accelerant was highly dependent on its boiling range. Almost all target components were present on wool and silk samples for longer periods than on the polyester and cotton samples. As an example, pentadecane and branched hexadecane were readily identified on wool and silk up to 12 h. Only trace amounts of them were detected on cotton and nothing was recovered from polyester after this period. This could be explained by the volatility of the accelerant components and sorption characteristics of the substrates.

In order to compare the evaporation rates for gasoline and diesel fuel on the substrates, the target components were studied under fixed conditions in the interval of 1 to 15 h. The percentage evaporation rates of the accelerant loss are shown in Fig. 3. It should be noted that wool could be more interesting than silk in reserving accelerant components for periods of time not more than 10 h. On the other hand, silk samples could be more interesting at relatively longer times. This information could be very important for the fire investigators in sample collection timelines. However, no significant differences in the evaporation times were detected between the polyester and cotton samples and between wool and silk samples.

Delayed analysis after burning. In order to establish a time interval after which the accelerants could no longer be identified, the substrate materials were burned after adding 200 μL of each accelerant. The fire residues were then determined after various times of extinguishing starting from 1 and up to 15 h. In addition, we studied the effect of weather conditions on the fire debris residues; this stage was designed to determine the actual time for the survival of the fire accelerant after extinguishing the samples. These experiments could be used to answer one of the most frequently asked questions by fire investigators: how long will flammable liquids remain on substrate materials.

Chromatograms recorded for the fire debris samples are shown in Fig. 4. The overall residues of species were found to be reduced with time by an order of magnitude, which is not surprising. Moreover, an important decrease in quantity occurred during the first three hours over almost all chromatograms. As an example, the decreasing quantity for pentadecane reached 47% in the case of wool, in comparison with 58% for 1,3,5-trimethylbenzene residues (about 10% more), as described in Fig. 3.

It is concluded that there are no fire residues remained in the burnt polyester and cotton samples after 15 h in all gasoline and diesel residues. Using the same experimental conditions, diesel accelerant residues have been detected for about 20 and 24 h after extinguishing in the of case of wool and silk samples, respectively. The same observations were done in the case of gasoline residues, though with lower percentages. The expected reason may be referred to the
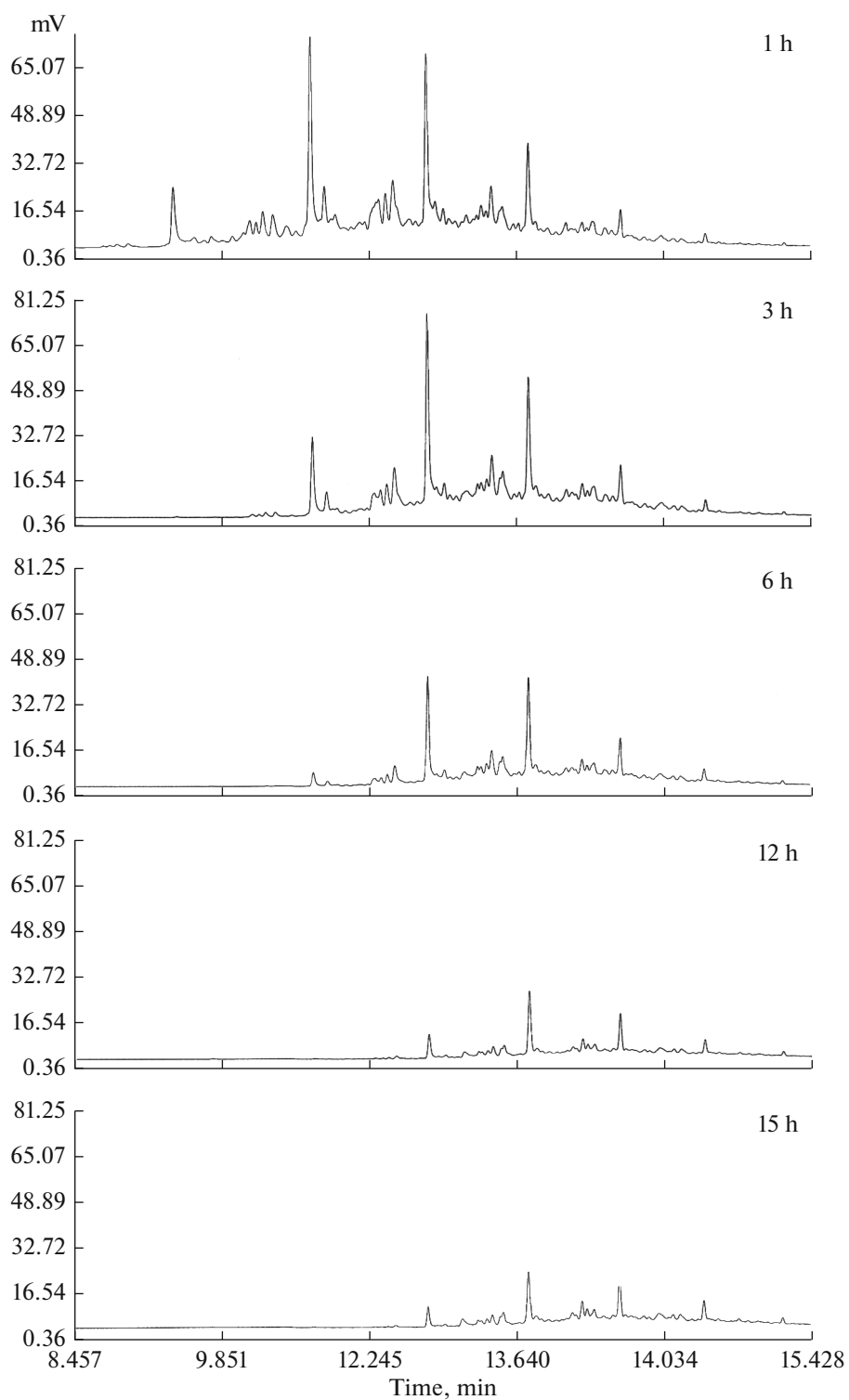
Fig. 4. Total ion chromatograms of the SPME extract from silk samples burnt with diesel fuel after various periods of time since extinguishing.

adsorption behavior of the gasoline and diesel accelerants on the substrate materials, which was more readily adsorbed on the silk and wool surfaces.

A method has been successfully developed for the determination of gasoline and diesel debris using SPME prior to identification by GC–MS.

Results show that the polydimethylsiloxane SPME fiber is capable of detecting as low as 200 μL of each accelerant at optimum conditions. In addition to the kind of the fire accelerant itself and the surrounding conditions, the evaporation rate of the accelerant is highly dependent on the absorption characteristics of the substrate. On any substrate type, the diesel fuel components preserved longer than gasoline components. Under fixed conditions, both accelerants persisted longer on wool and silk than on polyester and cotton. Collecting fire debris from wool could be more interesting for medium periods, while silk samples could be more informative at relatively longer periods. In conclusion, the results indicated that SPME is an easy, fast and effective method for sampling accelerants in fire debris determination.

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