A HOME-MADE SPME FIBER COATING FOR ARSON ANALYSIS

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Abstract

A number of adsorbents are available commercially as coatings for SPME fibers but some analytical methodologies might demand specific properties for the extraction of selected compounds, special coatings that have particular volume and a selectivity towards particular analytes. This paper presents a simple, fast, effective and environmental friendly methodology for the determination of accelerants in arson samples using headspace solid-phase microextraction coupled to gas chromatography. A new fiber prepared by sol-gel method, containing 1:1 molar ratio of octyltriethoxysilane (C_8-TEOS): methyltrimethoxysilane (MTMOS) was employed in this technique. The efficiency of the new fiber coating prepared by sol–gel technology for the determination of accelerants was compared to that of commercial PDMS/DVB fibers. Polydimethylsiloxane divinylbenzene (PDMS/DVB) is the most common fiber coating for the extraction of hydrocarbon compounds. Compared with commercial PDMS/DVB fiber, the new homemade fiber exhibited higher extraction capability and good selectivity for accelerants. The homemade fiber was also applied for the simulated arson samples. The home-made SPME adsorbent was shown to be a good alternative to commercially available fiber for the determination of accelerants in arson cases.

Abstrak

Pelbagai jenis gentian penjerap bagi teknik SPME wujud di pasaran. Namun demikian, ciri-ciri khas bagi pengekstrakan sebatian yang terpilih, salutan khas dengan isipadu tertentu dan keterpilihan terhadap analit tertentu diperlukan dalam beberapa kaedah analisis. Kertas kerja ini membentangkan suatu kaedah yang mudah, pantas, efektif dan mesra alam sekitar untuk menentukan bahan penggalak kebakaran dalam sampel kebakaran yang disengajakan dengan menggunakan teknik pengekstrakan fasa pepejal mikro yang dihubungkan dengan kromatografi gas. Gentian baru yang digunakan dalam teknik ini disediakan melalui kaedah "sol-gel", di mana ia terdiri daripada C_8-TEOS dan MTMOS dalam nisbah 1:1. Keberkesanan gentian penjerap baru yang disediakan melalui teknologi "sol-gel" untuk penentuan bahan penggalak kebakaran dibandingkan dengan gentian penjerap yang diperolehi secara komersil (PDMS/DVB). Gentian PDMS/DVB adalah gentian yang biasa digunakan dalam pengekstrakan sebatian hidrokarbon. Berbanding dengan gentian PDMS/DVB, gentian buatan sendiri yang baru menunjukkan kapasiti pengekstrakan yang lebih tinggi dan keterpilihan yang baik bagi bahan penggalak kebakaran. Gentian buatan sendiri ini juga diaplikasikan pada sampel simulasi kebakaran yang disengajakan. Gentian buatan sendiri untuk teknik SPME menunjukkan suatu alternatif yang baik kepada gentian komersial bagi penentuan bahan penggalak kebakaran dalam kes kebakaran yang disengajakan

Introduction

Arsons are particularly difficult crimes to prove due to the usual lack of physical evidence associating a suspect to the crime. The accelerants most commonly used by offenders because of their volatility, availability and flammability are petrol, kerosene and diesel. The more volatile components of an accelerant evaporate at a faster rate than the heavier components so that overall chemical profile of the accelerant will change during the fire and before sampling [1, 2].

It is difficult to conclusively determine if a sample of an accelerant was the same as that to initiate or propagate a fire, because of the universal composition of the common accelerants. The chemical components of the common accelerants are aliphatic and aromatic hydrocarbons and oxygenated hydrocarbons such as alcohols. The oxygenated hydrocarbons are to a degree water soluble and therefore washed away during the extinguishing of the blaze, so that little trace remains [3-6].

The amount of accelerant remaining at the fire scene available for sampling is governed by the initial loading of the accelerant, volatility of the accelerant, severity of the fire, water solubility of the accelerant, porosity of the substrate material, dryness of the area after the fire and the elapsed time between the fire and sampling [3-6].

An important aspect of an investigation of a suspected arson case involves the chemical analysis of the debris remaining after the fire. Currently, accelerant extraction and analytical techniques have been refined to improve sample turnover and to reduce the number of inconclusive findings. For this purpose, solid-phase micro extraction (SPME) have been introduced. The major advantage of SPME is that it uses no solvents and can be used for either direct sampling or sample clean-up. It is fairly economical and is a relatively simple and sensitive technique. The qualities that enable an SPME adsorbent to be successfully used for accelerant extraction and analysis are its selectivity towards accelerant components which separates and concentrates the accelerant from the headspace to yield a sample that is suitable for introduction to GC-FID [7].

Recently, many novel coatings have been developed using different techniques and technology for use in SPME. Compared with commercially available SPME adsorbents, the new materials exhibited higher thermal stability (350 °C), solvent stability (organic and inorganic) and extraction capability [8-19]. However, up to now, none of the novel fibers have been evaluated for the determination of accelerants in arson analysis. This paper presents a recent development in the forensic aspects of fire investigation. As a preliminary study, a home-made SPME adsorbent comprising of sol-gel derived C_8-coating was developed and evaluated for the determination of accelerants in arson samples, with the aim of improving the quality of ignitable liquid residue analysis.

Experimental

Chemicals and Materials

Samples of diesel and unleaded gasoline were purchased from a petrol station in Skudai, Johor while kerosene was obtained from a grocery shop at Taman Universiti, Skudai, Johor. Samples of carpet were purchased from a carpet retail shop in Taman Ungku Tun Aminah, Skudai, Johor.

Apparatus

A glass apparatus (400 cm^3) for sample preparation step of headspace SPME was specially designed [20]. A Supelco SPME holder, commercially available PDMS/DVB fibers (Bellefonte, Pennsylvania, U.S.A.), and home-made sol-gel derived C_8-coated fibers containing (1:1, C_8-TEOS:MTMOS) [21] were employed for the extraction of accelerants.

Instrumentation

Gas chromatography was conducted using a Hewlett-Packard 6890 GC (Wilmington, Delaware, U.S.A.). The HP 6890 gas chromatograph was equipped with FID and a HP ChemStation for data processing. An Ultra-1 capillary column (Agilent) of dimensions 25 m x 0.20 mm x 0.11 µm film thickness was used. Helium was used as the carrier gas at a flow rate of 1.2 mL/min. The injection port temperature was set at 250 °C and FID temperature at 310 °C. SPME injections were performed using a split mode injection (1:5).

Preparation of Spiked Fire Debris sample

A sample of carpet (15 cm x 10 cm) placed on a sheet of aluminium foil was ignited with a fire starter and left to burn until about 1/3 remained on the aluminium foil. Fire was extinguished and the partially burnt carpet was exposed to the surrounding air for 30 minutes to cool down. 100 µL of accelerant (petrol, kerosene and diesel) were individually spiked on to the burnt carpet fire debris sample. The spiked sample was placed in the glass apparatus prior to headspace SPME .

Procedures for Headspace SPME

The spiked fire debris sample was placed in the sample preparation apparatus that was immersed in a hot water bath and heated for 15 min at 100 °C. The C_8-coated fiber was exposed in the headspace and the fiber extracts were analyzed using GC-FID. The oven temperature was initially set at 40 °C, programmed at a rate of 10 °C/min until a final temperature of 270 °C. The headspace SPME procedure was repeated using PDMS/DVB fiber for comparison.

Results And Discussion

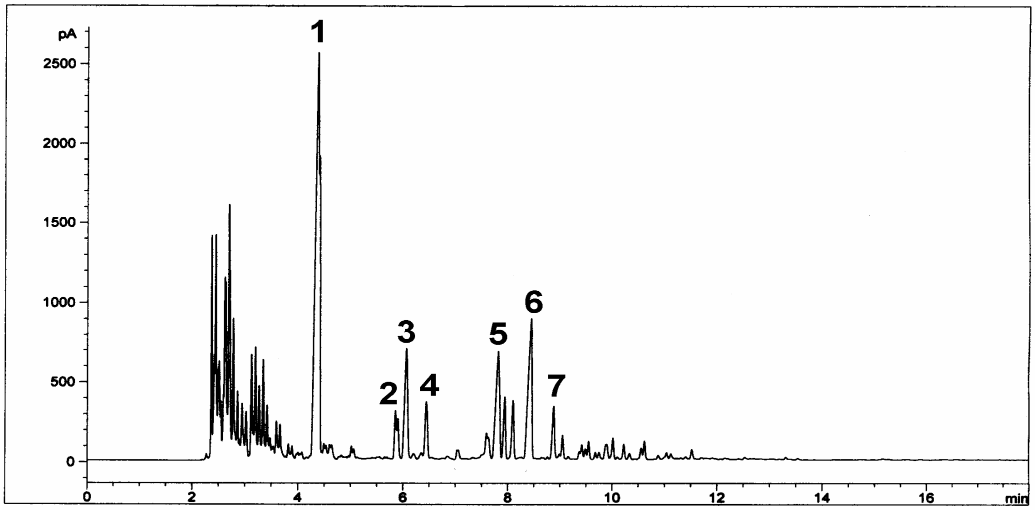
Selectivity of C_8-coated fiber for accelerants

In order to examine selectivity of the home-made SPME fiber towards petroleum based accelerants, burnt carpet samples were individually spiked with known amount of gasoline, kerosene and diesel. The samples were subjected to headspace SPME using sol-gel derived C_8-coated fiber and the GC profiles were compared with that from direct injection. As seen in Figure 1 (b), all the hydrocarbon components in gasoline spiked burnt carpet sample were recovered by using C_8-coated fiber and the chromatogram was comparable with the profile of gasoline from direct injection (Figure 1 (a). The hydrocarbon components in kerosene (Figure 2) and diesel (Figure 3) spiked burnt carpet sample were also effectively extracted using the home-made fiber and similar comparisons were obtained with direct injection of the respective accelerants. This indicated that the home-made SPME fiber favored the extraction of hydrocarbons, thus providing a good selectivity towards accelerants. The GC profiles of gasoline, kerosene and diesel spiked samples obtained in this study were in good agreement with those obtained by Borusiewicz [1] using Tenax as adsorbent and Yong [20] using commercially available fibers.

Extraction capability of the C_8-coated fiber

The extraction capability of the sol-gel derived C_8-coated fiber was determined by comparing it with the commercially available PDMS/DVB fiber. PDMS/DVB fiber was selected for comparison because previous work done in this lab [20] proved that the fiber has the highest sensitivity towards hydrocarbon compounds and most suitable for accelerants identification. Both C_8-coated fiber and PDMS/DVB fiber is capable of extracting early, middle and late eluting hydrocarbon compounds sufficiently. However, the C_8-coated fiber showed a slightly higher extraction capability by contrast with conventional PDMS/DVB fiber for all the accelerants as shown in Figure 4. This result was comparable to that reported by Gbatu *et al.* [8]. A higher extraction capability could be due to the existence of higher surface area for the C_8-coated fibers [8]. Up to now, all the headspace SPME extractions were carried out with the optimized conditions of the commercially available PDMS/DVB fiber [20]. A study is now underway to optimize the extraction and desorption time of the C_8-coated fiber. The optimized conditions of the C_8-coated fiber might result in faster extraction time as reported by Gbatu *et al.* [8].

(a)



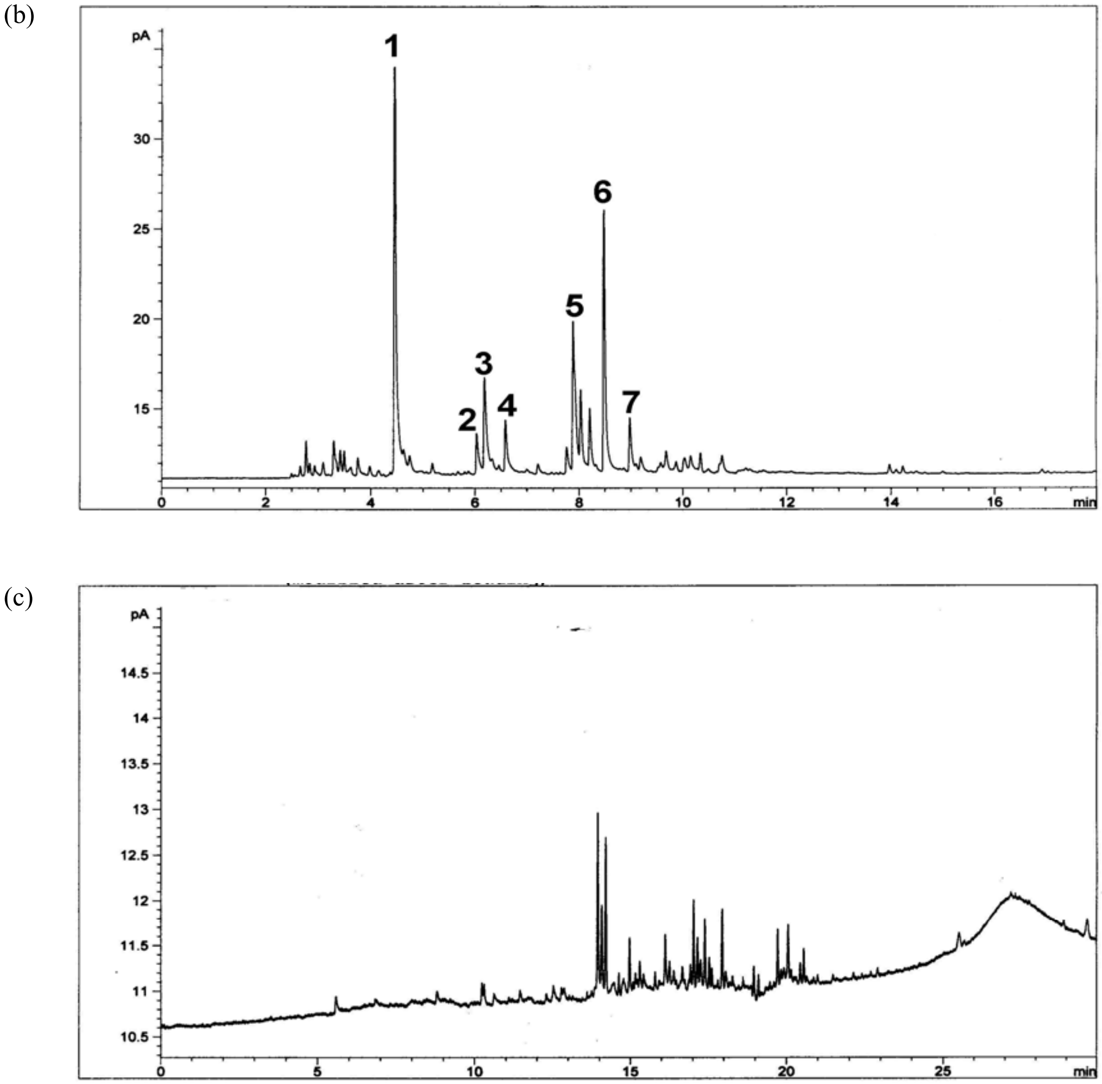
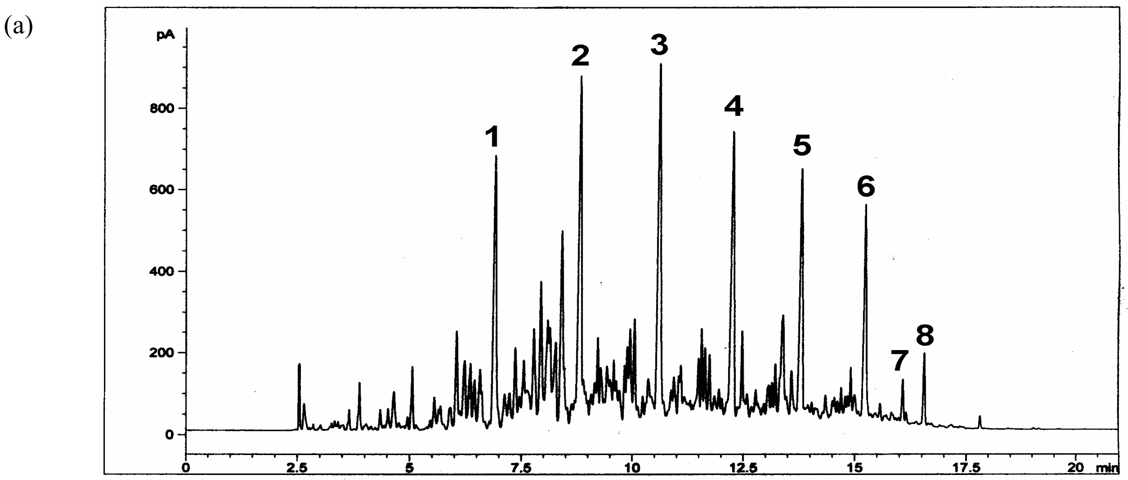
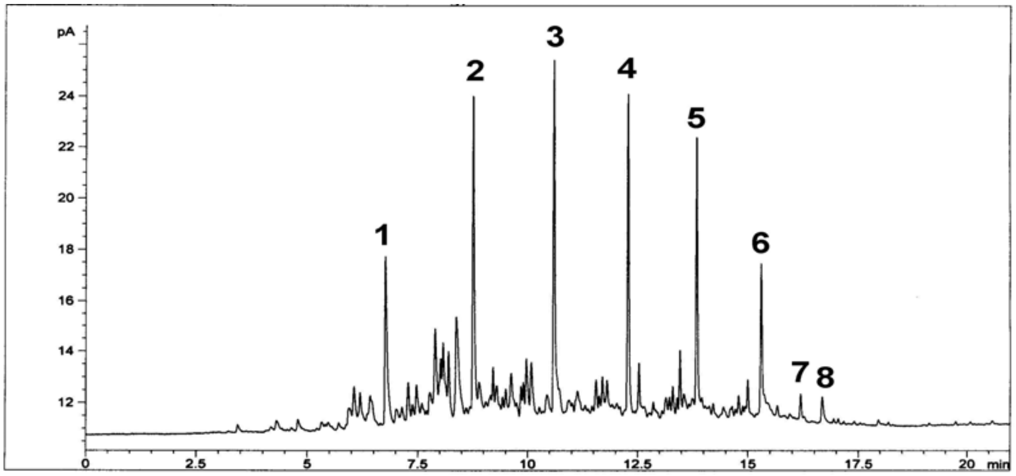


Figure 1: GC profiles of (a) direct injection of gasoline, (b) gasoline spiked burnt carpet sample and (d) the blank burnt carpet sample using C_8-coated fibers. Peak identities: (1) methylbenzene, (2) ethylbenzene, (3) 1, 3-dimethylbenzene, (4) 1, 2- dimethylbenzene, (5) 1-ethyl-2-methylbenzene, (6) 1, 2, 4-trimethylbenzene, (7) 1, 2, 3- trimethylbenzene.





(b)

Figure 2: GC profiles of (a) direct injection of kerosene and (b) kerosene spiked burnt carpet sample using C_8-coated fibers.Peak identities: (1) C_9, (2) C_{10}, (3) C_{11}, (4) C_{12}, (5) C_{13}, (6) C_{14}, (7) 2, 6-dimethylnapthalene, (8) C_{15}

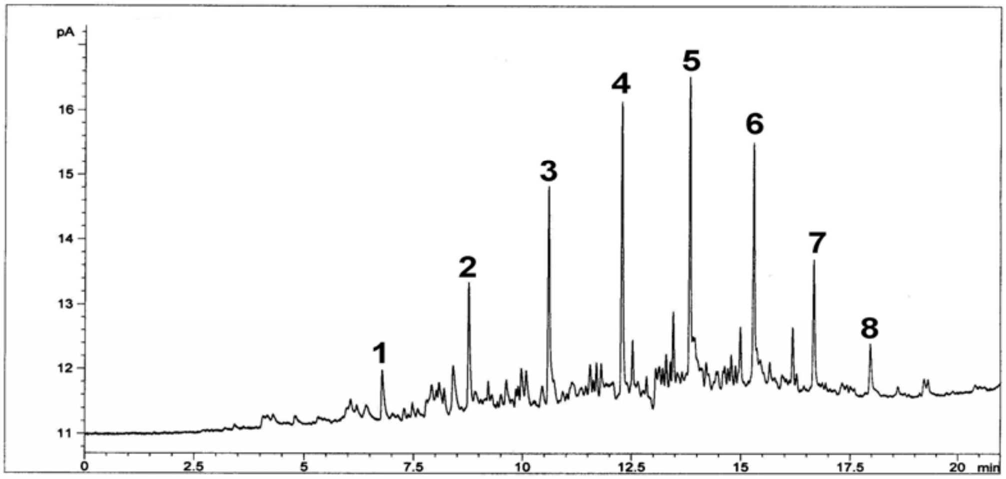
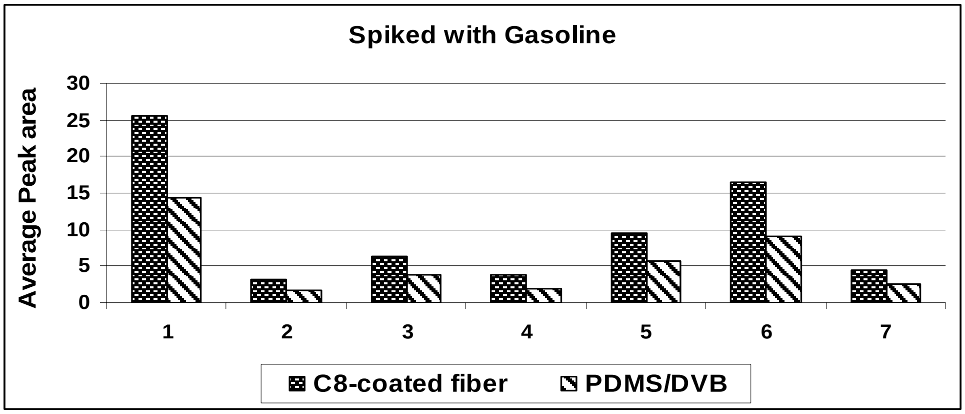


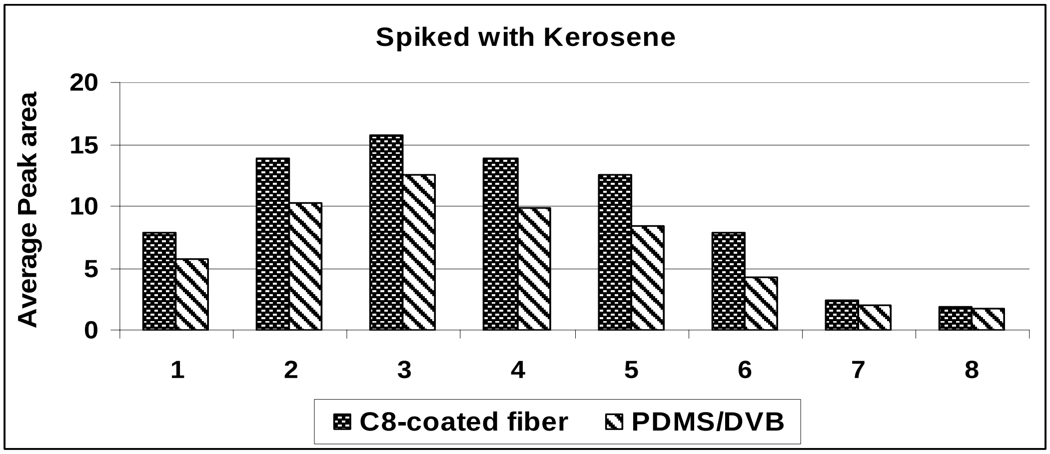
Figure 3: GC profiles of direct injection of diesel spiked burnt carpet sample using C_8-coated fibers. Peak identities: (1) C_9, (2) C_{10}, (3) C_{11}, (4) C_{12}, (5) C_{13}, (6) C_{14}, C_{15}, (7) C_{16}

(a)



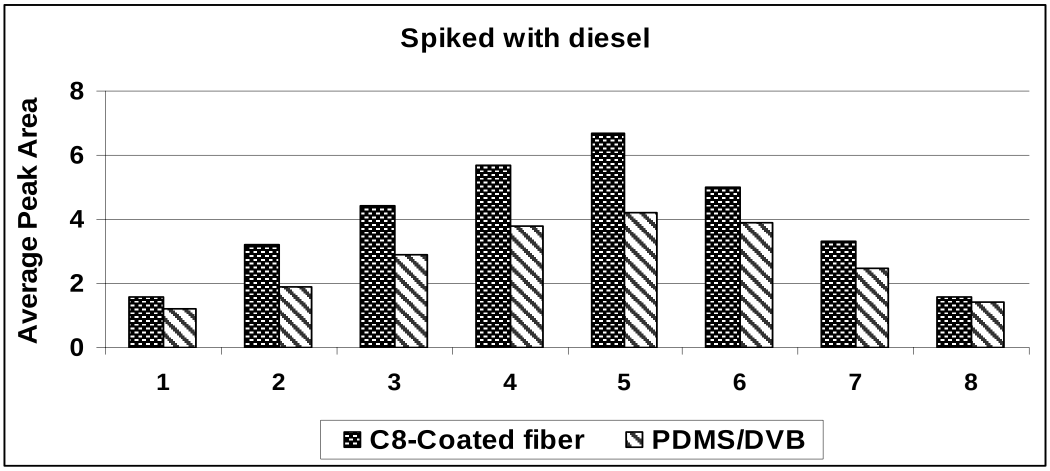
Label identities: (1) methylbenzene, (2) ethylbenzene, (3) 1, 3-dimethylbenzene,(4) 1, 2-dimethylbenzene, (5) 1-ethyl-2-methylbenzene, (6) 1, 2, 4-trimethylbenzene, (7) 1, 2, 3-trimethylbenzene.

(b)



Label identities: (1) C_9, (2) C_{10}, (3) C_{11}, (4) C_{12}, (5) C_{13}, (6) C_{14}, (7) 2, 6-dimethylnapthalene, (8) C_{15}

(c)



Label identities: (1) C_9, (2) C_{10}, (3) C_{11}, (4) C_{12}, (5) C_{13}, (6) C_{14}, C_{15}, (7) C_{16}

Figure 4: Comparison of sol-gel derived C_8-coated fiber and commercially available PDMS/DVB fiber in extracting hydrocarbon compounds from (a) gasoline, (b) kerosene and (c) diesel spiked burnt carpet

Conclusions

The sol-gel derived C_8-coated fiber was successfully evaluated for the determination of accelerants in arson samples. The home-made fiber was capable of extracting hydrocarbon compounds from simulated arson samples and showed a good selectivity towards accelerants. The C_8-coated fiber exhibited a slightly higher extraction capability by contrast with conventional PDMS/DVB fiber. The experiments performed proved that the developed fiber could be successfully applied for arson analysis.

Acknowledgements

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