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Headspace sorptive extraction for the detection of combustion accelerants in fire debris

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ABSTRACT

A novel method for separation and identification of ignitable liquid residues in fire debris by gas chromatography and mass spectrometry is presented. Preconcentration of the analytes was carried out using the simple headspace sorptive extraction (HSSE) technique. Polydimethylsiloxane stir bars were used as the enrichment phase, and parameters affecting both the adsorption and desorption stages were carefully optimized. Extraction was carried out at 50 °C for 1 h. Stir bars were desorbed thermally in the GC injection port, thus avoiding the use of organic solvents. The results for five ignitable liquids, including gasoline and diesel fuel, using HSSE were compared with those obtained with a solid-phase microextraction method, with HSSE appearing as a more sensitive alternative.

1. Introduction

The destructive nature of fire makes it difficult to obtain criminal evidence from the fire scene. In many cases, the chance of identifying the arsonist is related with the possibility of collecting, analyzing and tracking any combustion accelerant that may have been used to encourage the fire. The special relevance of such evidence has led to the development of various techniques for the analysis of fire debris that enable investigators to establish whether or not a fire was started intentionally with a high degree of sensitivity and reliability. The main contribution of these analytical techniques has been to qualitatively identify some compounds, whose presence in the fire debris may indicate that some kind of combustion accelerant was used to start the fire. Although a wide range of products can be used as combustion accelerants, the most common are gasoline, diesel, kerosene and turpentine [1]. Information about the type of accelerant used in arson may help investigators track down the suspected arsonist.

Gas chromatography (GC) is the most used analytical technique for the analysis of accelerants in fire debris. Ignitable liquids are composed primarily of hydrocarbons, and so a universal detector has to be coupled to GC. Flame ionization detection (FID) has traditionally been used for this purpose, but its use has been declining due to the identification capabilities of mass spectrometry (MS) [2–4]. In fact, the American Society for Testing and Materials (ASTM) has made MS the standard method for the investigation of fire debris [5]. On the other hand, the modalities of two-dimensional GC [6] and tandem mass spectrometry [7] have been proposed to remove interferences originated by fire debris pyrolysates.

Different sample preparation techniques have been used for isolating ignitable liquid residues from fire debris [2,8,9]. Solvent extraction [10], which is a time consuming technique [11], has been substituted in most applications by passive headspace concentration, because of its simplicity and the lower level of interference provided. Passive headspace concentration has been carried out with activated charcoal strips (ACS) [12–15].Passive adsorbents other than ACS and which can be thermally desorbed due to their thermal stability have also been checked [16,17]. Of note is the Radiello passive commercial sampler which also uses activated carbon as absorbent and CS_2 for desorption [18]. Solid-phase microextraction (SPME) overcomes the inherent disadvantages of very long adsorption times as well as the use of toxic organic solvents required when ACS is used, such as CS_2, dichloromethane or pentane [19–24]. SPME has been recommended as the ASTM standard for fire debris analysis as a screening test [25]. On the other hand, a polymer particle-packed needle device has been presented for the concentration of ignitable liquids

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as an interesting alternative to SPME [26]. Also, in order to increase the extraction efficiency of compounds with high boiling points, dynamic headspace extraction has been presented [27,28]. A miniaturized liquid-liquid microextraction (LLME) technique has also been applied in headspace mode for fire debris analysis [29], using benzyl alcohol as the extraction phase.

Even though SPME has proved to be a rapid and highly sensitive preconcentration technique that allows the detection of combustion accelerants even at trace levels, it has some major drawbacks, such as the low robustness of the fibers, their limited useful life, their cost and their low capacity which results in higher displacement rate. Headspace sorptive extraction (HSSE) is a microextraction technique derived from the application of stir bar sorptive extraction (SBSE) in headspace mode [30]. In this technique, a 1 or 2 cm stir bar coated with a thick film of 0.5 or 1 mm of polydimethylsiloxane (PDMS), meaning a total volume between 24 μL and 126 μL of PDMS, is hung in the headspace of a vial containing the sample. The heating of this vial, led to the evaporation of the analytes to the headspace, from where they are absorbed into the stir bar coating, which acts as extraction phase. Once equilibrium between phases is reached, the stir bar is removed from the vial and submitted to desorption prior to GC analysis. The introduction of the retained compounds into the GC system is accomplished by a thermal desorption in a specific injector, comprising a thermal desorption unit (TDU) and a programmed temperature vaporizing (PTV) injector. This preconcentration technique provides higher recoveries and so higher sensitivity than SPME, due to the larger amount of extracting phase involved (24–126 μL *versus* 0.5 μL). In addition, the robustness of the stir bar assembly facilitates its application, reaching useful life about 100 cycles in headspace mode.

Despite the advantages of HSSE over SPME, to the best of our knowledge, it has not been previously applied for the preconcentration of combustion accelerants in fire debris. The present work proposes an HSSE–TD–GC–MS procedure for the detection of ignitable liquid residues in fire debris.

2. Material and methods

2.1. Instrumentation

Commercial stir bars (20 mm length) coated with a 0.5 mm layer of PDMS (48 μL) were obtained from Gerstel (Mullheim an der Ruhr, Germany), and were conditioned in an empty thermal desorption tube at 275 °C for 0.5 h with helium at a flow desorption rate of 50 mL min^{-1} prior to their use. Inserts for Twister® headspace vials were tried (Gerstel). The sample introduction system into the gas chromatograph was composed of a thermal desorption unit (TDU-2) equipped with an autosampler (MPS-2) and a programmed temperature vaporization (PTV) cooled injector system (CIS-4) provided by Gerstel. The experimental conditions used for the sample introduction system are summarized in Table 1.

GC analyses were performed on an Agilent 6890 N (Waldbronn, Germany) gas chromatograph equipped with a 30 m × 0.25 mm × 0.25 μm VF-23MS (50% diphenyl–50% dimethylpolisiloxane) capillary column. The oven temperature program and other chromatographic conditions are summarized in Table 1. An Agilent 5973 quadrupole mass selective spectrometer equipped with an inert ion source was employed for detection purposes, working under scan mode in the 40–400 *m*/*z* range. Identification of the compounds was confirmed by spectra comparison with a mass spectra library.

All analyses were performed in 15 mL clear glass vials. To prevent analyte evaporation, the vials were sealed with hole-caps and PTFE-silicone septa were used. Laboratory-made systems, consisting of a drilled block provided with an electronic temperature control system, were used for controlling the temperature during the sample extraction step.

Table 1
Experimental conditions of the TD–GC–MS procedure.

Thermal desorption unit	
Mode	Splitless
Temperature program	50–240 °C at 380 °C min^{-1}, held 10 min
Desorption flow and pressure	50 mL min^{-1}, 7 psi
Cooled injector system	
Mode	Solvent venting
Liner	Tenax, 1 mm i.d.
Temperature program	15–300 °C (5 min) at 650 °C min^{-1}
GC–MS	
Capillary column	VF-23MS, 50% diphenyl-50% dimethylpolysiloxane 30 m × 0.25 mm, 0.25 μm
Carrier gas	Helium (1 mL min^{-1})
Oven program	40 °C held 8 min 40–90 °C at 25 °C min^{-1} 90–120 °C at 30 °C min^{-1} 120–150 °C at 15 °C min^{-1} 150–200 °C at 10 °C min^{-1}, held 2 min
Transfer line temperature	280 °C
Quadrupole temperature	150 °C
Ion source temperature	230 °C
Ionization	Electron-impact mode (70 eV)

2.2. Samples and analytical procedure

Different combustion accelerants, representing three of the eight main classes of the ASTM E 1618-06 ignitable liquid classification, including gasoline, diesel fuel (petroleum distillate), fire starter or barbecue lighter (BBQ), industrial solvent and turpentine (others–miscellaneous) were purchased from local stores. Working solutions (0.1% v/v) of these accelerants were prepared by dilution with methanol.

Soil and sawdust samples obtained from a local garden and a local shop, respectively, were used as debris simulants. Spiked samples were prepared by adding different volumes of the working solutions, in the range 10–100 μL, to 1 g of sample previously placed in glass vials.

Real fire debris of different accelerants were obtained by burning a sawdust–soil mixture (roughly 1:1) spiked with the undiluted accelerant and ignited by a propane torch in the open air, which was allowed to burn until mostly charred. About 1 g of the debris was placed in the extraction vessel (15 mL glass vials) for the HSSE procedure. A homemade magnetic holder was used to expose the PDMS stir bar to the vial headspace for 60 min at 50 °C (Fig. 1). Once extraction was accomplished, thermal desorption was carried out by placing the desorption tube in the TDU-2 connected to the PTV injector, and conducted to the GC–MS system.

For comparison purposes, a 100 μm PDMS SPME fibre was employed for accelerant preconcentration using previously reported extraction conditions and 240 °C and 2 min as desorption temperature and time, respectively.

3. Results and discussion

Preliminary experiments were carried out to optimize chromatographic separation using a mixture of the most widely used accelerants, gasoline and diesel, whose components include a wide number of analytes. In order to facilitate the rapid identification of the compounds, the oven program temperature selected provided