



An Analysis of Background Interference on Fire Debris

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Abstract

In this study, the controlled burn experiments of carpets with and without gasoline in this study and commonly encountered substrates produced complex chromatograms producing peaks that were identified by mass spectrometry and comparison with reference standards and each other. The result shown that many of the compounds frequently encountered as a result of either combustion products or pyrolysis products of carpets detected in fresh gasoline as well. These compounds as background interferences that detect whether the gasoline exist in carpet combustion products or not

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1. Introduction

According to the United States Fire Administration, the US has one of the highest fire death rates in the industrialized world at 14.5 deaths per million population and during the year 2000, 4045 Americans lost their lives and another 22 350 were injured as the result of fire; During this time, an estimated 75 000 incendiary or suspicious structure fires resulted in 505 civilian deaths and \$1.3 billion in property damage ^[1]. Arsons are particularly great challenges to investigate due to usual lack of physical evidence associating a suspect to the crime. That's because much of evidence at the scene is destroyed by the combustion and thermal degradation. And there are many outside interferences that are similar with petroleum products present in the fire. As a result of only the existence of the accelerants in fire debris is not a definitive indicator for an arson suspected.

The usage frequency of gasoline that is composed of hundreds of compounds is the highest and its composition make identification of fire debris very difficult. Currently, many scientists devoted to study accelerants and advanced technologies were used to analyze accelerants. Some persistence studies were conducted to determine the evaporation and persistence of petrol on different matrix. Lentini et al. ^[2] investigated the volatile components detectable in a wide variety of common objects, ranging from household products to shoes, clothes and carpet. They concluded that carpet samples can contain a number of compounds found in petrol. The evaporation of petrol from soil has been examined ^[3,4], and studies have been performed regarding the transfer and persistence of petrol on hands after filling a car ^[5], and on clothing and shoes while pouring petrol around a room ^[6]. K. Cavanagh et al ^[7], reported the theory that is a natural occurrence of petrol on the carpet or carpet mats of motor vehicles that would interfere with the potential determination of arson residues and he presented determine what levels of background interference due to the carpet matrix are likely to be encountered in the general population of motor vehicles. Folkman et al. ^[8] discovered that petrol was detectable on shoes after a period of 48 h, and on carpet after 7 days. The carpet in that study was left in an outdoors environment, at temperatures ranging from 5 to 15 °C.

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The study of accelerants component was conducted to determine the background interference on fire debris from different matrix. MS. Fernande et al^[9]. studied the common household items that were partially burnt and then sampled for volatile pyrolytic products using passive headspace adsorption. The adsorbed volatiles were then thermally desorbed and analyzed with capillary column gas chromatography. On comparing the results with those for corresponding unburnt samples, it was found that only a small proportion of the volatiles detected in the burnt items were pyrolytic products, the rest of the volatiles were attributed to residues originally present in the unburnt items. Scott A. Stout^[10] studied two cases suspected pipeline releases with gas chromatography/mass spectrometry (GC-MS). In his paper, the petroleum fingerprinting was used to investigate the reason of cases. Bertsch^[11] studied the nature of volatiles produced during the pyrolysis of carpet material. He found that while the fibre in carpets did not produce significant amounts of hydrocarbons, the backings often did, generating copious amounts of alkylbenzenes, benzene, toluene, ethylbenzene, styrene and alkylstyrenes, naphthalene and methylnaphthalenes, and other diagnostic components of petrol. Muller et al^[12], put the hand into a sealed bag with a charcoal at room temperature or with a gentle warming of the hand. The gasoline is extracted from the strip by dichloromethane then examined by GC-MS. Tsuyoshi Kaneko et al^[13] employed the GC-AED method to measure total sulfur contents to discriminate between legal diesel fuel and illegal fuel. M.I. Cervera et al^[14] detected 23 selected volatile organic compounds in environmental and wastewater samples using SPME-GC-MS/MS. The projected difference resolution (PDR) and Fuzzy rule-building expert systems (FuRESS) were applied to classify individual ignitable liquids (ILS) in Weiyang Lu's^[15] report. In her study the gasoline and kerosene collected from different locations in the United States were identified by gas chromatography/mass spectrometry (GC/MS) followed by above method of chemometric analysis.

The solid-phase microextraction (SPME) was invented by Pawliszyn in the early 1990s^[16]. It is a much simpler method that uses no pre-chemistry or solvents in which a phase-coated fused silica fibre is exposed to the headspace of the sample^[17-18]. Eric S et.al^[19], reported the effectiveness of headspace SPME as a solvent-free sampling technique for the recovery of accelerants. K.G.Furton et al^[20] presented the experimental results for explosive and ignitable liquid residues demonstrating the relative effects of major controllable variable and optimized the method of SPME. Elisabeth Rianawati et al^[21] optimized and validated the SPME method for analysis of polycyclic aromatic hydrocarbons in rainwater and stormwater.

An examination of the scientific literature has indicated that some matrix contained the hydrocarbons; the backings often did, generating copious amounts of alkylbenzenes, benzene, toluene, ethylbenzene, styrene and alkylstyrenes, naphthalene and methylnaphthalenes, and other diagnostic components of petrol. But there is no research on the combustion residues of carpet. The aim of this research is to use micro solid phase extraction techniques (SPME) and GC-MS to extract and identify, respectively, the household carpets with and without gasoline combustion residuals' compounds that are present in gasoline to find the background interference from combustion residuals. The analytical results will be used to determine which, if any, of these compounds may be used to identify suspected arson in fire investigation.

2. Experimental

2.1. Materials and Reagents

Hexane (purity =100.00%) is purchased from Honeywell. Gasoline is purchased from Chinese National Petroleum Corp (CNPC) in Guangzhou. Carpet samples (Pile:80% wool, 20% nylon; Inner layer: latex; Backside: 100% cotton) are purchased from IKEA of Sweden AB, 34381Almhult.

2.2. Instrumentations

A manual SPME holder and fibers coated with polydimethylsiloxane (PDMS, 100um film thickness) are purchased from Supelco (Bellefonte, PA, USA). Before usage, the fiber is conditioned according to the manufacturer's instruction (30 min at 250 °C).

After SPME, all extracts are analyzed by gas chromatograph-mass spectrometry (GC-MS) which is used in the entire experiment. The injector port is set to 250°C and the carrier gas used is helium (He) at a constant flow of 1.0 ml/min. The split ratio was 10:1 and the electron impact mode is applied for MDS operation, choosing 70eV as the electron energies, while the ion source temperature is set to 230°C. The scan range is 18-350 and the solvent delay is 3 min. The details of the program used in GC-MS analysis are as follows: The initial temperature of the GC oven is 40°C and hold for 5 min. The temperature is increased from 40 to 150°C at a rate of 3°C/min and hold at 150°C for 3 min. The temperature is then increased from 150 to 250°C at a rate of 20°C/min and hold for a final 2 min. The total run time is 52.67 min.

2.3 The samples preparation

Carpet sample is divided into two parts with 10cm×10cm (1[#], 2[#]). Sample 1[#] is complete combustion and the sample 2[#] with 1ml gasoline is complete combustion as well. Then, SPME under the conditions of the extraction temperature at 40°C for 30min and the GC-MS desorption time for 5min.

3. Results and discussion

3.1. Compositions of fresh gasoline

Fresh gasoline is subjected to GC-MS analysis as described above. The result for analyses fresh of gasoline and chromatograms are shown in Fig 1 and Fig 2 and the most frequently encountered compounds from analysis fresh gasoline of all 38 substrates are listed in Table.2. Some compounds such as n-alkanes, aromatic hydrocarbons, Indan and naphthalene etc are detected in fresh gasoline. Those compounds that are not all compositions in gasoline are regarded as a standard reference. There may be additional compounds of interest present in the chromatograms that not listed due to Matching Degree is less than 90% or content is more less than others etc.

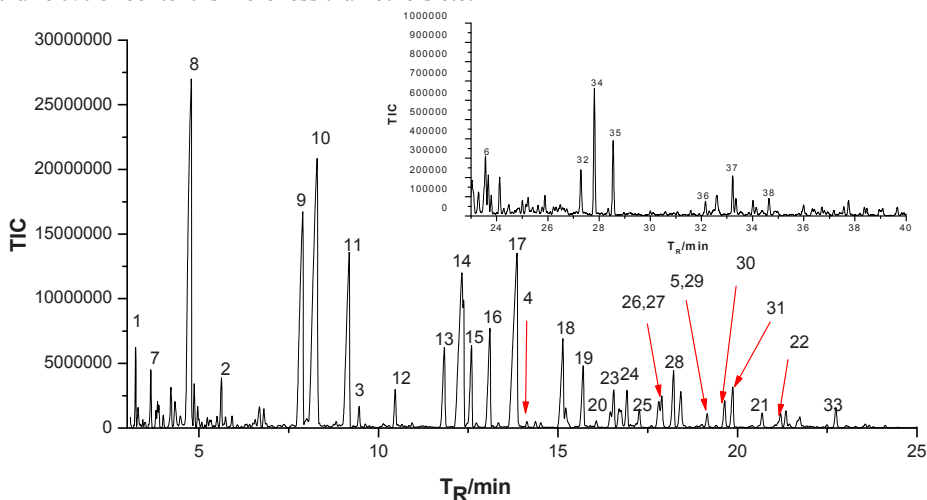


Fig 1 Chromatogram of combustion products of fresh gasoline

Table 1 Commonly encountered compounds resulting from fresh gasoline

Number	Name	TR/min	Formula	Types
1	Heptane	3.239	C7H16	n-alkanes
2	Octane	5.626	C8H18	
3	Nonane	9.466	C9H20	
4	Decane	14.139	C10H22	
5	Undecane	19.006	C11H24	
6	Dodecane	23.796	C12H26	
7	Cyclohexane, methyl-	3.661	C7H14	Cyclane
8	Toluene	4.782	C7H8	C1
9	Ethylbenzene	7.889	C8H10	C2
10	P-xylene	8.288	C8H10	
11	O-xylene	9.185	C8H10	
12	Benzene, (1-methylethyl)-	10.466	C9H12	C3
13	Benzene, propyl-	11.831	C9H12	
14	Benzene, 1-ethyl-3-methyl-	12.326	C9H12	

15	Benzene, 1,3,5-trimethyl-	12.595	C9H12	
16	Benzene, 1,2,3-trimethyl-	13.105	C9H12	
17	Benzene, 1,2,4-trimethyl-	13.858	C9H12	
18	Benzene, 1-ethyl-2-methyl-	15.147	C9H12	
19	Indane	15.706	C9H10	Indane
20	Indene	16.070	C9H8	Indene
21	1H-Indene, 2,3-dihydro-4-methyl-	20.690	C10H12	
22	Indan, 1-methyl-	21.203	C10H12	
23	Benzene, 1-methyl-4-propyl-	16.557	C10H14	C4
24	Benzene, 1-methyl-2-(1-methylethyl)-	16.926	C10H14	
25	Benzene, (1-methylpropyl)-	17.272	C10H14	
26	Benzene, 2-ethyl-1,4-dimethyl-	17.808	C10H14	
27	Benzene, 2-ethyl-1,3-dimethyl-	17.892	C10H14	
28	Benzene, 1-methyl-4-(1-methylethyl)-	18.222	C10H14	
29	Benzene, 2-ethyl-1,4-dimethyl-	19.158	C10H14	
30	Benzene, 1,2,3,4-tetramethyl-	19.644	C10H14	
31	Benzene, 1,2,4,5-tetramethyl-	19.872	C10H14	
32	Benzene, pentamethyl-	27.286	C11H16	C5
33	Naphthalene	22.747	C10H8	Naphthalene
34	Naphthalene, 2-methyl-	27.822	C11H10	
35	Naphthalene, 1-methyl-	28.552	C11H10	Naphthalene-n methyl-
36	Naphthalene, 2,3-dimethyl-	32.601	C12H12	
37	Naphthalene, 2,7-dimethyl-	33.221	C12H12	
38	Naphthalene, 1,8-dimethyl-	34.651	C12H12	

3.2. Background interference from burned carpets

The most abundant components of the chromatogram have been identified through the use of mass spectrometry and listed in the captions of the figures. The mass spectra of burned carpet without gasoline for peaks of interest are compared with the spectra under the same chromatographic and mass spectrometer conditions (Table 2 and Table 3) used in the analysis of combustion residues of carpet with gasoline and fresh gasoline. Fig 2 illustrates the resulting chromatogram after burning a 10 cm by 10 cm swatch of carpet (1[#]) without gasoline using the above conditions. Fig. 3 illustrates the chromatogram resulting from the analysis of the extract after burning a 10 cm by 10 cm swatch of carpet (2[#]) with 1ml gasoline using the above conditions. The analysis of the resulting chromatograms and mass spectra data from these experiments indicates that some of the compounds extracted must be created through the combustion process and are not due to the background of the substrate. Table 2 and Table 3 list the most information of combustion products of carpet samples with and without gasoline.

Results are shown in Table 2, Naphthalene is detected in sample 1[#] and fresh gasoline. The presence of these products could interfere with ignitable liquid residues (ILR) identification, particularly in cases where the quantity of the ILR present is very small.

As shown in the fig 3, there are four compounds, that are Toluene, Ethylbenzene, Benzene, propyl-, Benzene, (1-methylethyl) - only appear in sample 2[#] and fresh gasoline. They could be taken as characteristic products of carpet with gasoline. This paper exhibits the background chromatographic profile are obtained from one of carpets (Pile: 80% wool, 20% nylon; Inner layer: latex; Backside: 100% cotton). There will be different background interference if the carpet's materials are different.

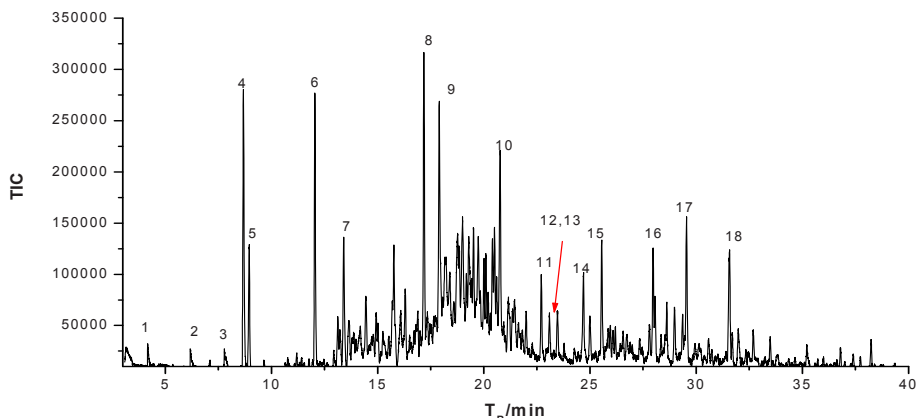


Fig 2 Chromatogram of combustion products of carpet sample (1#) without gasoline

Table 2 Commonly encountered compounds resulting from combustion products of carpet sample (1#) without gasoline

Number	TR/min	Name	Formual
1	4.175	Pyridine	C5H5N
2	6.176	Pyridine, 2-methyl-	C6H7N
3	7.779	Pyridine, 3-methyl-	C6H7N
4	8.679	Cyclohexanol	C6H12O
5	8.950	Styrene	C8H8
6	12.047	Benzaldehyde	C7H6O
7	13.407	Phenol	C6H6O
8	17.176	Acetophenone	C8H8O
9	17.903	Phenol, 4-methyl-	C7H8O
10	20.764	Benzyl nitrile	C8H7N
11	22.709	Naphthalene	C10H8
12	23.090	Benzene,2-cyclopenten-1-yl-	C11H12
13	23.468	1H-Indene, 1-ethenyl-2,3-dihydro-	C11H12
14	24.694	Benzene, cyclopentyl-	C11H14
15	25.547	Benzenepropanenitrile	C9H9N
16	27.967	Indole	C8H7N
17	29.547	Benzene, 3-cyclohexen-1-yl-	C12H14
18	31.575	Biphenyl	C12H10

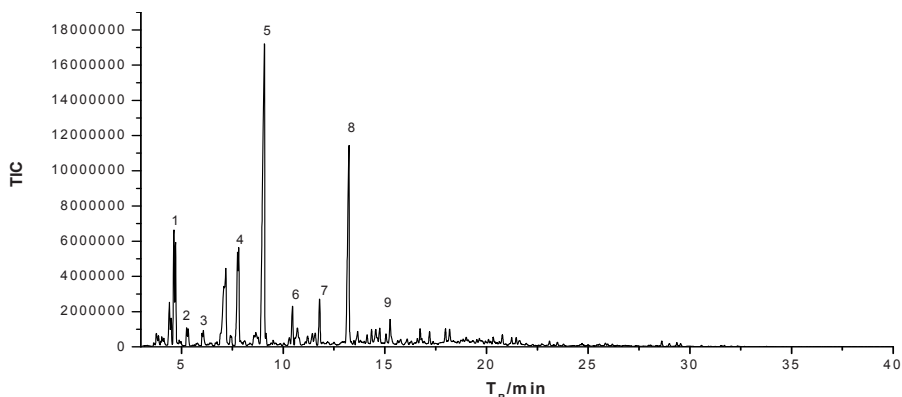


Fig. 3 Chromatogram of combustion products of carpet sample (2#) with 1ml gasoline

Table.3 Commonly encountered compounds resulting from combustion products of carpet sample (2#) (with 1ml gasoline)

Number	TR/min	Name	Formual
1	4.620	Toluene	C7H8
2	5.248	Cyclopentanone	C5H8O
3	5.999	Pyridine, 2-methyl-	C6H7N
4	7.819	Ethylbenzene	C8H10
5	9.076	Styrene	C8H8
6	10.459	Benzene, (1-methylethyl)-	C9H12
7	11.796	Benzene, propyl-	C9H12
8	13.238	.alpha.-Methylstyrene	C9H10
9	15.258	Benzene, 1-propenyl-	C9H10

4. Conclusions

The compounds that could interfere with the analysis ILR, gasoline is selected in study, may originate from one or more sources such as materials themselves, combustion products or pyrolysis products during the burning. The controlled burn experiments of carpets with and without gasoline in this study and commonly encountered substrates produced complex chromatograms producing peaks that were identified by mass spectrometry and comparison with reference standards and each other.

The result shown that many of the compounds frequently encountered as a result of either combustion products or pyrolysis products of carpets such as Toluene, Ethylbenzene, Benzene, propyl-, Benzene, (1-methylethyl)- that detected in fresh gasoline as well. So the existing of gasoline is not determined if the target compounds detected in combustion products. Pyridine, 2-methyl- and Styrene are detected in both samples (1[#], 2[#]). All above compounds as background interferences that detect whether the gasoline exist in carpet combustion products or not. In addition, alkanes, including n-alkanes and branched alkanes, and many of the aromatic compounds used to identify some ignitable liquids, such as Benzene,1,3-dimethyl-, Benzene, propyl- may be found in the burn products. Therefore, forensic chemists must be aware that the presence of these products could interfere with ILR identification, particularly in cases where the quantity of the ILR present is very small.

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References

- [1] José R. Almirall, Kenneth G. Furton. Characterization of background and pyrolysis products that may interfere with the forensic analysis of fire debris. *J. Anal. Appl. Pyrolysis*. 71 (2004) 51-67.
- [2] J.J. Lentini, J.A. Dolan, C. Cherry. The petroleum-laced background. *J. Forensic Sci.* 45 (5) (2000) 968-989.
- [3] S.H. Kang, C.S. Oulman. Evaporation of petroleum products from contaminated soils. *J. Environ. Eng.* May (1996) 384-386.
- [4] D.C. Mann, W.R. Gresham. Microbial degradation of gasoline in soil. *J. Forensic Sci.* 35 (4) (1990) 913-923.
- [5] M. Darrer, O. Delemont, E. Du Pasquier, J. Papilloud, J.C. Martin. Collection and persistence of gasoline on hands in: Proceedings of the Second European Meeting of Forensic Science, Cracow, Poland, 12–16 September 2000.
- [6] S.A. Coulson, R.K. Morgan-Smith. The transfer of petrol on to clothing and shoes while pouring petrol around a room. *Forensic Sci. Int.* 122 (2000) 135-141.
- [7] K. Cavanagha, E. Du Pasquiera, C. Lennardb. Background interference from car carpets—the evidential value of petrol residues in cases of suspected vehicle arson. *Forensic Science International* 125 (2002) 22-36.
- [8] T.E. Folkman, A. M. Kuehl, R.J. Groves, A.D. Beveridge. Evaporation rate of gasoline from shoes, clothing, wood and carpet materials and kerosene from shoe sand clothing. *Can.Soc. Forensic Sci. J.* 23 (2/3) (1990) 49-59.
- [9] MS Fernandes, CM Lau and WC Won. The effect of volatile residues in burnt household items on the detection of fire accelerants. *science&. justice* Volume 42(2002) 7-15.
- [10] Scott A. Stout. Applications of petroleum fingerprinting in known and suspected pipeline releases-- two case studies. *Applied Geochemistry* 18 (2003) 915-926.
- [11] W. Bertsch, Volatiles from carpet: a source of frequent misinterpretation in arson analysis, *J. Chromatogr. A* 674 (1994) 329-333.
- [12] Dan Muller ,Aharon Levy, Ran Shelef. *Forensic Sci. Int.* 206 (2011) 150-154.
- [13] Tsuyoshi Kaneko, Hiroaki Yoshida, Shinichi Suzuki. The determination by gas chromatography with atomic emission detection of total sulfur in fuels used as forensic evidence. *Forensic Science International* 177 (2008) 112-119.

- [14] M.I. Cervera, J. Beltran, F.J. Lopez, F. Hernandez. *Anal Chim Acta* 704 (2011) 87- 97.
- [15] Weiyang Lu, J. Graham Rankin etc. Ignitable liquid identification using gas chromatography/mass spectrometry data by projected difference resolution mapping and fuzzy rule-building expert system classification. *Forensic Science International* 220 (2012) 210–218.
- [16] C.L. Arthur, J. Pawliszyn, *Anal. Chem.* 62 (1990) 2145–2148.
- [17] J.V. Hinshaw, *LCGC Europe* 16 (December 01, 2003) 803.
- [18] S. Bell, *Forensic Chemistry*, Prentice Hall, 2005.
- [19] Eric S. Bodle, James K. Hardy. *Anal.Chim. Acta* 589 (2007) 247-254.
- [20] K.G.Furton, J.R. Almirall, M. Bi, J. Wang, L. Wu, J. *Chromatogr.A* 885 (2000) 419-432.
- [21] Elisabeth Rianawati, Rajasekhar Balasubramanian. *Physics and Chemistry of the Earth* 34 (2009) 857-865.