

Effects of Automobile Fluids for the Detection of Gasoline in an Arson Investigation

W.A. Rushan Fernando¹, W.P.A.R.D. Bandara²

^{1,2}Senior Assistant Government Analyst, Government Analysts Department, Sri Lanka

Abstract:- In this paper, GC-MS analysis of gasoline traces on engine oil, brake oil, hydraulic oil, and power steering oil has been carried out using *Alstoniascholaris* wooden slips as the substrate. The GC-MS analysis was conducted with electron impact ionization at 70 eV and a flow rate of 1.5 ml/min. Only indane with 1,2,3,5-tetramethylbenzene and only dodecane were identified, respectively, as interferences with gasoline target compounds related to hydraulic oil and engine oil. After burning, indane and 1,2,3,5-tetramethylbenzene were disappeared.

Keywords:- Gas Chromatography-Mass Spectrometry, Auto Mobile fluids, Substrate.

I. INTRODUCTION

In recent decades, fire incidents have become more impactful on public properties compared to the past. Natural causes such as lightning, electrical failures and accidental fuel leaks with high heat or sparks are potential initiators of fires. Not only do accidental fires occur, but people also engage in deliberate and malicious burning of property to gain income from insurance companies during financial crises in businesses¹.

A motor vehicle contains various types of flammable materials, including solid combustibles and automobile fluids such as engine oil, brake oil, hydraulic oil, and power steering oil. Although forensic scientists collect correct samples from a fire-damaged motor vehicle, interpreting the presence of ignitable liquids in those fire debris samples is challenging due to interfering products. Therefore, understanding which compound comes from what substrate and how they relate to each other is crucial for better

identification of what belongs to a possible ignitable liquid and what does not².

The most frequently used ignitable liquids to initiate fires in arson cases are gasoline, favored by arsonists due to its high flammability and availability. A comprehensive study was conducted, where out of 1040 individual items submitted for analysis, 17.6% were from motor vehicles. Of these motor vehicle sample items, 48.1% contained ignitable liquid residues. Gasoline was the most frequently detected ignitable liquid, accounting for 78.4% of positive results in motor vehicle samples³.

De Araujo et al. published a comprehensive review of portable analytical platforms for forensic chemistry, highlighting the use of portable Gas Chromatography-Mass Spectrometry (GC-MS) for analyzing Ignitable Liquid Residues⁴. Therefore GC is a well-known separation method used to resolve complex mixtures of volatile compounds in fire debris samples. Capillary columns are highly effective in characterizing trace-level volatiles isolated from fire debris when coupled with mass spectrometry. This technique provides the distribution and names of hydrocarbon components, allowing for library searches to characterize the column effluents. The resulting Total Ion Chromatograms can serve as a powerful tool to identify the types of fire accelerants².

A number of compounds in gasoline have been identified as target compounds in the GC analysis of fire debris samples. According to the ASTM E1618-14 standards, the molecules listed in Table 1 are the main target compounds for gasoline⁵. The compounds detected in the fire debris sample should be compared not only for their presence but also for their chromatographic pattern match.

Table 1: Gasoline target compounds

Gasoline peak number	Compound	Compound type
P1	n-propylbenzene	C3-alkylbenzene
P2	1-ethyl-3-methylbenzene	C3-alkylbenzene
P3	1-ethyl-4-methylbenzene	C3-alkylbenzene
P4	1,3,5-trimethylbenzene	C3-alkylbenzene
P5	1-ethyl-2-methylbenzene,	C3-alkylbenzene
P6	1,2,4-trimethylbenzene	C3-alkylbenzene
P7	1,2,3-trimethylbenzene	C3-alkylbenzene
P8	Indane	Aromatics
P9	1,2,4,5-tetramethylbenzene	C4-alkylbenzene
P10	1,2,3,5-tetramethylbenzene	C4-alkylbenzene
P11	Dodecane	Straight chain alkane
P12	2-methylnaphthalene	Polynuclear aromatic
P13	1-methylnaphthalene	Polynuclear aromatic

This research was conducted to identify traces of gasoline in fire debris, which included various types of automobile fluids. The study also aimed to investigate potential interferences in the analysis of gasoline in fire debris comprising different types of automobile fluids.

II. METHODOLOGY

A. Chemicals and Materials

Acetone - 99.9 % was purchased from Sisco Research Laboratories Pvt. Ltd., India. Activated Charcoal Strips was purchased from Arrowhead Forensics, USA. Freshly prepared metallic containers specially made for fire debris analysis was purchased from local market. GC glass vials (2 ml) was purchased from Agilent technologies, USA.

B. Instruments and Equipment

TX4 Digital Vortex Mixture with IR sensor was purchased from VelpScientifica, Italy. Oven, DK-600DT was purchased from Yihder Technology Co. Ltd., Taiwan.

The Agilent 7890B Gas Chromatograph, equipped with an HP-5MS column, a 5977A Mass Detector, a 7693 Autosampler, and Agilent ChemStation software, was purchased from Agilent Technologies, USA.

C. Automobile fluids, gasoline and wooden slips for test sampling

Engine oil, brake oil, hydraulic oil and power steering oil were purchased from local market.

Gasoline was obtained from the distributed center of the oil refining, Ceylon Petroleum Corporation, Sri Lanka.

Clean *Alstoniascholaris* wooden slips used as the substrate to make samples were prepared ourselves locally.

D. Preparations of test Automobile fluid samples

➤ Non- heated automobile fluid samples

Approximately 1 ml of each automobile fluid sample was poured into separate metallic containers, and activated charcoal strips were suspended using twine above the samples, following the initial step of passive headspace extraction with activated charcoal². The metallic containers

were then sealed with metallic lids to create an airtight environment.

➤ Partially burnt automobile fluid samples

Approximately 1 ml of each automobile fluid sample was poured into separate metallic containers containing 20 g of wooden slips. They were ignited with a flame and allowed to burn, consuming approximately half of their volume. The fire was extinguished by covering the containers with their metallic lids. Subsequently, the partially burnt remains were treated in a similar manner.

➤ Partially burnt automobile fluid samples after spiking with gasoline

Approximately 1 ml of each automobile fluid sample was poured into separate metallic containers with 20 g of wooden slips. Subsequently, these samples were spiked with 1 ml of gasoline and partially burnt and follows the procedure described above.

➤ Substrate sample

Approximately 20g of *Alstoniascholaris* wooden slips were placed into a metallic container and burnt it partially.

➤ Substrate sample spiking with gasoline

The substrate samples as mentioned above were spiked with 1ml of gasoline and partially burnt as described earlier. Next, for all those samples follow the next steps of heated passive headspace extraction technique as mentioned below. Firstly, metallic containers containing the samples were heated in the oven at 80°C for 8 hours to release the volatiles and allow them to adsorb onto activated charcoal strips. Afterward, the samples were removed from the oven and allowed to cool down to room temperature. Subsequently, the activated charcoal strips were carefully removed from the metallic containers and inserted into GC glass vials. The test samples were then extracted into acetone using a vortex mixture. Finally, these test samples were analyzed by GC-MS.

➤ GC-MS Analysis

Following method and the program mentioned in Table 2, were applied for the analysis of test samples and reference materials.

Table 2: GCMS program method

Gas	High purity (99.9995%) Helium
Injector temperature (°C)	250
Oven maximum temperature(°C)	300
Oven temperature program	Initial 40 °C, hold 2.0 min 1 st ramp 5 °C/min to 90 °C, hold for 0.0 min 2 nd ramp 14 °C/min to 250 °C, hold for 10.0 min
Carrier pressure(psi)	11.9
Total run time(min)	33.4
Flow rate(ml/min)	1.5
Injection volume and mode(µl)	1.0, split less
Ionization method	Electron impact ionization (EI) 70 eV
Scan mode	Sim/scan
Source temperature(°C)	230
Quadrupole temperature(°C)	150
Scanning mass range	30-550

III. RESULTS AND DISCUSSION

Gasoline is a mixture of aromatic compounds with less abundant aliphatic hydrocarbons. These chemicals are volatile and can potentially be separated using Gas Chromatography techniques, owing to their differences in boiling temperatures. The variations in chemical behaviors, influenced by differences in boiling points, result in characteristic fingerprints in GC analysis. Generally, these fingerprints cover a series of peaks in the chromatogram, representing various molecules. Consequently, these fingerprints are valuable for the qualitative analysis of fire debris in fire investigations.

Moreover, the fingerprint pattern may deviate due to matrices that burn along with the flammable liquid. One of the primary objectives of this research is to identify traces of gasoline residues in fire debris samples containing

automobile fluids using the unique characteristics or patterns of fingerprints in the GC chromatogram.

The nearly unchanging nature of gasoline over time and across different locations makes it chemically unique. The predictable and stable formulations result in easily identifiable gas chromatographic peak profiles, which can serve as an analytical tool in fire investigations.

In the identification of gasoline residues in fire debris samples containing automobile fluids, this study utilized the range of retention times over which peaks eluted in the fire debris samples spiked with gasoline.

Figure 1 displays the numbered target peaks in standard gasoline chromatograms, and the retention times of these target peaks are tabulated in Table 3.

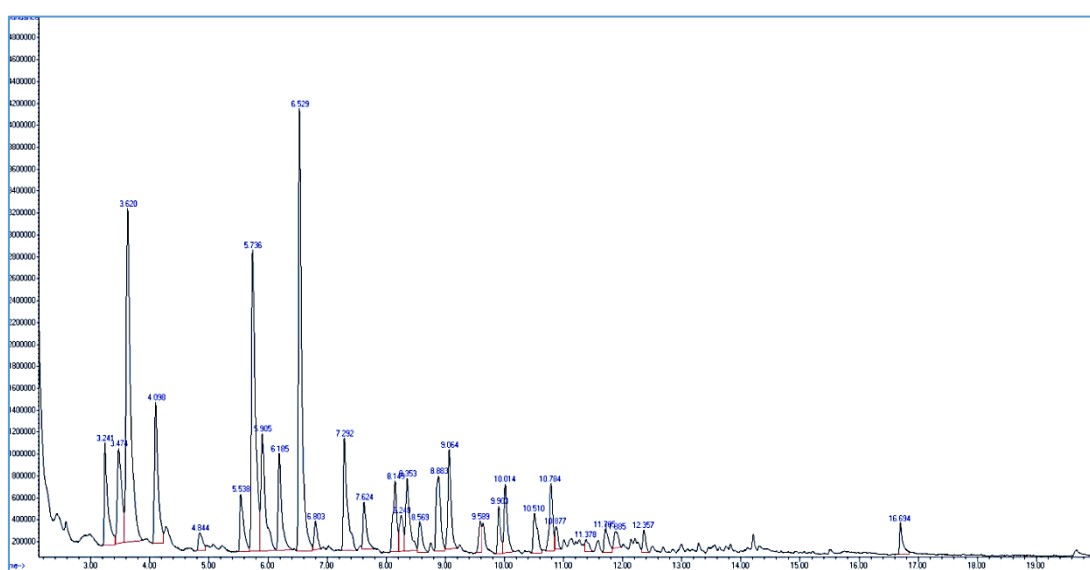


Fig. 1: Chromatogram of standard gasoline

Table 3: Retention times of the target peaks in the chromatogram of standard gasoline.

Target peak No.	Compound Name	Retention Time (min)
P1	n-propylbenzene	5.54
P2	1-ethyl-3-methylbenzene	5.74
P3	1-ethyl-4-methylbenzene	5.75
P4	1,3,5-trimethylbenzene	5.91
P5	1-ethyl-2-methylbenzene	6.19
P6	1,2,4-trimethylbenzene	6.53
P7	1,2,3-trimethylbenzene	7.29
P8	Indane	7.63
P9	1,2,4,5-tetramethylbenzene	9.90
P10	1,2,3,5-tetramethylbenzene	10.02
P11	Dodecane	12.36
P12	2-methylnaphthalene	14.11
P13	1-methylnaphthalene	14.31

The chromatograms of partially burnt automobile fluid samples, after spiking with gasoline, were compared with a specific standard for the purpose of identifying traces of

ignitable liquid residues. The chromatograms of the test samples are shown in Figures 2 to 5.

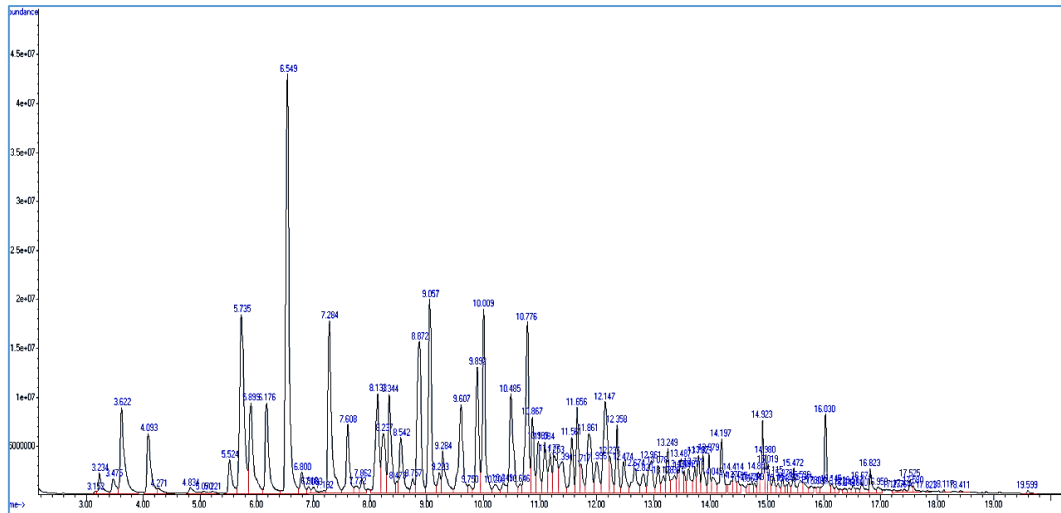


Fig. 2: Chromatogram of partially burnt engine oil (sample 1) spiked with gasoline

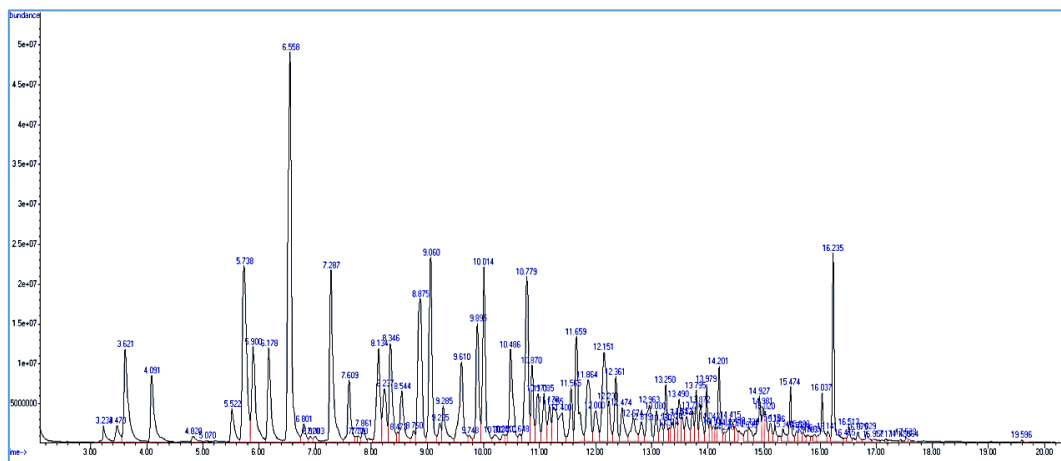


Fig. 3: Chromatogram of partially burnt break oil (sample 2) spiked with gasoline

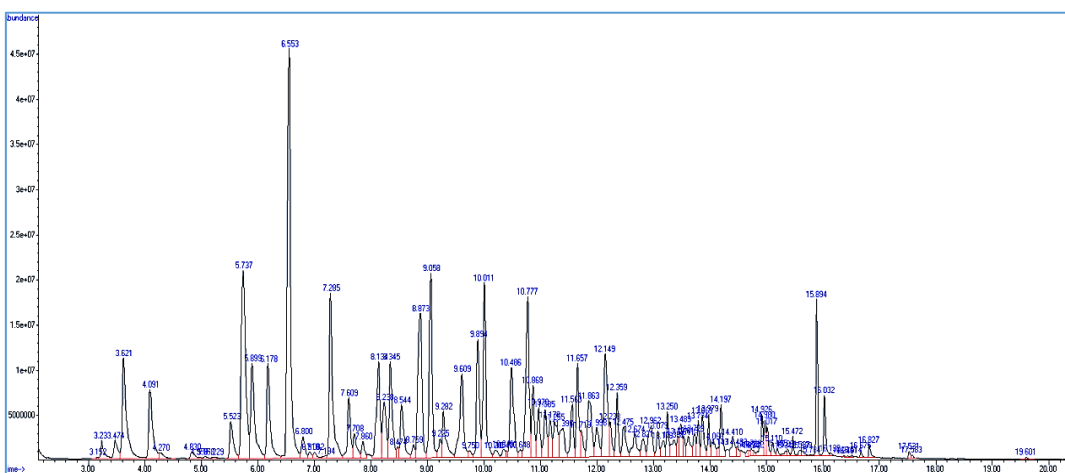
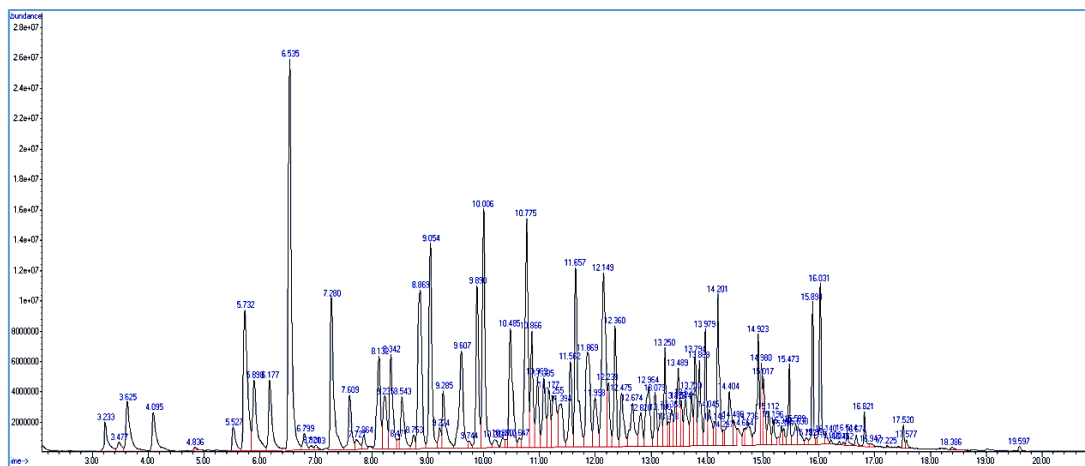


Fig. 4: Chromatogram of partially burnt hydraulic oil (sample 3) spiked with gasoline



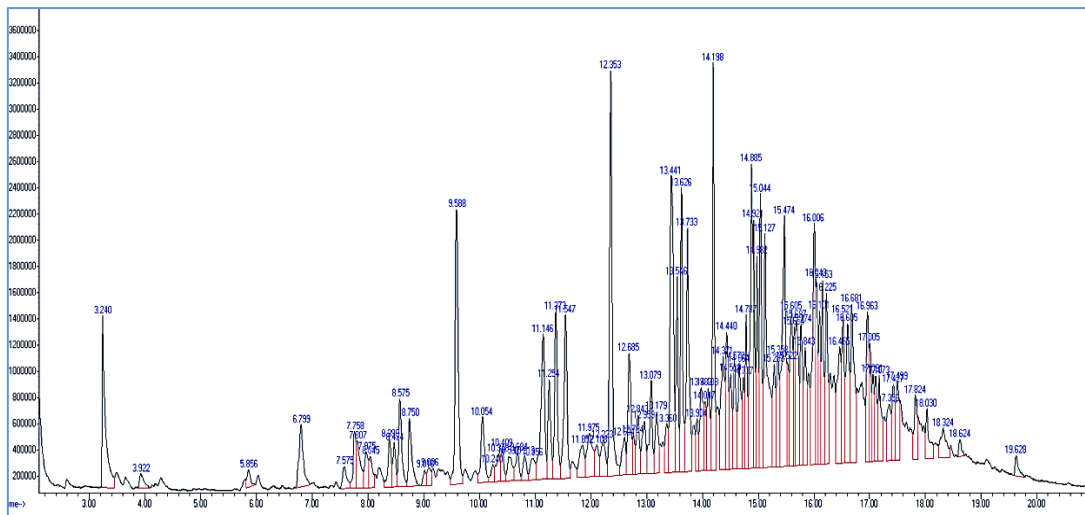


Fig. 6: Chromatogram of neat engine oil

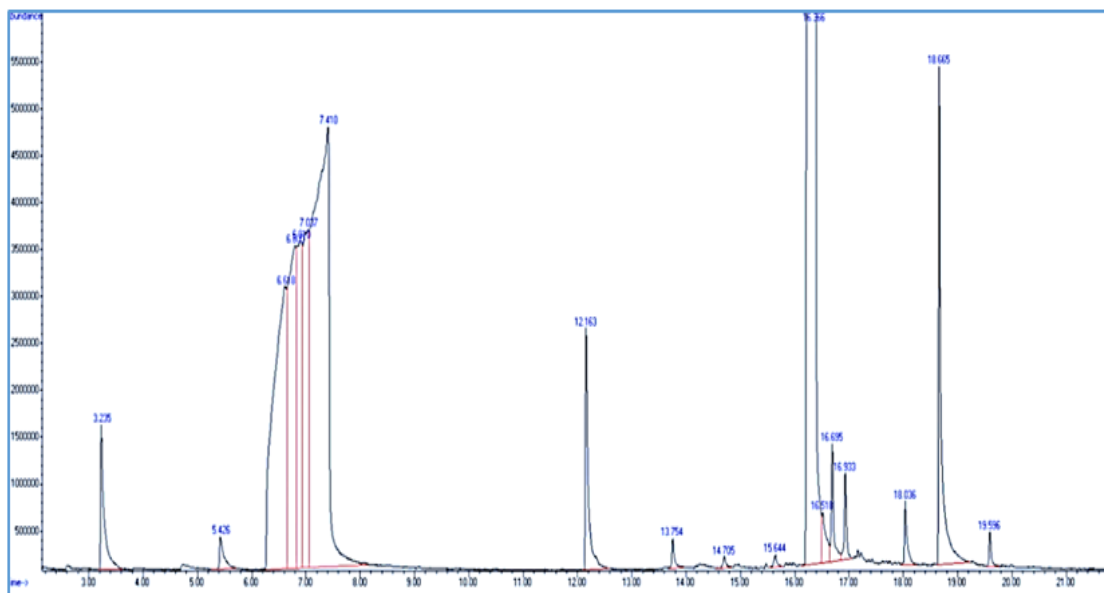


Fig. 7: Chromatogram of neat brake oil

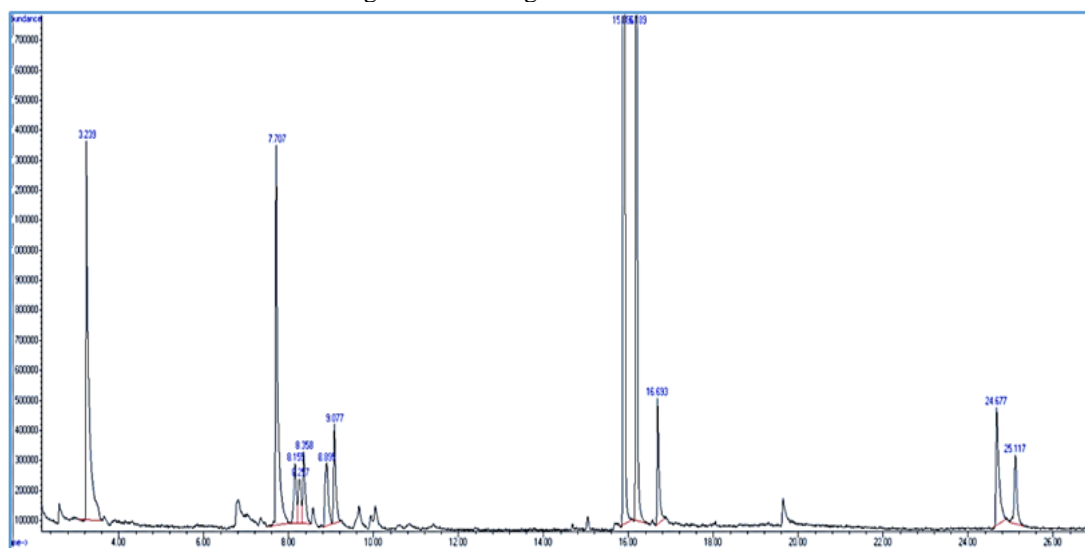


Fig. 8: Chromatogram of neat hydraulic oil

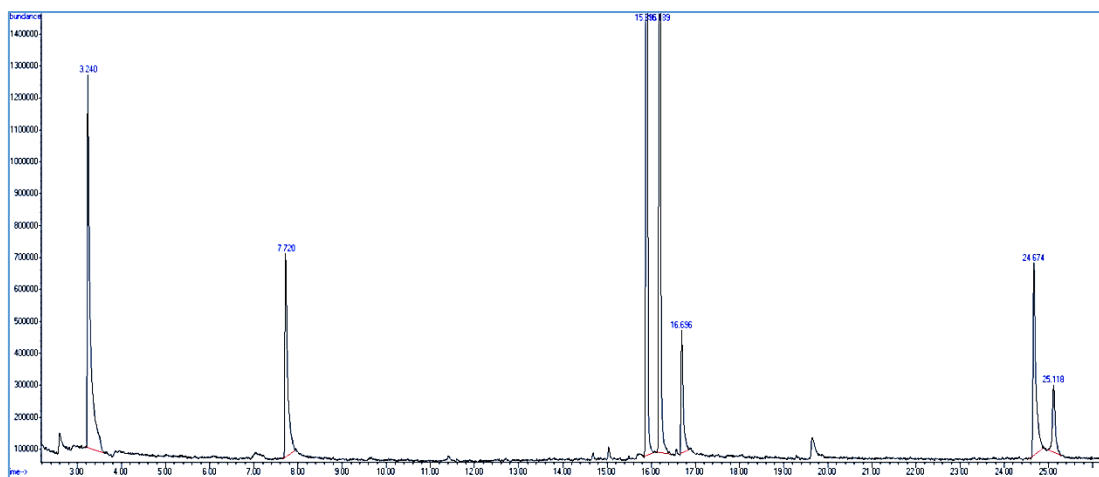


Fig. 9: Chromatogram of neat power steering oil

Table 5: Interfering compounds in the chromatograms of neat automobile fluids with gasoline target compounds.

Target Compound	Target peak No.	Retention time (min)			
		Engine oil	Brake oil	Hydraulic oil	Power steering oil
n-propylbenzene	P1	-	-	-	-
1-ethyl-3-methylbenzene	P2	-	-	-	-
1-ethyl-4-methylbenzene	P3	-	-	-	-
1,3,5-trimethylbenzene	P4	-	-	-	-
1-ethyl-2-methylbenzene	P5	-	-	-	-
1,2,4-trimethylbenzene	P6	-	-	-	-
1,2,3-trimethylbenzene	P7	-	-	-	-
Indane	P8	-	-	7.65	-
1,2,4,5-tetramethylbenzene	P9	-	-	-	-
1,2,3,5-tetramethylbenzene	P10	-	-	10.04	-
Dodecane	P11	12.35	-	-	-
2-methylnaphthalene	P12	-	-	-	-
1-methylnaphthalene	P13	-	-	-	-

According to the Table 5 indane, 1,2,3,5-tetramethylbenzene and dodecane were identified as interferences with gasoline target compounds. Brake oil and power steering oil did not contain any interferences.

Comparing these interfering compounds and considering their availability in the chromatograms, the identification of gasoline in samples containing engine oil and hydraulic oil was straightforward even though the mentioned interferences were present.

Table 6: Interfering compounds in the chromatograms of partially burnt automobile fluids with gasoline target compounds.

Target Compound	Target peak No.	Retention time (min)			
		Engine oil	Brake oil	Hydraulic oil	Power steering oil
n-propylbenzene	P1	-	-	-	-
1-ethyl-3-methylbenzene	P2	-	-	-	-
1-ethyl-4-methylbenzene	P3	-	-	-	-
1,3,5-trimethylbenzene	P4	-	-	-	-
1-ethyl-2-methylbenzene	P5	-	-	-	-
1,2,4-trimethylbenzene	P6	-	-	-	-
1,2,3-trimethylbenzene	P7	-	-	-	-
Indane	P8	-	-	-	-
1,2,4,5-tetramethylbenzene	P9	-	-	-	-
1,2,3,5-tetramethylbenzene	P10	-	-	-	-
Dodecane	P11	12.36	-	-	-
2-methylnaphthalene	P12	-	-	-	-
1-methylnaphthalene	P13	-	-	-	-

According to Table 6, no interfering compounds were identified in fire debris samples containing brake oil, hydraulic oil, and power steering oil. Only dodecane, straight chain alkane was identified in the partially burnt engine oil sample. Therefore, other compounds disappeared after burning and did not interfere with identifying traces of gasoline in fire debris.

When considering interferences due to substrate material, it can be divided into two main categories: substrate background products, present on any substrate prior to the fire, and combustion products formed during the

burning of the substrate⁶. Extracting and analyzing the volatile compounds from unburnt (fresh) substrate is the only way to determine the substrate background products⁶.

The GC-MS chromatogram obtained from the burned *Alstoniascholaris* wooden slips, which were used as the substrate material for this research, is shown in Figure 10. No substrate background products could be identified due to its natural nature. According to the chromatogram shown in Figure 11, it did not produce any interferences even though the substrate was subjected to pyrolysis.

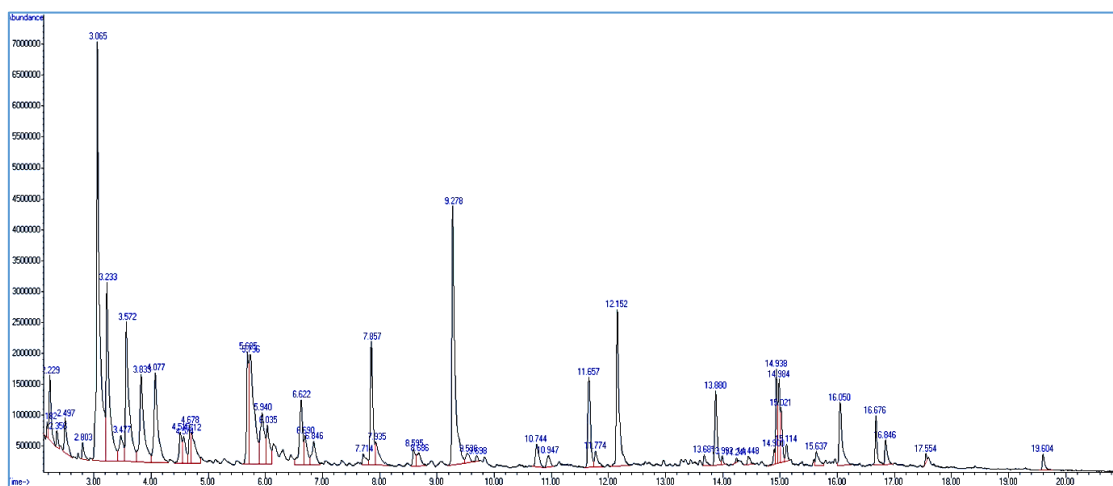


Fig. 10: Chromatogram of burnt neat wooden slips

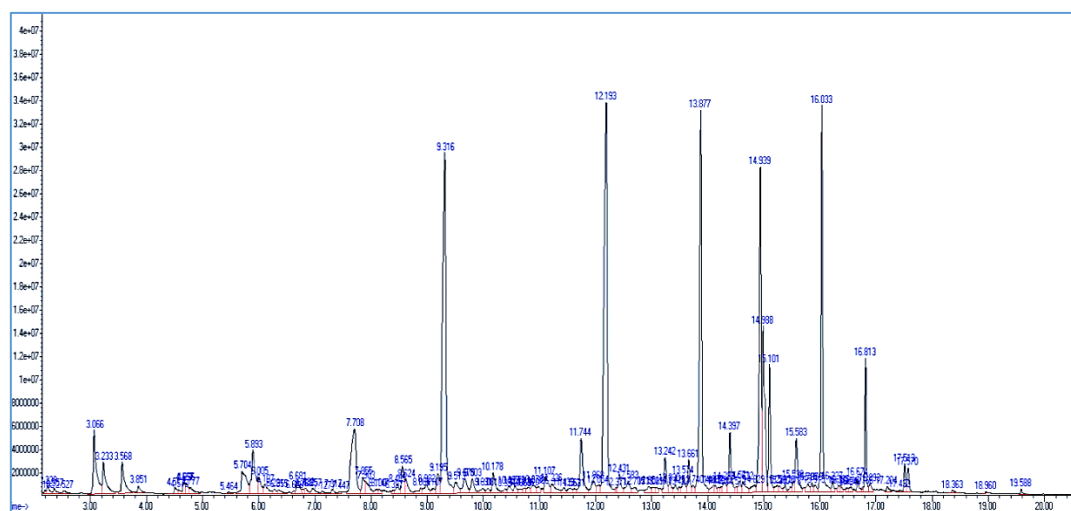


Fig. 11: Chromatogram of pyrolysis wooden slips

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