

GERSTEL AppNote 269

An Automated Dynamic Headspace Approach for the Determination of Ignitable Liquid Residues from Mock Arson Evidence

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Keywords

Arson, Ignitable Liquid Residue, Fire Debris, Forensic, Dynamic Headspace, Thermal Desorption, Gas Chromatography-Mass Spectrometry

Abstract

In forensic investigations, analyzing ignitable liquid residues (ILRs) obtained from crime scenes is critical for establishing whether a fire was deliberately set and potentially identifying a perpetrator. Traditional methods for extracting ILRs from fire debris, such as solvent, static headspace, and solid phase microextraction (SPME) extractions, often have significant drawbacks. These methods can destroy the sample, involve lengthy manual procedures, require harmful solvents, and have long incubation times. An extraction technique such as dynamic headspace (DHS) offers several advantages over traditional extraction methods, including non-destructive sample handling, improved sensitivity, automated extraction, and the elimination of hazardous solvents. This study demonstrates an automated DHS approach to extract three commonly used ignitable liquids from mock arson evidence.

Introduction

Determining ignitable liquid residues (ILRs) is essential in investigating arson and suspicious fires. Arson, the criminal act of deliberately burning property, leaves minimal clues once the fire is extinguished. The arsonist is no longer present, and evidence is often destroyed. However, detecting ILRs on fire debris can link accelerants to an offender.

The American Society for Testing and Materials (ASTM) has established several procedures for extracting ILRs from substrates,

often employing a headspace approach followed by Gas Chromatography-Mass Spectrometry (GC-MS). While ASTM 1386 specifies a solvent extraction method for ILRs from fire debris, modern crime laboratories prefer evidence-preserving techniques such as static headspace, passive headspace with activated charcoal strips (ACS), or SPME [1-6]. Despite their advantages, these methods face challenges, including using carbon disulfide for eluting analytes off ACSs, long incubation times of up to 16 hours, competition effects, and volatility bias.

There are nine ignitable liquid classes: gasoline, petroleum distillate, isoparaffinic, aromatic, naphthenic-paraffinic, normal alkane, dearomatized, oxygenated, and miscellaneous products. Gasoline is its own ignitable liquid class, subcategorized based on carbon range as "light/medium" (C4-C13) [8]. In this study, gasoline was the ignitable liquid of interest for temperature optimization and reproducibility experiments due to its common use in arson [7]. Automotive part cleaner, categorized as a "light" (C4-C9) aromatic, and diesel fuel, categorized as a "heavy" (C8-C20+) petroleum distillate, were two additional ignitable liquids in this study to show the versatility of the DHS unit [8]. The DHS 3.5+ is demonstrated as an automated and exhaustive solution for determining ILRs on mock arson evidence. The DHS 3.5+ benefits this work as its larger sorbent capacity minimizes analyte breakthrough, especially for ignitable liquids subcategorized as "light" or with a broad carbon range, such as gasoline. GERSTEL's DHS module promotes more efficient extractions by continuously sweeping the sample headspace with inert gas. Unlike static headspace, passive headspace, and SPME, this allows little to no analyte discrimination during sampling.

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Experimental

Instrumentation

GERSTEL MPS Robotic^{PRO} with Dynamic Headspace 3.5⁺ (DHS 3.5⁺) on Agilent 8890/5977B GC-MSD. The DHS 3.5⁺ module is shown in Figure 1.



Figure 1: DHS 3.5⁺ module used for automated ignitable liquid extraction from mock arson evidence.

Analysis Conditions DHS 3.5⁺

DHS 3.5⁺

Trap	Tenax [®] TA
Incubation	100 °C
Sampling	Sample 100 °C Trap 25 °C Volume 750 mL (50 mL/min)

TD 3.5⁺

Pneumatics mode	Splitless
Temperature	40 °C (0 min); 720 °C/min; 280 °C (3 min)

CIS 4

Liner	Glass bead-filled
Pneumatic mode	Solvent vent (50 mL/min), split 75:1
Temperature	-120 °C; 12 °C/s; 275 °C (3 min)

Analysis Conditions Agilent 8890 GC

Pneumatics	He; P _i = 7.0699 psi Constant flow = 1 mL/min
Column	30 m DB-5ms UI (Agilent) d _i = 0.25 mm d _f = 0.25 μm
Oven	40 °C (2 min); 5 °C/min; 180 °C (0 min); 20 °C/min; 280 °C (0 min)

Analysis Conditions 5977B Inert Plus MSD

Full Scan	40-350 amu
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Sample Description

Adhesive tile squares, gasoline, diesel fuel, and an automotive parts cleaner were purchased from local stores.

Sample Preparation

Optimization & Reproducibility: All ignitable liquids were diluted 1:1000 in ethanol. 100 μL of diluted gasoline was spiked into three 20 mL screw-capped vials for temperature optimization at 60 °C, 80 °C, and 100 °C. After determining the optimal extraction temperature, three additional vials were prepared in triplicate to evaluate reproducibility.

Mock Arson Evidence: A 10 cm x 10 cm tile square was ignited using a lighter and allowed to burn for 10-30 seconds. The substrate was not burned to completeness, as typical arson evidence is obtained from areas with minimal charring to ensure the highest probability of recovering ILRs. When a substrate is charred, most of the ignitable liquid is consumed.

Approximate 1 cm x 1 cm cuttings of each tile square were taken as evidence of fire debris, totaling three samples. Cuttings were made along the edges of burn patterns, one of the highest probability locations of recovering ILRs, as seen in Figure 2. The cuttings were then placed in individual 20 mL screw-capped vials. According to ASTM 2154 and 1618, as little as 0.1-1 μL of neat ignitable liquid deposited on a sample would be sufficient for identification and classification [2, 6]. To meet these requirements, 100 μL of the 1:1000 diluted gasoline, automotive parts cleaner, or diesel fuel was spiked into the respective vials.

An approximate 1 cm x 1 cm tile square, unburnt and unexposed to ILRs, was used as a method blank.

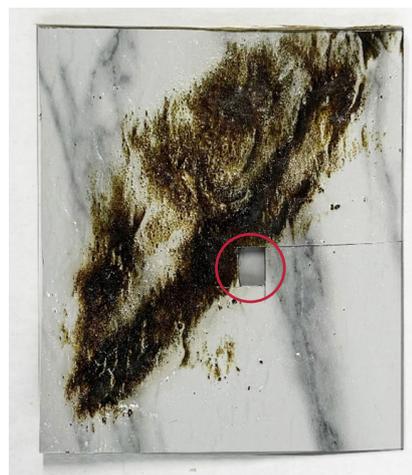


Figure 2: Exemplary cutting of mock fire debris evidence.

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Sample Introduction

The samples were incubated at 100 °C for 3 minutes and then extracted for 15 minutes at 50 mL/min helium flow for a total trap volume of 750 mL. The analytes were trapped at 25 °C on a Tenax® TA packed tube. The tubes were desorbed at 280 °C for 3 minutes with a 50 mL/min helium flow, and analytes were trapped in the CIS 4 inlet using a glass bead-filled liner at -120 °C. When desorption was complete, analytes were transferred to the column in split mode (75:1) by rapidly heating the inlet to 275 °C.

Results and Discussion

Gasoline is a complex, refined petroleum product comprised of several aromatic hydrocarbons, with a carbon range of C4-C12, that are used to characterize it as an ignitable liquid. Gasoline is an individual class of ignitable liquid because of its unique chro-

matographic fingerprint, whereby several target compounds are organized into groups. These groups are informally named Three Musketeers, Castle Group, Gang of Four, Twin Towers, and Five Fingers. Often, forensic scientists use informal terminology when testifying in court to explain significant findings in layman's terms when speaking to a jury. Figure 3 shows the total ion chromatogram of gasoline with five extracted ion insets representing each group. The Three Musketeers represent C2 alkyl benzenes, the Castle Group C3 alkyl benzenes, the Gang of Four C4 benzenes, the Twin Towers methylnaphthalenes, and the Five Fingers dimethyl and ethylnaphthalenes. The Five Fingers group implies that five compounds are present. However, not all isomers within this group can be detected accurately, and only two compounds are used as targets for gasoline identification.

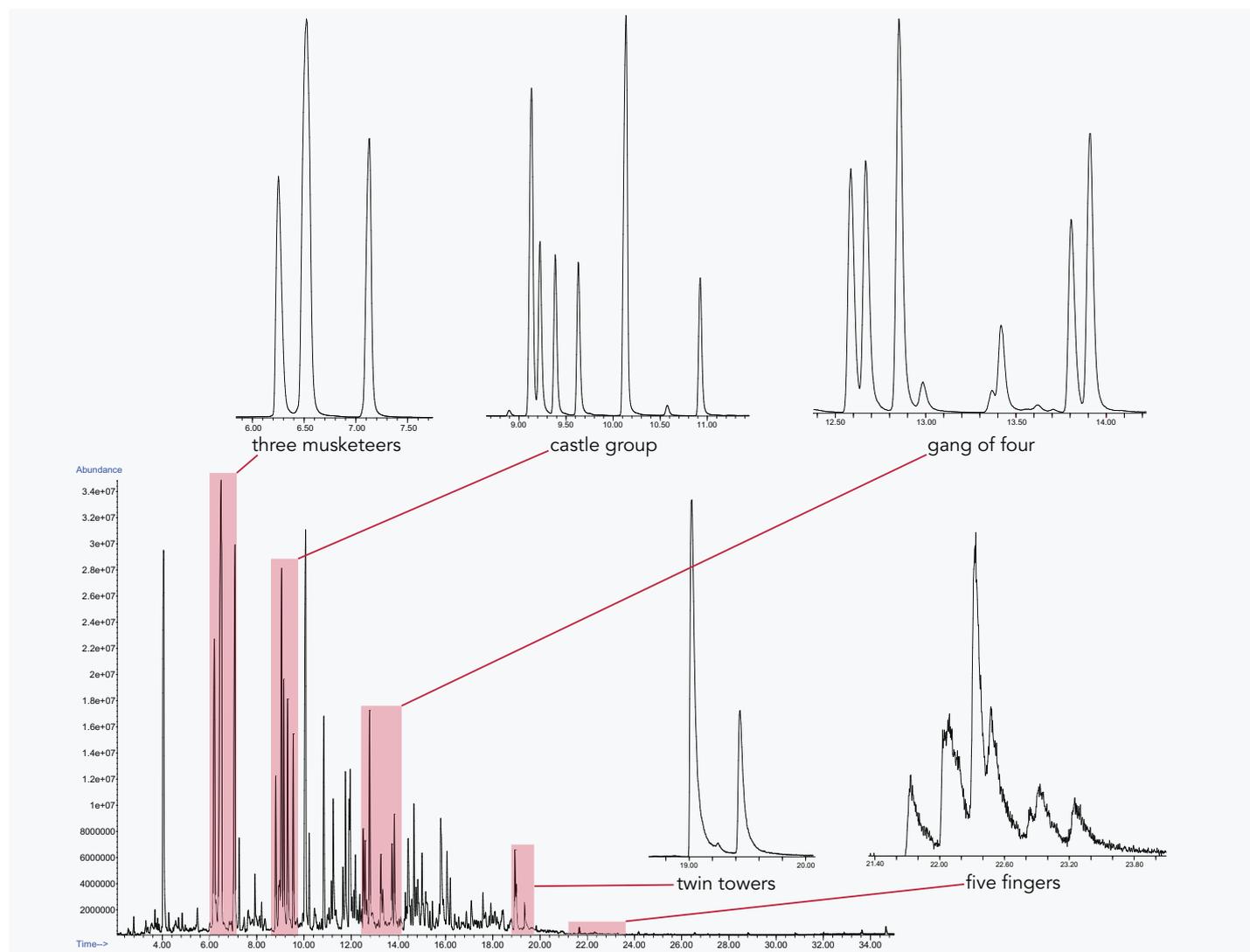


Figure 3: Total ion chromatogram of gasoline with extracted ion insets for informally named target groups.

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A temperature optimization study was conducted to monitor the signal of mandatory target analytes for identifying gasoline according to ASTM 1618 [2]. These target analytes are in bold in Tables 1 and 2. ASTM practices for separating ignitable liquids from arson evidence involve incubation and extraction temperatures ranging from 60 °C to 140 °C. Specifically, SPME methods utilize temperatures between 60 °C and 80 °C to reduce discrimination against high-volatility analytes [6]. Temperatures below 60 °C insufficiently volatilize compounds greater than C15, while temperatures above 140 °C can induce secondary reactions. Due to the latter, optimization temperatures of 60 °C, 80 °C, and 100 °C were chosen. Table 1 lists the peak areas for the gasoline target compounds when extracted at these three temperatures. The analyte signal for all target compounds produced the highest peak area when extracted at 100 °C. Moreover, the higher extraction temperature more effectively diffused 1,3- and 2,3-dimethyl naphthalene into the sample headspace to be concentrated onto the Tenax® TA trap.

Table 1: List of gasoline analytes for temperature optimization study with area counts normalized to 100 °C. (ASTM 1618 target analytes in **bold**).

Compounds	m/z	60 °C	80 °C	100 °C
Ethylbenzene	91	89.61	102.28	100.00
m/p-Xylene	91	90.17	102.79	100.00
o-Xylene	91	87.64	104.73	100.00
Propyl benzene	91	84.53	102.58	100.00
m-Ethyl toluene	105	89.31	102.63	100.00
p-Ethyl toluene	105	84.36	100.44	100.00
Mesitylene	105	88.86	100.76	100.00
o-Ethyl toluene	105	88.70	101.06	100.00
1,2,4-Trimethylbenzene	105	89.55	101.41	100.00
1,2,3-Trimethylbenzene	105	87.54	100.82	100.00
Indane	117	88.69	101.17	100.00
1,2,4,5-Tetramethylbenzene	119	82.33	101.23	100.00
1,2,3,5-Tetramethylbenzene	119	82.14	101.10	100.00
5-Methylindane	117	84.50	93.49	100.00
4-Methylindane	117	83.30	93.37	100.00
4,7-Dimethyl indane	131	78.81	84.46	100.00
2-Methyl naphthalene	142	88.71	91.06	100.00
1-Methyl naphthalene	142	90.23	91.31	100.00
1,3-Dimethyl naphthalene	156	62.86	80.19	100.00
2,3-Dimethyl naphthalene	141	66.31	78.95	100.00
Dodecane	57	83.00	90.11	100.00

Figure 4 shows the stacked view of total ion chromatograms obtained for three replicates of diluted retail gasoline. This visualizes the excellent reproducibility achieved with the DHS extraction technique. Additionally, Table 2 lists the peak areas obtained for each compound when extracted at their respective base peak ions. Several analytes, in addition to the gasoline target compounds, were identified for temperature optimization and reproducibility studies for comprehensiveness. All compounds' percent relative standard deviations (%RSD) fell below 5.00%, with an average %RSD of 4.50%. Reproducibility is imperative to forensic science as the results must show that methods can be consistently verified across different analysts and laboratories to ensure admissibility in court.

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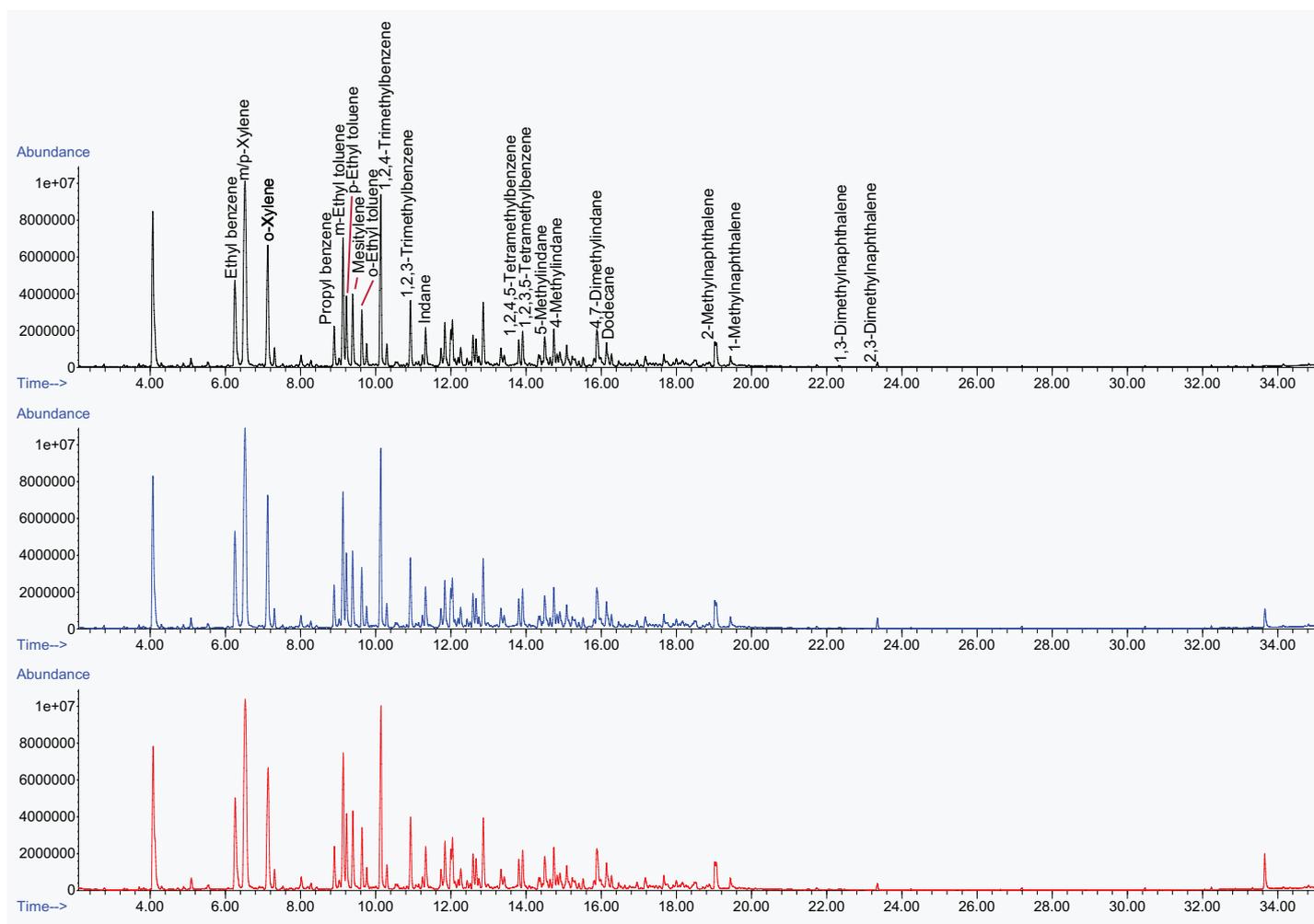


Figure 4: Stacked view of total ion chromatograms for gasoline replicates (n=3).

Table 2: List of gasoline analytes for reproducibility study with extracted base peak ion peak areas and %RSDs. (ASTM 1618 target analytes in **bold**).

Compounds	m/z	Replicate 1	Replicate 2	Replicate 3	%RSD
Ethylbenzene	91	80,834,894	86,529,019	86,004,991	3.73
m/p-Xylene	91	179,927,451	189,782,509	188,599,333	2.89
o-Xylene	91	86,911,239	92,570,276	93,102,873	3.78
Propyl benzene	91	27,545,425	29,493,876	30,232,846	4.77
m-Ethyl toluene	105	76,039,590	80,973,134	82,257,220	4.12
p-Ethyl toluene	105	37,440,568	39,767,951	39,261,204	3.15
Mesitylene	105	31,428,293	33,202,775	34,075,446	4.10
o-Ethyl toluene	105	30,790,381	33,015,763	33,879,196	4.89
1,2,4-Trimethylbenzene	105	98,510,274	104,163,032	107,057,054	4.21
1,2,3-Trimethylbenzene	105	28,694,582	30,454,361	31,477,603	4.66
Indane	117	18,194,260	19,322,887	19,868,113	4.46
1,2,4,5-Tetramethylbenzene	119	12,325,213	13,188,750	13,057,325	3.62

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Table 2 (cont.): List of gasoline analytes for reproducibility study with extracted base peak ion peak areas and %RSDs. (ASTM 1618 target analytes in **bold**).

Compounds	m/z	Replicate 1	Replicate 2	Replicate 3	%RSD
1,2,3,5-Tetramethylbenzene	119	18,473,771	19,614,205	20,253,999	4.64
5-Methylindane	117	12,024,049	12,809,281	13,487,548	5.73
4-Methylindane	117	15,595,901	17,927,825	18,353,781	5.59
4,7-Dimethyl indane	131	8,961,582	9,533,456	10,706,003	9.14
2-Methyl naphthalene	142	14,647,128	13,751,232	13,586,036	4.08
1-Methyl naphthalene	142	6,098,266	5,665,559	5,744,870	3.95
1,3-Dimethyl naphthalene	156	782,895	839,669	811,109	3.50
2,3-Dimethyl naphthalene	141	182,090	195,723	184,203	3.92
Dodecane	57	2,795,905	3,057,151	3,103,325	5.55
				Avg % RSD	4.50

Figure 5 shows the total ion chromatogram obtained for the method blank. This method blank determines whether existing adhesive tile- or contamination-related VOCs will interfere with identifying ignitable liquids on mock arson evidence. Compounds identified included aromatic hydrocarbons, esters, alkanes, chlori-

nated alkanes, and phthalates. Some of these compounds, like aromatics and alkanes, will overlap with classes of ignitable liquids, so it is crucial to understand the chromatographic profile of the substrate before evaluating the ILRs present in fire debris.

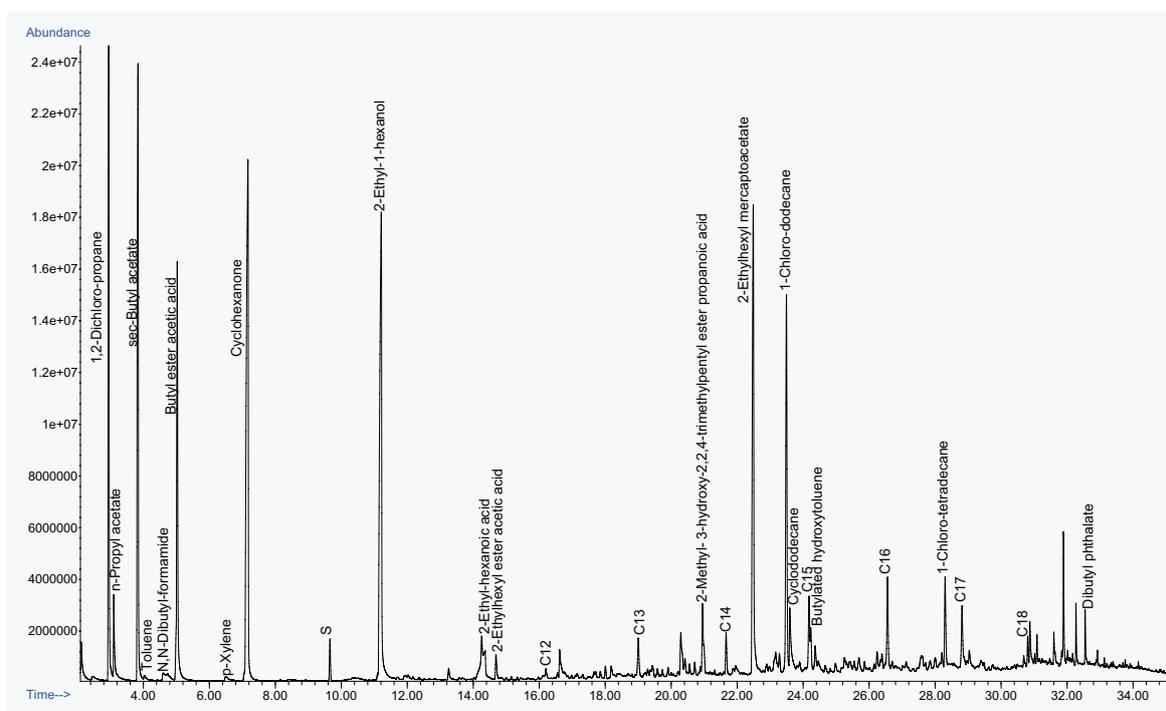


Figure 5: Total ion chromatogram of method blank.

Figure 6 shows the total ion chromatogram obtained for fire debris in which gasoline was used as the ignitable liquid. The typical gasoline fingerprint can be extrapolated from the chromatogram,

allowing the identification of target compounds listed in ASTM 1618. 1,3-Dimethylnaphthalene coeluted with 2-ethylhexyl mercaptoacetate, a compound found in the method blank.

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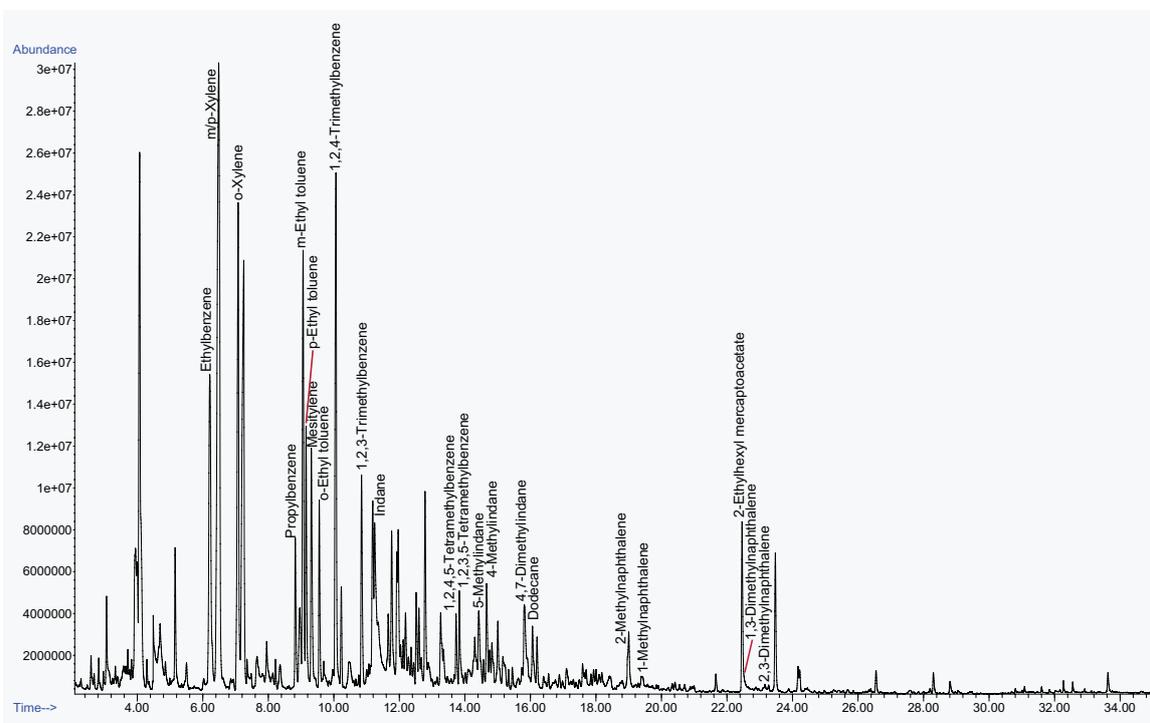


Figure 6: Total ion chromatogram of gasoline mock arson evidence.

Figure 7 shows the total ion chromatogram obtained for fire debris in which automotive parts cleaner was used as the ignitable liquid. Automotive car parts cleaners are classified as light aromatic products [9]. A prominent toluene peak was identified in the chro-

matogram, with the remaining peaks being attributed to the floor tile—the automotive parts cleaner packaging listed toluene as the main ingredient.

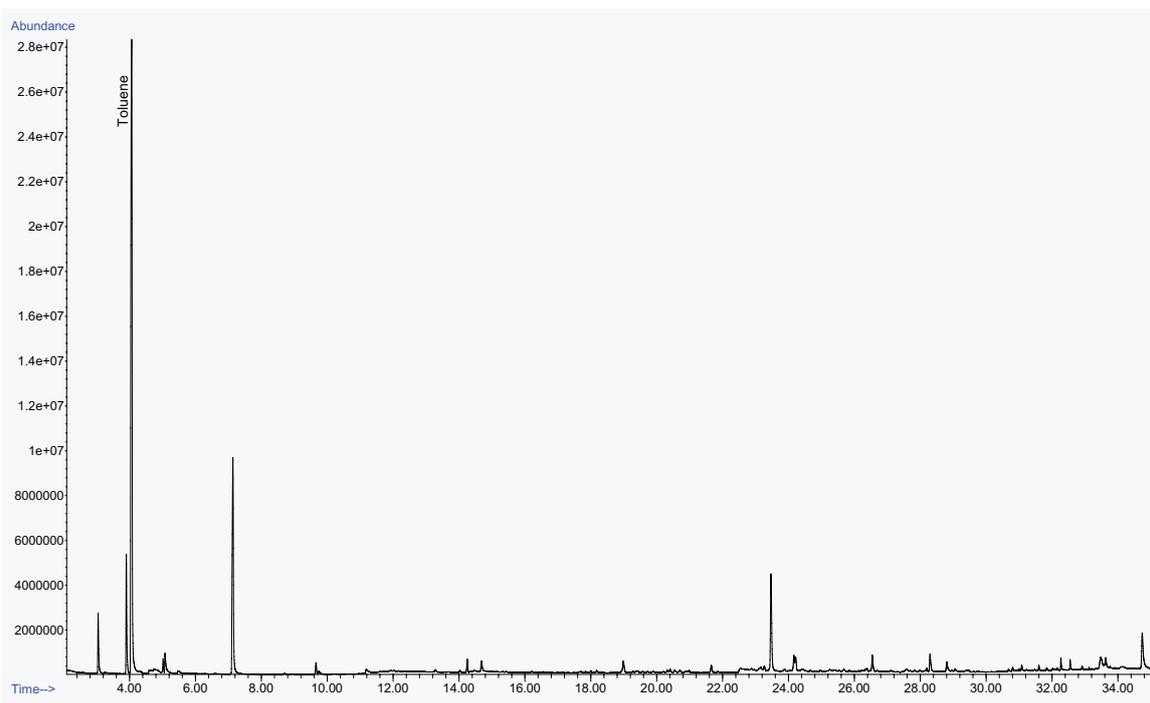


Figure 7: Total ion chromatogram of automotive part cleaner mock arson evidence.

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When ignitable liquid containers, such as gas tanks and spray cans, are left at crime scenes, investigators are provided with a potential source of the fire. Moreover, it allows forensic scientists to match the ILRs on fire debris with the ignitable liquid left at the scene.

Figure 8 shows the total ion chromatogram obtained for fire debris in which diesel fuel was used as the ignitable liquid. Diesel fuels are classified as heavy petroleum distillates with notable aromatics

and a Gaussian distribution pattern of consecutive alkanes [9]. Alkanes from C10 to C20 were identified in the chromatogram in addition to aromatics, indane, and naphthalene-related compounds. Diesel fuel, like gasoline and automotive parts cleaners, can also be easily obtained. Because diesel fuel is a heavy petroleum distillate, it is composed of less volatile hydrocarbons, making it safer for arsonists to ignite over other ignitable liquids.

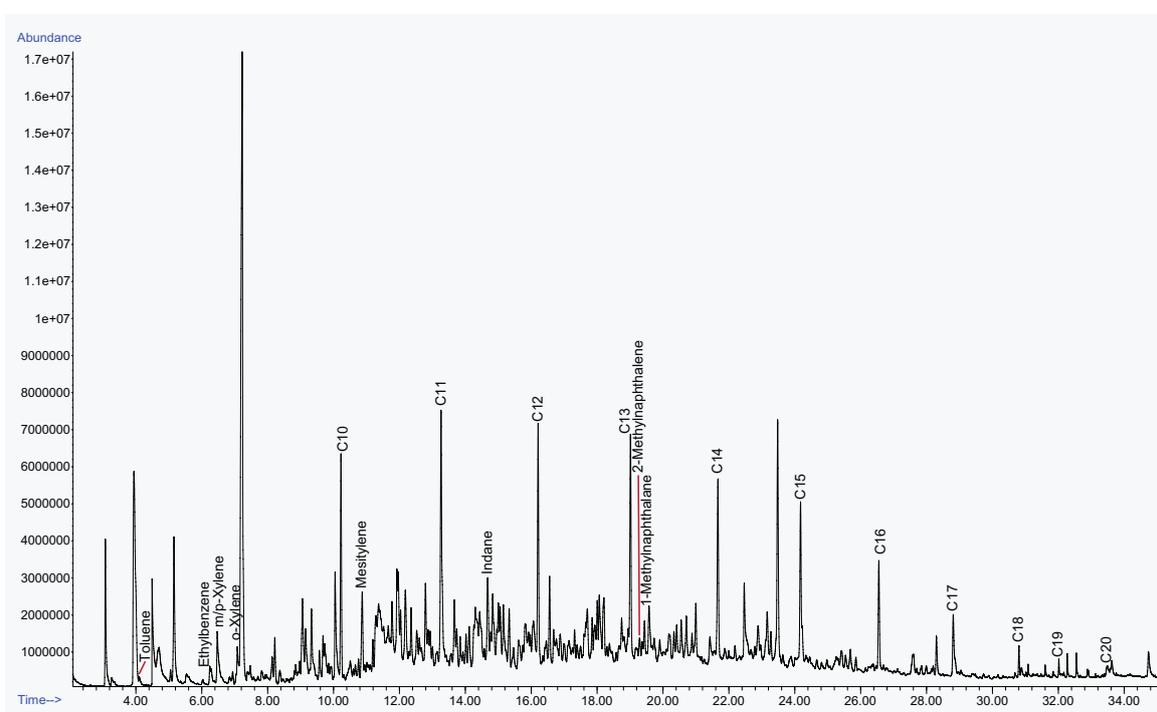


Figure 8: Total ion chromatogram of diesel fuel mock arson evidence.

Conclusion

This study demonstrated the capabilities of the GERSTEL DHS 3.5+ to effectively extract three ignitable liquids from mock arson evidence. The key benefits of the GERSTEL DHS 3.5+, especially in forensics, are its automation, exhaustive extraction nature, and non-destructive, solvent-free means of extracting to preserve the original sample. Additionally, the TD 3.5+ thermal desorption tubes ensure a larger sorbent capacity, thus minimizing the likelihood of analytes breaking through the trap. This is relevant for more volatile compounds in light classes of ignitable liquids or for more comprehensive capturing across a full carbon range, like with gasoline's complex makeup.

References

- [1] ASTM 1386 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction.
- [2] ASTM 1618 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry.
- [3] ASTM 1387 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography.
- [4] ASTM 1412 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal.

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- [5] ASTM 1413 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration onto an Adsorbent Tube.
- [6] ASTM 2154 Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME).
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