

TECHNICAL NOTE

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The Detection and Analysis of Ignitable Liquid Residues Extracted from Human Skin Using SPME/GC

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ABSTRACT: A simple, fast, inexpensive, and sensitive technique for the detection and identification of flammable or combustible liquid residues on the skin of arson suspects is presented. The use of solid phase microextraction (SPME) for the analysis of ignitable liquid residues has been demonstrated and it is shown in this work that this technique is effective in extracting these liquid residues at extremely low quantities. Microliter quantities of controlled spikes of gasoline, diesel fuel, and charcoal lighter fluid were deposited on the hands of a volunteer and extracted after several time intervals. The SPME technique can recover very small amounts of liquid deposits on skin up to 3.5 h after exposure, depending on the class of the ignitable liquid residue used.

KEYWORDS: forensic science, solid phase micro-extraction, fire-debris, flammable or combustible liquid residues, skin extraction

Solid-phase microextraction (SPME) was first reported by Pawliszyn (1,2) as a sensitive technique for the pre-concentration of organic compounds for their subsequent analysis. This portable device is easy to use, very fast and its operation has been previously described for the analysis of flammable or combustible liquid residues from fire debris by the authors (3–5). SPME uses a sorbent-coated fiber to extract compounds for their subsequent thermal desorption directly into the injection port of a GC or HPLC (6). SPME offers the advantage over traditional extraction techniques by integrating the sampling, extraction, concentration and sample introduction into a single step. A variety of applications have been reported to date including the analysis of compounds of environmental interest (7–9), food and flavor compounds (10,11) and other forensic applications (12) which have included the headspace extraction of drugs from urine (13). Presently, we report the application of this technique to the analysis of flammable or combustible liquid residues on human skin. The analytes of interest include gasoline, diesel fuel, and charcoal lighter fluid as examples of three

different classes of flammable or combustible liquid residues that may be found at the scene of a suspected arson. This technique enables a fire investigator, in collaboration with a chemist, to detect ignitable liquid residues directly from a suspect's skin very quickly after the suspect has been identified. A field portable Gas Chromatograph may be used to obtain results at the crime scene or a field portable version of the SPME device may also be used for remote sampling followed by analysis in the laboratory.

Experimental

Analytical Conditions

The ignitable liquid residues tested in this study were charcoal lighter fluid (Sure-Glow, Pitt Penn Oil Co., Creighton, PA), gasoline (Fina, 87 octane), and the heavy petroleum distillate (HPD) diesel fuel (Exxon, Dodge Island barge sample). GC separations were performed on a Hewlett Packard 5890 gas chromatograph using a capillary column: DB-5 ms, 30 m, 0.25 mm ID, and 0.25 μm film thickness (J & W Scientific, Folsom, California.). The injection port temperature was maintained at 250°C and a flame ionization detector was used and maintained at a temperature of 310°C. Helium was used as a carrier gas with a flow rate of 1 mL/min (33.33 cm/s) in the splitless injection mode. The GC oven was programmed to hold the initial temperature at 35°C for 1 min then ramped at a rate of 15°C/min to 70°C, held for 5 min and ramped at a rate of 4°C/min to 195°C, held for 6.5 min then ramped at 20°C/min to 270°C and finally held for 3 min. Although a variety of fiber types are currently commercially available (Supelco, Bellefonte, PA) the Polydimethylsiloxane (PDMS) coated fiber with a 100 μm film thickness was found to offer the best extraction efficiency (3–5) for the flammable or combustible liquid residues tested.

Sampling Procedures

Gasoline on Hand Skin, Sampling With and Without Heating—A series of 10 μL spikes of the gasoline were deposited on the hand of a volunteer subject. Following several time intervals after exposure, (5 s, 5 min, 10 min, 15 min, 30 min, 45 min, 75 min, and 90 min) the hand with gasoline was covered with a 17 cm by 30 cm nylon bag, the PDMS SPME fiber was inserted into the bag and the fiber was exposed to the headspace over the hand for 15 min. A heating lamp was placed 30 cm above the bag and turned on for 5 and 15 min in-

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tervals, to provide gentle heating of the headspace over the hand. The volunteer was seated in an air conditioned laboratory between the deposit of the residues and the sampling. The SPME fiber was retracted and inserted into the injection port of the GC for analysis. The same sampling procedure was used without heating the headspace for comparison of extraction efficiencies. A new volunteer or a clean hand was used between time interval experiments where a fresh volume of residue was deposited prior to sampling.

Sampling with Different Size Bags—A larger bag (45 cm by 30 cm) was also used to determine the effect of bag size on sampling efficiency for the gasoline liquid residue.

Diesel on Hand Skin—A 10 μL spike of diesel fuel was deposited on the hand of a volunteer and sampled 5 s later and 3.5 h later. The bag was heated for 5 min as described above, and the

headspace was sampled for 10 min after the deposition of the diesel fuel.

Charcoal Lighter Fluid on Hand Skin—Samples of 3 and 10 μL of the charcoal lighter fluid were spiked on the hand of a volunteer. After 5 s and 2 h, the hand was covered with the bag, the heating lamp was turned on for 1 min and 5 min (for the 2 h interval experiment) and sampled with the SPME fiber for 2 more min (10 min sampling for the 2 h interval experiment).

Results and Discussion

Detection of Gasoline Spikes on Skin

Figure 1 is the chromatogram resulting from a 15 min SPME sampling of a hand with no flammable or combustible liquid residue spikes, after heating for 5 min. Figure 2 is the chromatogram of a 1

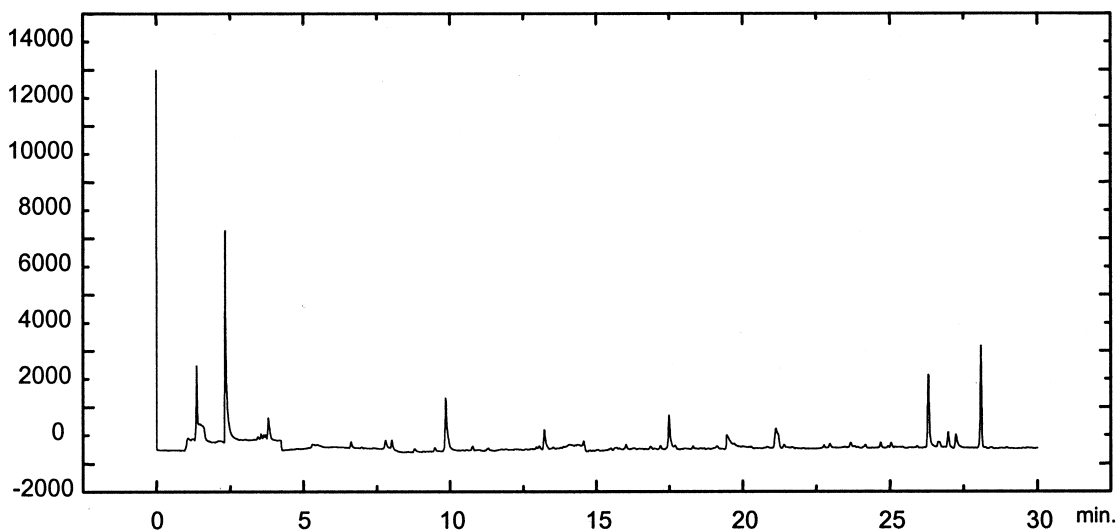


FIG. 1—Chromatogram of a 15 min SPME extraction of the headspace over a hand with no flammable or combustible liquid residue added after 5 min of heating the bag.

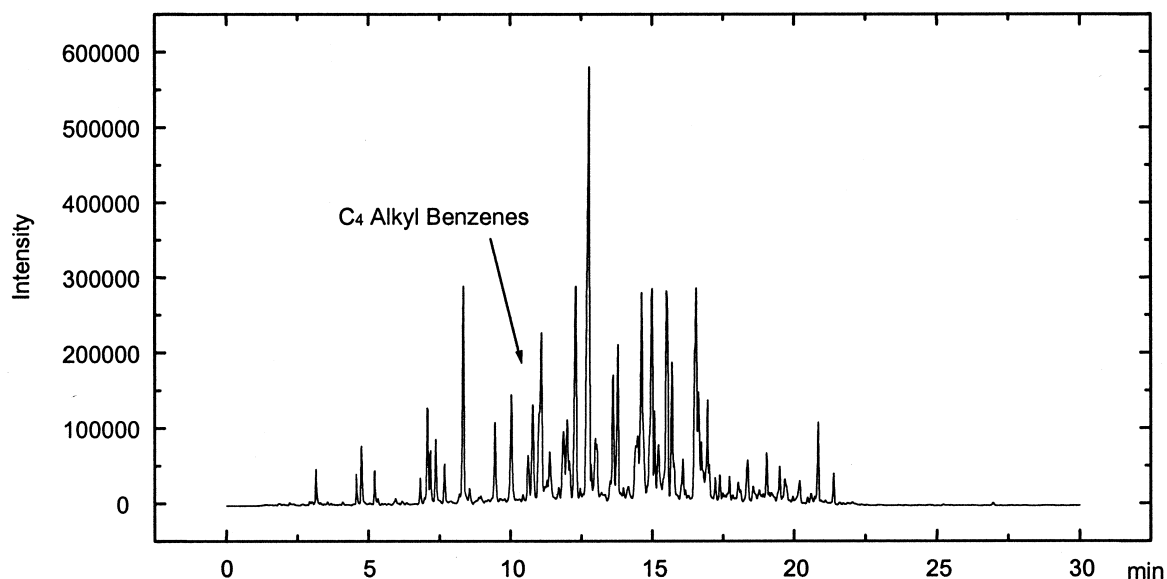


FIG. 2—Chromatogram of a 15 min SPME extraction of a 1- μL spike of 97% evaporated gasoline on a Kimwipe[®] sampled from a 1 quart can.

μL spike of a 97% evaporated gasoline spike on a Kim Wipe and deposited in an empty paint can immediately followed by headspace extraction with the SPME for 15 min. Figures 3–10 are the SPME chromatograms of gasoline spikes on the hand of a volunteer for the different time intervals and the different SPME sampling times. A comparison of Fig. 3 (sampling 5 s after exposure), Figure 4 (sampling 5 min after exposure) and Fig. 5 (sampling 10 min after exposure) illustrates that most of gasoline components, especially the low boiling components evaporated during the first 10 min after being applied on the hand. Figures 6, 7, 8, 9 and 10 represent sampling after 15, 30, 45, 75, and 90 min, respectively. Detectable amounts of some of the components of the gasoline residues can be observed even 90 min after application on the hand, although at this level (re-

sults from a 10 μL spike), the gasoline can not be identified after 75 min and 90 min as per ASTM guidelines (14).

It was also observed that the headspace volume can also affect the SPME recovery of the liquid residues. The amount of recovery of the gasoline by SPME on the hand depended on the size of the bag used to cover the hand. A higher recovery of gasoline was obtained when the smaller bag was used to cover the hand.

The sampling temperature can also influence the recovery of gasoline from skin. Although heating can increase the evaporation rate of gasoline from skin, when the heating lamp is used for a prolonged amount of time the heat has a secondary effect. Heating also causes the partial desorption of the analytes that are in equilibrium between the fiber surface and the headspace in the heated bag. The

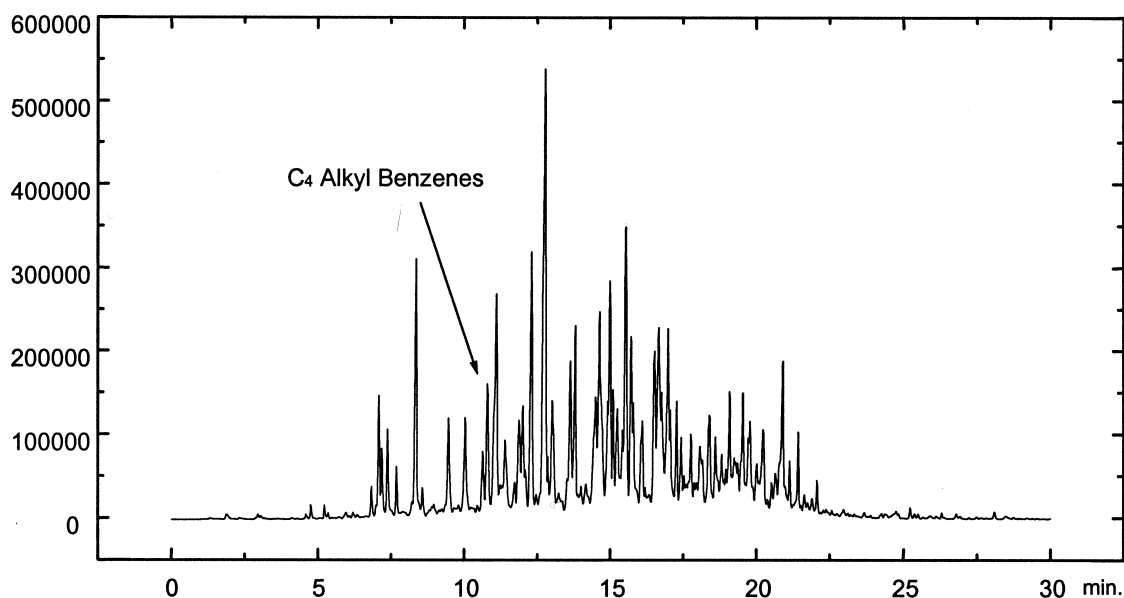


FIG. 3—Chromatogram of a 15 min SPME extraction of a 10- μL spike of gasoline on a hand sampled 5 s after exposure and heated for 5 min with a heat lamp.

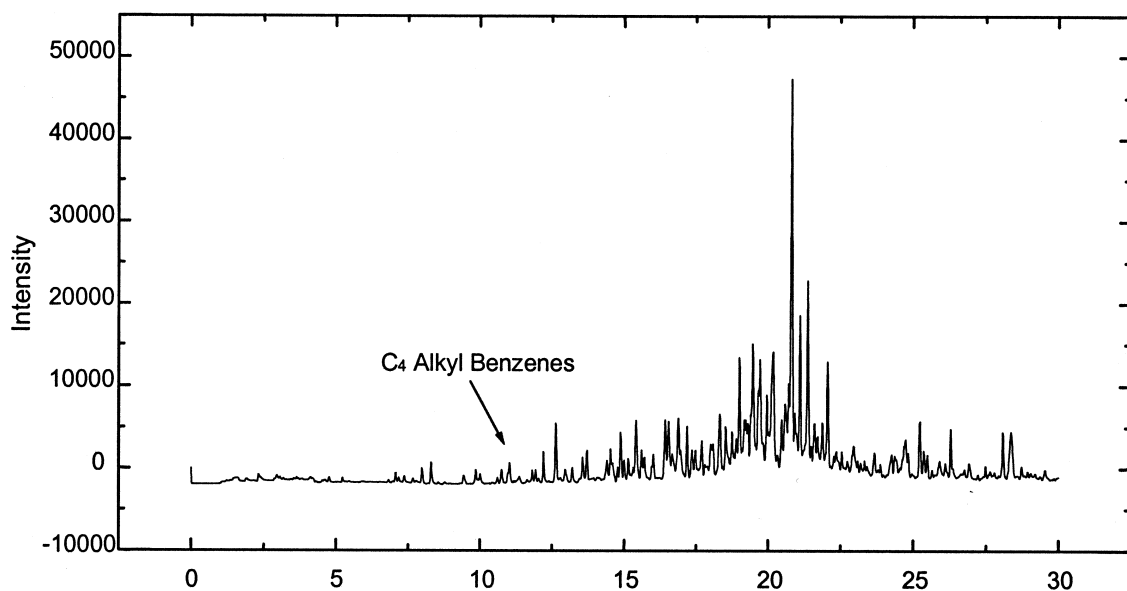


FIG. 4—Chromatogram of a 15 min SPME extraction of a 10- μL spike of gasoline on a hand sampled 5 min after exposure and heated for 5 min with a heat lamp.

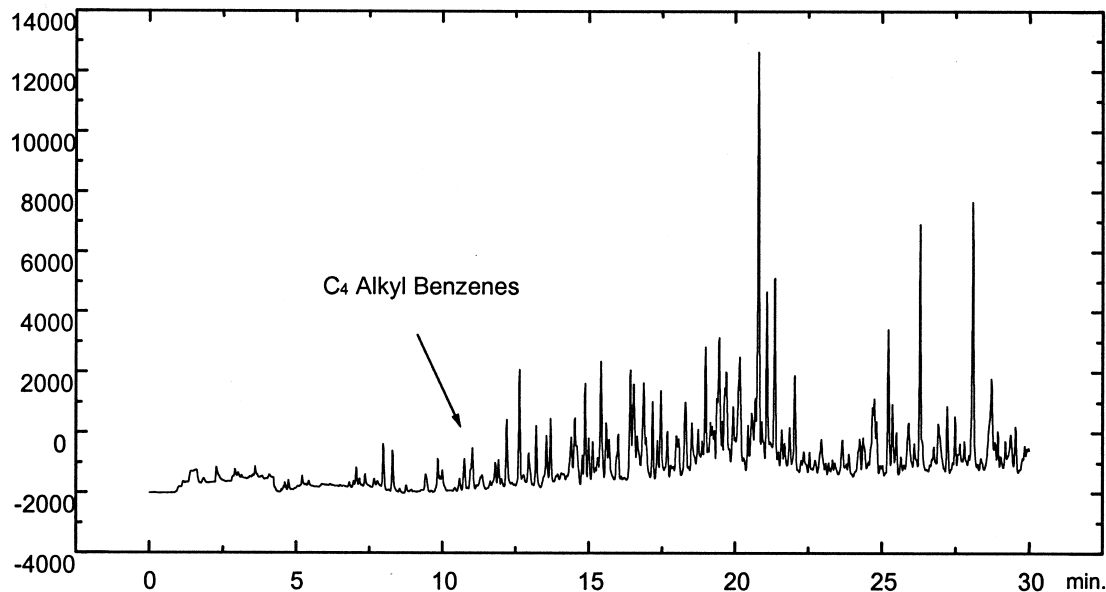


FIG. 5—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of gasoline on hand sampled 10 min after exposure and heated for 5 min with a heat lamp.

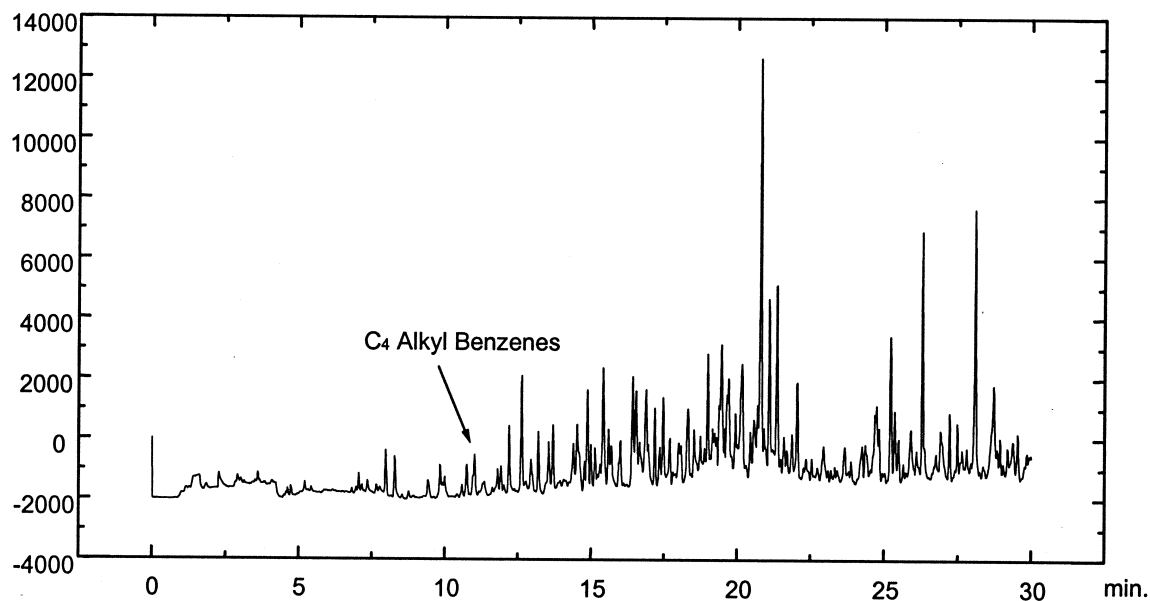


FIG. 6—Chromatogram of 15 min SPME extraction of a 10- μ L spike of gasoline on a hand sampled 15 min after exposure and heated for 5 min with a heat lamp.

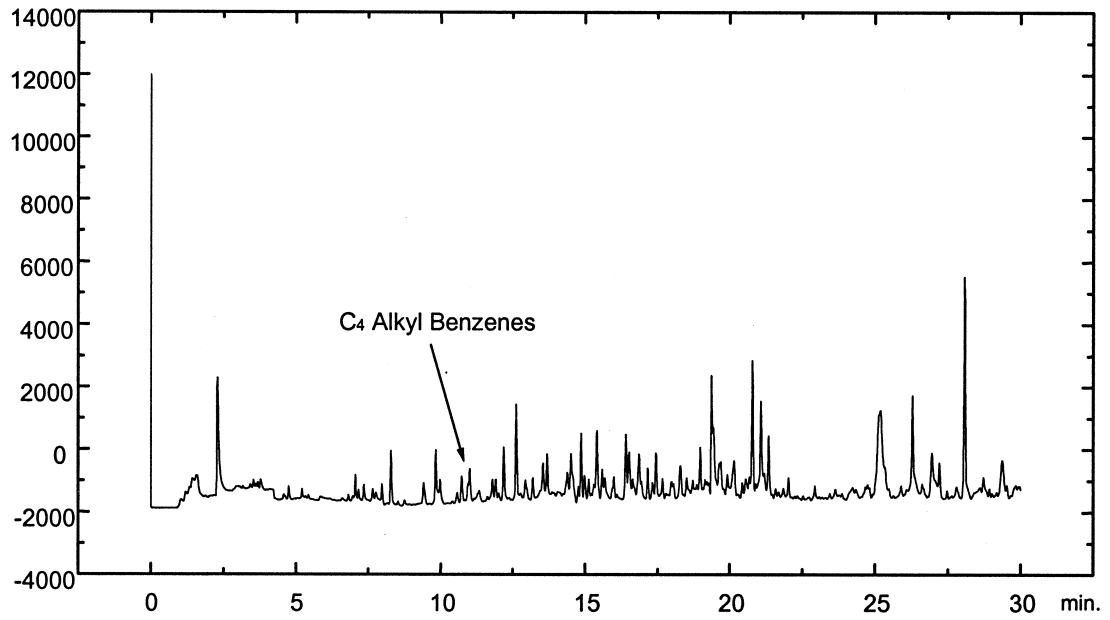


FIG. 7—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of gasoline on a hand sampled 30 min after exposure and heated for 5 min with a heat lamp.

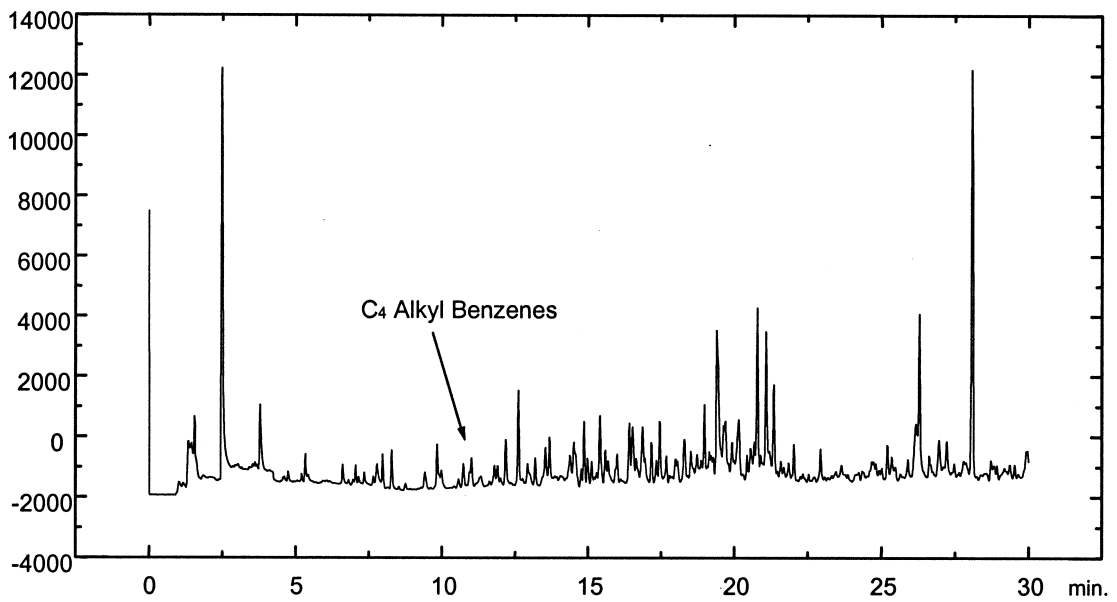


FIG. 8—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of gasoline on a hand sampled 45 min after exposure and heated for 5 min with a heat lamp.

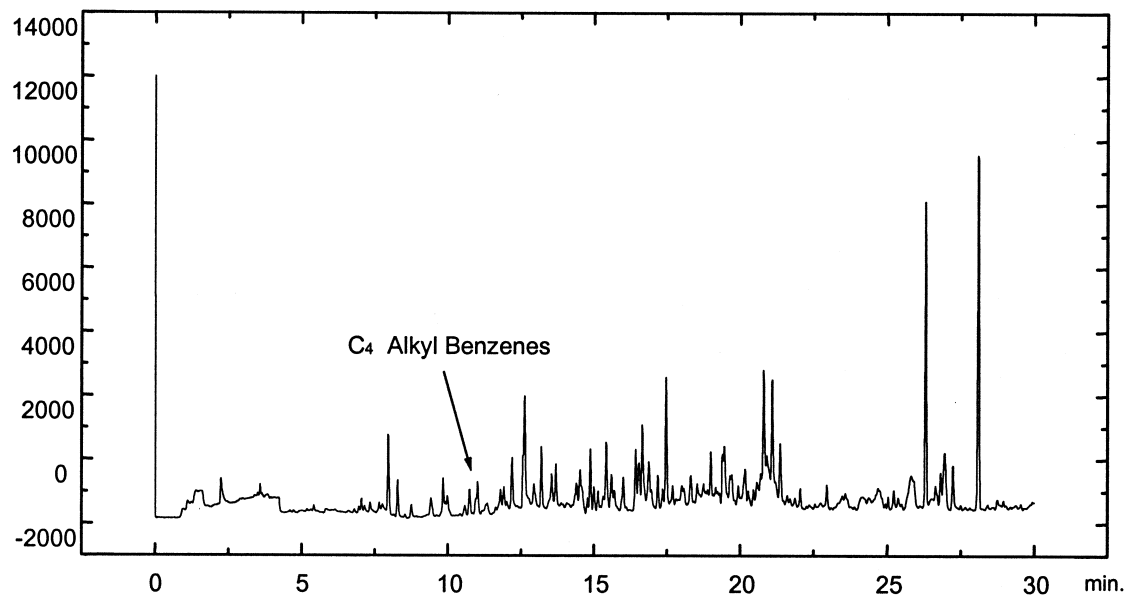


FIG. 9—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of gasoline on a hand sampled 75 min after exposure and heated for 5 min with a heat lamp.

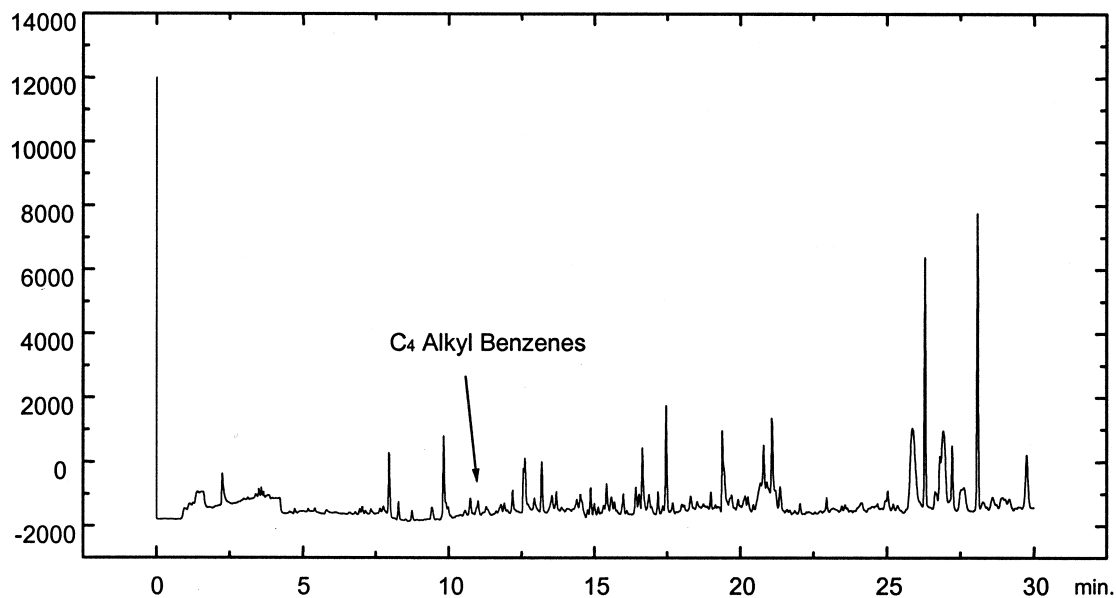


FIG. 10—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of gasoline on a hand sampled 90 min after exposure and heated for 5 min with a heat lamp.

overall effect of prolonged heating is to produce reduced extraction efficiencies and it was found that the method of heating for 5 min prior to SPME sampling provided for the best recovery.

The test results were found to be reproducible affording chromatograms with peaks of similar intensities for the same sampling experiments.

Detection of Diesel Fuel Spikes on Skin

The chromatograms shown in Figs. 11 and 12 are the result of SPME extractions of diesel fuel spikes on skin, sampled 5 s, and 3.5 h after application, respectively. Although the low boiling components are not observed after 3.5 h, preventing the identification

of a HPD (Class V or IV) as per ASTM guidelines (14), some of the expected peaks are observed.

Detection of Charcoal Lighter Fluid Spikes on Skin

Figures 13 and 14 are the chromatograms resulting from SPME extractions of charcoal lighter fluid spikes, sampled 5 s and 2 h after application on the hand. Charcoal lighter fluid can be identified even 2 h after exposure.

Conclusions

A fast and simple method to detect and characterize flammable or combustible liquid residues directly from human skin is reported

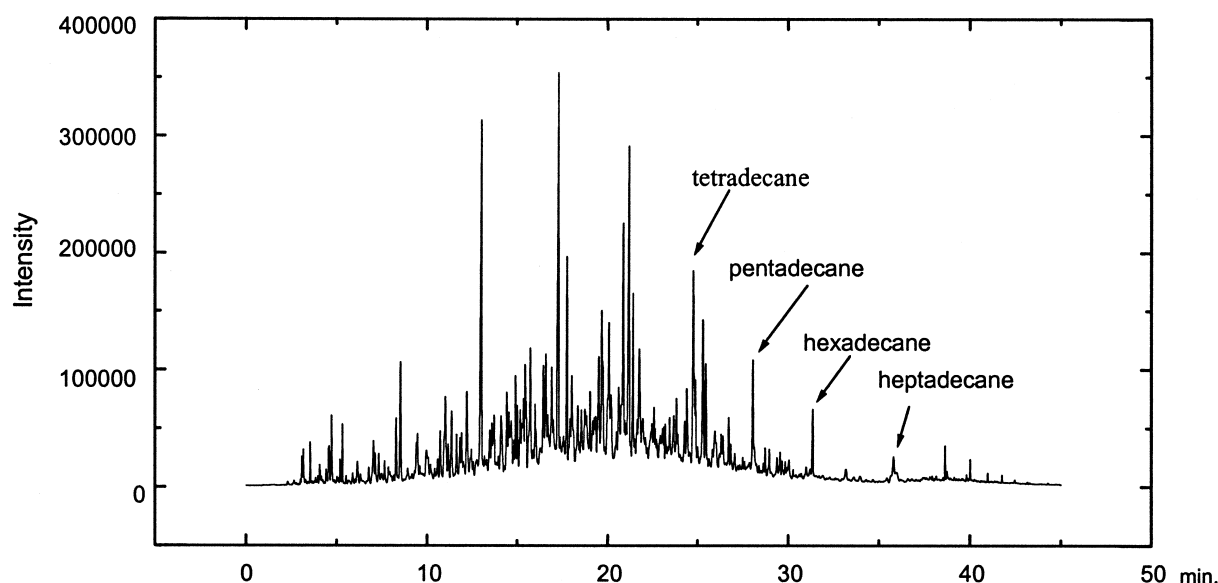


FIG. 11—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of diesel fuel on a hand sampled 5 s after exposure and heated for 5 min with a heat lamp.

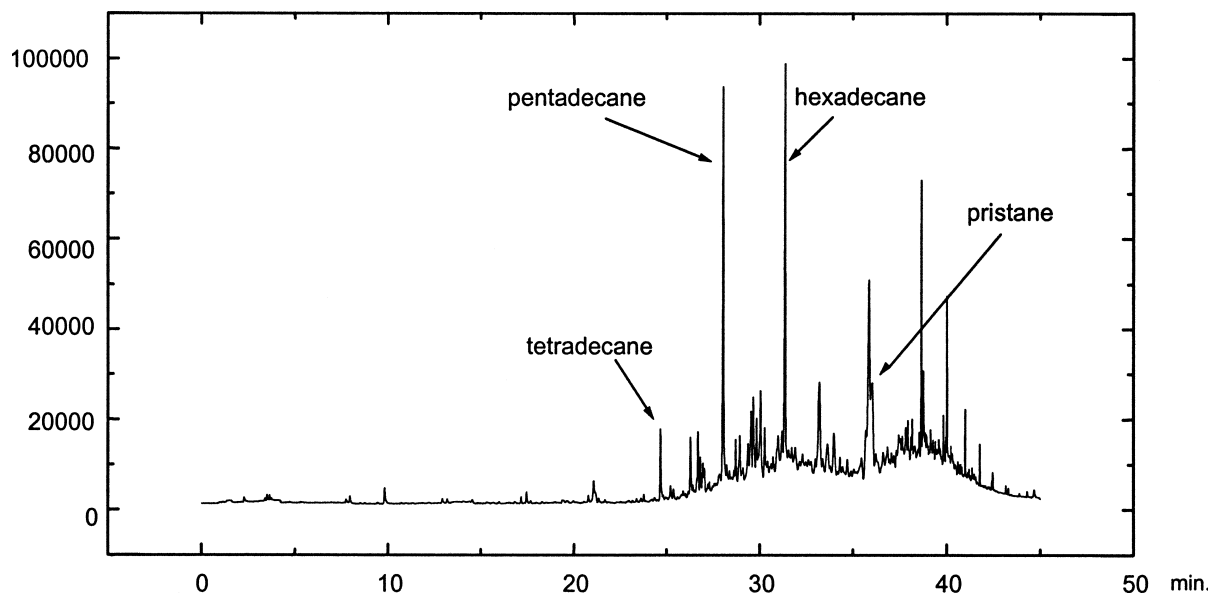


FIG. 12—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of diesel fuel on a hand sampled 3.5 h after exposure and heated for 5 min with a heat lamp.

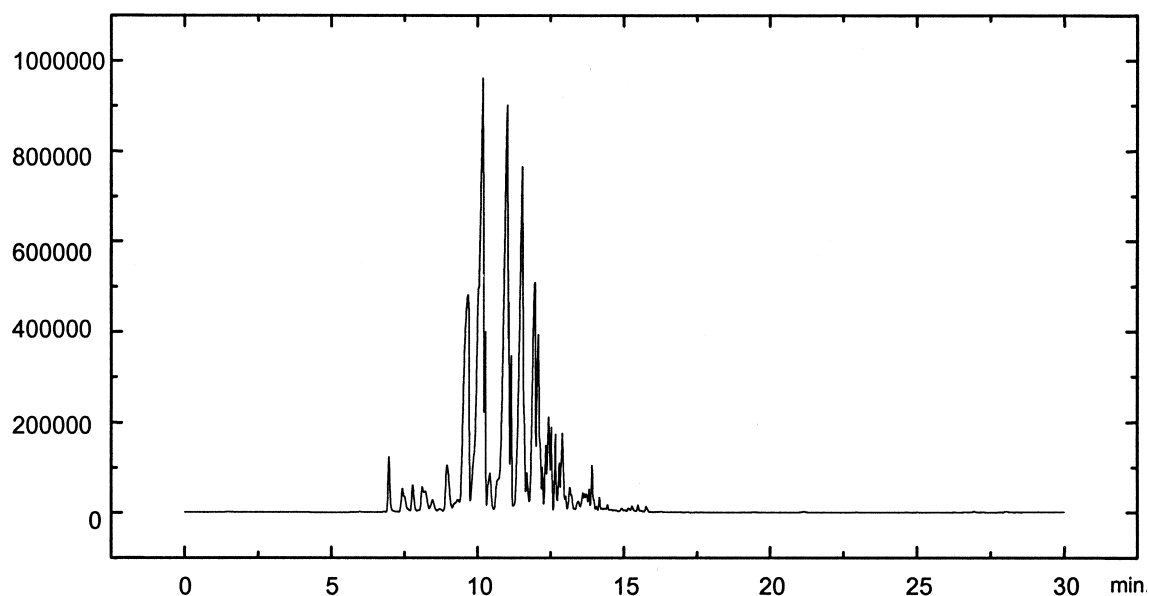


FIG. 13—Chromatogram of a 3 min SPME extraction of a 3- μ L spike of charcoal lighter fluid 5 s after exposure and heated for 1 min with a heat lamp.

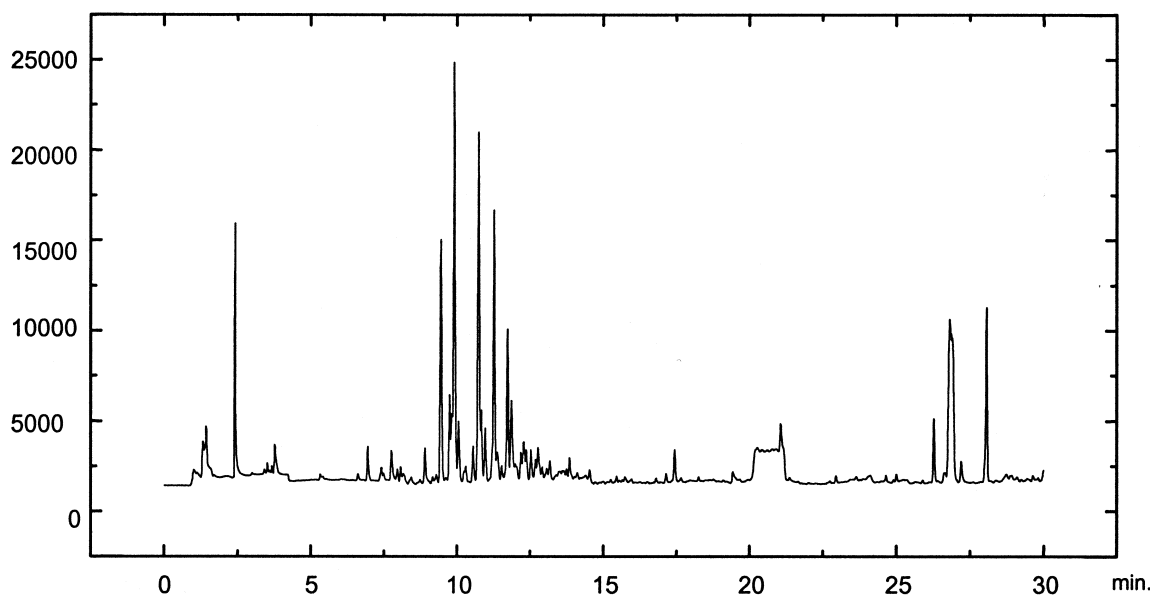


FIG. 14—Chromatogram of a 15 min SPME extraction of a 10- μ L spike of charcoal lighter fluid 2 h after exposure and heated for 5 min with a heat lamp.

for the first time. This technique allows for the rapid analysis (within 15 min) of ignitable liquid residues that are exposed and adsorbed on human skin and would enable the fire investigation team to positively identify a flammable or combustible liquid residue very quickly. The portable SPME unit can be used at the scene of the fire along with a portable gas chromatograph or it can be used to collect the sample for subsequent analysis in a laboratory.

The SPME technique can recover very small amounts of ignitable liquid deposits on skin depending on the class of the flammable or combustible liquid residue used and time after exposure.

This method can be used in conjunction with an accelerant detection canine (ADC) team at a crime scene by first identifying a possible suspect at the crime scene using the ADC team. The

SPME method can then confirm the ADC alert by chemically identifying the presence of a flammable or combustible liquid residue on the skin of the suspect. The simplicity of use for this commercially available apparatus makes it suitable for use by field investigators in coordination with a chemist.

Small quantities of flammable or combustible liquid residues (i.e., 10 μ L spikes) were used to illustrate the sensitivity of the SPME extraction method. It is expected that in real world situations, a greater amount of liquid residues may be splashed on the hands of a suspect, making the determinations and identifications of the residues more conclusive. In order to be used in actual casework, the full range of flammable or combustible liquid residues would need to be characterized from human skin and any possible

background levels evaluated. Validation studies using ADC teams, investigators and chemists would also be required prior to field implementation.

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