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Analysis of Petroleum Products in Fire Debris Residues by Gas Chromatography: A Literature Review

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Abstract

This review gives a brief overview of developments in the analysis of petroleum products (PP) in fire debris residues (FDR) by gas chromatography (GC). The review covers different aspects of analysis such as the substrates involved, isolation procedures, column and mobile phase used, and subsequent detection in tabular form. This paper covers detection of PP such as petrol, kerosene, and diesel in various types of samples of interest to fire debris analysts. Solid phase microextraction is most frequently used along with gas chromatography-mass spectrometry (GC-MS) for the extraction and identification of PP from FDR. Chemometric tools should be used to improve the

significance and reliability of results obtained from the analysis of FDR. However, the potential utility of portable GC-MS in fire debris analysis cannot be ignored, and its proper development and validation is required before using it for this purpose.

تحليل المنتجات النفطية في بقايا مخلفات الحريق بواسطة الكروماتوغرافيا الغازية : (مراجعة علمية) المستخلص

تستعرض هذه المراجعة بشكل موجز التطورات المنجزة في مجال تحليل المنتجات النفطية في بقايا مخلفات الحرائق بطريقة كروماتوغرافيا الغاز. وتغطي المراجعة جوانب مختلفة من التحليل مثل المواد الداخلة، وإجراءات الفصل، والعمود المستخدم، والطور المتحرك المستخدم، والكشف اللاحق للمواد بشكل مجدول.

وتغطي هذه الورقة الكشف عن المركبات النفطية مثل البنزين والكيروسين والديزل في أنواع مختلفة من العينات التي تهم فريق تحليل بقايا مخلفات الحريق. ويتم غالباً استخدام تقنية الطور الصلب للاستخلاص منتهي الصغر للعينات جنباً إلى جنب مع تقنية الفصل الكروماتوغرافي الغازي المقترنة بمطياف الكتلة (GC-MS) وذلك من أجل استخلاص وتحديد هوية المركبات النفطية من بقايا مخلفات الاحتراق. كما ينبغي استخدام أدوات القياس الكيميائي (الكيموميتري) لتحسين مدلول وموثوقية النتائج المستحصل عليها تحليل بقايا مخلفات

Keywords: Forensic Science, Forensic Chemistry, Fire Debris Analysis, Petroleum Products, Arson, Gas Chromatography-Mass Spectrometry

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الحريق. ومع ذلك، لا يمكن تجاهل الفائدة المحتملة لجهاز فصل الغازات المحمول في تحليل الحطام من الحرائق، ولا بد من تطويره الصحيح والتحقق من صحته قبل استخدامه لهذا الغرض.

الكلمات المفتاحية: علوم الأدلة الجنائية، الكيمياء الجنائية، تحليل مخلفات الحريق، المنتجات النفطية، الحريق المتعمد، كروماتوغرافيا الغاز، مطياف الكتلة.

1. Introduction

Fire involves the oxidation of fuel and emits energy in terms of heat and radiations. During the burning process, heat and radiations are emitted due to oxidation of fuel by atmospheric oxygen. Therefore, fuel, oxidizer, and heat are three basic essential components to initiate fire [1]. Any chemical substance (solid, liquid, or gas) used to start a fire or increase the intensity or speed at which it spreads is known as fuel. Liquid fuels include highly inflammable and volatile liquids such as petroleum products (PP) (petrol, kerosene, and diesel) or oxygenated organic solvents, and are frequently used by criminals due to their easy availability, cost-effectiveness, simple handling and storage. These substances can be used to intentionally start or spread fire. These substances are defined as an ignitable liquid (IL) based upon their physical and chemical properties but as an accelerant based upon how they are being used, i.e., intention behind its use. Therefore, not all inflammable liquids found at a fire scene are accelerants and conversely, not all accelerants used to commit arson are liquids [1,2].

A complex chemical substance produced during the petroleum refining of crude oil is known as PP. It is a mixture of multiple components with a wide range of boiling points [3]. ILs can be classified into three broad classes: petroleum products (PP) (petrol, kerosene, and diesel); naturally derived ILs like turpentine and limonene; and oxygenated organic solvents like alcohols and acetone. Petroleum de-

rived ILs can be further classified into light (C4-C9), medium (C8-C13), and heavy (C9-C20+) products based on boiling range and specific chemical composition. ILs can also be broadly classified into 2 broad classes: petroleum and nonpetroleum liquids, depending on their source. Petroleum based ILs originate from crude oil and include petrol, kerosene, and diesel whereas nonpetroleum based ILs are derived from other sources and include turpentine and oxygenated organic solvents like ethers and alcohols [2,4].

Fire may be accidental, spontaneous, or intentional in nature depending on intention. Accidental fire may be due to faulty wiring, overheated electric motors, and cigarette smoking, etc. Spontaneous fire occurs due to natural heat produced in poorly ventilated containers or areas. Fire in containers containing rags wetted with certain types of highly unsaturated oils such as linseed oil is spontaneous in nature due to slow heat producing chemical oxidation between air and oil. Intentional fire includes arson [1,5]. Arson is defined as any willful and malicious burning of property for some illegal purpose, especially with criminal or fraudulent intent. It also involves attempt to burn (with or without intent to defraud) a dwelling house, public building, motor vehicle, and personal property. It is wilful destruction of property by fire [5]. Motives to commit arson are plentiful and can include criminal intent such as concealing crimes (theft or murder), revenge, financial gain (insurance claims), vandalism, part of a series of crimes, an act of terrorism with motivations such as racial and religious hatred, or for political reasons [1,5]. In India, "bride burning" for dowry presents another aspect of such crimes, and it also includes cases of homicidal or suicidal burning. Kerosene is most frequently used to commit bride burning in India [4,6].



Fire scenes are very difficult to investigate because of the destructive nature of fire. The fire itself destroys the physical evidence at its origin. Most of the evidences are destroyed during the burning process and others are destroyed during the fire extinguishing process. Investigators have to search through debris which is often water soaked or covered with foam from fire extinguishers. The involvement of personnel from different departments (fire brigade, hospital, police station, insurance companies, forensic science laboratory, etc.) also increases the complexity of investigation at the fire scene. It is considered as one of the easiest crimes to commit and also one of the hardest crimes to investigate. A scientific and systematic methodology should be adopted in a careful manner to collect evidences from fire scenes.

Arson is the one crime that destroys rather than creates evidence as it progresses [1,5]. ILs are not frequently present in unintentional fires. The unexplained presence of these liquids thus strongly indicates a fire of suspicious origin [7]. Detection and identification of these PP are, therefore, helpful in determining the origin and cause of fire [1,4].

Fire debris analysis is an examination of FDR in order to detect and identify ignitable liquid residues (ILR). FDR are most frequently received in cases of suspicious fires such as arson cases, for the detection and characterization of trace amounts of IL. FDR may contain partially or completely burnt clothes, carpet, wood, soil, hairs, paper, concrete, wire, and skin recovered from the body of victim or the accused. These samples are referred to forensic science laboratories for the detection and characterization of traces of petroleum residues [1,2].

Thus, detection of PP is of prime importance. Many classical physical and chemical methods were used for the

detection and identification of PP in FDR. But these methods were time-consuming, less sensitive, and non-specific. Therefore, sophisticated instrumental analytical techniques such as gas chromatography (GC), gas chromatography – mass chromatography (GC-MS), gas chromatography – mass chromatography – mass chromatography (GC-MS-MS), and multidimensional gas chromatography (GC×GC) are frequently used to analyse trace amounts of PP in FDR.

Thus, on the basis of frequent use of PP in arson cases, we target the detection of petrol, kerosene, and diesel in various complex matrices of forensic interest by conventional as well as modern GC methods. The aim of this is to give an overview on analysis (including extraction procedure, separation, and identification) of PP in fire debris by GC methods. Table-1 provides important experimental information about the analysis such as the substrates involved, isolation procedures, column and mobile phase used, and subsequent detection using various GC and GC-MS methods.

2. Analysis of Petroleum Products (PP)

Development of GC methods that are capable of detecting trace amounts of PP in FDR has become increasingly important in the field of forensic science. Routine analyses rely on the visual comparison of a gas chromatogram using controlled samples of standard PP. Sandercock [8] provided an overview of the scientific literature describing best practices in the fields of fire scene investigation as well as ignitable liquid residue analysis. The most up-to-date information regarding the most appropriate tools for the analysis and interpretation of FDR are presented by Martin-Alberca et al. [9] who reviewed different aspects of analysis and interpretation of FDR such as current stan-



Table 1- Characteristics of the GC methods used for the analysis of petroleum products in fire debris samples.

S.No.	Analyte(s)	Matrix	Extraction Technique(s)	Column (Dimensions)	Carrier gas (flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
1.	Paraffin wax, liquid paraffin, gear oil, light oil, lubricating oil, engine oil	NR	NR	OV-1 glass capillary (50 m x 0.25 mm)	H2 (4 mL/min)	FID	280 °C	NA	[27]
2.	Petrol	NR	NR	DB-1 (60 m x 0.25 mm x 1 μm)	H2 (45 cm/sec)	FID	NR	NA	[28]
3.	Petrol, naphtha, varsol, kerosene, stove oil, diesel, furnace oil	Pine Wood	Steam distillation	Stainless steel (2.4 m x 3 mm)	N2 (25 mL/min)	FID	150 °C, 150 °C	NA	[29]
4.	Petrol, kerosene, diesel	Hardwood charcoal	Hot headspace, steam distillation, adsorption wire technique	OV 1 (25 m) 15% Carbowax 20M on chromosorb W packed column (3 m x 6.35 mm)	N2 (10 psi=inlet pressure) N2 (60 mL/min)	FID	NR	NA	[30]
5.	Petrol	Carpet padding	Solvent extraction, steam distillation, direct headspace, sorbent trap/thermal desorption	Supelcoport stainless steel (12' x 1/8")	N2 (20 mL/min)	FID	230 °C, 230 °C	NA	[31]
6.	Petrol, kerosene, diesel	Filter paper	Headspace, Dynamic adsorption/ elution	OV-101 Stainless steel (6 m x 3.175 mm)	NR	FID	NR	NA	[32]

Continued in next page



Table 1- (continued)

S.No.	Analyte(s)	Matrix	Extraction Technique(s)	Column (Dimensions)	Carrier gas (flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
7.	Petrol, kerosene, diesel	Paper	Headspace, Passive adsorption/ elution	DB-5 (30 m × 0.32 mm × 1 μm)	H ₂ (70 cm/sec)	FID	250 °C	NA	[33]
8.	Petrol, MPD, HPD	NR	Passive adsorption/ elution	SPB-1 (30m × 0.32 mm × 0.25 μm)	He (2 mL/min)	FID	250 °C, 290 °C	NA	[34]
9.	Petrol, kerosene, diesel	Wood, kim wipes	Passive adsorption/ elution	DB-1 (12 m × 0.25 mm × 0.25 μm)	He (25.6 cm/sec)	FID	275 °C, 280 °C	NA	[35]
10.	Petrol, diesel, lighter fluid	Water	Solvent extraction, SPME	HP-1 (30 m × 0.2 mm × 0.25 μm)	He (1 mL/min)	FID	220 °C, 300 °C	NA	[36]
11.	Petrol	Burned pine, wood, plastic	SPME, Passive adsorption/ elution	HP-1 (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	FID	220 °C, 300 °C	NA	[37]
12.	Petrol, diesel, charcoal lighter fluid	Human hand	SPME	DB-5MS (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	FID	250 °C, 310 °C	NA	[38]
13.	Petrol, diesel, kerosene	Carpet	SPME	Ultra-1 (25 m × 0.20 mm × 0.11 μm)	He (1.2 mL/min)	FID	250 °C, 310 °C	NA	[39]
14.	Petrol, diesel, kerosene	Fabric curtain	Headspace single drop microextraction	Ultra-1 (25 m × 0.20 mm × 0.1 μm)	He (1.5 mL/min)	FID	NR	NA	[40]
15.	Petrol	Human hand	Passive adsorption/ elution	DB-5 (30 m × 0.32 mm × 1.0 μm)	He (2 mL/min)	FID	250 °C, 280 °C	NA	[41]

Continued in next page



Table 1- (continued)

S.No.	Analyte(s)	Matrix	Extraction Technique(s)	Column (Dimensions)	Carrier gas (flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
16.	Petrol, kerosene, diesel, white and methylated spirits, mineral turpentine, isopropanol	Tissue paper, soil, unburnt carpet and wood, burnt carpet and wood	Passive adsorption/ elution	DB-1 (25 m) Carbowax (30 m)	H2 (30 mL/min)	FID	For DCM extracts (260 °C, 260 °C) For water extracts (150 °C, 150 °C)	NA	[42]
17.	130 accelerants including petrol, kerosene, diesel	NR	SPME	PETROCOL DH 50.2 (50 m × 0.2 mm × 0.5 μm)	N2 (1 mL/min)	FID	270 °C	NA	[43]
18.	Petrol, dodecane	Carpet	Passive adsorption/ elution	Stainless steel (3.65 m × 3.18 mm)	N2 (30 mL/min)	PID	NR	NA	[44]
19.	Petrol, kerosene, diesel	Carpet, carpet padding, wood	Dynamic adsorption/ elution	OV-1 (1.2 m × 1.2 mm × 1.0 μm) OV-1 (20 m × 0.25 mm × 0.25 μm)	NR	MS	NR	35-250	[45]
20.	Petrol	Carpet, carpet padding, tiles, form, pine, roof shingles, synthetic polymers	Passive adsorption/ elution	Fused silica (15 m × 32 mm)	NR	MS	NR	NR	[46]
21.	Petrol, diesel	NR	NR	HP-1 (25 m × 0.20 mm × 0.50 μm), HP-5 (25 m × 0.20 mm × 0.50 μm), HP-5MS (30 m × 0.25 mm ×	He (1.0 and 0.6 mL/min)	MS	280 °C	NR	[47]

Continued in next page



Table 1- (continued)

S.No.	Analyte(s)	Matrix	Extraction Technique(s)	Column (Dimensions)	Carrier gas (flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
22.	Petrol, diesel	NR	NR	HP-1 (25 m × 0.20 mm × 0.50 μm)	He (0.8 mL/min)	MS	250 °C	NR	[48]
23.	Petrol, diesel	NR	Passive adsorption/ elution	HP-1MS (30 m × 0.25 mm × 0.25 μm)	H2 (1.1 mL/min)	MS	250 °C	30-300	[49]
24.	Petrol, paint thinner, solid charcoal starter, white spirits	NR	NR	HP-1 (30 m × 0.25 mm × 0.25 μm)	He (1.2 mL/min)	MS	300 °C	20-400	[50]
25.	Petrol, kerosene, diesel	Tissue paper	Passive adsorption/ elution	BP-1 (25 m × 0.25 mm × 0.25 μm)	He (Head pressure = 120 kPa and 35 kPa)	FID, MS	NR	NR	[51]
26.	Petrol	NR	Steam distillation, Passive adsorption/ elution	HP-1 (25 m × 0.2 mm × 0.33 μm)	He (0.5-1 mL/min)	MS	250 °C	40-500	[52]
27.	Petrol, barbecue lighter fluid	Wood, carpet	SPME	DB-5 (30 m × 0.25 mm × 0.25 μm)	NR	FID, MS	275 °C, 300 °C	50-260	[53]
28.	Petrol, diesel	Wool, silk, polyester, cotton	SPME	TR-5MS-SQC (15 m × 0.25 mm × 0.25 μm)	He (2 mL/min-For petrol)	MS	250 °C-for petrol,	40-300	[54]
29.	Petrol, diesel, barbecue lighter, turpentine, industrial solvents	Soil, sawdust	HSSE, SPME	VF-23MS (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	NR	40-400	[55]

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Table 1- (continued)

S.No.	Analyte(s)	Matrix	Extraction Technique(s)	Column (Dimensions)	Carrier gas (Flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
30.	Petrol	Wood, paper, carpet	SPME	HP-5MS (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	280 °C	40-400	[56]
31.	Petrol, diesel	Carpet	SPME	DB-5MS (30 m × 0.25 mm × 0.25 μm)	He (1.6 mL/min)	MS	250 °C	50-500	[57]
32.	Petrol, kerosene, diesel, lighter fluid, camp fuel, cement thinner, cleaner, paint thinner, lamp oil	Paper	Passive adsorption/ elution	HP-1MS (30 m × 0.25 mm × 0.25 μm)	H2 (1.1 mL/min)	MS	320 °C	30-300	[59]
33.	Petrol, diesel, C1-C4 alcohols, acetone	Filter paper	Passive adsorption/ thermal desorption	Elite-1 (30 m × 0.25 mm × 1.0 μm)	He	MS	NR	NR	[60]
34.	Petrol, diesel	Human hand	Passive adsorption/ elution	AT-1 (30 m × 0.25 mm × 0.25 μm)	He (3.2 mL/min)	MS	NR	30-300	[61]
35.	Petrol, diesel	Filter paper	Passive adsorption/ elution	HP-1 (25 m × 0.2 mm × 0.5 μm)	He (100kPa)	MS	NR	33-300	[62]
36.	Petrol	Cloth, paper towel	Passive adsorption/ elution	Rtx-1 (30 m × 0.25 mm × 0.25 μm)	0.68 mL/min	MS	NR	10-400	[64]
37.	Petrol, MPD, HPD	Wood, tile, carpet	Passive adsorption/ elution	DB-1 (60 m × 0.32 mm × 0.25 μm)	He (2 mL/min)	MS	260 °C	50-200	[65]
38.	Petrol	Wood	Passive adsorption/ elution	DB-1 (60 m × 0.25 mm × 1.0 μm)	He	MS	NR	29-200	[66]

Continued in next page



Table 1- (continued)

S.No.	Analyte(s)	Matrix	Extraction Technique(s)	Column (Dimensions)	Carrier gas (flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
39.	Petrol, diesel	Carpet (nylon, polyester, wool), wallpaper, synthetic floor	Passive adsorption/ elution	SBP-5 (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	275 °C	37-400	[67]
40.	Petrol	Car carpet	Passive adsorption/ elution	DB-5MS (30 m × 0.25 mm × 0.25 μm)	He (1.7 mL/min)	MS	250 °C	40-200	[68]
41.	Diesel	Wood, chipboard, plastic, carpet	Passive adsorption/ thermal desorption	Elite-1 (30 m × 0.25 mm × 1.0 μm)	He	MS	NR	NR	[69]
42.	Petrol	Water, blood, juice	Passive adsorption/ thermal desorption	DB-5MS (30 m × 0.25 mm × 0.5 μm)	NR	MS	NR	NR	[70]
43.	NR	Polyethylene bags	Passive adsorption/ thermal desorption	DB-5MS (30 m × 0.25 mm × 0.5 μm)	NR	MS	NR	NR	[71]
44.	NR	Gloves	SPME	HP-5MS (30 m × 0.25 mm × 0.25 μm)	He (1.2 mL/min)	MS	NR	25-350	[72]
45.	Petrol, diesel	Rest of Chemical Ignition Molotov Cocktails	SPME	HP-5MS (12 m × 0.2 mm × 0.33 μm)	He (0.8 mL/min)	MS	250 °C	10-400	[73]
46.	Petrol, kerosene, diesel	NR	Passive adsorption/ elution	DB-1 (30 m × 0.25 mm × 0.25 μm) BP-5 (30 m × 0.32 mm × 0.5 μm)	N ₂ (1 mL/min) He (1 mL/min)	FID, MS	265 °C 280 °C	45-500	[74]

Continued in next page



Table 1- (continued)

S.No.	Analyte(s)	Matrix	Extraction Technique(s)	Column (Dimensions)	Carrier gas (Flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
47.	Petrol, lubricant, fuel oils	Water	Passive adsorption/ elution	Elite (1.30 m)	NR	MS	NR	35-350	[75]
48.	Petrol	Car carpet	Passive adsorption/ elution	HP-5MS (30 m × 0.25 mm × 0.25 μm)	He (1.2 mL/min)	MS	280 °C	30-350	[76]
49.	Petrol, kerosene, diesel, extraction solvent, universal diluter	Carpet, wood, unpainted chipboard	Passive adsorption/ thermal desorption	Elite-1 (30 m × 0.25 mm × 1.0 μm)	He	MS	NR	NR	[77]
50.	Petrol	Carpet	SPME	5MSI (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	250 °C	30-300	[78]
51.	Petrol	Human hand	Passive adsorption/ elution	HP-5MS (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	250 °C	10-450	[79]
52.	Petrol	NR	SPE	HP-5MS (30 m × 0.25 mm × 0.25 μm)	He (1.2 mL/min)	MS	280 °C	30-350	[80]
53.	51 accelerants including Petrol, kerosene, diesel	Wood, carpet	Passive adsorption/ elution	Supleco (25 m × 0.2 mm × 0.5 μm)	He (40 mL/min)	MS	NR	NR	[82]
54.	Petrol, kerosene	Carpet, wood	Passive adsorption/ elution	DB-5MS (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	250 °C	50-550	[84]
55.	Petrol	Soil	Passive adsorption/ elution	DB-5MS (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	250 °C	40-300	[85]
56.	Petrol, kerosene, torch fuel, lamp oil, paint thinner	Carpet	Passive adsorption/ elution	HP-1MS (30 m × 0.25 mm × 0.25 μm)	He (1 mL/min)	MS	250 °C	50-550	[86]

Table 1- (continued)

S.No.	Analyte/s	Matrix	Extraction Technique/s	Column (Dimensions)	Carrier gas (flow rate)	Detector	Injector & Detector Temp.	m/z Range	References
57.	Petrol, kerosene, diesel, turpentine	Carpet, rubber and foam underlay	SPME	MXT-5 (5 m × 0.1 mm × 0.4 μm)	NR	MS	270 °C	45-500	[87]
58.	Petrol, diesel, mineral spirits, paint thinner, paint remover, lighter fuel, turpentine	Carpets	SPME	Rtx-5MS (30 m × 0.25 mm × 0.25 μm)	He (2 mL/min)	MS	270 °C	45-200	[89]
59.	Petrol	Soil	Passive adsorption/ elution	SPB-5 (7.5 m × 0.20 mm × 0.20 μm)	He	MS/MS	300 °C	40-290	[90]
60.	Petroleum distillates (petrol, kerosene, charcoal lighter fluid, paint thinners)	Carpet, paper, wood, plastic, cloth	Dynamic adsorption/ elution	DB-5 (30 m × 0.25 mm × 1 μm) DB-225 (30 m × 0.25 mm × 0.25 μm)	H2 (1 mL/min)	FID	280 °C, 280 °C	NA	[94]
61.	Petrol, kerosene, diesel	NR	Solvent extraction	BPX50 (30 m × 0.25 mm × 0.50 μm) BPX1 (2 m × 0.1 mm × 0.10 μm)	NR	MS	325 °C	NR	[95]
62.	White spirit	NR	NR	DB-1 (30 m × 0.25 mm × 0.5 μm) DB-17 (1 m × 0.1 mm × 0.2 μm)	He (Head pressure= 120 kPa)	FID, MS	250 °C, 280 °C	30-200	[97]

NA- Not Applicable

NR- Not Reported

dard and new sample extraction procedures, novel statistical tools, and distortion effects (microbial action, matrix effect, acidification effect) on chemical fingerprints of neat ILs or ILRs. Most of the reviews provide information regarding different sample preparation methods used for the analysis of the ILs in FDR [10-12].

Analysis of FDR is a two-step process. The first step involves the isolation and concentration of PP from matrices while the second step involves the chromatographic separation, analysis, and identification of PP. The authenticity of the second step completely depends on the efficiency of first step [10]. Techniques used for the isolation of PP from different substrates have changed over time. In the 1950's and 1960's, steam distillation, vacuum distillation, and solvent extraction procedures were used to extract PP from substrates and were considered as conventional extraction procedures [13,14]. In the early 1970's, headspace (HS) extraction procedures were introduced in fire debris analysis and are considered as modern extraction procedures [13,15]. These HS extraction procedures include direct (heated) HS extraction, carbon strip method, solid phase micro-extraction (SPME), and purge and trap HS extraction. The current standardized procedures which provide technical information and quality consensus guidelines for the isolation of ILs, analysis of fire debris, classification of ILs and ILR samples, and interpretation of ILR extracted from FDR are all well documented [16-20].

2.1. Chromatography-Flame Ionization Detection (GC-FID) Methods

Gas chromatography was first applied to fire debris analysis in 1960 [22]. Prior to that, ILR were analysed by different techniques [23-26]. Flame ionization detector (FID) is the most popular detector used with GC. Its

response is not influenced by change in the flow rate of mobile phase, and it works as a standard detector for the analysis of hydrocarbons due to its high sensitivity, low noise, and large linear response range [21].

Lloyd [27] observed that visual inspection of chromatograms is sufficient to discriminate different types of PP of high relative molecular mass and suggested the use of capillary GC for this purpose. Table-1 presents the characteristics of GC and GC-MS methods for analysis of PP in FDR. According to Mann [28], boiling point range, relative concentration of major versus minor components, aliphatic and aromatic hydrocarbon content, and presence of additives are useful parameters to distinguish different classes of ILs.

Yip and Clair [29] used the oven heating method over steam distillation because of its simplicity, rapidity, and absence of interfering peaks from substrates. Twibell et al. [30] suggested that the adsorption wire procedure is the most sensitive while the hot HS method is the least sensitive. They also concluded that steam distillation has intermediate sensitivity for the extraction of PP from FDR. They advocated the use of capillary columns over packed columns due to their high sensitivity and greater resolution. Nowicki and Strock [31] used the charcoal adsorption/elution technique over HS and solvent extraction methods for the isolation of PP from FDR. Frenkel et al. [32] used the adsorption tube method over the HS method due to its high sensitivity. The use of Zeolite 4A (0.4 nm pores, 2 g/1ml of water) molecular sieves was suggested in order to eliminate the interference caused by water. In contrast to this, Reeve et al. [33] recommends the use of the direct HS injection technique over the charcoal adsorption technique for the isolation of PP from FDR due to its simplicity, high sensitivity, and minimum sample preparation requirement. Waters and Palmer [34] suggested the use of passive HS concentration technique in multiple analyses of FDR due



to their non-destructiveness and reduced susceptibility to contamination. Newman et al. [35] studied the effects of different parameters such as adsorption time, adsorption temperature, strip size, and concentration of sample on the adsorption of PP. They observed that diesel and kerosene products are difficult to discriminate at incubation temperatures less than 60 °C. However, higher temperature (>90 °C) is not recommended due to pyrolysis and decomposition of substrates. Newman et al. [35] recommended using 8 mm × 8 mm strip size and heating at 50-70 °C for 16-24 hrs to produce efficient results.

Different studies [36-38] advocated the use of the SPME technique over conventional solvent extraction and ACS methods for the isolation of residues of ILs from human hands, aqueous samples, and FDR. IL was deposited on the hand of a subject and then covered with a nylon bag. SPME fiber was inserted into the bag and exposed to HS over the hand for 15 min. The fiber was then inserted into the injection port of a gas chromatograph [38]. Ahmad et al. [39] developed a sol-gel based C8 (octyltriethoxysilane and methyltrimethoxysilane in ratio of 1:1) coated with home-made SPME fiber for the isolation of PP from arson samples. This fiber showed higher extraction recoveries than conventional PolyDiMethylSiloxane/DiVinylBenzene (PDMS/DVB) fiber.

Sanagi et al. [40] used HS single drop microextraction (HS-SDME) GC method for the analysis of PP in FDR. They carried out HS-SDME as follows: a 10 mL aliquot of the sample solution was placed in a 15 mL headspace vial. The sample solution was continuously stirred at 1500 rpm. The microsyringe was pre-rinsed more than 8 times with the organic solvent in order to eliminate carry-over. Then organic solvent was drawn into a microsyringe which was then inserted into the headspace after piercing the vial septum and suspended over the sample solution in a fixed position relative to the headspace vial. The plunger was pushed

in such a way that the organic solvent was suspended on the tip of the syringe needle. After 20 min of extraction, the drop was withdrawn into the syringe by pulling back the plunger. The syringe needle was removed from the sample vial, and the extract was introduced directly into the GC injection port for further analysis. No interferences due to burnt matrix were observed. They suggested that the HS-SDME-GC method is rapid, efficient, sensitive, and simple and can be used as an excellent alternative method for the analysis of PP in FDR.

Darrer et al. [41] observed significant evaporation of petrol within 30 min of its deposition on hands and recommends the use of PVC gloves for effective and efficient collection of petrol from hands due to low background noise or reduced amount of volatile compounds detected from it. Coulson et al. [42] observed that air foam (used as fire extinguisher) did not cause significant interferences in detection and identification of hydrocarbon fuels in FDR. Bodle and Hardy [43] developed SPME-GC method for the identification of PP. They suggested that Soft Independent Model Classification Analogy (SIMCA), a statistical tool, can be an effective class predictor of PP. The accuracy of classification by SIMCA models for previous and current ASTM systems was 98.5% and 97.2%, respectively.

2.2. Gas Chromatography-Photoionization Detection (GC-PID) Method

This detector is based on measuring the current resulting from photoionization of an analyte by ultraviolet radiation at a suitable electrode. Its high sensitivity for aromatic hydrocarbons, higher selectivity, and large linear response range enhances its utility in the analysis of complex hydrocarbon mixtures [21]. Higgins et al [44] suggested the replacement of a conventional convection oven with a microwave oven for sample heating in order to reduce analysis time and enhance the sensitivity of IL vapour collection.



2.3. Gas Chromatography-Mass Spectrometry (GC-MS) Methods

GC-MS is an extremely versatile approach in which two techniques based on completely different principles are coupled together. In GC-MS, GC separates the components of a sample while MS identifies them. Compounds are separated on the basis of their relative affinity with the stationary phase of the column. Components eluting from the chromatographic column are then introduced to the MS via a specialized interface. Coupling of MS with GC not only detects the analytes but also provides the pinpoint identification of analytes. Therefore, MS provides a powerful detection tool in combination with gas chromatography [21]. GC-MS is commonly used for the analysis of PP residues in fire debris [20, 45].

Bertsch et al. [45] advocated the use of GC-MS and macro-programming for noise reduction and automated data processing for the detection of ILs in arson debris. Sellers and Bertsch [46] recommended the replacement of a qualitative approach with a semi-quantitative approach for the analysis of FDR. Analysis of blank was suggested after strong positive debris samples. Choodum and Daeid [47] developed and validated a GC-MS method to analyse hydrocarbon residues. Different parameters such as carrier gas flow rate, column temperature programming, and inlet temperature were optimized to obtain better resolution and sensitivity in a shorter time. Excellent intra-day and inter-day precision were obtained for this method. Choodum and Daeid [48] recommend the use of 100% dimethylpolysiloxane HP-1 column over 5% phenylmethylpolysiloxane HP-5 and HP-5MS columns for the analysis of ILs in FDR.

Locke et al. [49] proposed the use of eight internal standards to monitor the efficiency of the extraction procedure. However, in contrast to this, Salgueiro et al. [50] suggested the use of internal standards for quality control in the detection of ILs in FDR. The present procedure checks the con-

servation of samples during storage, isolation of analytes from activated charcoal strip (ACS) and fire debris, and the repeatability of GC-MS.

Tranthim-Fryer [51] presented a simple, sensitive, and cost effective carbon wire adsorption/solvent extraction technique for the analysis of PP and volatile organic compounds in arson debris samples by GC and GC-MS. Water vapors did not cause any interference in detection and identification of PP. He suggested that this method allows further examination of samples at a later date (if required) and can be useful for laboratories not having a thermal desorption unit or pyrolyzer. Frontela et al. [52] suggested that although the adsorption/elution method is faster than distillation, the latter is highly efficient to extract PP from FDR. Steffen and Pawliszyn [53] recommend the use of the HS SPME method for the isolation of PP from FDR by employing GC and GC-MS. They suggested that the ion selective mode of MS can be used to distinguish between interferences generated from FDR and trace amounts of PP. Aqel et al. [54] detected petrol and diesel in simulated FDR, even 24-hours after the extinguishment of fire, using SPME-GC-MS. They suggested that silk samples are more useful for the recovery of accelerants.

Cacho et al. [55] advocated the use of an efficient and sensitive simple HS sorptive extraction (HSSE) technique for the isolation of PP from fire debris prior to the analysis by GC-MS. For HSSE procedure, 1g of debris (soil and sawdust) was placed in 15 ml glass vials. A polydimethylsiloxane (PDMS) stir bar was exposed to HS vial for 60 min at 50 °C. Commercial stir bars coated with 0.5 mm of PDMS were used as extracting phase. A thermal desorption unit (TDU) equipped with an autosampler and a programmed temperature vaporization (PTV) cooled injector system was used for sample introduction into a gas chromatograph. The limit of detection was in the range of 0.1 - 0.7 ng/g, depending on the nature of the PP. Lloyd



and Edmiston [56] recommend using the use of Carboxen/PDMS fibers for extracting hydrocarbons from FDR due to their high efficiency for aromatic hydrocarbons as compared to aliphatic hydrocarbons. Fettig et al. [57] suggested the use of mixed polymeric (Divinylbenzene/Carboxen/Polydimethylsiloxane, DVB/CAR/PDMS) SPME fiber for isolating PP from FDR due to its ability to adsorb analytes of different polarities. Smale et al. [58] suggested that using a Passive HS Residue Extraction Device (PHRED) is a more sensitive and effective technique than cat litter, absorbent matting, and cotton pads for extracting ILR from concrete surface.

Sandercock [59] recommends using activated carbon cloth (ACC) over ACS for the isolation of ILs from fire debris, as ACC gave more concentrated extracts than ACS and was more cost effective. It was observed that a high amount of water vapors in fire debris causes significant decrease in the recovery of alkane compounds. Borusiewicz and Zieba-Palus [60] advocated the use of Tenax TA over Carbotrap 300 for isolating non-polar, high boiling compounds of PP from FDR due to its higher efficiency and affinity for non polar, high boiling compounds. They suggested the use of Carbotrap 300 over Tenax TA for isolating polar, volatile compounds of PP from FDR. Tenax TA can be readily reused when cleaning of adsorbed remnants is required in Carbotrap 300. Muller et al. [61] developed a simple, sensitive, and innovative method for the detection of trace amounts of ILR on a suspect's hands. They observed that the process of adsorption can be accelerated by heating the hands to 45 °C using a hair dryer or light bulb. However, they observed that this method cannot distinguish between fuel used as an arson accelerant and fuel used for legitimate purposes. Lentini and Armstrong [62] observed no significant differences in the eluting abilities of carbon disulfide and diethyl ether. Use of diethyl ether over carbon disulfide (as extracting solvent) was suggested

due to less health risks posed to laboratory personnel.

Smith [63] observed that interference caused by combustion and pyrolysis products of matrices can be eliminated by mass chromatography. This method provides a rapid detection of specific compounds even in the presence of intense background interferences. Gilbert [64] advocated the potential utility of extracted ion profiles in distinguishing an IL from interference due to pyrolysis or other contaminants and suggested that individual extracted ion profiles are better than summed extracted ion profiles in identifying ILs. Keto and Wineman [65] recommended using target compound chromatograms (TCC) for the identification of petroleum based PP. They observed that target compound patterns for fresh and weathered petrol, medium petroleum distillates, and heavy petroleum distillates are specific and can be used for their identification in high background FDR. They also observed that pyrolysis products have different target compound chromatograms from PP and thus did not cause a risk of false identification of residual PP. Barnes et al. [66] compared different petrol samples by using the sequential peak ratio method and target ion response. They observed that wood does not cause any interference in the comparison process. They suggested that such comparisons are useful in comparing petrol (extracted from debris) to unevaporated petrol samples and in associating an evaporated petrol sample with its source and discriminating it from other sources of petrol.

Sellers and Bertsch [46] observed that urban air is another key source of interferences in addition to pyrolyzates and background matrices in the analysis of arson debris. Almirall and Furton [67] characterized the background and pyrolysis products that are generated during control burning of different substrates. They observed that many substrate backgrounds, combustion or pyrolysis products, are also target compounds of ILR mixtures and can interfere with the identification process. They also observed that ILs



and substrate backgrounds have different chromatographic patterns. They suggested that negative control samples of substrates present at fire scenes should be collected and analysed before actual samples of interest.

Cavanagh et al. [68] observed that car carpets exhibit some of the compounds that may interfere with the detection and identification of petrol residues. Borusiewicz [69] observed that fire extinguishers (foam, powder, snow) did not cause any interference in the isolation, detection, and identification of diesel from FDR, and suggested that the use of fire extinguishers should be rapid as this factor plays a significant role in the recovery of PP from FDR. Borusiewicz [70] recommended that a routine analytical procedure used for analyzing FDR can also be applied to analyze atypical aqueous samples (juice, blood, and polluted water) for the detection of trace amounts of ILs in them. He observed that such kinds of atypical matrices produce unusual matrix effects. Borusiewicz and Kowalski [71] detected pentamethylheptane, limonene, and even n-alkanes and n-alkenes in polyethylene bags using GC-MS. Grafit et al. [72] detected carbon disulfide, toluene, xylenes, aldehydes (C5-C9), naphthalene derivatives, etc, in gloves using GC-MS. Martin-Alberca et al. [73] analyzed acidified ILR in fire debris by SPME-GC-MS. Significant differences, in terms of relative abundance of aromatic compounds, was observed in chromatographic profiles of acidified and non-acidified neat and weathered petrol samples. They suggested that the presence of tert-butylated compounds can indicate the existence of acidified petrol in fire debris. McCurdy et al. [74] analysed PP in FDR with conventional GC and GC-MS methods and compared this with vapour phase ultraviolet spectroscopy. They observed that vapour phase ultraviolet spectroscopy is not capable of analysing alkanes or polycyclic aromatic hydrocarbons. The authors suggested that this technique can be used as an additional technique for the analysis of PP in FDR. However, it is not

able to detect UV non-absorbing compounds, which form the major component of PP. Zadora et al. [75] reported two cases in which the GC-MS method was used to identify PP in FDR, including water. They observed that residues of PP can be detected in samples even several months after their collection.

Cavanagh-Steer et al. [76] observed that deposition of target compounds onto carpet depends on occupation and suggested that the presence of larger volumes of petrol on carpet is indicative of intentional addition of petrol to that surface. They observed that the evaporation level of petrol increases with time between deposition and analysis. They noted significant evaporation of petrol from car carpets within 24 hours of its deposition. It was observed that less than 100 μ L petrol could not be detected after 24 hrs of deposition on car carpet. They suggested that the presence of petrol (fresh or slightly evaporated) in a significant amount on motor vehicle carpets indicates the addition of petrol to a vehicle interior and eliminates the potential contamination due to normal vehicle usage. Borusiewicz et al. [77] studied the effect of different factors (type of burned material and accelerant, time of burning, availability of air) on the detection of traces of PP. No significant relationship between time of burning and the detectability PP traces was observed. They also observed that variation in air availability did not significantly affect the detection of PP traces. They suggested that type of substrate effects interference in the identification process while type of IL and burning time is less significant. Dhabbah et al. [78] advocated the collection of thin carpets from fire scenes because of longer retention of petrol on thin carpets. They suggested that amount of fuel, carpet thickness, and adsorption capacity of carpet play key roles in the presence and survival of petrol residues. They developed a SPME-GC-MS method for the identification of residues of petrol on carpet. They observed that petrol can be detected in samples after a few



hours after extinguishing the fire. Montani et al. [79] recommends the use of non powdered latex gloves for collecting residues of petrol from a suspect's hands because it emits the least interfering volatiles. They developed a simple and effective sampling kit which is efficient in preventing external and cross contaminations.

Sandercock and Du Pasquier [80] observed that polar compounds cannot be used to distinguish between different petrol samples due to insignificant variation from sample to sample. They suggested that two-ring polycyclic aromatic hydrocarbons can be used to distinguish between different petrol samples. Linear discriminant analysis (LDA) divides 35 samples into 32 unique groups. Waddell et al. [81] classified ILs into 2 major groups: aliphatic and aromatic, by applying hierarchical cluster (HCA) analysis on their total ion spectrum data. Tan et al. [82] recommends the use of multivariate pattern recognition techniques such as Principal Component Analysis (PCA) and SIMCA for classifying PP in to their respective classes. Detection limits of correct classification depended on sample class and were in the range of 5-50 μL . They suggested that carpet is a better source than wood for collection of ILR.

Doble et al. [83] suggested that PCA can be used to classify petrol samples into either premium or regular class while Artificial Neural Networks (ANN's) can classify petrol into premium or regular groups and into seasonal formulation based subgroups. The accuracy of correctly classifying samples as either premium or regular petrol using Mahalanobis distance calculated from PC scores was 80-93%. Only 48-62% of samples were correctly classified into their summer or winter subgroups. Approximately 97% of samples were correctly classified into their summer or winter subgroups using ANN's, and 93.2% of samples were correctly classified into regular or premium class by using LDA. Prather et al. [84] recommends the use of statistical procedures such as Pearson Product Moment Cor-

relation Coefficient (PPMC), HCA, and PCA to associate ILR to standard liquids, even in the presence of evaporation and matrix interferences, but not to a specific level of evaporation. Turner et al. [85] used PCA to study the effect of seasons on microbial degradation of petrol in soil and observed that n-alkanes are most readily degraded by micro-organisms followed by mono-substituted alkyl benzenes and benzaldehyde. They also observed the remarkable changes in composition of petrol during fall, winter, and spring seasons while little to no changes are observed in soil samples collected during an unusually hot and dry summer season. They advocate the prompt preservation and analysis of soil samples in order to properly classify ILR. Smith et al. [86] used a mathematical model to determine the chemical composition of IL at various evaporation levels. Strong to moderate PPMC coefficients were observed between modeled and experimentally derived chromatograms for petroleum distillates and gasoline.

Visotin and Lennard [87] suggested the use of a portable GC-MS for the analysis of residues of ILs in fire debris at the fire scene. The procedure involves sampling for 3 min using SPME fiber and subsequent analysis within 2 min. Although this method's sensitivity and resolution is very good, its rate of false negative results is low. Leary et al. [88] advocate the use of a field-portable GC-MS for the analysis of explosives, FDR, and counterfeit drugs at the scene of a crime. Portable GC-MS provides real-time, on-field, rapid presumptive results for the analysis of fire debris samples. It ensures collection of relevant samples from the scene. Robust analytical ability, small size, minimal consumables, and limited power usage are some of the added advantages of portable GC-MS over laboratory based GC-MS. However, loss of high mass resolution and mass accuracy, low performance characteristics, and technological feasibility and false battery alarms are some of its major limitations. The effect of environmental conditions



such as rain, sunlight, snow, and the presence of any detectable volatile organic compound in air should be considered during its operation on the scene [87-88].

2.4. Gas Chromatography-Differential Mobility Spectrometry (GC-DMS) Method

Lu et al. [89] compared the performance of differential mobility spectrometry (DMS) and MS in the detection and classification of ILs from fire debris using projected difference resolution (PDR) and observed that resolution of GC-DMS is higher than GC-MS. However, performance and efficiency of GC-MS is better than GC-DMS. Neat samples were classified with 100% accuracy.

2.5. Gas Chromatography-Tandem Mass Spectrometry (GC-MS-MS) Method

Sutherland [90] reported a case in which he presented the potential utility of the GC-MS-MS technique in analyzing FDR (soil). He suggested that GC-MS-MS can be used to confirm the identity of ultra trace amounts of several petrol components with a very high degree of certainty by enhancing signal to noise ratio. The use of GC-MS-MS for the identification of PP in FDR was recommended due to its high sensitivity and selectivity [91-93].

2.6. Multidimensional Gas Chromatography (GC×GC) Method

Jayatilaka and Poole [94] and Taylor et al. [95] identified petroleum distillates in FDR by multidimensional GC method and suggested that present method is less influenced by interfering co-eluting and matrix components and can be used to identify PP in contaminated arson samples with improved certainty. The dynamic HS method is recommended over the static HS method for extraction purposes due to its higher total recovery [94]. Pert et al. [12] also advocated the utility of multi-dimensional GC (GC×GC) in the analysis of FDR because it eliminates the interferences

due to pyrolyzed products. Frysinger and Gaines [96] used multi-dimensional gas chromatography (GC×GC) to analyze ILs in FDR. Multidimensional GC is frequently used to analyze samples containing ILR [8]. Martin-Alberca et al. [9] suggested the use of GC×GC-FID and GC×GC-MS for the analysis of FDR. Sampat et al. [97] determined the chemical profile of neat white spirit using GC×GC-FID and GC×GC-MS. Brand-to-brand differences and production variations with time were studied using PCA. They observed limited variation in chemical composition of white spirits during their productions. However, substantial variation in chemical composition of white spirits was found over time.

3. Conclusion

This review has shown that the trend of extraction procedure is changing from conventional steam distillation to more sophisticated SPME procedures, and no single extraction method is ideal for the isolation of different PP from variety of substrates of forensic importance as every extraction procedure has its own merits and demerits, and is used on the basis of availability. Nowadays, SPME and ACS are the most frequently used methods for the isolation of trace amounts of PP from fire debris.

Advances in instrumentation have opened the doors for utilization of more sophisticated analytical techniques such as GC, GC×GC, and GC-MS in the analysis of FDR. GC-MS is the most widely used technique for the analysis of FDR due to its sensitivity, selectivity, and reproducibility. It can be used to pinpoint the identity of PP present in trace amounts in fire debris. Major limitations of this technique are that it is destructive in nature and cannot discriminate the source of peak based on retention time as well as mass spectra. Therefore, a more sophisticated and



advanced GC-MS-MS technique is used for the analysis of FDR. GC-MS-MS can easily eliminate the interferences caused by combustion or pyrolysis products in the PP identification process.

The use of chemometric tools in statistical evaluation of results can be used to compare results of similar samples with slight variation in their chemical composition in order to differentiate samples on the basis of weathering grade, brand, or ASTM class, and to associate ILRs with their corresponding ILs, or even to compare data gathered from different laboratories or methodologies.

It is, therefore, concluded that no single extraction method is universally effective for the isolation of different PP from FDR. GC is a powerful analytical technique for the analysis of the PP in different kinds of FDR. However, the sensitivity and discriminatory power of the technique can be greatly improved by utilizing modern extraction methods like HS enrichment and SPME and by hyphenating it with more selective and specific detectors such as MS. The progress in passive HS concentration using new SPME fibers and methodologies improves the extraction ILs from debris. Although more sophisticated and sensitive multidimensional GC (GC×GC) and GC-MS-MS techniques are used for analyzing FDR, GC-MS is the most effective and frequently used technique for this purpose. Chemometric tools should be used to improve the significance and reliability of results obtained from the analysis of FDR. Development and validation of more sensitive and efficient GC-MS methods for the detection of PP residues in FDR is suggested. However, the potential utility of portable GC-MS in fire debris analysis cannot be ignored, and its proper development and validation is required before using it for this purpose.

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Conflict of interest

The authors declare that they have no conflict of interest.

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