Implementation of SPME and Rapid GC-MS as a Screening Approach for Forensic Fire Debris Applications

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Highlights:

- SPME used as sampling technique for rapid GC-MS analysis of ignitable liquids.
- Rapid GC inlet conditions optimized and compound LODs as low as 27 ng/mL achieved.
- Gasoline and diesel fuel analyzed using SPME-rapid GC-MS workflow.
- Mock burn samples analyzed, and major compounds identified using SPME-rapid GC-MS.

Abstract: Analysis of ignitable liquids in fire debris samples can be a time-consuming process, from extraction of volatile compounds to instrumental analysis. Rapid gas chromatography-mass spectrometry (GC-MS) is a screening technique that can be utilized prior to confirmatory GC-MS analysis to provide an informative screening approach and reduce the need to further analyze negative samples. Though rapid GC-MS is fast (less than two minutes), extraction techniques such as passive headspace extraction remain a bottleneck for decreasing overall workflow times. In this work, solid phase microextraction (SPME) was implemented with rapid GC-MS for ignitable liquid analysis for a faster, more sensitive screening approach compared to extraction with passive headspace. Using optimized inlet conditions, limits of detection as low as 27 ng/mL per compound were achieved. Gasoline and diesel fuel were extracted and analyzed, and major compounds in each liquid were identified in the resulting chromatograms. Extracted ion profiles (EIPs) and deconvolution methods were useful for additional compound identifications. Lastly, the SPME-rapid GC-MS workflow was extended to the analysis of gasoline and diesel fuel in mock burn samples using carpet and wood substrates. From SPME sample extraction to rapid GC-MS instrumental analysis and data processing, the total workflow for a single sample was reduced to under 20 min. These results indicate that SPME is a suitable injection technique for rapid GC-MS to provide a fast and sensitive screening approach for fire debris applications.

Keywords: Solid phase microextraction, Rapid GC-MS, Screening, Ignitable liquids, Fire debris, Forensic science

1. Introduction

Ignitable liquid identifications are a critical part of fire debris analysis and fire investigations as a whole, as the presence of such liquids can be an indicator of an intentionally set fire [1, 2]. Samples submitted to a forensic laboratory typically undergo sample preparation using a standard extraction technique, the most common being passive headspace extraction [3], followed by analysis *via* gas chromatography-mass spectrometry (GC-MS) [4]. Chromatographic profiles are visually compared to reference chromatograms (often generated in-house) of known ignitable liquids to identify the liquid class (if present) based on the major compounds present and their relative abundances. The complexities of these samples can vary widely, as components related to substrates and/or other debris (matrix) from a fire scene will often be present and can complicate ignitable liquid identifications. To mitigate the effects of matrix interferences, total ion chromatograms (TICs) and extracted ion profiles (EIPs) are frequently used in tandem during visual comparisons, as EIPs can be useful for minimizing substrate- or matrix-specific compounds.

Due to the intrinsic complexity of ignitable liquids themselves, lengthy GC-MS methods (≈30 min/injection) are required for full separation and complete compound elution. Extraction processes themselves can also be time-intensive, especially passive headspace, which can take upwards of 10 h to 20 h to complete. Despite the success of such a technique, the entire workflow process (from sample preparation to instrumental analysis) can quickly become time consuming. As such, screening sample contents could decrease the total analysis time by eliminating the need to perform GC-MS confirmatory analyses on negative samples that do not contain ignitable liquids, conserve laboratory supplies and consumables (more cost-effective), and reduce overall instrument wear.

Alternative techniques for fire debris analysis have been reported, ranging from field-portable [5-7] to lab-based [8-11]. Recently, rapid GC-MS has been developed as a screening tool for forensic applications [12, 13]. The technique consists of an instrument attachment that is configured to a traditional benchtop GC-MS instrument. Separation occurs *via* a short (2 m) chromatography column, which connects to the mass spectrometer. Previous efforts focused on an initial application of the technique to ignitable liquid analysis using direct liquid injection [14]. Liquid extracts were prepared using passive headspace extraction with activated charcoal strips (ACS), and the extract was subsequently analyzed by rapid GC-MS. The results were successful, in that ignitable liquid components were identified in each sample, with analysis times under two

minutes. While the time per injection was greatly reduced, total workflow times remained lengthy due to the sample preparation process. For workflow times to be meaningfully reduced, a faster extraction technique is required. Solid phase microextraction (SPME) is suitable for this purpose, as the fiber can be directly injected into the instrument inlet. SPME for ignitable liquid analysis is well established and outlined in ASTM E2154 [15]. Not only does the solvent-less technique eliminate the use of hazardous extraction chemicals such as carbon disulfide or dichloromethane, it is highly sensitive (low ng levels) and selective [16].

Applications of SPME for ignitable liquid extractions have been well reported since the mid-1990s, shortly following the initial development of the technique [17]. Furton, Almirall, and Bruna reported on the applications of SPME for extraction of gasoline and petroleum distillates from burned debris and aqueous solutions [18, 19]. Major compounds in all liquids were identified, even in the presence of pyrolysis products, substrate interferences, and water. Compared to passive headspace with ACS, sensitivities with SPME improved by an order of magnitude, as thermal desorption from the fiber occurs directly in the GC inlet [18]. Steffen and Pawliszyn also used SPME to extract gasoline and lighter fluid from burned carpet and wood samples. Compounds corresponding to each ignitable liquid were successfully identified [20].

Studies have also been reported on the effects of fiber coating, adsorption time, and adsorption temperature on collection efficiencies for ignitable liquids and related analytes. In general, it has been reported that fiber thickness is proportional to analyte volatility for extraction efficiency (*i.e.*, a thicker fiber is more suitable for adsorption of highly volatile compounds) [16, 21-24]. While fibers with different chemistries (*e.g.*, polydimethylsiloxane (PDMS), carboxen, divinylbenzene, or a combination of each) can preferentially adsorb compounds of different classes, PDMS is most commonly used for ignitable liquid applications. Despite the successful application of SPME to fire debris samples in the literature, many analyses are still performed using traditional GC-MS or other instrumental techniques. To date, SPME has yet to be utilized with rapid GC-MS for sample extraction and injection.

In this work, the implementation of SPME with rapid GC-MS is investigated for a fast workflow for fire debris screening. Instrument inlet parameters were optimized specifically for SPME injection to maximize instrument response. Gasoline and diesel fuel were analyzed using the SPME-rapid GC-MS workflow, and major compounds were identified in the resulting chromatographic data. The use of TICs, EIPs, and deconvolution methods for compound

identification were investigated, as well as an evaluation of mass spectral quality as a function of coelution. Lastly, mock burn samples were collected and analyzed to assess the performance of SPME for ignitable liquid extractions in the presence of matrix interferences. This work is a continuation of efforts investigating the utility of rapid GC-MS for fire debris applications. As such, the implementation of SPME as an extraction and injection technique could decrease total workflow times, conserve laboratory resources, and minimize analyst exposure to hazardous solvents.

2. Materials and Methods

2.1 Reagents and Materials

All compounds and materials were used as received. Instrument optimization and limit of detection determination were performed using a neat test mixture (no solvent) containing approximately 0.1 mol of each of the following compounds: *p*-xylene (analytical standard, Sigma-Aldrich, St. Louis, MO, USA), *n*-nonane (>98.0 %, Tokyo Chemical Industry Co., Tokyo, Japan), 1,2,4-trimethylbenzene (TMB) (98 %, Sigma-Aldrich), *n*-decane (≥99 %, Sigma-Aldrich), 1,2,4,5-tetramethylbenzene (TEMB) (98 %, Sigma-Aldrich), naphthalene (99 %, Sigma-Aldrich), and *n*-tridecane (analytical standard, Sigma-Aldrich). *n*-Tetradecane (≥99.0 %, Sigma-Aldrich) was used as a diluent for detection limit determinations. For any samples that were analyzed using direct liquid injection *via* traditional GC-MS (*i.e.*, test mixture, burn sample extracts), samples were diluted in dichloromethane (≥99.9 %, Sigma-Aldrich). Gasoline and diesel fuel were obtained from the National Institute of Standards and Technology (NIST) Fire Department.

A 30-µm PDMS fiber (1-cm length, 24 ga) (Supelco, St. Louis, MO, USA) was used for all SPME sampling. Prior to first use, the fiber was conditioned in the traditional GC inlet at 250 °C for 30 min (in accordance with manufacturer recommendations). Epoxy-lined, pint-size paint cans (Uline, Pleasant Prairie, WI, USA) were used for packaging of mock burn samples. Lined, quart-size paint cans (Uline) were used for extraction of all samples.

2.1.1 Solid Phase Microextraction (SPME)

For liquid sample (*i.e.*, test mixture) SPME extractions, a 10-µL aliquot was transferred to a GC vial fitted with a vial insert. The vial was then placed (uncapped) inside of a quart-size paint can to dilute by volume (approximately 1:1000). Solid samples (*i.e.*, mock burn samples) were

transferred to a quart-size paint can (for consistency with the liquid sample extractions); no further sample preparation was conducted. For an individual extraction (liquid or solid sample), the paint can was sealed with a lid precut with a center opening. The SPME fiber assembly was inserted through the opening and suspended in the sample headspace. The fiber was extended, exposing it to the sample, for an adsorption time of 5 min. The fiber was then retracted, the fiber assembly removed from the paint can, and the fiber immediately injected into the rapid GC-MS inlet for analyte desorption and analysis. The fiber was held in the inlet for a designated injection time, subsequently retracted, and the assembly was removed from the inlet.

2.2   Rapid GC-MS and Traditional GC-MS

An Agilent 3971 QuickProbe GC-MS (Agilent Technologies, Santa Clara, CA, USA) was used for all rapid GC-MS analyses. The system is connected to an Agilent 8890 gas chromatograph and a 5977B mass spectrometer, equipped with a 7693 autosampler (Agilent Technologies). Configuration of the rapid GC-MS attachment to the traditional GC-MS instrument is described in detail elsewhere [14]. Briefly, the attachment connects to the traditional benchtop GC and houses its own chromatography column, a DB-1ht QuickProbe GC column (2 m length x 0.25 mm outer diameter x 0.10 µm inner diameter, Agilent Technologies). For traditional GC-MS analysis, a 100% PDMS column (DB-1, 30 m length, 0.25 mm outer diameter x 0.25 µm inner diameter, Agilent Technologies) was used. The use of a three-port inert tee allows for the benchtop instrument to be configured for traditional and rapid GC analyses, and the end of each GC column connects to individual tee inputs. The output line is a DB-1ms Ultra Inert QuickProbe GC column (1 m length x 0.18 mm outer diameter x 0.18 µm inner diameter, Agilent Technologies), which connects directly to the MS transfer line.

A rapid GC-MS temperature program previously developed for ignitable liquids was utilized for all analyses: initial temperature of 35 °C, hold 10 s, ramp 2 °C/s to 100 °C, ramp 4 °C/s to 280 °C, hold 10 s [14]. The total analysis time was 98 s (1.63 min). The temperature of the conventional GC oven was held, isothermal, at 280 °C, such that analytes would not degrade and would remain in the vapor phase when traveling from the rapid GC column to the MS. A 2-mm ultra-inert, splitless, straight liner (Agilent Technologies) was used. The following sample injection order was used for all rapid GC-MS analyses: system blank, fiber blank(s), sample, fiber blank(s), system blank. A system blank consisted of running the rapid GC temperature program with no fiber or sample

inserted in the inlet and was conducted to reduce background levels due to inlet exposure to ambient conditions.

For traditional, liquid injection GC-MS analyses, the following temperature program was utilized, adapted from the National Center for Forensic Science (NCFS) method for fire debris analysis: initial temperature of 40 °C, hold 3 min, ramp 10 °C/min to 280 °C, hold for 4 min [25]. The method included a 5 min solvent delay. The inlet temperature was set to 250 °C, operating in split mode (20:1 split ratio) at 48.745 kPa (7.0699 psi). A 1-µL injection volume was used. Helium conservation mode was turned on. Samples were analyzed in triplicate, with a solvent blank injection before and after the replicate group for each sample.

Ultra-high purity helium (99.999 %) was used as the carrier gas for all GC-MS analyses (rapid and traditional) at a flow rate of 1 mL/min. For rapid GC-MS, the carrier gas pressure used was 103.421 kPa (15 psi). The MS parameters were the same for both rapid and traditional GC-MS analyses. The transfer line was set to 280 °C. A 70-eV electron ionization source was used, with a source temperature of 230 °C. The quadrupole temperature was set to 150 °C. A scan range of m/z 40 – m/z 550 was utilized, at a scan rate of 5.9 scans/s (N = 1). The threshold was set to 50 counts, and a gain factor of 3 arbitrary units (a.u.) was utilized. The MS was tuned using the Autotune tune type for the duration of the entire study.

2.3   Data Processing

MassHunter GC-MS Data Acquisition software (MassHunter Workstation Software, GC-MS Data Acquisition, version 10.0, Build 10.0.284.1, Agilent Technologies) was used for all data acquisition. Data analysis, including initial compound identification, retention time determination, peak integration, and extracted ion profile (EIP) generation, was performed using MassHunter Qualitative Analysis Navigator (version B.08.00, Agilent Technologies). EIPs were generated for compound classes consistent with those defined in the NCFS Ignitable Liquids Reference Collection Database and ASTM E1618 for ignitable liquid analysis using the following m/z values: alkane (m/z 57, m/z 71, m/z 85, m/z 99), aromatic (m/z 91, m/z 105, m/z 119, m/z 133), cycloalkane (m/z 55, m/z 69, m/z 83, m/z 97), indane (m/z 117, m/z 131, m/z 145, m/z 159), and polynuclear aromatic (PNA) (m/z 128, m/z 142, m/z 156) [4, 25]. Additional compound identifications were performed using the NIST Mass Spectral Search Program (NIST MS Search, version 2.3). Deconvolution was performed using MassHunter Unknowns Analysis (version B.09.00/Build 9.0.647.0, Agilent Technologies);

method parameters are listed elsewhere [14]. The NIST 2020/2017/EPA/NIH Mass Spectral Library was used for all library search and MS Search comparisons. Raw data was exported to Microsoft Excel (Microsoft Office 365, Microsoft Corporation, Redmond, WA, USA) for additional processing.

2.4   Optimization and Limit of Detection (LOD)

Optimization of rapid GC-MS inlet parameters was conducted using a 2^3 full-factorial design-of-experiments (**Supplementary Data, Table S1**). Three parameters were optimized, with two levels (low, high) per factor: injection time (5 s, 10 s), inlet temperature (250 °C, 280 °C), and split ratio (split, splitless). Injection time corresponded to how long the SPME fiber was held in the inlet. For each experiment, five replicate analyses were performed, and the average peak height was calculated for each compound. Main effects plots were generated using the average peak intensities and corresponding 95 % confidence interval for each level and factor.

Instrument sensitivity for SPME injection was determined by calculating the limits of detection (LODs) for each compound in the test mixture. To achieve concentrations low enough for accurate LOD determinations, solutions were prepared at five different dilution factors (approximately 1:5, 1:10, 1:15, 1:25, 1:50; exact concentrations listed in **Supplementary Data, Table S2**) in *n*-tetradecane, as this is a compound commonly found in ignitable liquids but did not interfere with elution of test mixture components. Ten replicates of each solution were analyzed, with the order of solutions analyzed randomly using the Random Number Generator in Microsoft Excel. Using peak intensities, LODs were calculated at the 90 % confidence level *via* the NIST ASTM E2677 Limit of Detection Web Portal Data Entry Page [26]. Uncertainties were determined by calculating the standard deviation across the 10 replicates for each concentration.

2.5   Ignitable Liquid Analysis and Mock Burn Sample Preparation and Analysis

Neat gasoline and diesel fuel were analyzed using the SPME collection procedure and rapid GC-MS analysis method in Section 2.1.1 and 2.2, respectively. Five replicate analyses were conducted for each liquid, with fiber blanks analyzed in between each sample analysis. If carryover was observed in the blank injection immediately following a sample, additional fiber blanks were

analyzed until carryover was not present. Major compounds were identified in the raw TICs, relevant EIPs, and deconvolved TICs.

For the mock burn samples, medium-pile carpet and wood (untreated) were used as substrates. Pieces measured approximately 6 cm by 5 cm. Individual samples were prepared by depositing 1 mL of gasoline or diesel fuel onto a given substrate. The sample was ignited and allowed to burn until flames self-extinguished. Each sample was transferred to a clean, lined paint can (pint-size) and sealed with a lid. This process was repeated for all four combinations of ignitable liquid and substrate, for two sample replicates of each. To understand the composition of each substrate without ignitable liquid (negative samples), clean, unburned substrates were packaged individually in a similar manner to the positive burn samples (those containing ignitable liquid). Additionally, to identify any pyrolysis products associated with each substrate, pieces of the carpet and wood were burned as-is and packaged consistent with all other samples. For these negative substrate samples, which had difficulty igniting or sustaining flames, a 1-mL aliquot of isopropyl alcohol (99.9 %, Fisher Chemical, Fair Lawn, NJ, USA) was added to assist in flame generation. For the unburned and burned substrates, two replicates of each sample were collected.

For SPME extraction of the burn samples, each sample was transferred to a lined, quart-size paint can and extracted according to the procedure described in Section 2.1.1. Cans were first sealed with fully closed lids (no center opening). Consistent with ASTM E2154 [15], each positive sample was heated at 80 °C for 5 min to assist with desorption of volatiles. Negative, unburned samples were heated for 10 min. Following desorption, each sample was immediately removed from heat. The paint can lid was replaced with a lid precut with a center circular opening (the precut lid was washed with methanol in between each sample analysis to prevent carryover). The SPME fiber was suspended in the sample headspace for 5 min for positive samples and 10 min for negative samples. Longer heating and adsorption times were used for negative samples to enable lesser volatile compounds within the substrates to desorb into the headspace and adsorb onto the SPME fiber. Ideally, the same heating and adsorption times would be utilized for all samples (positive or negative); however, for this work, longer times for positive samples resulted in column overload due to the ignitable liquid volume used for spiking, whereas shorter times for negative samples were insufficient for compound detection (low signal-to-noise ratio). All samples were analyzed *via* rapid GC-MS analysis according to the procedure and method detailed in Section 2.2.

3. **Results and Discussion**

3.1 *Assessment of SPME injection reproducibility and optimization of inlet parameters*

3.1.1 *SPME injection reproducibility*

The compatibility of SPME as a rapid GC-MS injection technique was initially assessed using a seven-component test mixture containing compounds present in many ignitable liquids. With the exception of naphthalene, the components of the test mixture were consistent with those used in previous work [14]. All seven compounds were identified in the resulting total ion chromatogram (TIC), in which baseline resolution was achieved for most compounds (**Figure 1**). Due to the timescale of the rapid GC-MS technique, solvent delays or detector off-times are not always feasible. Thus, SPME is an advantageous alternative injection technique due to its solvent-less nature, especially for other mixtures containing early-eluting volatile components (more volatile than those in the test mixture) that would otherwise coelute with the solvent.
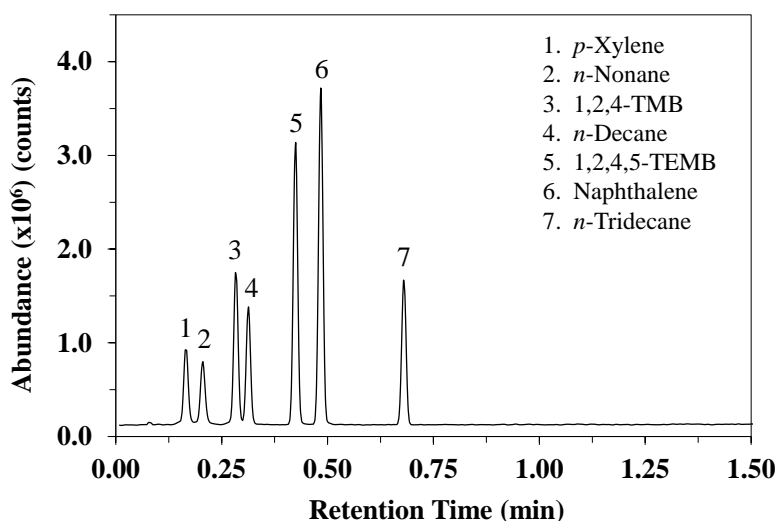

Figure 1. *Total ion chromatogram (TIC) of test mixture collected using solid phase microextraction (SPME) analyzed by rapid gas chromatography-mass spectrometry (GC-MS). TMB = trimethylbenzene; TEMB = tetramethylbenzene.*

To assess the reproducibility of the injection technique, average retention times and peak heights were calculated for compounds across replicate test mixture injections ($n = 10$). Retention time percent relative standard deviations (% RSDs) ranged from ≈0.6 % (naphthalene) to ≈1.5 %

(1,2,4-TMB). (**Table 1**). Comparatively, retention time reproducibility for SPME injection was within the range calculated for direct liquid injection in previous work (% RSDs of 0.5 % to 2.1 %) [14]. For comparison of raw peak intensities, % RSDs ranged from ≈16 % (*p*-xylene) to ≈28 % (naphthalene) (**Supplementary Data, Table S3**). Higher variability compared to liquid injection rapid GC-MS and/or traditional GC-MS (with autosampler capabilities) was not unexpected for SPME injection considering increased variability inherent in the manual injection process as well as expected headspace nonuniformity across sample replicates. Given these caveats, the data demonstrates adequate reproducibility. To evaluate chromatographic pattern reproducibility, raw peak intensities were normalized to that of the most abundant compound (naphthalene) in each replicate analysis. Aside from *n*-tridecane, % RSDs ranged from ≈3 % to 14 % (**Table 1**). These values demonstrate that reproducible chromatograms (in terms of relative abundances and chromatographic pattern) are generated using SPME as the injection technique.

Table 1. *Average retention times (t_R) and peak heights (normalized), respective standard deviations, and % relative standard deviations (RSDs) for test mixture compounds across replicate measurements (n = 10). Peak height data is not provided for naphthalene, as it was used for normalization. TMB = trimethylbenzene; TEMB = tetramethylbenzene.*

Compound	Avg. t_R (min)	St. Dev. (min)	% RSD	Avg. Peak Height (Counts)	St. Dev. (Counts)	% RSD
p-Xylene	0.166	0.002	1.00	0.21	0.03	14
n-Nonane	0.206	0.003	1.52	0.17	0.01	9.3
1,2,4-TMB	0.284	0.002	0.802	0.53	0.05	9.3
n-Decane	0.313	0.003	1.04	0.38	0.02	4.9
1,2,4,5-TEMB	0.422	0.003	0.749	0.89	0.03	2.9
Naphthalene	0.482	0.003	0.554	-	-	-
n-Tridecane	0.676	0.004	0.571	0.4	0.2	51

Across raw and normalized average peak intensities, the greatest variation was observed for *n*-tridecane (% RSDs of ≈56 % and 51 %, respectively) (**Table 1, Supplementary Data, Table S3**), likely caused by competitive adsorption. Of the compounds in the test mixture, *n*-tridecane is the heaviest, largest, and least volatile. As a result, it is one of the last compounds that would vaporize into the headspace and compete for SPME fiber active sites, leading to greater adsorption variability [27, 28]. Despite this inherent limitation of SPME sampling, the injection technique overall was still demonstrated to be reproducible for the test mixture.

3.1.2   Optimization of inlet parameters

To maximize rapid GC-MS instrument response, optimization was performed for injection time, inlet temperature, and split ratio. The optimal level for each factor was determined by that which resulted in maximum peak heights for test mixture compounds. Irreproducible peak intensities were observed for *n*-tridecane, likely due to competitive adsorption effects. Therefore, optimal parameters were determined using the remaining six compounds in the test mixture. Maximum response was observed at the "high" level for all three factors (10 s injection time, 280 °C inlet temperature, and splitless injection) (**Figure 2**). This response was logical, as these levels facilitated analyte desorption, volatilization, and column loading. For split ratio only, respective peak intensities per compound between the low and high levels were statistically significant at the 95 % confidence interval (**Figure 2C**, **Supplementary Data, Table S4**). However, while splitless injections led to higher peak intensities, subsequent fiber blank injections exhibited analyte carryover. To maximize response and minimize carryover for this factor, the optimized method ultimately utilized split injections. For injection time and inlet temperature, the "high" levels were used (10 s and 280 °C, respectively).
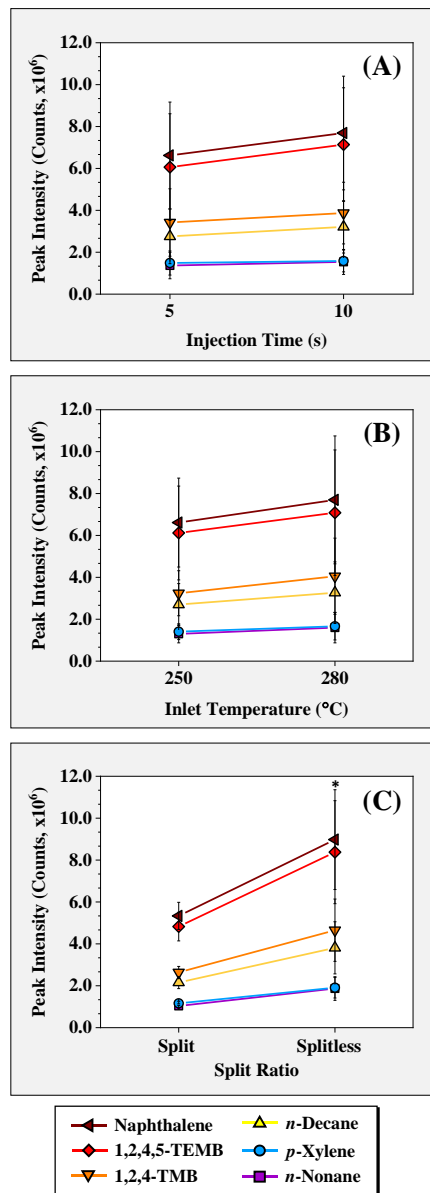
Figure 2. *Main effects plots showing average peak intensities at each factor level from optimization of inlet (A) injection time, (B) inlet temperature, and (C) split ratio. Error bars represent the 95 % confidence intervals, at which the differences between split ratio level responses were statistically significant (indicated by asterisk). TMB = trimethylbenzene; TEMB = tetramethylbenzene. Low values are on the left, high values are on the right.*

These determinations were further supported by main effects plots of % RSDs for compound intensities. A 10 s injection time and split injection both resulted in lower intra-parameter variability (**Supplementary Data, Figure S1**). While an inlet temperature of 280 °C was chosen for the optimized method, greater variability was observed at this temperature compared to 250 °C (**Supplementary Data, Figure S1B**). These results warrant further examination, such as

investigating more than two temperatures or varying only inlet temperature (while holding other parameters constant). However, as a wide range of % RSDs was observed at both levels, an inlet temperature of 280 °C was sufficient for the purposes of this work.

3.2 Limit of Detection (LOD)

Using the optimized inlet conditions, the sensitivity of SPME-rapid GC-MS was evaluated using five concentrations of test mixture solutions (approximately 200 µg/mL, 100 µg/mL, 80 µg/mL, 50 µg/mL, and 20 µg/mL). Consistent with the injection reproducibility and optimization studies, inconsistent abundances for *n*-tridecane were observed across replicate measurements. As a result, its calculated LOD was an order of magnitude greater than the LODs for the remaining six compounds in the mixture (**Table 2**), with an uncertainty greater than the LOD itself (110 ng/mL ± 120 ng/mL). (Note: uncertainties were determined by taking the difference between the LOD at the 90 % confidence level (LOD90) and the 90 % upper confidence limit (UCL) from **Table 2**). This large variability is likely due to competitive adsorption, described in Section 3.1.1.

Table 2. *Limits of detection (LOD) for each compound in the test mixture calculated at the 90 % confidence level (LOD90), as well as the respective 90 % upper confidence limit (UCL) (n = 10). TMB = trimethylbenzene; TEMB = tetramethylbenzene.*

Compound	LOD90 (ng/mL)	90 % UCL (ng/mL)
p-Xylene	27	33
n-Nonane	39	53
1,2,4-TMB	33	41
n-Decane	41	54
1,2,4,5-TEMB	36	45
Naphthalene	34	42
n-Tridecane	110	230

Excluding *n*-tridecane, LODs ranged from 27 ng/mL ± 6 ng/mL (*p*-xylene) to 41 ng/mL ± 13 ng/mL (*n*-decane) (**Table 2**). These results represent the LODs for individual compounds in a simple mixture, rather than for a complex mixture as a whole, such as an ignitable liquid. However, the LODs indicate the high sensitivity of the rapid GC-MS technique with SPME injection. Sensitivities using SPME improved by an order of magnitude compared to those calculated using direct liquid injection in previous work, for which LODs were in the low µg/mL range [14]. Greater

sensitivities with SPME injection is well-established [16], as thermal desorption occurs directly in the GC inlet. Many studies have reported similar sensitivities for ignitable liquids [18-20, 22, 29]. Overall, the LODs determined for SPME injection demonstrated that this technique is highly sensitive for compounds that are among those present in ignitable liquids, and the extraction technique could be used to obtain increased sensitivity during sample screening.

3.3   Analysis of ignitable liquids and assessment of mass spectral quality

3.3.1   Ignitable liquid analysis

To assess the utility of SPME-rapid GC-MS for ignitable liquid screening, neat gasoline and diesel fuel were sampled and analyzed to identify the major compounds present in the resulting chromatographic data. For all samples, major compounds were first identified using the raw TICs. Given the timescale of rapid GC-MS, baseline resolution was not expected, nor necessary, as the technique is intended for screening, rather than confirmation. For the purposes of fire debris screening, this work aimed at investigating the ability to identify some, not all, of the major compounds listed in ASTM E1618 as indicators of certain ignitable liquid classes [4]. To combat the limitation of compound identification in sample TICs due to coelution, additional data processing techniques and tools were utilized. As a second level of identification, extracted ion profiles (EIPs) were generated from the TICs using mass-to-charge values for relevant compounds and compound classes commonly found in ignitable liquids (Section 2.3) [4]. Lastly, a third level of data processing was employed by applying deconvolution to the sample data, as this tool proved useful for compound identification in previous work [14].

In the TIC for gasoline, 11 compounds were identified, all eluting within the first minute of analysis. Among these were compounds commonly used for gasoline identification, such as xylene, C_3- and C_4-alkylbenzenes, naphthalene, and methylnaphthalene (**Figure 3A**). Of the isomeric compounds for which the specific isomer could not be differentiated, the general compound or compound class (without isomeric position) to which the highest spectral search score was attributed, is reported here. For this and all subsequent samples, difficulty with isomer differentiation was expected given the degree of coelution observed.
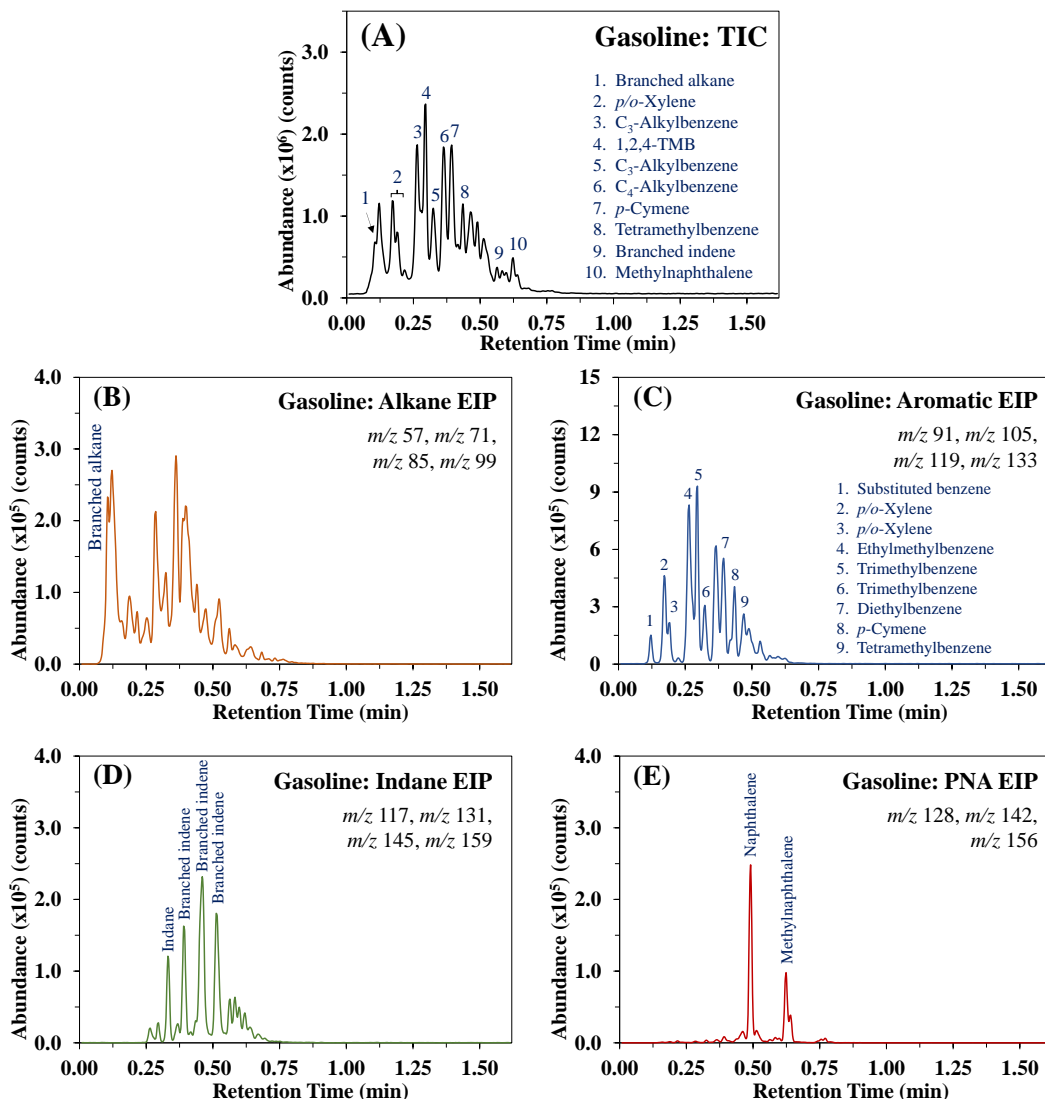
Figure 3. *(A) Total ion chromatogram (TIC) for neat gasoline analyzed using solid phase microextraction (SPME)-rapid gas chromatography-mass spectrometry (GC-MS), as well as extracted ion profiles (EIPs) for the (B) alkane, (C) aromatic, (D) indane, and (E) polynuclear aromatic (PNA) classes.*

Of the five compound classes for which EIPs were generated, compounds were present in the alkane, aromatic, indane, and polynuclear aromatic (PNA) profiles (**Figure 3B – 3E**, **Supplementary Data, Table S5**). In the alkane EIP, only a branched alkane was identified (**Figure 3B**), likely due to the extent of coelution and low compound abundances (approximately 10^5 counts). Conversely, the aromatic, indane, and PNA EIPs enabled identification of additional compounds in the gasoline sample. In the aromatic EIP, these compounds included two xylene isomers, ethylmethylbenzene, trimethylbenzenes, and C_4-alkylbenzenes (**Figure 3C**). Many of these

compounds were also identified in the TIC, but improved resolution and decreased background levels were observed in the EIP. Generation of the indane EIP resulted in identification of indane and several branched indenes (**Figure 3D**), which were not identifiable in the TIC, as these compounds were masked by the high abundance of the alkylbenzenes that eluted at similar retention times. Lastly, naphthalene and methylnaphthalene were identified in the PNA EIP (**Figure 3E**). In addition to the compounds already identified in the TIC and EIPs, other compounds, such as substituted benzenes and branched alkanes, were identified using deconvolution (**Supplementary Data, Table S5**). An example of the gasoline TIC after applying deconvolution is shown in **Supplementary Data, Figure S2A**. Furthermore, specific compound identities of some components (*e.g.*, 2,5-dimethylheptane) were determined using deconvolution, whereas only structural class (*e.g.*, branched alkane) assignment was possible using the TIC and EIPs due to limitations from coelution (**Supplementary Data, Table S5**).

Analysis of diesel fuel using SPME-rapid GC-MS also resulted in the identification of major compounds using all three levels of data processing (TIC, EIPs, and deconvolution) (**Supplementary Data, Table S6**). Despite a high background observed in the TIC (**Figure 4A**), substituted benzenes were still identified. While not one of the major compound classes present in diesel fuel, aromatic compounds are still known to be present at lower abundances [4]. Following TIC analysis, EIPs were generated, with relevant compounds present in the alkane and aromatic profiles (**Figure 4B and 4C**). Lower background levels and improved resolution were observed, while additional compounds were identified compared to the TIC. Normal alkanes $C_{10} - C_{13}$ were identified in the alkane EIP (**Figure 4B**) and were among the most abundant compounds present, which is characteristic of diesel fuel. In the aromatic EIP, xylene, C_3- and C_4-alkylbenzenes were observed (**Figure 4C**). Combined, these compounds align with those commonly found in diesel fuel. Lesser abundant compounds were further identified using deconvolution, including *n*-nonane, branched alkanes, and alkylbenzenes (**Supplementary Data, Table S6 and Figure S2B**).
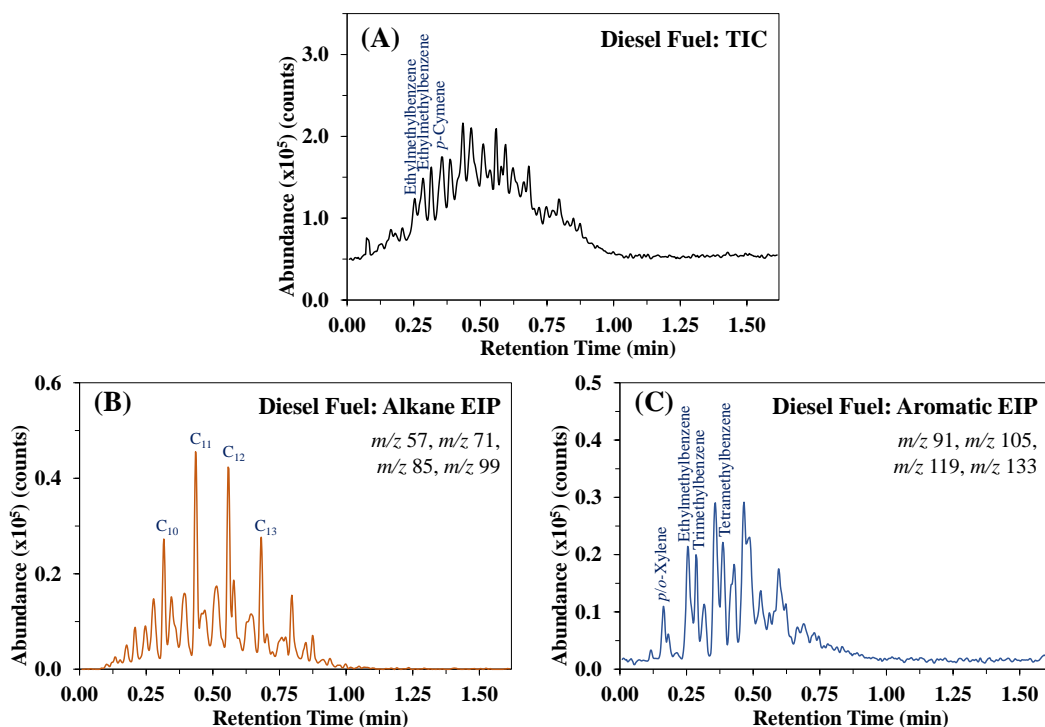
Figure 4. *(A) Total ion chromatogram (TIC) for neat diesel fuel analyzed using solid phase microextraction (SPME)-rapid gas chromatography-mass spectrometry (GC-MS), as well as extracted ion profiles (EIPs) for the (B) alkane and (C) aromatic classes.*

Even for complex mixtures such as gasoline and diesel fuel, the use of multiple data analysis tools enabled successful identification of characteristic compounds commonly used for ignitable liquid classifications. For both liquids, the number of compounds identified increased with each level of data processing. For gasoline, 11 compounds were identified in the TIC, whereas 16 compounds were identified across all relevant EIPs (31 % increase), and 21 compounds were identified using deconvolution (24 % increase compared to EIP identifications). For diesel fuel, only three compounds were identified in the TIC, but this number increased to eight compounds across EIPs (63 % increase) and 11 compounds using deconvolution (27 % increase compared to EIP identifications). Based on the compounds identified in gasoline and diesel fuel, preliminary ignitable liquid classifications (*i.e.*, gasoline and petroleum distillate, respectively) could be made based on the compounds listed for classification in ASTM E1618 [4], demonstrating the success of SPME-rapid GC-MS as a screening technique for these liquids.

3.3.2   Mass spectral quality assessment

Because the rapid GC-MS instrumentation is configured with EI-MS detection capabilities, compound identification is still performed through spectral comparisons to the NIST GC-MS EI mass spectral library. However, due to the extent of coelution present in the chromatograms of gasoline and diesel fuel, it was anticipated that mass spectral quality could be reduced. This hypothesis was evaluated by investigating spectral search scores for background-subtracted spectra extracted from the TICs and EIPs (using NIST MS Search software) and for deconvolved spectra (using MassHunter Unknowns Analysis). Due to the high background in the diesel fuel TIC, compound identifications were most consistent (in terms of compound identities and scores) using scores from the NIST MS Search software (compared to library search scores) and from forward searches of the deconvolved spectra. Thus, only these scores are discussed for diesel fuel compound identifications.

For most compounds identified in gasoline, library search scores were higher for deconvolved mass spectra than they were for mass spectra extracted from the TIC or EIPs (**Figure 5, Supplementary Data, Table S5**). Score comparisons for a subset of compounds identified are shown in **Figure 5, top**. While search scores were higher for the deconvolved mass spectra, the magnitude of the increase was not uniform across compounds. For several compounds, such as xylene and methylnaphthalene, larger than average increases were observed (**Figure 5, top**), likely because the compounds were low in abundance and suffered from coelution. It should be noted that library search scores for some compounds identified in both the TIC and EIPs differed slightly due to differences in retention times at which the mass spectra were generated. Overall, search scores for most compounds were between 80 a.u. – 90 a.u. (on a scale of 0 a.u. to 100 a.u.) (**Figure 5, bottom**), regardless of how the spectra were generated. Despite the high degree of coelution in the chromatographic data, these score breakdowns demonstrate that the mass spectra generated using SPME-rapid GC-MS are of adequate quality for compound identification during sample screening.
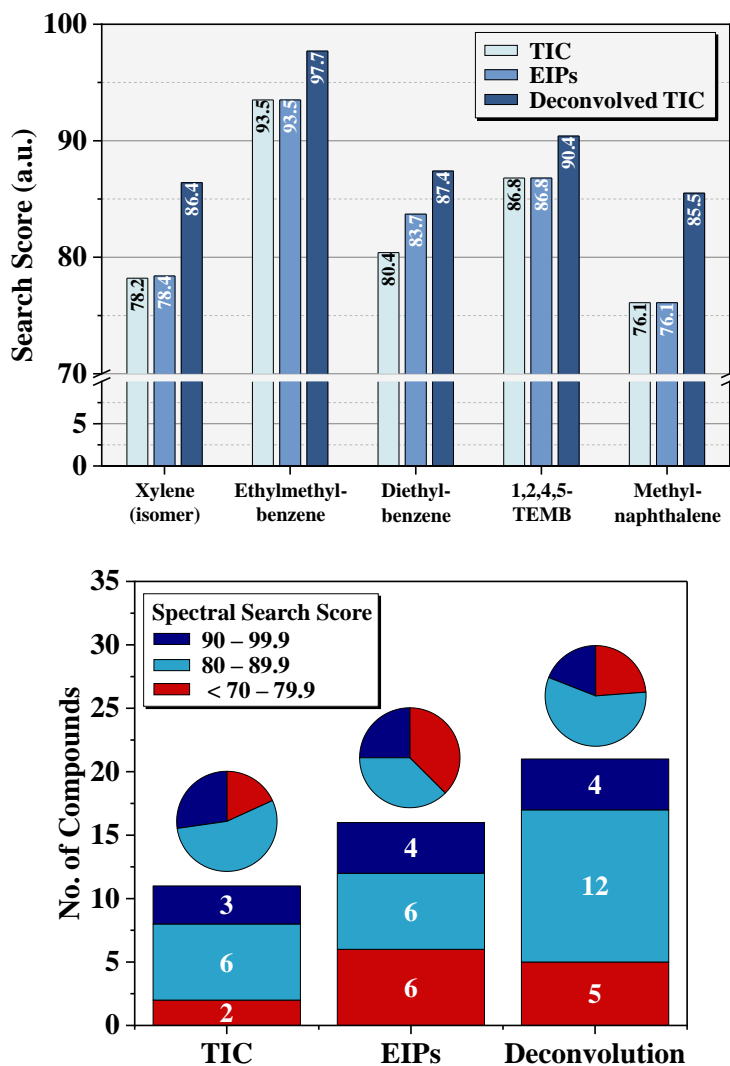
Figure 5. *(Top) Mass spectral library search scores for a subset of compounds in neat gasoline identified using mass spectra extracted from the total ion chromatogram (TIC) and relevant extracted ion profiles (EIPs) compared to search scores using the deconvolved mass spectra. TEMB = tetramethylbenzene. (Bottom) Breakdown of the spectral scores for compounds identified in gasoline using the TIC, EIPs and deconvolution.*

The effects of coelution on two alternative scoring metrics, match factors (MFs) and reverse match factors (RMFs), were also investigated. The spectra for many compounds exhibited extraneous high mass-to-charge ions ($m/z > 200$) at low abundance and were attributed to coeluting compounds from either the sample or background (*e.g.*, column bleed, contaminants), an example of which is provided in **Figure 6**. For instances like this, consideration of RMFs in addition to MFs was useful for compound identification. Unlike MFs, RMFs look for ions in the library spectrum

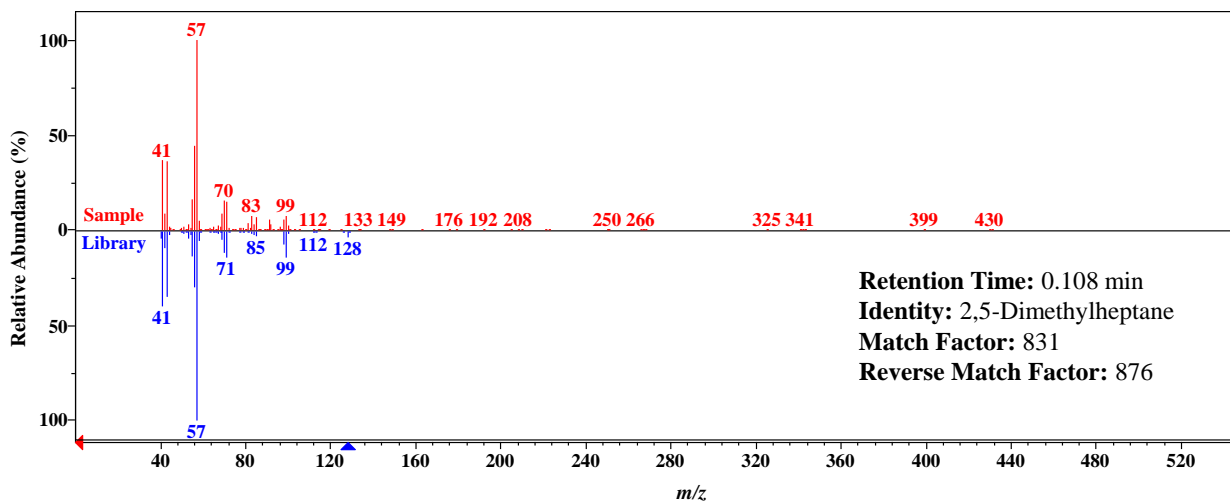that are also in the sample spectrum; therefore, the extraneous ions are ignored in the scoring process [30].

Figure 6. *Head-to-tail mass spectral comparison for a branched alkane (red) eluting at 0.108 minutes identified in the total ion chromatogram (TIC) of neat gasoline compared to the library mass spectra of the compound with the highest match factor (2,5-dimethylheptane) (blue).*

Comparisons of MFs/RMFs for a subset of compounds in gasoline are shown in **Supplementary Data, Table S7**. Similar to the library search scores for gasoline (**Figure 5**), a greater increase between MFs and RMFs for spectra generated from the TIC and/or EIPs was observed for certain compounds (*e.g.*, xylene and naphthalene). These compounds were present at lower abundances in the TICs and affected by coelution more so than compounds of greater abundances. A similar trend was also observed for the deconvolved spectral search scores. Increases between MFs and RMFs, while not as great in magnitude compared to those for spectra generated from the TIC and EIPs, were still apparent. The largest increase was observed for naphthalene, consistent with the spectrum generated from the EIP (**Supplementary Data, Table S7**).

In addition to gasoline, higher RMFs (compared to the corresponding MFs) were observed for compounds in diesel fuel identified in the TIC and EIPs; this trend was especially evident for compounds identified only in the EIPs (**Supplementary Data, Table S6**Error! Reference source not found.). For these compounds, especially xylene, *n*-decane, and *n*-undecane, the RMFs were approximately 30 % greater than the corresponding MFs. Taking into consideration all data

generated for both ignitable liquids, deconvolution was ideal for identifying the greatest number of compounds. In terms of mass spectral comparisons, the joint use of deconvolution and RMFs (if available) is recommended for the highest confidence in compound identifications. However, if such data processing cannot be performed, RMF scoring based on spectra generated from TICs and/or EIPs is the recommended scoring metric for compound identifications.

3.4   Analysis of mock burn samples

To further evaluate the capability of SPME-rapid GC-MS for ignitable liquid screening, mock burn samples were generated and analyzed by SPME-rapid GC-MS. Carpet and wood were used as substrates, as these are common household flooring materials. For the analyses of the negative unburned and burned substrate samples, several compounds were identified in the chromatograms of both substrates. Alkenes were the dominant compounds identified in the unburned and burned carpet samples (**Supplementary Data, Figure S3A and S3B**). In the wood samples, terpineol was identified in both the unburned and burned samples (**Supplementary Data, Figure S3C and S3D**). Additional terpenes were identified in both wood samples, such as 3-carene (indistinguishable from α-pinene at this retention time) and β-pinene in the unburned sample and carene and limonene in the burned sample. While not present at high abundances (approximately 10^5 counts), the compounds in both carpet and wood samples were identified as possible interferences for the subsequent positive sample analyses.

For the carpet sample spiked with gasoline, major compounds identified in the TIC included C_3- and C_4-alkylbenzenes and methylnaphthalene (**Figure 7A**). Indane and naphthalene were also identified using deconvolution (indicated by asterisks). As expected, effects of evaporation were evident in the TIC compared to that of unevaporated gasoline (**Figure 3A**), as compounds at earlier retention times ($t_R < 0.50$ min) were either not present or present at lower abundances. Conversely, compounds at later retention times ($t_R > 0.50$ min) were the dominant compounds in the chromatogram, which is consistent with gasoline at higher evaporation levels in burn samples. Despite evaporation, additional compounds corresponding to gasoline were identified in the relevant EIPs, including xylene and additional alkylbenzenes in the aromatic EIP (**Figure 7C**), indane and branched indenes in the indane EIP (**Figure 7D**), and naphthalene and methylnaphthalene in the PNA EIP (**Figure 7E**). Branched alkanes were identified using solely deconvolution, due to the low abundances of these compounds relative to others in the TIC and alkane EIP (**Figure 7B**).
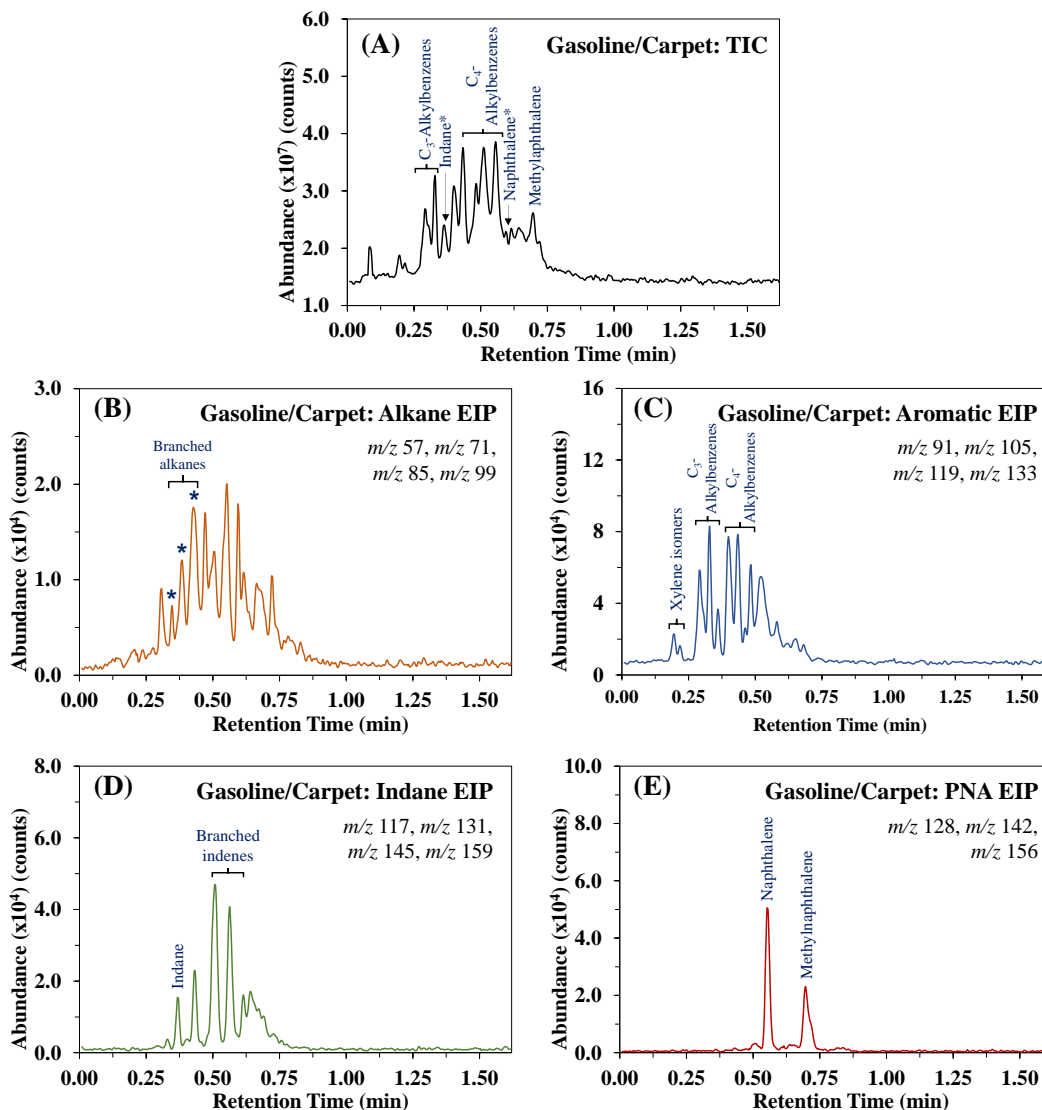
Figure 7. *(A) Total ion chromatogram (TIC) for gasoline/carpet mock burn sample, with extracted ion profiles (EIPs) for the (B) alkane class, (C) aromatic class, (D) indane class, and (E) polynuclear aromatic (PNA) class. Asterisks (*) indicate compounds that were presumptively identified using deconvolution.*

Similar results were observed for the wood sample spiked with gasoline. Compounds associated with gasoline were identified in the TIC, as well as the alkane, aromatic, indane, and PNA EIPs (**Supplementary Data, Figure S4**). These compounds included C_2-, C_3-, and C_4-alkylbenzenes, normal and branched alkanes, naphthalene, and methylnaphthalene. Consistent with

the carpet sample, deconvolution was useful for identifying additional compounds that were unable to be identified in the TIC or EIPs, such as additional alkanes, indane, and branched indenes.

For the diesel fuel burn samples, identification of compounds using the TIC alone was difficult due to coelution and high background levels, which was consistent with the analysis of the neat liquid; however, major compounds were identified using relevant EIPs and deconvolution. For the diesel fuel and carpet sample, *n*-decane, *n*-undecane, and *n*-dodecane were identified in the TIC (**Figure 8A**), with the latter two identified using deconvolution. These normal alkanes were again identified in the alkane EIP (**Figure 8B**), and *p*-xylene and substituted benzenes were present in the aromatic EIP (**Figure 8C**). The wood sample with diesel fuel yielded analogous chromatographic results to the carpet sample. The TIC for the burn sample (**Supplementary Data, Figure S5A**) was visually similar to that of the carpet sample with diesel fuel. Normal alkanes *n*-decane, *n*-undecane, *n*-dodecane, and *n*-tridecane were all identified in the TIC, with *n*-tridecane identified using deconvolution. The same compounds were identified in the alkane EIP, and in the aromatic EIP, *p*-xylene and substituted benzenes were identified (**Supplementary Data, Figure S5B and S5C**). As with the carpet burn sample, all of these compounds are utilized for diesel fuel classification during fire debris analysis. Despite the presence of additional peaks in the TICs and EIPs of both the carpet and wood samples spiked with diesel fuel, the corresponding compound identities could not be definitively determined due to low mass spectral search scores. However, as rapid GC-MS is a screening technique, identification of a subset of compounds, rather than every compound, is sufficient for gauging the contents of a sample to determine the need for confirmatory analysis.
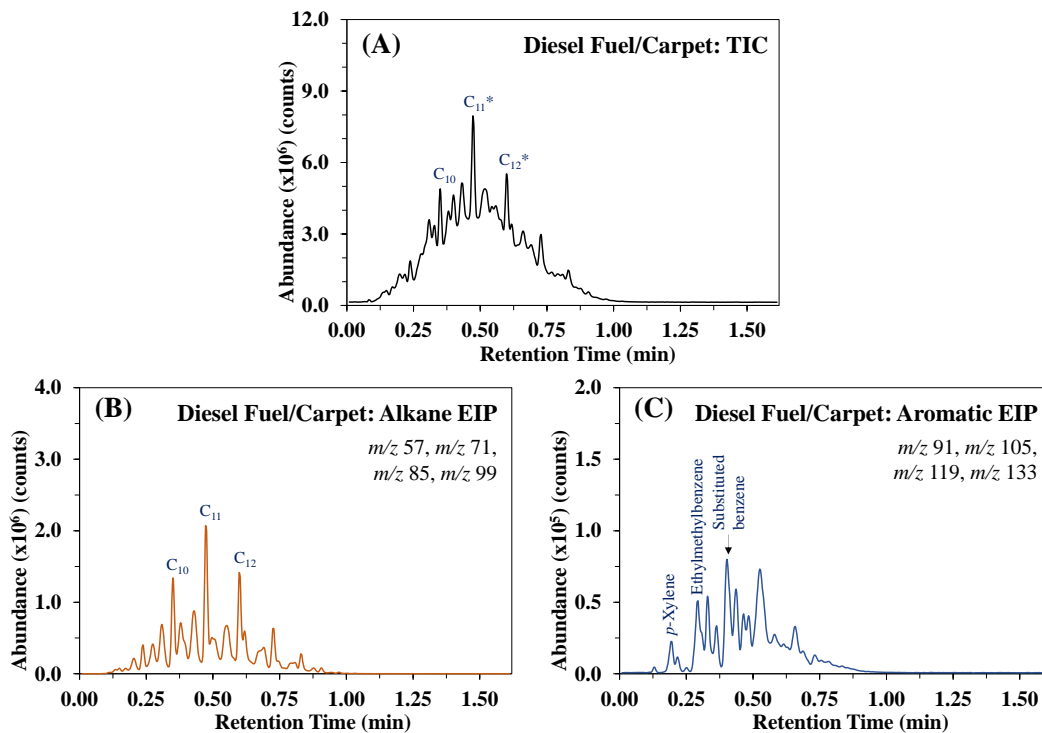
Figure 8. (A) Total ion chromatogram (TIC) for diesel fuel/carpet mock burn sample, with extracted ion profiles (EIPs) for the (B) alkane class and (C) aromatic class. Asterisks (*) indicate compounds that were presumptively identified using deconvolution.

In general, for all burn samples, regardless of ignitable liquid or substrate, compounds corresponding to either substrate were not identified in the sample TICs or EIPs, or when using deconvolution. While some substrate interferences are expected for burn samples, a relatively high volume of ignitable liquids was used to spike the substrates (1 mL), mainly for proof-of-concept purposes. This volume likely caused any substrate compounds in the burn sample chromatograms to be masked by ignitable liquid compounds, which were an order of magnitude more abundant than the substrate compounds identified in the negative samples (**Supplementary Data, Figure S3**). It is also possible that the lack of substrate component identifications was due to competitive adsorption during SPME extraction and displacement of compounds present at low concentrations by those present at higher concentrations. In future studies, smaller volumes of ignitable liquids will be used to more accurately assess the sensitivity of the technique in the presence of matrix interferences. The high abundances of ignitable liquid components observed in this work are unlikely to be observed in real-world samples; nonetheless, successful identification of these compounds still highlights the utility of rapid GC-MS with SPME injection. Analysis workflow

times (from extraction and analysis to data interpretation) were under 20 min, demonstrating the rapid nature of the workflow. While work involving more realistic burn samples is necessary for fully investigating the performance of SPME-rapid GC-MS for fire debris analysis, these results indicate that the technique is a promising tool for such applications.

4. Conclusions

In this work, the implementation of SPME with rapid GC-MS was investigated as a viable screening technique for ignitable liquids with applications in fire debris analysis. Instrument inlet parameters were optimized for SPME injection to maximize instrument response while also limiting carryover. Using the optimized instrumental method, the sensitivity of rapid GC-MS when coupled with SPME injection was determined, with compound LODs in the low ng/mL range (as low as 27 ng/mL). Such low sensitivities are common for SPME injection and are especially advantageous for samples that may have low quantities of analyte present, such as fire debris.

SPME-rapid GC-MS was extended to the analysis of neat gasoline and diesel fuel, and major compounds in the corresponding chromatograms were identified. Due to the rapid timescale of the instrumental technique, coelution was observed throughout the TICs of both liquids, hindering the identification of many compounds. However, the use of EIPs and deconvolution enabled identification of additional compounds in each liquid, many of which are utilized for ASTM ignitable liquid classifications. As rapid GC-MS is intended solely for screening, the use of extra data processing tools (*e.g.*, EIPs or deconvolution) is not required; these techniques are simply demonstrated as additional resources to aid in preliminary identifications. However, EIPs are already commonly used by fire debris analysts to minimize substrate interferences. Further, deconvolution is performed using existing computer software and takes approximately 30 s to complete for a given sample (from file upload to data processing). Thus, there is a relatively low barrier for implementation of these tools in fire debris analysis.

For SPME-rapid GC-MS application to mock burn samples, major compounds in gasoline or diesel fuel were identified using all forms of data processing. While the amount of ignitable liquids present was likely greater than in real-world samples, the ability to identify major compounds and recognize the chromatographic pattern of each liquid demonstrated the promise of SPME-rapid GC-MS for fire debris screening. Future work includes analysis of mock burn samples with varying concentrations of ignitable liquids, specifically lower levels more likely to be present in fire debris

samples to determine a threshold for reliable identifications. Ongoing work currently involves the extension of rapid GC-MS to ignitable liquids of different ASTM classes using direct liquid injection. Future work will focus on analysis of these liquids using SPME extraction to compare chromatographic profiles across injection techniques. Lastly, future efforts will involve the investigation of different fiber coatings and thicknesses (*e.g.*, carboxen/PDMS, divinylbenzene) to assess collection efficiencies and to collect high-mass compounds more reproducibly. In general, the results of this work indicate that SPME can be successfully used as an alternative sampling technique for rapid GC-MS analyses, specifically for ignitable liquids. With total workflow times of < 20 min, SPME-rapid GC-MS shows promise as a fast and informative screening technique for fire debris analysis.

CRediT authorship contribution statement

Briana A. Capistran (ORCID: 0000-0001-6937-0403): Conceptualization, Investigation, Data curation, Formal Analysis, Writing – Original Draft, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Disclaimer

Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by NIST, nor does it imply that such products are necessarily the best available for the purpose.

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Supplementary Data:

Table S3. Design of experiments utilized for inlet optimization, using a 2^3 full-factorial design.

Experiment	Injection Time (s)	Split Ratio	Inlet Temperature (°C)
1	5	Split	250
2	10	Split	250
3	5	Splitless	250
4	10	Splitless	250
5	5	Split	280
6	10	Split	280
7	5	Splitless	280
8	10	Splitless	280

Table S4. Exact concentrations (in µg/mL) of test mixture compounds in each of the five solutions used for limit of detection (LOD) analysis (dilution factors for each solution listed for reference). TMB = trimethylbenzene; TEMB = tetramethylbenzene.

Compound	Concentration (µg/mL)				
	1:5	1:10	1:15	1:25	1:50
p-Xylene	0.196	0.0981	0.0654	0.0393	0.0196
n-Nonane	0.237	0.119	0.0790	0.0474	0.0237
1,2,4-TMB	0.222	0.111	0.0741	0.0444	0.0222
n-Decane	0.263	0.132	0.0877	0.0526	0.0263
1,2,4,5-TEMB	0.248	0.124	0.0827	0.05496	0.0248
Naphthalene	0.237	0.118	0.0790	0.0474	0.0237
n-Tridecane	0.341	0.170	0.114	0.0682	0.0341

Table S5. Raw average peak heights, respective standard deviations, and % relative standard deviations (RSDs) for test mixture compounds across replicate measurements ($n = 10$). TMB = trimethylbenzene, TEMB = tetramethylbenzene.

Compound	Avg. Peak Height (Counts)	St. Dev. (Counts)	% RSD
p-Xylene	323939	53690	16.574
n-Nonane	263800	50192	19.026
1,2,4-TMB	804302	155173	19.2929
n-Decane	578715	140158	24.2188
1,2,4,5-TEMB	1376489	361146	26.2368
Naphthalene	1552695	438393	28.2343
n-Tridecane	612128	340376	55.6054

Table S6. Average peak intensities and respective 95 % confidence intervals (CIs) for test mixture compounds (excluding *n*-tridecane) for inlet split ratio optimization ($n = 5$). (*) indicates statistical significance. TMB = trimethylbenzene, TEMB = tetramethylbenzene.

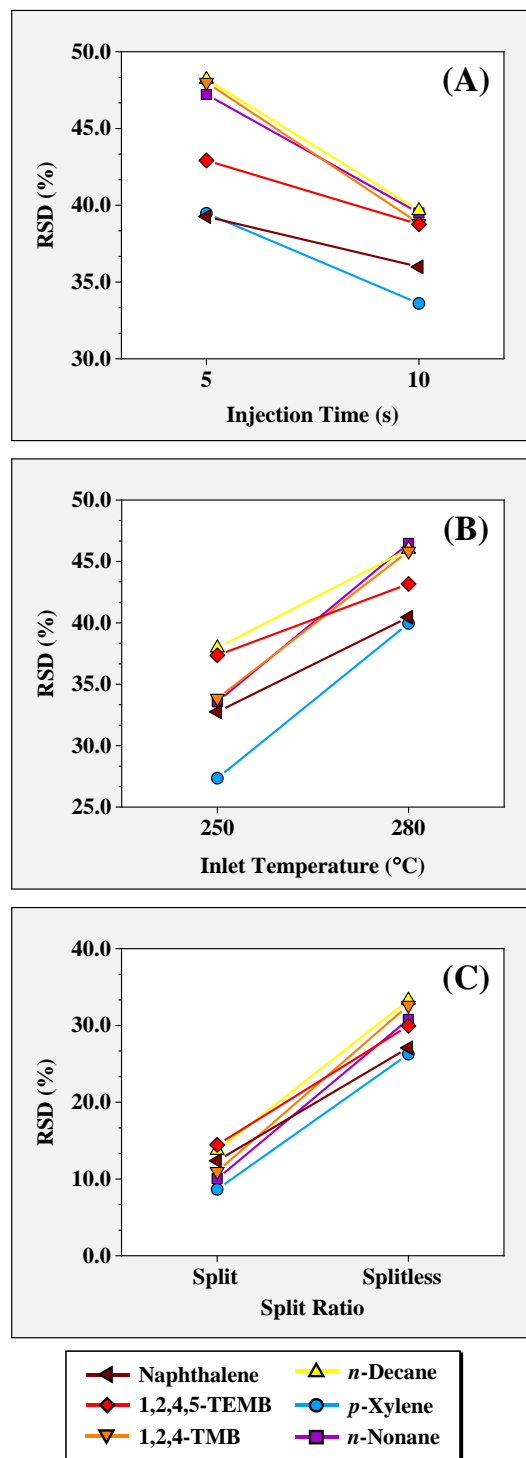| Compound	Split	Splitless
	Avg. Intensity ± 95 % CI (Counts)	Avg. Intensity ± 95 % CI (Counts)
p-Xylene	116105 ± 9835	190845 ± 49101*
n-Nonane	103448 ± 10167	190845 ± 56330*
1,2,4-TMB	263860 ± 28377	465145 ± 48685*
n-Decane	215578 ± 28994	381100 ± 124375*
1,2,4,5-TEMB	482391 ± 68292	837699 ± 245854*
Naphthalene	533590 ± 64680	897637 ± 238222*

Figure S9. Main effects plots for % relative standard deviations (RSDs) calculated for replicate peak intensities of test mixture compounds for optimization of (A) injection time, (B) inlet temperature, and (C) split ratio. TMB = trimethylbenzene; TEMB = tetramethylbenzene. Low values are on the left, high values are on the right.

Table S7. Library search scores, match factors (MFs), and reverse match factors (RMFs) of compounds identified in neat gasoline using the total ion chromatogram (TIC) and relevant extracted ion profiles (EIPs), and after applying deconvolution to the TIC. Retention times (t_R) are taken from the deconvolved TIC.

| t_R (min)	TIC (11 compounds)	Library Search Score	MF	RMF	EIPs (16 compounds)	Library Search Score	MF	RMF	Deconvolution (TIC) (21 compounds)	MF	RMF
0.108	Branched alkane	85.8	831	876	Branched alkane (Alkane)	85.8	831	876	2,5-Dimethylheptane	85.2	94.8
0.121					Substituted benzene (Aromatic)	79.3	728	757			
0.172	o/p-Xylene	90.5	902	971	o/p-Xylene (Aromatic)	90.5	901	971	o/p-Xylene	98.1	99.8
0.183									3-Ethylhexane	73.8	99.8
0.190	o/p-Xylene	78.2	785	964	o/p-Xylene (Aromatic)	78.4	783	961	o/p-Xylene	86.4	94.3
0.224									Substituted benzene	80.2	81.5
0.264	Ethylmethylbenzene	93.5	933	954	Ethylmethylbenzene (Aromatic)	93.5	933	954	Substituted benzene	97.7	99.4
0.284									Branched alkane	84.3	98.5
0.295	Trimethylbenzene	93.0	891	927	Trimethylbenzene (Aromatic)	91.7	891	927	C_3-Alkylbenzene	98.3	99.8
0.323	C_3-Alkylbenzene	80.6	770	859	C_3-Alkylbenzene (Aromatic)	80.6	770	859	C_3-Alkylbenzene	80.6	99.9
0.331					Indane (Indane)	77.4	710	829	Indane	80.4	91.9
0.359									Branched alkane	84.7	98.4
0.364	1,3-Diethylbenzene	80.4	772	885	1,3-Diethylbenzene (Aromatic)	83.7	795	902	Diethylbenzene	87.4	99.8
0.368									Cymene isomer	88.5	98.1
0.393	p-Cymene	87.7	810	826	p-Cymene (Aromatic)	87.7	810	826	C_4-Alkylbenzene (Cymene isomer)	87.5	99.1
0.398									Branched alkane	75.2	92.9
0.435	1,2,4,5-Tetramethylbenzene	86.8	839	902	1,2,4,5-Tetramethylbenzene (Aromatic)	86.8	839	902	1,2,4,5-Tetramethylbenzene	90.4	97.2
0.460					Branched indene (Indane)	79.7	739	773	Branched indene	83.1	88.9
0.490					Naphthalene (PNA)	91.3	656	900	Naphthalene	72.1	97.8
0.513	Branched indene	85.2	774	788	Branched indene (Indane)	88.6	778	798	Branched indene	79.2	90.9
0.582					Branched indene (Indane)	77.8	692	757	Branched indene	60.0	92.3
0.623	1-Methylnaphthalene	76.1	726	921	1-Methylnaphthalene (PNA)	76.1	726	921	Methylnaphthalene	85.5	96.6
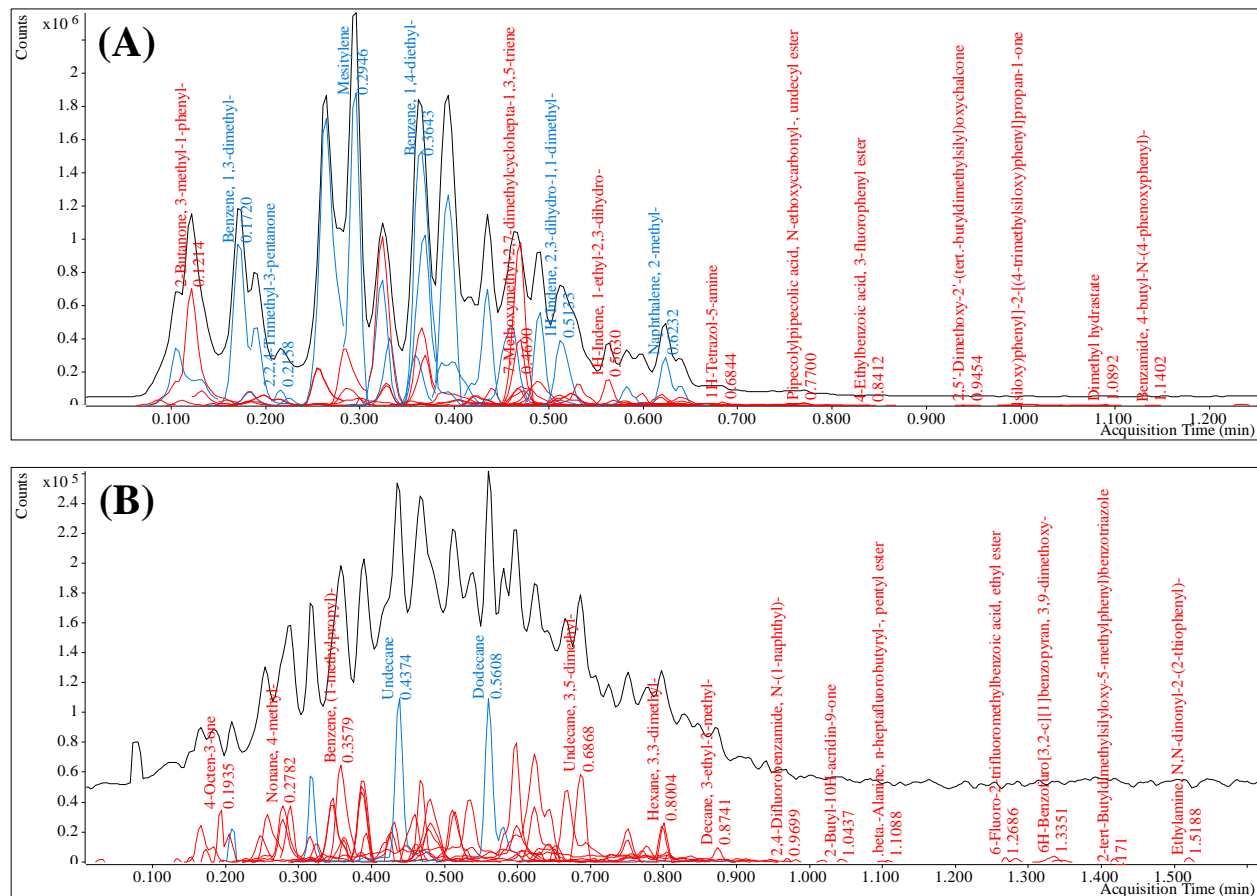
Figure S10. Total ion chromatograms (TICs) for neat (A) gasoline and (B) diesel fuel with deconvolution applied (red and blue traces). Compounds consistent with those used for ASTM classifications for both liquids are outlined in blue.

Table S8. Match factors (MFs) and reverse match factors (RMFs) of compounds identified in neat diesel fuel using the total ion chromatogram (TIC) and relevant extracted ion profiles (EIPs), and after applying deconvolution to the TIC. Retention times (t_R) are taken from the deconvolved TIC.

t_R (min)	TIC (3 compounds)	MF	RMF	EIPs (8 compounds)	MF	RMF	Deconvolution (TIC) (11 compounds)	MF
0.166				o/p-Xylene (Aromatic)	562	938	C_2-Alkylbenzene	73.0
0.210							n-Nonane	72.1
0.257	C_3-Alkylbenzene	620	835	C_3-Alkylbenzene (Aromatic)	620	835	C_3-Alkylbenzene	74.4
0.287	C_3-Alkylbenzene	607	844	C_3-Alkylbenzene (Aromatic)	607	844	C_3-Alkylbenzene	77.4
0.318				n-Decane (Alkane)	573	855	n-Decane	83.2
0.358							C_4-Alkylbenzene	67.7
0.387	C_4-Alkylbenzene	643	725	C_4-Alkylbenzene (Aromatic)	643	725	C_4-Alkylbenzene	75.7
0.437				n-Undecane (Alkane)	614	848	n-Undecane	88.9
0.558				n-Dodecane (Alkane)	612	685	n-Dodecane	90.7
0.683				n-Tridecane (Alkane)	574	668	Alkane	73.1
0.797							Branched alkane	69.5

Table S9. Match factors (MFs) and reverse match factors (RMFs) for a subset of spectral comparisons for spectra generated from the total ion chromatogram (TIC) and extracted ion profiles (EIPs) of neat gasoline, as well as the deconvolved spectra following TIC deconvolution. TEMB = tetramethylbenzene. Scores from comparisons of spectra generated from the TIC or EIPs are on a scale of 0 a.u. to 999 a.u. Scores for comparisons of spectra generated from deconvolution are on a scale of 0 a.u. to 99.9 a.u.

Compound	TIC		EIP		Deconvolution	
	MF	RMF	MF	RMF	MF	RMF
o/p-Xylene	785	964	783	961	86.4	94.3
Trimethylbenzene	891	927	891	927	98.3	99.8
C_3-Alkylbenzene	770	859	770	859	80.6	99.9
Diethylbenzene	772	885	795	902	87.4	99.8
1,2,4,5-TEMB	839	902	839	902	90.4	97.2
Naphthalene			656	900	72.1	97.8

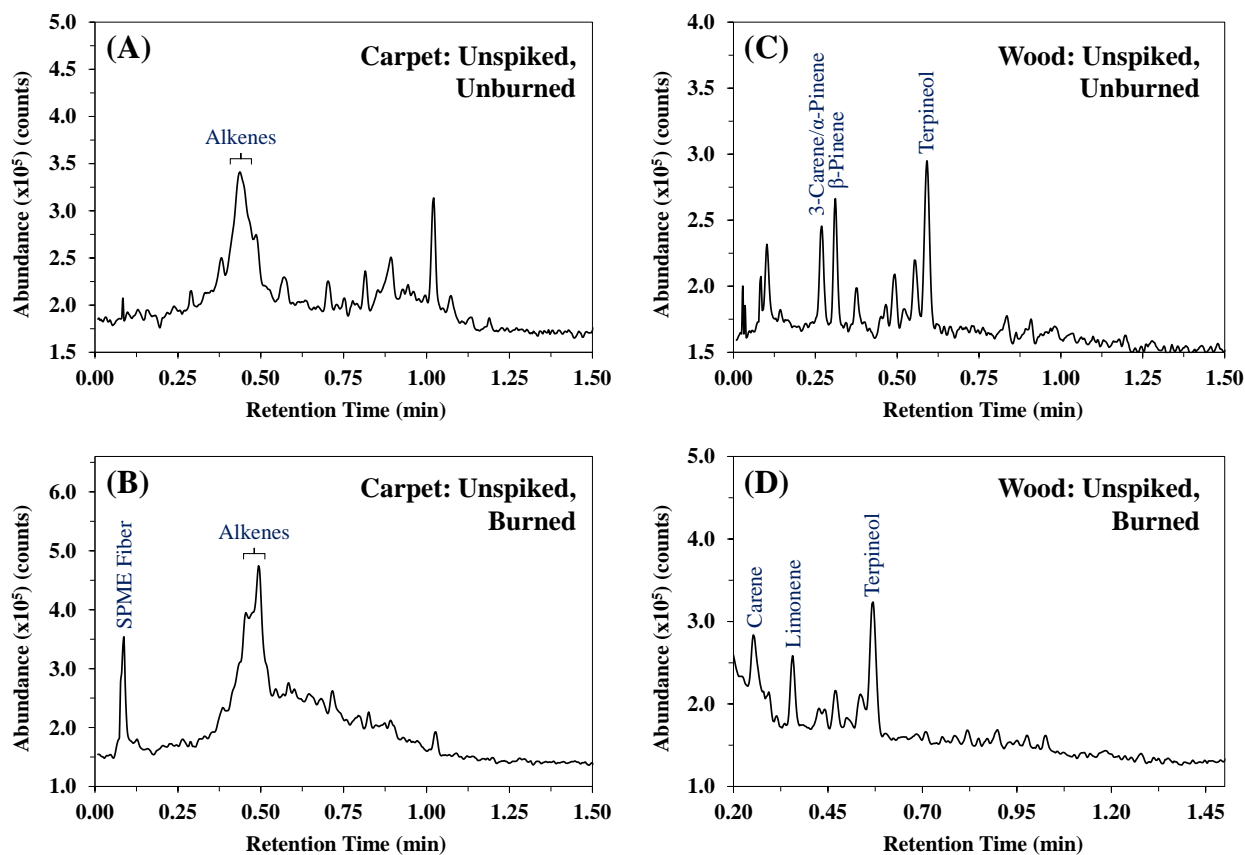| Key:	650 – 699 / 65 – 69.9	700 – 749 / 70 – 74.9	750 – 799 / 75 – 79.9	800 – 849 / 80 – 84.9	850 – 899 / 85 – 89.9	900 – 949 / 90 – 949.9	950 – 999 / 95 – 99.9

Figure S11. Total ion chromatograms (TICs) for negative substrate samples analyzed using solid phase microextraction (SPME)–rapid gas chromatography-mass spectrometry (GC-MS) for (A) unburned carpet, (B) burned carpet, (C) unburned wood, and (D) burned wood.
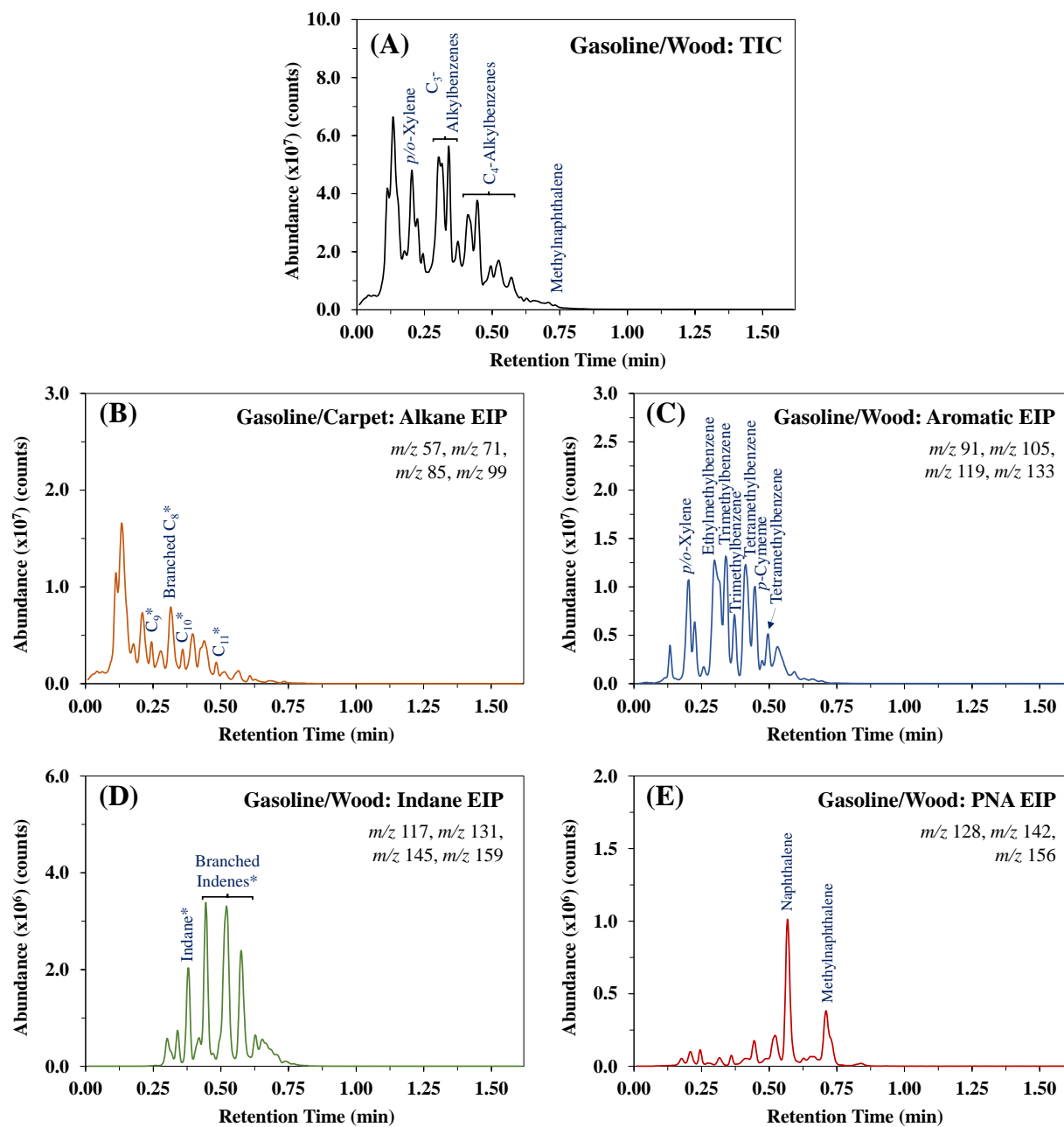
Figure S12. (A) Total ion chromatogram (TIC) for gasoline/wood simulated burn sample, with extracted ion profiles (EIPs) for the (B) alkane class, (C) aromatic class, (D) indane class, and (E) polynuclear aromatic (PNA) class. Asterisks (*) indicate compounds that were identified using deconvolution.
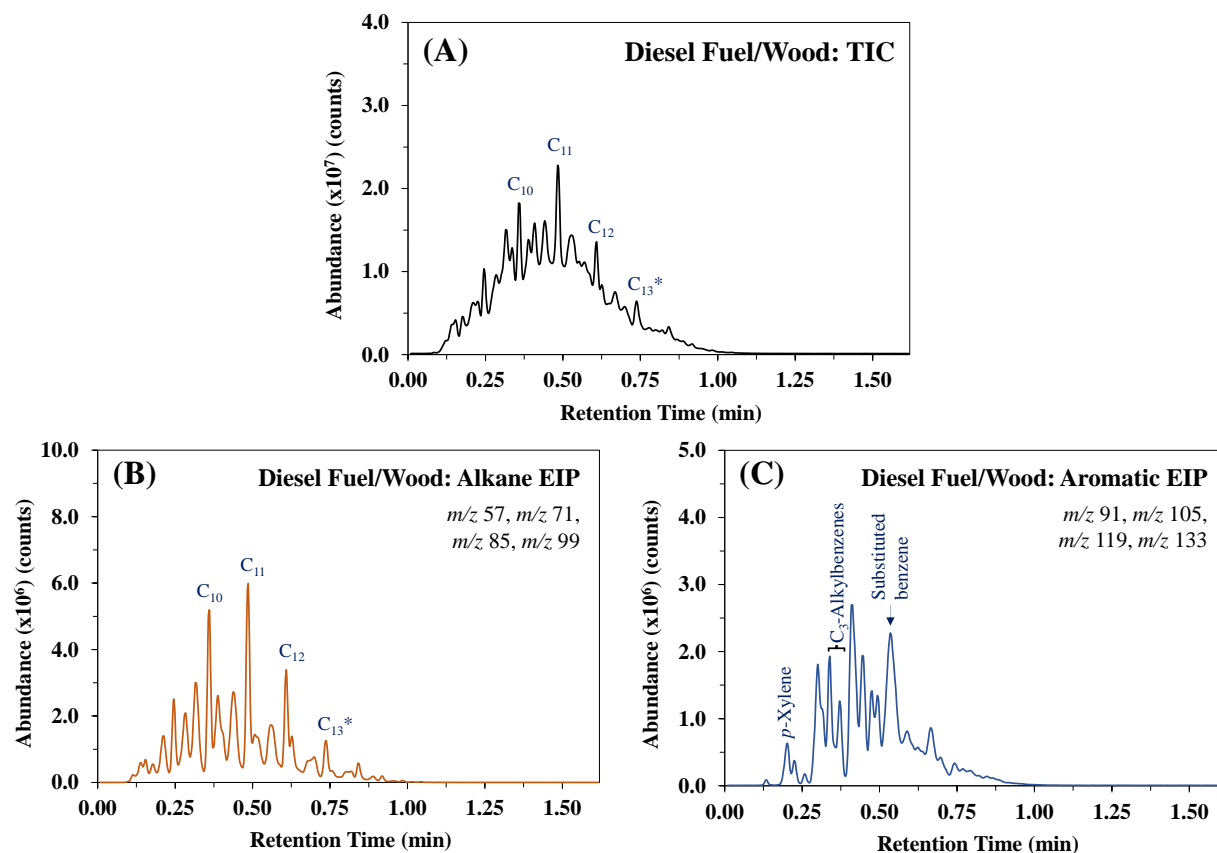
Figure S13. (A) Total ion chromatogram (TIC) for diesel fuel/wood simulated burn sample, with extracted ion profiles (EIPs) for the (B) alkane class and (C) aromatic class. Asterisks (*) indicate compounds that were identified using deconvolution.