

Determination of Gasoline Residues on Carpets by SPME–GC–MS Technique

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Abstract The analysis of traces ignitable liquids on a burned carpet could provide information to a forensic investigation. While the research on this field is still limited, this study illustrates the capabilities of the solid-phase microextraction coupled with gas chromatography-mass spectrometry to detect and identify gasoline residue from fire debris. The technique proved to be rapid, simple and efficient; it does not require specific skills or solvents for the extraction. The obtained results indicate that the amount of fuel used to ignite the carpet samples and a carpet thickness, play an important role on the presence and survival of the gasoline residues. This depends on the adsorption capacity of the burned carpet, where it is preferred to take samples from thin carpets rather than thick one, i.e., gasoline traces were detected up to 5 h, above carpet of 5 mm thickness using 2 mL accelerant.

Keywords Forensic science · Arson · Ignitable liquids · Gasoline · GC-MS · SPME · Carpet

الخلاصة

يُعد تحليل بقايا آثار مسرعات الاشتعال على السجاد من أهم الطرق التي يمكن أن توفر معلومات مهمة في التحقيقات الجنائية لمعرفة أسباب الحرائق. وعلى الرغم من أن الدراسات في هذا المجال مازال محدودة يقوم هذا العمل على دراسة قدرة طريقة استخلاص الطور الصلب الدقيقة ، والتحليل بتقنية كروماتوغرافيا الغاز مع طيف الكتلة لكشف بقايا البنزين وتحديدها من مخلفات الحرائق. فقد أثبتت هذه الطريقة فعالية عالية إلى جانب بساطة تنفيذها وسرعتها ، حيث إنها لا تتطلب مهارات محددة أو استخداماً لأي مذيبات في عملية الاستخلاص. وتشير النتائج التي تم الحصول عليها من هذه الدراسة إلى أن كمية الوقود المستخدمة لإشعال عينات السجاد إضافة إلى سماكته تلعب دوراً هاماً في إمكانية بقاء مخلفات البنزين بعد الحرق ، وهذا يعتمد على سعة امتزاز عينات السجاد المحترقة ، حيث يفضل اختيار عينات من السجاد ذات سماكة أقل بدلاً من العينات السميكة ، وذلك لزيادة احتمال بقاء آثار مسرعات الاشتعال عليها مدة أطول. فمن خلال هذه الدراسة تم الكشف عن آثار البنزين مدة وصلت إلى خمس ساعات باستخدام عينات من السجاد ذات سمك 5 ملم سمك تم حقنها بـ 2 مل من البنزين.

1 Introduction

Arson fires are usually started by the use of ignitable liquid accelerants. Accelerants such as gasoline, diesel and kerosene are used by many arsonists to increase the rate and intensity of the fire; these accelerants are a main choice for arsonists because of the low cost and availability [1]. Even the use of a small amount of an ignitable liquid can cause considerable monetary losses as well as endanger in human lives.

Arson crimes are often difficult to detect due to the lack of physical evidence associating a suspect to the crime, in addition to the complex nature of the accelerants and the fire itself, the combustion process and associated heat create damage that leave small traces of the substance at the crime scene [2,3]. An important aspect of an investigation of a suspected arson case involves the chemical analysis of the debris resulting from the fire.

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One of the major objectives of the investigators at the crime scene is to search and collect the fire debris that contains traces of ignitable compounds; the presence of various target components suggests the presence of ignitable liquid residues. Forensic chemists are tasked with the extraction, isolation, concentration, identification and analysis of these target compounds that could be used to accelerate a fire that was set intentionally.

The detection and analysis of these ignitable liquid residues are routinely carried out in order to determine which type of liquid accelerant was used, thus giving investigators important information that can be useful in explaining the cause and propagation of the fire, gaining intelligence on a series of offenses, and even pointing to or excluding suspects [4,5].

GC-MS is one of the most widely used techniques by forensic chemists and investigators in arson analysis [6–8], but analysis of these residues is not always straightforward. In most cases, extraction procedures have to be employed prior to GC analysis, to concentrate analytes and to remove extraneous matrix interference.

Several traditional and modern techniques for sample preparation of ignitable liquids, such as solvent extraction, steam distillation, passive and dynamic headspace methods, have been developed and validated in the literature, for the extraction and collection of fire debris residues [1,9–16].

Since the introduction of SPME by Pawliszyn in the early 1990s [17], it has been gaining great interest for the sampling and pre-concentration of the analytes of interest in a single, simple step prior to GC-MS analysis of the target analytes [18–25]. In comparison with the other traditional techniques, SPME is a simple method that requires no solvent desorption stage or complicated extraction apparatus.

Several arson researches have been explored using SPME for the extraction of volatile organic accelerants from fire debris [25–34]. SPME is a powerful extraction technique, it consists of a phase coated fused silica fiber, and the fiber is coating with an immobilized polymer that exposed to the headspace of the sample [35,36]. The analytes are extracted from the headspace by absorption into the polymer coated onto a quartz fiber that is housed within a needle similar to a syringe needle. Within several minutes, the absorbed analytes can be desorbed by thermal desorption in GC injection port and directly inserted for analysis [37,38].

In this study, polydimethylsiloxane SPME fiber was tested for detection and identification of gasoline accelerant from burned carpets materials. More than 50 carpet samples were analyzed using SPME and GC-MS. Different parameters were tested including amount of gasoline, carpet thickness and delayed time after burning.

2 Experimental

2.1 Chemicals and Materials

Gasoline samples were regular grade (95 octane) and obtained from local petrol stations in Riyadh, Saudi Arabia.

Polyester carpet samples with different thickness (5, 15 and 25 mm) and 10 × 10 cm square-shaped pieces of polyester carpets were donated by a local carpet supply house (Riyadh, Saudi Arabia).

2.2 SPME Fibers

SPME fiber (100 μm polydimethylsiloxane, PDMS-100) was purchased from Supelco (Bellefonte, PA, USA). Before using 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.

2.3 GC-MS Analysis

All determinations were performed using a GC-MS system constituted by an Agilent 6890N gas chromatograph coupled with Agilent 5973 Mass selective detector. Chromatographic separation of the analytes was obtained by an Agilent 5MSI capillary column with the following dimensions: length 30 m; internal diameter 0.25 mm; and film thickness 0.25 μm . The column, with a constant helium flow of 1.0 mL min^{-1} , was submitted to the following temperature program: Initial temperature was 35 °C, held for 2 min, ramped at 10 °C min^{-1} to 220 °C, held at 220 °C for 2 min, ramped at 30 °C min^{-1} to 300 °C, held at 300 °C for 10 min. The total running time was 35 min while the injector temperature was set at 250 °C.

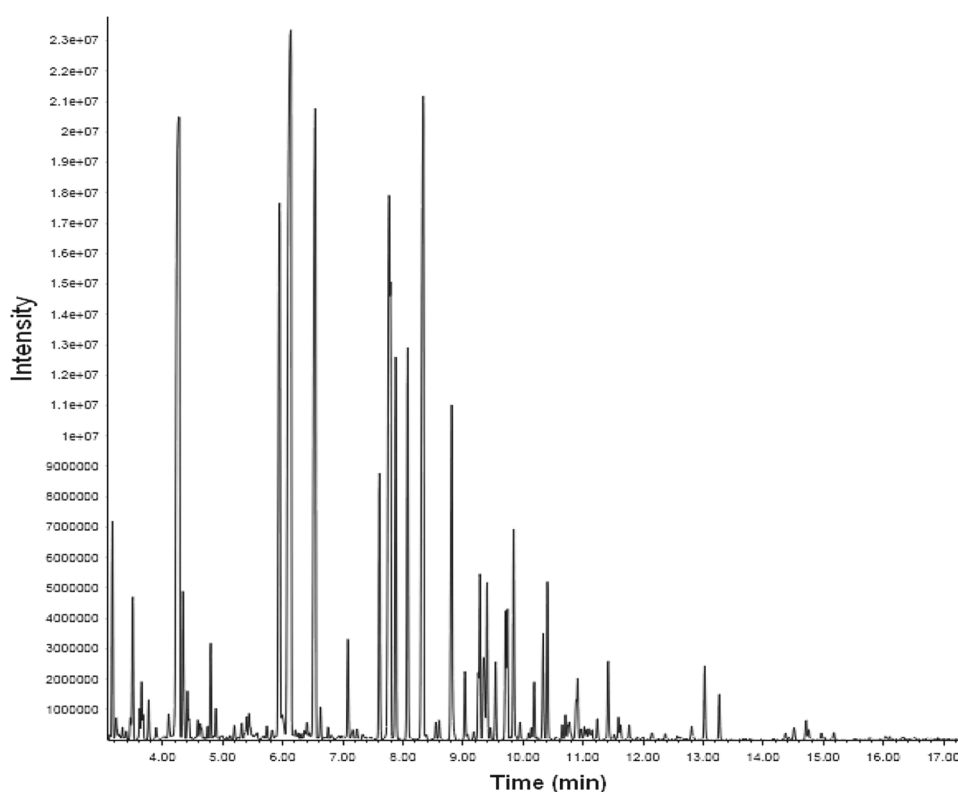
The mass selective detector was operated in scan mode in the mass range of 30–300 units to detect the ions produced by electron ionization (70 eV) at 230 °C ion source temperature. The injections were carried out in a splitless mode for the SPME method and in a split mode with 10:1 ratio for a reference samples.

2.4 Extraction and Samples Collection

The first part of the study was designed to evaluate gasoline as a reference ignitable liquid. Then, carpet samples with 5, 15 and 25 mm thicknesses were saturated with different gasoline volumes (1, 2 and 3 mL) for 1 min, burned for 1 min and extinguished. The burning carpets were extinguished by placing under an inverted 1000-mL beaker.

Nylon bags with 12" × 18" dimension (Tritech Forensics, Executive Park Blvd Southport NC, USA) were used for collection of the fire debris samples after burning. The extraction protocol performed according to the solid-phase micro-extractor manual provided by its manufacturer. The

Fig. 1 Reference total ion chromatogram of the gasoline accelerant by GC-MS



nylon bags containing fire debris were pierced, and the SPME fiber part was placed in direct contact with the fire debris retrieved from an arson scene for 1 min to extract accelerants and adjusted in the GC injection port for 10 sec. The extracted compounds were then directly injected into a port of the GC-MS.

The effect of time on sampling and analysis of the debris was studied; fire debris samples were collected for analysis after varying times ranged between 0.5 and 12 h from the subjection to the carpet samples. In all parts of the study, carpets were directly transferred to the nylon bags. A passive headspace extraction of the volatile compounds was carried out in an oven at 50 °C for 30 min.

The same procedure was repeated with each carpet thickness for five different periods of time (0.5, 1, 2, 3 and 5 h) after application; in the present stage, 2 mL of gasoline was drawn along the carpet samples in a circular shape; and each carpet 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. The resulting extracts were then examined for the presence of trace amounts of gasoline. In all cases, three replicates were collected for each analysis and the average values were considered.

2.5 Gasoline Identification Criteria

The identification of gasoline was carried out based on the criteria recommended by the American Society for Testing and

Materials (ASTM) E 1618 standards [39], and these guidelines state that to conclude the presence of gasoline, a group of several compounds including C3 and C4-alkylbenzenes in addition to various aliphatic compounds must be present.

A number of target compounds such as toluene, ethylbenzene, propylbenzene, 1,2,3-trimethylbenzene and 1,3,5-trimethylbenzene were chosen to determine the presence or absence of gasoline. 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 their mass spectra against a reference library.

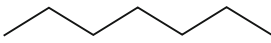
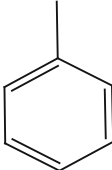
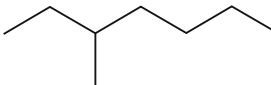
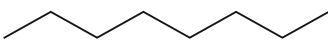
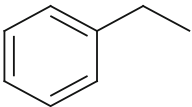
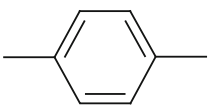
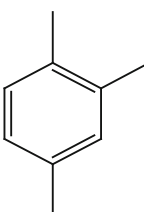
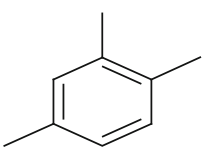
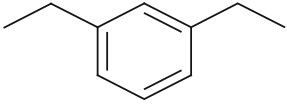
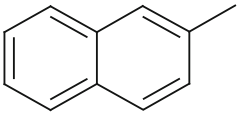
3 Results and Discussion

3.1 Reference Data

Reference spectrum recorded for gasoline accelerant is shown in Fig. 1. Gasoline contains many highly volatile components that elute during the first 15 min with high intensity. Table 1 lists the mass channels for the present compounds with their masses and retention times. In order to check the presence of gasoline in carpet samples during this study, some of these compounds were used as distinctive chromatographic peaks which were considered as an identifiable fingerprinting for accelerator in GC analysis.



Table 1 Target components of gasoline considered during this study

Compound name	Chemical structure	Molecular mass	Retention time (min)
n-Heptane		100	3.171
Toluene		92	4.263
3-Methyl heptane		114	4.349
Octane		114	4.784
Ethyl benzene		106	5.964
p-Xylene		106	6.123
1,2,4-Trimethyl benzene		120	7.851
1,2,5-Trimethyl benzene		120	8.292
1,3-Diethyl benzene		134	9.247
1-Methyl naphthalene		142	13.276

Examination of the gasoline background spectrum reveals some clear peaks at masses m/z 92 (C_7H_8), m/z 100 (C_7H_{16}), m/z 106 (C_8H_{10}), m/z 120 (C_9H_{12}), m/z 134 ($C_{10}H_{14}$) and m/z 142 ($C_{11}H_{10}$).

It should be noted that there is a possibility for presence of some lighter masses, observed under ($m/z < 60$), which are the products of the larger aromatic fragmentation species present in petrol samples. However, under our current aim of providing characteristic fingerprints for gasoline accelerant residues, it should not be too problem-

atic as the proportion of fragments produced in our case remains constant over repeated experiments with all gasoline samples.

3.2 Effect of Fuel Amount

In order to determine the best accelerant volume that gives more gasoline residues, carpet samples with same dimension (10×10 cm) and 15 mm fixed thickness were burned for 2 min after adding different gasoline amounts.



As shown in Fig. 2, studying the effect of gasoline contents showed that the highest peak responses have been achieved when the gasoline content was 2 mL. This volume corre-

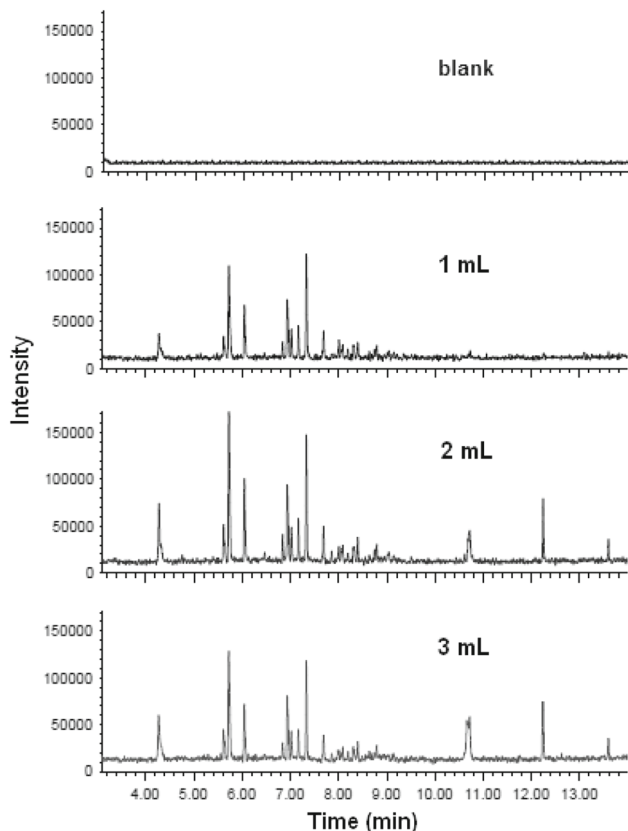
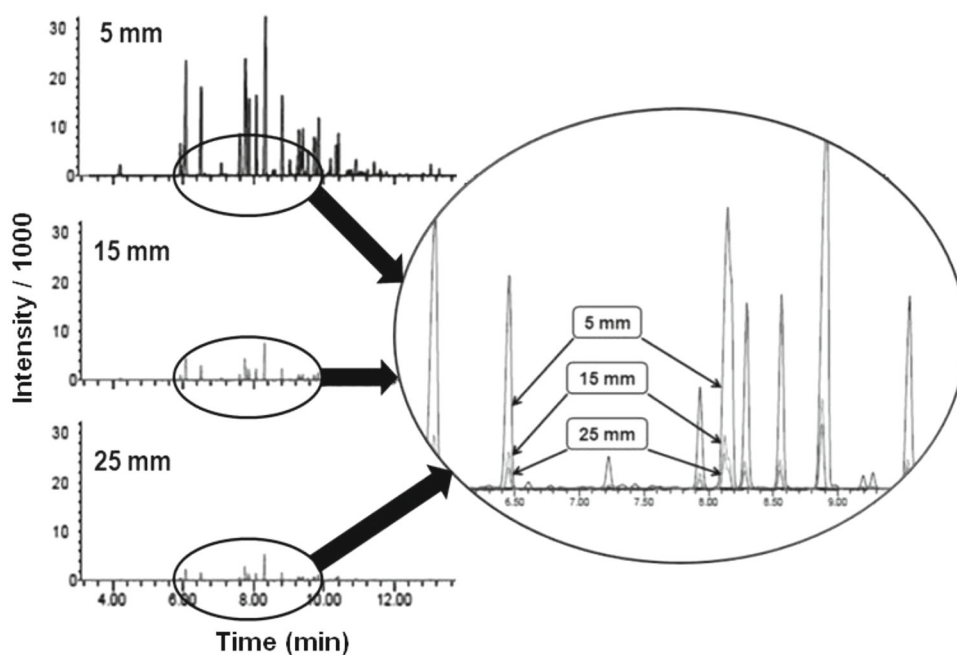


Fig. 2 Total ion chromatograms of the SPME extract from burnt carpet samples of different gasoline volumes (blank, 1, 2 and 3 mL)

Fig. 3 Total ion chromatograms of the SPME extract from burnt carpet samples of different thickness (5, 15 and 25 mm)



sponds to the optimum value of the carpet capacity of adsorption. Two milliliter gasoline volume has been set for next experiments. Furthermore, there is an indication for presence of some additional peaks at 14.237, 15.472, 17.536, 19.262, 21.428 and 22.753 min, which may be attributable to burnt carpet contents.

3.3 Effect of Carpet Thickness

In the present stage, several experiments were conducted for different carpet samples thicknesses (5, 15 and 25 mm). All samples were soaked with a specific gasoline amount (2 mL) as optimized in the last section.

Figure 3 shows the influence of carpet thickness on the amounts of fire debris residues. A trend to lower intensity is observed when the carpet thickness increased. 5 mm carpets thickness exhibited the most residues contents. The overall intensities for the all mass channels are two or more orders of magnitude lower using 15 mm carpet thickness, and about the same magnitudes using 25 mm carpet samples thickness.

3.4 Delayed Analysis After Burning

Carpet samples with the three used thickness were burned in this stage of work after adding 2 mL of gasoline accelerant. The fire residues were then analyzed after various times of extinguishing starting from 0.5 and up to 5 h. In addition to study 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 carpet samples. These experiments could be used to answer one of the most frequently asked questions by fire investiga-



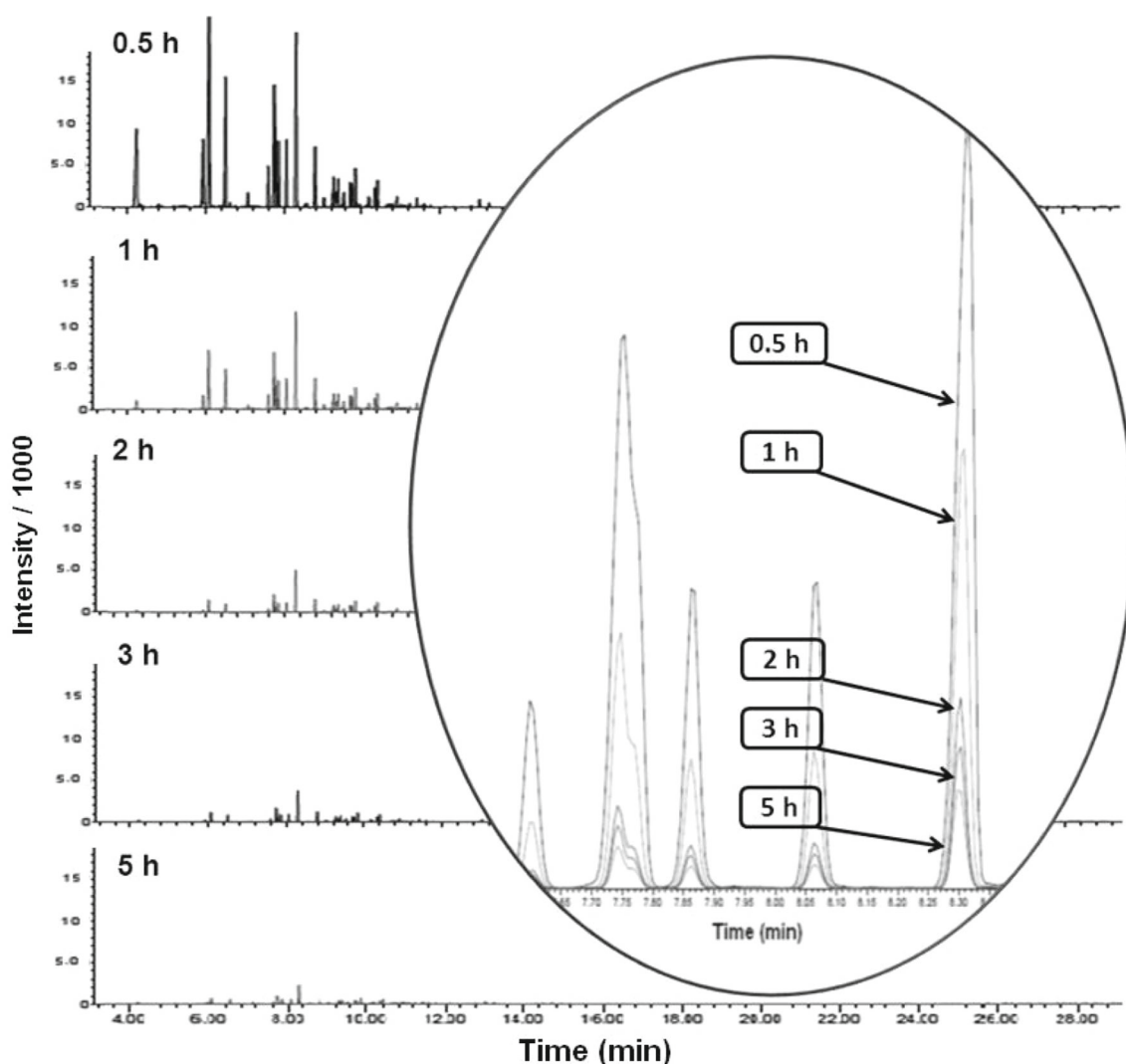


Fig. 4 Total ion chromatograms of the SPME extract from burnt carpet samples with 5 mm thickness after periods of times (0.5, 1, 2, 3 and 5 h) from extinguishing

tors; how long will flammable liquids remain on carpets or other materials.

Chromatograms recorded for the fire debris samples analyzed above 5 mm thickness carpets, after periods of times from extinguishing, are shown in Fig. 4. The overall residues of species were found to be reduced with the time by an order of magnitude, which is unsurprising. Moreover, an important decrease in quantity occurred during the first half-hour overall chromatograms shows strong similarities with those obtained with the two other thickness.

It is concluded that there are no fire residues remain in the burnt 5 mm carpet samples after 5 h. Using the same experimental conditions, no gasoline residues have been detected after about 3 and 2 h in the case of 15 and 25 mm thickness carpet samples, respectively. The expected reason may be referred to the adsorption behavior of the gasoline accelerant on the carpet materials, which was more readily adsorbed

on the thin carpet surface, so the gasoline is exposed to more radiant heat. On the other hand, no sufficient amounts of the accelerant have been reached to the textile of the carpets in the other cases.

The obtained results were compared with those of previous studies that evaluated the persistence of gasoline on various substrates; the same observations were founded in all studies. With the exception of 5 mm thickness carpets, which permitted to detect gasoline accelerator for a period of time up to 5 h after extinguishing, all other values are in a good agreement with our obtained values [24,30,40]. This observation supports the trend reported in this work.

4 Conclusion

Ignitable liquid identification is an important topic in arson crime investigation, because liquids such as gasoline and

kerosene are commonly used as accelerants in arson crimes. In the present study, a method has been developed for the extraction, analysis and identification of gasoline fuel using SPME then analysis by GC-MS. The developed method was rapid, simple and efficient. Based on the finding results, the presence of gasoline could only be established in samples collected directly after few hours from extinguishing the fire.

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