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GC-MS of Ignitable Liquids Using Solvent-Desorbed SPME for Automated Analysis

ABSTRACT: Solid-phase microextraction (SPME) is well documented with respect to its convenience and applicability to sampling volatiles. Nonetheless, fire debris analysts have yet to widely adopt SPME as a viable extraction technique, although several fire debris studies have demonstrated the utility of SPME coupled with gas chromatography-mass spectrometry (GC-MS) to identify ignitable liquids. This work considers the expansion of SPME sampling from the customary thermal desorption mode to solvent-based analyte desorption for the analysis of ignitable residues. SPME extraction fibers are desorbed in 30 μL of nonaqueous solvent to yield a solution amenable to conventional GC-MS analysis with standard autosampler apparatus. This approach retains the advantages of convenience and sampling time associated with thermal desorption while simultaneously improving the flexibility and throughput of the method. Based on sampling results for three ignitable liquids (gasoline, kerosene, and diesel fuel) in direct comparisons with the widely used activated charcoal strip (ACS) method this methodology appears to be a viable alternative to the routinely used ACS method.

KEYWORDS: forensic science, solid phase microextraction, fire debris analysis, ignitable liquid residues

Solid phase microextraction (SPME) is a recently established sampling approach first described by Arthur and Pawlizyn (1). Several excellent texts and reviews are available for SPME (2–5), and the technique has been used for a diversity of applications ranging from the analysis of combustion products in river water and soils (6–10) to the analysis of substances extracted from bodily fluids (11,12). Of direct relevance to this work, SPME has also been recently applied to the extraction of ignitable liquid residues from fire remains. In a series of publications by Furton, Almirall and Bruna beginning in 1995, SPME was shown to facilitate convenient and exceptionally sensitive ignitable liquid residue analysis versus the more commonly used activated charcoal strip (ACS) procedures (13–16). Likewise, Steffan and Pawlizyn demonstrated the applicability of SPME to fire debris samples analyzed via gas chromatography-mass spectrometry (GC-MS) in 1996 (17), and Bertsch and Ren have provided a recent review comparing this extraction methodology to other sample preparation methods for sample analysis in fire debris investigations (18).

SPME utilizes a sorbent-covered fiber for the adsorption of analytes of interest. This sorbent can be comprised of a variety of conventional stationary phases including polydimethylsiloxane (PDMS, e.g., 100 μm , 30 μm , and 7 μm thickness), polyacrylate (PA), and divinylbenzene-polydimethylbenzene, among others. As in conventional gas chromatography, the thickness of the stationary phase affects the selectivity as well as the total capacity of the fiber. Typically, thicker phases are more suitable for volatiles analysis, while thin coatings are more efficient for larger, more hydrophobic compounds (19). Adsorption of analyte(s) to the SPME

phase can take place either directly from the headspace above a sample or from insertion of the SPME fiber into an aqueous matrix. Analyte desorption also usually occurs in one of two ways, most frequently associated with the instrumentation utilized for component separation. When used in conjunction with high-performance liquid chromatography (HPLC), desorption is typically accomplished as the fiber is introduced into the HPLC injector and contacts the hydroorganic mobile phase (19,20). However, for the much more numerous GC applications including previous ignitable liquid residue studies (13–18), analytes are normally thermally desorbed as the fiber is inserted into the heated injection port (e.g., 250°C) of the GC instrument.

As noted, at the present time the fire debris analysis technique utilized by most forensic labs is the passive (static) headspace analysis using an activated charcoal strip (ACS) (21). Advantages of this methodology include its inherent simplicity, relative sensitivity, extract archivability, and amenability to automation, whereas disadvantages include exposure to carbon disulfide (CS_2) in those labs utilizing this traditional desorption solvent (an olfactory irritant and nervous system, developmental and reproductive hazard, (22)), lengthy adsorption conditions (typically 16 h at 60–80°C, (21)), and the loss of volatile analytes from the sample following ACS extraction.

SPME has yet to be widely accepted in the forensics community as an alternative for ACS; in fact, the ASTM standard for Fire Debris Analysis currently recommends the use of SPME as a screening test only (23). As demonstrated previously (13–18), considerable advantages do exist for SPME using the thermal desorption mode including increased sensitivity, simplicity in sample preparation, and the lack of expensive, toxic solvents. Nonetheless, it has been argued that SPME may in fact be overly sensitive, resulting in significant measurement of the petroleum-laced background that is inherent in products manufactured with petroleum derivatives (24). Other disadvantages of the SPME process include the limited fiber lifetime (typically less than 100 injections), inability to archive the

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SPME extract, and an inability to conveniently automate the analytical process using conventional GC autosamplers.

The primary purpose of this work is to develop a combination of the best features of both the ACS and SPME techniques for ignitable liquid residue analysis. Adsorbing analytes from fire debris samples on the SPME fiber reduces sample preparation time from 16 h to 10 min. Further, since an inconsequential fraction of material is actually removed from the ignitable liquid residue sample when SPME is employed, the analyst is afforded the opportunity to reanalyze the sample as needed. To overcome the limitation imposed by thermal desorption for SPME automation, the fiber is instead desorbed with a small quantity of organic solvent. In contrast to the ACS method in which as much as 700 μL of desorbing solvent (e.g., CS_2) is frequently used depending on autosampler vial geometry, the volume of solvent is reduced to 30 μL , thus avoiding unnecessary exposure to the analyst and reducing wastes. This approach provides the fire debris analyst with the opportunity to screen high priority cases in less than an hour from the time sample is made available, while routine samples can be stored in the injection solvent and analyzed using conventional autosampler devices at a more convenient time. Further, since the desorption solvent can be archived in a manner similar to the conventional ACS method, a significant limitation of the SPME method may be removed.

Methods

Apparatus

All analyses were conducted using a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 mass selective detector, HP7683 autosampler, and an HP-5 (5% phenyl) 30 m by 0.25 mm analytical column with 0.25 μm film thickness (Agilent Technologies, Wilmington, DE). The mass selective detector was operated in the scan mode monitoring a range of 33–370 m/z using a standard autotune. GC operating temperatures were optimized as follows: quadrupole temperature, 150°C; source temperature, 230°C; injector temperature, 250°C. Flow was maintained through the col-

umn at 1.00 mL/min. Temperature programming was optimized and utilized an initial temperature of 40°C for 4.00 min ramped to 280°C at 9°C/min.

The SPME syringe and SPME fibers, 7 and 100 μm polydimethylsiloxane (PDMS), and 85 μm polyacrylate (PA), were obtained from Supelco, Inc. (Bellefonte, PA) and conditioned per the manufacturer's recommendations. Reagent grade carbon disulfide (CS_2) was from J.T. Baker (Phillipsburg, NJ). Sampling vials (2 mL) were fitted with spring-centering liners to give a final volume of 100 μL (Agilent Technologies, Wilmington, DE). Quart-sized, lined paint cans (Devoe Paints, Spartanburg, SC) were used to contain each sample. Laboratory tissues (Kimberly-Clark, Roswell, GA) spotted with the appropriate ignitable liquid were placed in the paint cans as the medium for sample volatilization into the headspace. Gasoline (87-octane), kerosene, and diesel fuel were each obtained from Exxon, Inc. (Spartanburg, SC).

Extraction Procedure

The general procedure for volatiles extraction (see Fig. 1, Table 1) was to spot 2.0 μL of ignitable liquid (gasoline, kerosene, or diesel fuel) onto a laboratory tissue, place the tissue into a quart-sized paint can and subsequently seal the can with the lid hammered into place. For SPME analysis, the fiber assembly was inserted into the headspace of the can through a hole in the lid prepared using an awl. After a predetermined adsorption period at a controlled temperature, the fiber assembly was removed and analytes were either thermally desorbed in the heated GC injector or desorbed with an organic solvent rinse. In the case of solvent desorption, a portion (i.e., 1.0 μL) of the recovered sample was subsequently injected from the liquid phase into the GC-MS instrument for analysis using conventional autosampling apparatus with low-volume inserts.

In an effort to optimize sample recovery and response, a preliminary study was performed to determine the length of time required for adsorption of the ignitable liquids onto the SPME fibers. For example, a polyacrylate (PA) fiber with a phase thickness of 85 μm was placed in the headspace of a can containing 2 μL of kerosene

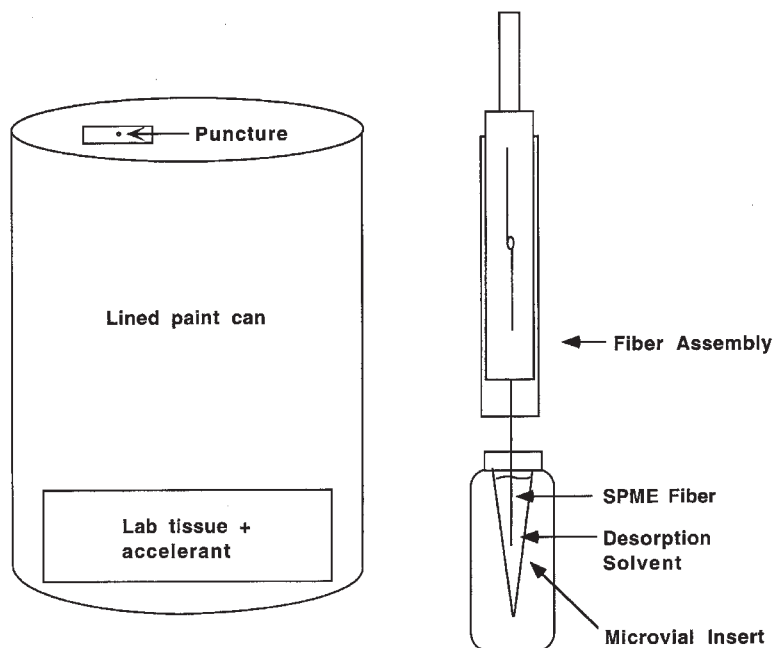
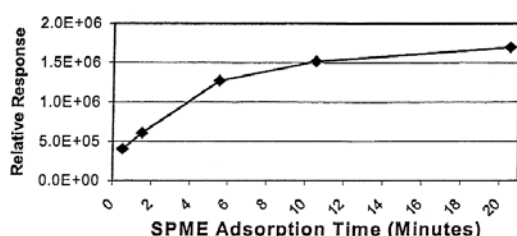


FIG. 1—SPME extraction procedure for ignitable liquids using solvent-based desorption.

TABLE 1—Comparison of ACS and SPME extraction protocols.

ACS Procedure	Solvent Desorbed SPME Procedure
Place evidence in sealed paint cans, placing small hole in can with awl	Place evidence in sealed paint cans, placing small hole in can with awl
Suspend activated carbon strip from cork using wire over hole in can	Place transparent tape over hole in can
Heat at 60°C for 16 h	Heat at 60°C, inserting SPME syringe into headspace for 10 min
Remove strip from cork, desorb with 700 μ L CS ₂ ; Place 100 μ L into GC autosampler vial	Retract fiber, desorb for 1 min into microvial containing 30 μ L CS ₂

FIG. 2—MS response as a function of SPME adsorption time for kerosene sample (85 μ m PA fiber; all other conditions as stated in text).

on a laboratory tissue. The can was maintained at an internal temperature of 60°C and the fiber was exposed to the sample headspace for increasing time intervals. The sample was then immediately thermally desorbed in the heated injection port and subjected to GC-MS analysis. As anticipated, analyte recovery was observed to increase as a function of adsorption time in Langmuir fashion (Fig. 2). However, based on the degree to which the response plateaus owing to fiber/headspace equilibration and the potential for displacement of lighter volatiles with heavier analytes (25), an adsorption time of 10 min was selected for all subsequent studies with all fiber phases as a suitable compromise between extraction speed and analyte sensitivity.

In a separate study designed to optimize conditions for solvent desorption, solutes were eluted from the SPME fiber using CS₂ at temperatures ranging from ambient - 60°C. For each temperature, several desorption times (0.50, 1.0, 5.0, and 10.0 min) were investigated in regard to sample recovery (i.e., standard peak area) and precision (%RSD). Desorption at ambient temperature for 1 min was determined to result in complete release of adsorbed analytes. Based on these parameters, GC injection modes (i.e., split, pulsed split, splitless, and pulsed splitless) were compared and adjusted for maximum sensitivity. The conditions producing optimal results consisted of a splitless injection with a flush of 25 mL/min at 0.5 min, albeit these injection conditions provided moderate broadening of the early eluting volatiles including ethyl-benzene, *o*-, *m*- and *p*-xylenes.

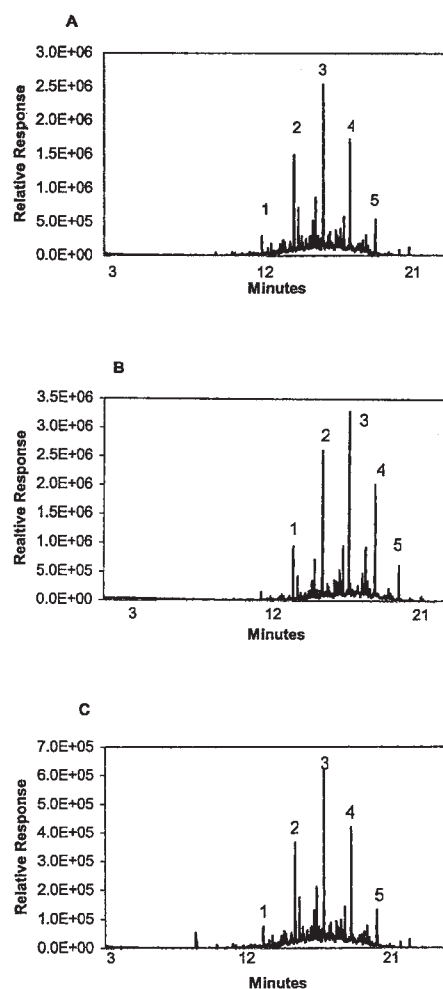
Results

SPME vs. ACS Extraction

In considering the use of SPME as a potential alternative to the established ACS procedure for fire debris analysis, of primary concern is the performance of the technique in providing the charac-

teristic chromatographic fingerprint used for ignitable liquid identification. Figure 3 shows a direct comparison of chromatograms obtained following ACS, SPME with thermal desorption, and SPME using CS₂ desorption for an extracted kerosene sample. The chromatographic pattern agrees well between these samples in the critical fingerprint region for alkanes C₁₁-C₁₈ with maximum response observed for tridecane, and demonstrates the utility of SPME analysis for kerosene extraction. While the SPME analysis utilizing solvent desorption provides reduced signal relative to the thermally desorbed sample (note reduction in signal intensity), the chromatographic profile is nonetheless clearly consistent with the presence of heavy petroleum distillate and displays sufficient sensitivity to permit confident determination of the presence of such an ignitable liquid.

Figure 4 provides a similar comparison for a sample of diesel fuel. It is noteworthy that in the conventional ACS procedure, diesel and kerosene are very difficult to differentiate based solely on the chromatographic profile due to the inefficiency of the charcoal strip in adsorbing and/or desorbing the higher molecular weight fractions of diesel fuel in particular. For example, "neat" diesel fuel injected directly into the GC (data not shown) yields an alkane profile that extends to linear chains in excess of 25 car-

FIG. 3—GC-MS total ion chromatograms obtained following extraction of kerosene standard using (A) ACS, (B) SPME with thermal desorption, and (C) SPME with CS₂ solvent desorption (100 μ m PDMS fiber, 1 = C₁₁, 2 = C₁₂, 3 = C₁₃, 4 = C₁₄, 5 = C₁₅; all other conditions as stated in text).

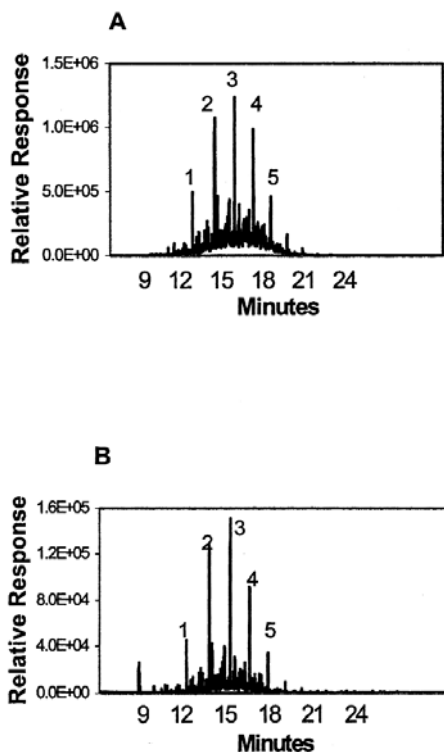


FIG. 4—GC-MS total ion chromatograms obtained following extraction diesel fuel standard using (A) ACS and (B) SPME with CS_2 solvent desorption (100 μm PDMS fiber, all other conditions as stated in text).

bons. In contrast, when the headspace of diesel fuel is absorbed onto the ACS matrix, response diminishes at the higher molecular weight region and peaks are not typically observed beyond the C_{18} alkane region. Based on our observations SPME analysis is quite consistent with the ACS procedure in this regard, and displays no inherent advantage or disadvantage in the analysis of these ignitable liquid residues relative to the established ACS approach.

Figure 5 provides a direct comparison of SPME utilizing solvent desorption versus the ACS procedure for a 50% evaporated gasoline sample. It has previously been noted that SPME is found to discriminate toward medium-heavy distillate compounds (25), and we observe a shift toward heavier molecular weight components of gasoline. The resulting chromatographic fingerprint, well known to fire debris analysts, is noticeably biased toward the heavier tetramethylbenzene and naphthalene fractions when SPME is compared against the ACS procedure, but is still of sufficient quality to be reliable in gasoline identification. In this regard, it is also noteworthy that the comparative signal (i.e., extractability) for kerosene was significantly greater than that of the gasoline via SPME, especially when adsorption was accomplished at ambient temperature as in Fig. 3.

As a final point for comparison, samples of nylon carpet were pyrolyzed and subjected to the identical treatment for both ACS and solvent-desorbed SPME extraction for both diesel fuel and gasoline (Fig. 5c) ignitable liquids. While some minor additional products of pyrolysis were observed at approximately equivalent relative intensities for both the SPME and the ACS procedures for the 50% evaporated gasoline samples in particular, this did not result in a significant difference in the identification of major product peaks associated with either ignitable liquid.

SPME Optimization

Several stationary phase sorbents are currently commercially available for use with SPME, in a variety of phase thicknesses depending on the phase composition. For example, Figs. 6 and 7 provide a direct comparison of extraction efficacy evidenced by the GC-MS chromatographic profiles of gasoline and kerosene using 100 μm PDMS, 7 μm PDMS, and 85 μm PA stationary phases. The 100 μm PDMS phase is observed to be generally more sensitive for both gasoline and kerosene as compared to the other two fibers. For gasoline, the 85 μm PA phase yielded chromatographic responses (i.e., total ion abundances) only slightly lower than that of the 100 μm PDMS fiber. However, the PA phase (often used for polar semivolatiles extraction) yielded a significantly diminished response for the heavier and more hydrophobic kerosene. The 7 μm PDMS fiber proved to be even less useful due to its reduced loading capacity and provided limited signal when assayed with conventional thermal desorption and or when desorbed with CS_2 .

Carbon disulfide has long been recognized as the solvent of choice for fire debris analysis due to its relatively low response with flame ionization detection (GC-FID) and excellent solvent

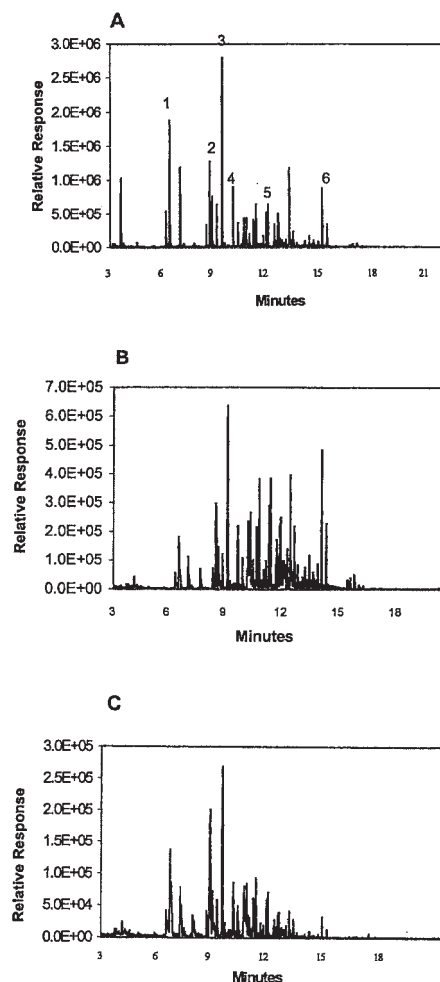


FIG. 5—GC-MS total ion chromatograms obtained following extraction of 50% evaporated gasoline standard using (A) ACS and (B) SPME with CS_2 solvent desorption. (C) SPME with CS_2 solvent desorption for pyrolyzed nylon carpet sample spiked with 2 μL 50% evaporated gasoline (100 μm PDMS fiber, 1 = *m*, *p*-xylenes, 2 = C_3 alkyl benzenes, 3 = 1,2,4-trimethylbenzene, 4 = 1,2,3-trimethylbenzene, 5 = tetramethylbenzenes, 6 = methyl-naphthalene; all other conditions as stated in text).

properties for ignitable liquid components. As GC/MS gradually replaces GC-FID as the industry standard for fire debris investigations, other solvents have been found useful for ACS desorption that do not exhibit the olfactory, health, and environmental concerns associated with CS₂ use (26), and such solvents may find use in the SPME method as well. In this study, methylene chloride, methanol, pentane, and diethyl ether were each evaluated and compared to CS₂ in the analysis of kerosene (i.e., monitoring tridecane) with solvent desorption using the 100 μm PDMS phase (Table 2). As indicated, methanol was observed to result in component signal intensities most promising in comparison to carbon disulfide, whereas pentane and ether were found to be somewhat less efficient in eluting tridecane from the fiber. Analysis of the residual material remaining on the fiber via thermal desorption in the heated GC injection port immediately following solvent desorption confirmed this general trend in solvent efficacy. For example, fibers eluted with CS₂ failed to show any significant carryover of ignitable liquid residue, whereas fibers eluted with the other solvents each demonstrated residual eluted material in relative proportion to their extraction efficiency.

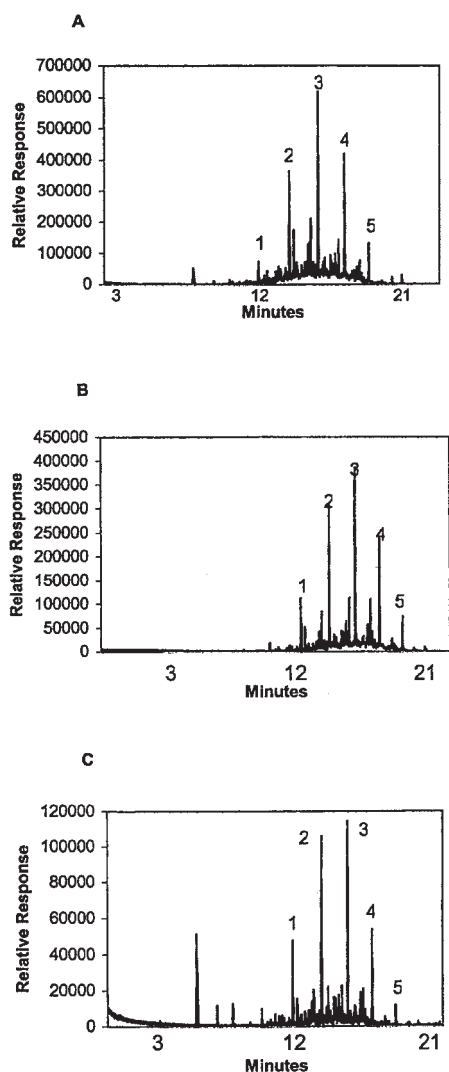


FIG. 6—GC-MS total ion chromatograms obtained following extraction of kerosene standard onto (A) 100 μm PDMS, (B) 7 μm PDMS, and (C) 85 μm PA fibers (Elution with 30 μL CS₂; all other conditions as stated in text).

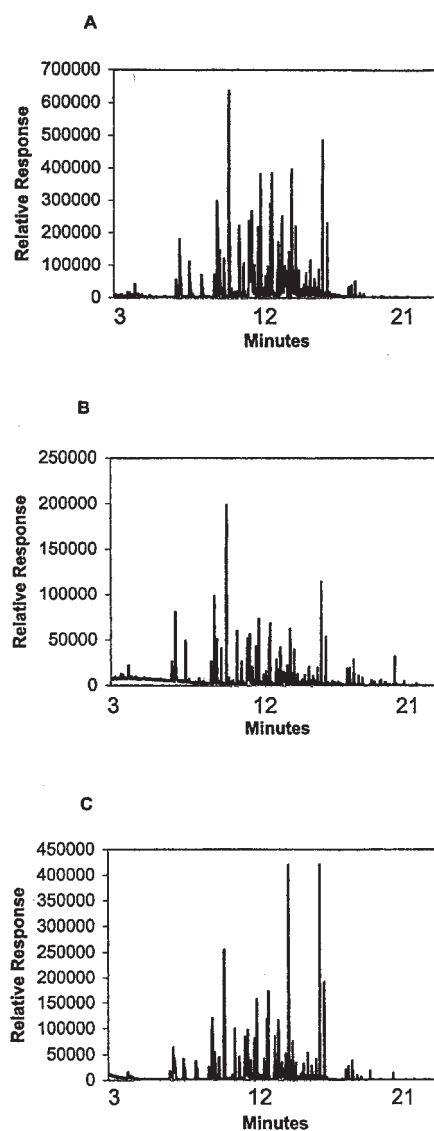


FIG. 7—GC-MS total ion chromatograms obtained following extraction of 50% evaporated gasoline standard onto (A) 100 μm PDMS, (B) 7 μm PDMS, and (C) 85 μm PA fibers (Elution with 30 μL CS₂; all other conditions as stated in text).

TABLE 2—Comparison of tridecane response in extracted kerosene sample using various SPME desorption solvents.

Solvent	MS Ion Abundance	Relative Extraction Efficiency*
Carbon disulfide	619 500	100
Methanol	442 750	71
Methylene chloride	392 000	63
Pentane	365 600	59
Ether	277 800	45

*Based on optimal efficiency obtained using CS₂. All desorptions were carried out on 100 μm PDMS using 30 μL of the specified solvent at ambient temperature for 1.00 min contact time.

Discussion

The procedure outlined in Table 1 for ignitable liquid residue analysis using SPME with solvent desorption offers some distinct advantages over either the conventional ACS procedure or other SPME approaches described previously. First and foremost, the time required for sample extraction is reduced from 16 h using the ACS procedure to only 10 min with either SPME methodology. This provides the analyst with the unique opportunity to either screen or fully analyze priority samples immediately on receipt (or in the field using portable GC-FID monitoring equipment). In addition, since an inconsequential amount of material is removed from the sample headspace as a result of the reduced volume of the extraction phase for SPME, multiple extractions can be performed without concern for altering volatile ignitable liquid concentrations, and/or the solvent extract can be archived for future use/reference.

In practice, thermally-desorbed SPME analysis is often considered a less attractive alternative to the ACS procedure as only one discrete sample can be processed at a time using the comparatively expensive SPME fiber/holder assembly. Further, this apparatus must be transported from the extraction setting to the GC-MS instrument for injection immediately following extraction. This sample throughput problem is conveniently remedied with the solvent desorption approach, as conventional autosampler microvials are used to recover and store the extracted analytes until chromatographic injection is convenient to the analyst (e.g., overnight run). As discussed above, the data obtained via SPME with solvent desorption appear to be at least as reliable using SPME as the conventional procedure, and the extreme sensitivity to the fire debris organic background is modulated by the extraction volume (which is fully adjustable). In the work presented here, significantly reduced quantities of organic solvent (i.e., 30 μ L) were found to be sufficient for fiber elution, reducing the amount of solvent waste and associated hazards by more than one order of magnitude versus the ACS procedure.

Although the performance of SPME extraction fibers is known to vary considerably as a function of extraction matrix, temperature, fiber age, etc., we have been able to successfully use each fiber for 50 or more injections prior to fiber failure with a relative standard deviation in response of 15–20%. While the precision of the SPME fibers has not yet reached the level of quantitative reproducibility enjoyed by some extraction techniques, the reliability of the technique to provide qualitative confirmation of the presence of ignitable liquids would not seem to be an issue.

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