Research Article

"COMPARATIVE STUDY OF HYDROCARBANS IN SEMIBURT AND COMPLETE BURNT PARTICALS IN ASH RESIDUE BY USING GC-MS/MS."

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Abstract

The present study is a comprehensive comparative analysis of hydrocarbon profiles in semi-burnt and completely burnt particulates isolated from Five ash residues generated during controlled combustion processes. Utilizing gas chromatography-tandem mass spectrometry (GC-MS/MS), achieved high-sensitive quantification and characterization of diverse hydrocarbon classes, including aliphatic hydrocarbons (AHCs), polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs (alkyl-PAHs), and oxygenated derivatives. The results revealed compositional differences driven by combustion efficiency, Semi-burnt particulates were significantly enriched in low-molecular-weight (LMW) compounds. The identification of saturated hydrocarbon residues created during thermal degradation processes is further supported by the presence of distinctive diagnostic ions, especially 85 m/z for aliphatic hydrocarbons. Phthalate esters were identified in only three samples (S2 –S4), while they were absent in S1 and S5, suggesting variability in the composition of the burnt substrates. The study confirms that GC–MS/MS is a robust and reliable technique for the identification and characterization of such residues in complex fire debris matrices, providing valuable insights for forensic interpretation and source attribution. These findings provide crucial mechanistic insights into the thermal alteration pathways of organic matter during combustion and have significant implications for improving source apportionment models for atmospheric particulate matter, refining environmental risk assessments of combustion-derived emissions, and developing more effective strategies for monitoring and mitigating the release of toxic organic pollutants from various combustion sources.

Keywords: Arson, fire debris, Hydrocarbons, Tandem Mass Spectrometry, PVC and Pollutants.

1. Introduction

Forensic analysis of fire scenes frequently hinges on the accurate detection and identification of ignitable liquid residues, which often serve as key evidence in establishing the cause and point of origin of a fire. In arson investigations, ignitable liquids are frequently employed as accelerants, and detecting them in fire debris is crucial for substantiating investigative conclusions and supporting legal actions. Hydrocarbons in semi-burnt (partially combusted) particulates retain more volatile components compared to completely burnt residues, where pyrolysis favours persistent polycyclic aromatic hydrocarbons (PAHs). (Dong et al., 2025)

Background of Fire Debris and Accelerants

Fires, especially those suspected of arson, leave behind complex matrices of ash, char, and particulates that challenge traditional analytical methods. Accelerants, flammable liquids used to initiate or spread fire, are typically petroleum distillates rich in aliphatic hydrocarbons and aromatic compounds. During combustion, these undergo cracking, dehydrogenation, and 705 ionization705ion. Semi-burnt particulates, exposed to lower temperatures, preserve lighter fractions, while complete burning volatilizes them, enriching residues with heavier naphthalenes, phenanthrenes, and chrysenes. (Petroleum Distillates, 2014)

Forensic standards like ASTM E1618 classify ignitable liquids into categories (Class 1: light petroleum distillates; Class 3: medium aromatics). However, heat-induced alterations blur these profiles—evaporation ratios shift, and pyrolysis products like alkylbenzenes mimic native compounds. Studies show gasoline loses 70–90% of volatiles in open burns, yet diagnostic ratios endure in protected areas (Birks et al., 2017). This necessitates advanced separation techniques to discern true accelerants from fire-generated interferents like styrene from plastics or furans from wood. Early methods

relied on charcoal stripping or solvent desorption with flame 706 ionization detection (FID), lacking specificity (Martín-Alberca et al., 2016). Headspace analysis improved volatile capture but missed semi-volatiles. Single-quadrupole GC-MS, the gold standard since the 1980s, excels at total ion chromatograms (TICs) for pattern matching but falters in complex matrices due to co-elution (Dimandja et al., 2000). Tandem – MS, introduced in the 2000s, uses multiple reaction monitoring (MRM) for enhanced selectivity of parent ions fragment to daughters, filtering noise (Van Der Gugten, 2020). For hydrocarbons, transitions like alkanes and naphthalene provide quantification limits <1 µg/g, surpassing GC-MS by 10–50 fold in burnt samples. Passive adsorption with activated charcoal tubes or solid-phase microextraction (SPME) precedes injection, often with dichloromethane or pentane extraction. Temperature-programmed GC separates C5–C40 compounds on non-polar columns like DB-5MS. MS/MS libraries (NIST and Wiley) aid identification, with extracted ion chromatograms (EICs) revealing subtle isomers. Recent advances incorporate comprehensive two-dimensional GC (GC×GC) for ultra-complex residues, but GC-MS/MS balances cost and performance. Thermal degradation varies across surfaces partially burned particles from surface ash still hold onto the original accelerants, whereas fully burned areas yield dehydrated, cyclized compounds. Additional environmental elements, such as rain, soil microbes, and firefighting foam, also contribute to the removal of water-soluble aromatics. Matrix effects reduce signal intensity, as soot and metals cause analyte ionization. Standard GC-MS has recognized limitations in fully burned fire debris because pyrolysis products, substrate effects, and evaporative loss can obscure ignitable liquid residues. (Detection of Ignitable Liquid Residues in Fire Debris by Using Direct Analysis in RealTime Mass Spectrometry (DART-MS), n.d.).

2. Material & Methodology:

Sample Preparation: Extraction and Cleanup

The complex nature of ash residues necessitates robust extraction and cleanup procedures to isolate non-target hydrocarbon components.

2.1. Extraction (Bumbrah et al., 2017)

Various extraction methods can be employed depending on the matrix and target analytes. For hydrocarbons in solid matrices such as ash, accelerated solvent extraction (ASE) or ultrasonic-assisted extraction (UAE) is commonly used. Solvents such as n-hexane / Acetone (4:1 v/v), dichloromethane (DCM) or mixtures like DCM/methanol (9:1 v/v) are effective for isolating a broad range of hydrocarbons, including PAHs and alkyl-PAHs.

Ash Debris Sample Collection

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Sample Weighing and Transfer to Extraction Vial

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Addition of Solvent Mixture

(n-Hexane: Acetone, 4:1 v/v)

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Solvent Extraction (Shaking / Mixing)

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Filtration of Extract

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Collection of Clear Extract

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Injection into GC–MS/MS System

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Identification of Hydrocarbon Compounds

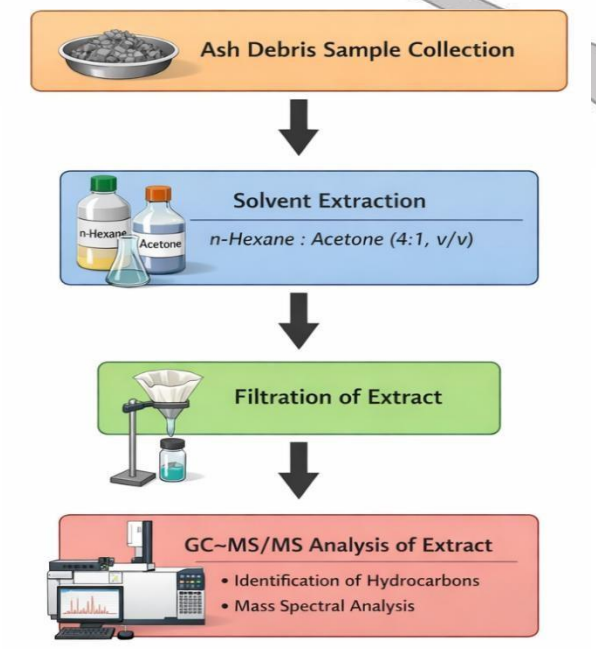


Fig: 1.1 Extraction Procedure

3. GC-MS/MS:

Gas Chromatography-Tandem Mass Spectrometry (GC-MS/MS) is the preferred analytical technique for the hydrocarbons. The hyphenated technique combines the high-resolution separation power of gas chromatography with the definitive molecular identification and quantification capabilities of mass spectrometry.

Table no 1.1 GC-MS/MS Parameters

Analytical Column	TG-5MS;30mx0.25mmIDx0.25µm
Injection volume	1 µL
Flowrate	1.0 ml/min
Mode	MRM mode
Inlet temperature	280ºC
Source temperature	220ºC
Transfer Line temperature	300ºC
Equilibration time	0.50 min
Max temperature	350ºC
Injector Port	Injector Port A
Preinjection cycles	5
Rinses	3
Solvent volume	1.0 Ml
Rinse volume	1.0 Ml

Solvent volumes	1.0 Ml
Oven Run Time	27.0Inute

Temperature Programming: GC-MS

Table:1.2Temperature Programming

Rate (ºC/min)	Temperature(ºC)	Hold time
0.0	40	10.0
5.00	150	0.00
20.00	250	5.00

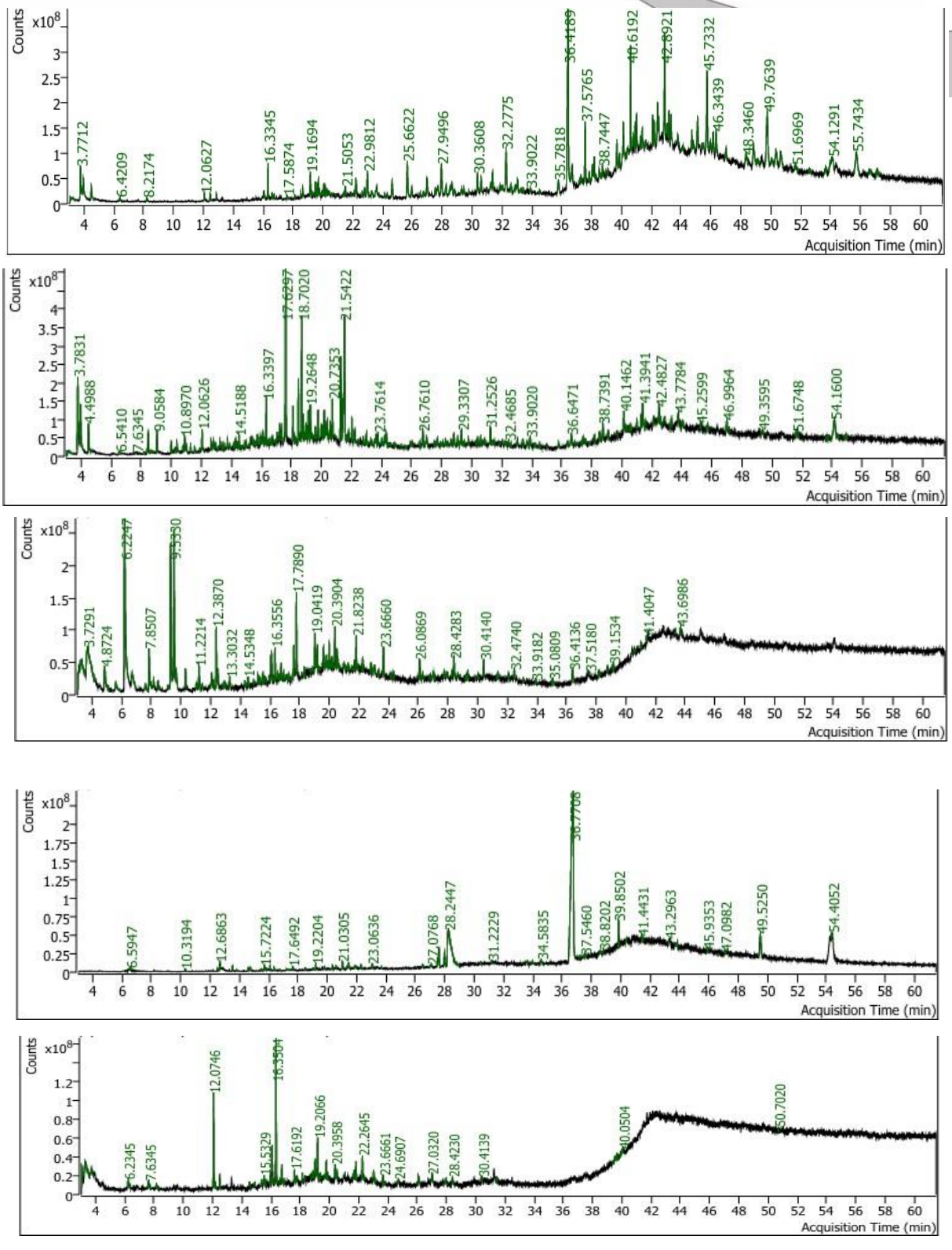
Result & Discussion:

For the identification of compounds present in the ash debris samples, GC–MS/MS analysis was performed and the obtained spectra were compared with the reference mass spectral library. Each detected compound produced multiple fragment ions (m/z values) due to electron ionization fragmentation. The use of the base peak ion is a common practice in GC–MS/MS reporting because it represents the most abundant and stable fragment ion in the mass spectrum of a compound. While several additional fragment ions were observed for each compound, the selected base peak provides a reliable diagnostic value when used together with retention time and library matching for compound identification.

S. No	RT (min)	Compound Name	Molecular Formula	Major m/z	Type
1.	3.7831	Ethylbenzene	C8H10	91	Major hydrocarbon
2.	3.9634	o-Xylene	C8H10	106	Major hydrocarbon
3.	13.1280	1-But-3-enylnaphthalene	C14H14	141	Aromatic hydrocarbon
4.	15.5222	Pentacosane	C25H52	85	Longchain hydrocarbon
5.	3.3505	2,5-Norbornadiene	C7H8	66	Hydrocarbon
6.	4.8724	1,3-Cyclohexadiene, 1,3,5,5-tetramethyl	C10H16	81	Hydrocarbon
7.	5.6217	Bicyclo [3.1.0] hex-2-ene, 4,4,6,6-tetramethyl	C10H16	93	Hydrocarbon
8.	6.2247	Benzene, 1,2,3-trimethyl	C9H12	105	Aromatic hydrocarbon
9.	7.8507	2,6-Octadiene, 2,4-dimethyl	C10H18	93	Hydrocarbon
10	8.1631	Decane, 5-ethyl-5-methyl	C13H28	85	Aliphatic hydrocarbon
11	43.6986	Tetrapentacontane	C54H110	85.1	Long-chain hydrocarbon
12	3.3205	Toluene	C7H8	91	Aromatic hydrocarbon
13	6.2345	Mesitylene	C9H12	105	Aromatic hydrocarbon
14	12.0746	Benzene, 1,3-bis(1,1-dimethylethyl)	C14H22	174.9	Aromatic hydrocarbon
15	12.5012	Decane, 5-ethyl-5-methyl	C13H28	85	Aliphatic hydrocarbon
16	21.0700	5,15-Dimethylnonadecane	C21H44	85	Branched hydrocarbon
17	31.4227	Tetrapentacontane	C54H110	85	Long-chain hydrocarbon
18	6.5947	Acetic acid, dimethoxy-, methyl ester	C5H10O4	76	Oxygenated compound
19	15.6587	Naphthalene, 6-(1,1-dimethylethyl)-1,2,3,4-tetrahydro	C14H20	173	Aromatic hydrocarbon
20	17.6492	Diethyl phthalate	C12H14O4	149	Phthalate ester
21	23.0636	1,2-Benzenedicarboxylic acid, butyl octyl ester	C20H30O4	148	Phthalate ester
22	34.5835	Triethylene glycol di(2-ethylhexoate)	C22H42O6	170	Plasticizer
23	11.5870	p-Cumenol	C9H12O	107	Aromatic compound
24	36.8610	Bis(2-ethylhexyl) phthalate	C24H38O4	149	Phthalate plasticizer

Table: 1.3 Components Found in Ash Residues

Fig 1.2- 1.6 (GC-MS/MS Chromatogram of fire debris sample)



The GC–MS chromatogram shows that a few key chemicals with high relative abundance predominate in the sample, with the remaining ingredients being present in trace or tiny levels. Higher retention durations correspond to less volatile, higher molecular weight molecules like long-chain hydrocarbons and oxygenated derivatives, while shorter

retention times correspond to more volatile, low molecular weight substance. This area percentage data indicates that while many additional compounds are present in smaller amounts, the sample contains a few main chemicals with great abundance, such as ester derivatives and aromatic hydrocarbons.

More volatile chemicals are represented by early retention time peaks, while less volatile and more complex molecules, such as esters and long-chain compounds, are represented by later peaks. The sample's complex nature is reflected in its overall chemically varied composition, which includes both hydrocarbon and oxygenated molecules. The GC–MS/MS analysis of the ash debris samples revealed the presence of several hydrocarbons and related organic compounds with different retention times and characteristic fragment ions (m/z values). Aromatic hydrocarbons, branching aliphatic hydrocarbons, and long-chain hydrocarbons make up the majority of the discovered substances, according to the analytical tables derived from the five datasets, with trace amounts of oxygenated derivatives and compounds associated to plasticizers, toluene, mesitylene, substituted benzene derivatives, branched decane/heptane derivatives, and long-chain hydrocarbons like pentacosane and tetracosane were among the detected hydrocarbons. These substances were found at various retention durations and had distinctive fragment ions (such as m/z 85, 91, 99, 113, etc.) that are commonly linked to hydrocarbon structures. Such hydrocarbon pieces show that the ash debris contains hydrocarbon remnants from burning. The presence of branched alkanes and aromatic hydrocarbons indicates that the burned material may contain elements from fuels, synthetic compounds, or petroleum-based chemicals. Furthermore, the detection of phthalate esters and other oxygenated chemicals in certain samples suggests that plastic materials or polymer-based goods that may have undergone thermal degradation during burning contributed to the contamination. During the GC–MS/MS analysis of the ash debris samples, several compounds exhibited common fragment ions in their mass spectra. Since many hydrocarbons undergo similar fragmentation paths during electron ionization (EI), it is expected that similar m/z values will repeat across various substances in hydrocarbon analysis. Because of this, fragment ions from structurally similar compounds are frequently same or closely related. Overall, the GC–MS/MS results' hydrocarbon distribution pattern shows that the ash debris contains a diverse variety of combustion products. The existence of both main and minor hydrocarbon components in the examined samples is confirmed by the differences in retention periods and diagnostic fragment ions among the identified compounds.

Conclusion

The current study shows that GC-MS/MS is a robust and analytically reliable method for qualitatively characterizing organic residues in complicated ash debris matrices. The study emphasizes that fire debris is a chemically complex system in which a variety of factors, such as the substrate's nature, the conditions of combustion, and interactions with the post-burn environment, influence the identified chemicals. The observed variation among samples highlights the necessity for case-specific interpretation in forensic investigations by supporting the idea that no single chemical profile can accurately represent all fire debris. Additionally, the identification of several constituent classes emphasizes the importance of thorough analytical methods for precise chemical profiling and source assessment. From a forensic perspective, the results validate the function of sophisticated instrumental methods in augmenting the value of evidence, allowing for more knowledgeable conclusions concerning the source and type of burned materials. As a result, combining GC-MS/MS analysis with methodical data interpretation offers a trustworthy framework for examining fire debris and advances forensic analytical techniques. Additionally, expanding the dataset with controlled burn experiments and known reference materials can significantly improve source attribution and interpretation in forensic investigations.

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