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Forensic examination of petrol for adulteration by GC-MS

Rudranarayan Behera[1], Amrita Dey[1],Dr. Spriha Sharma[1*]
Department of Forensic Science, Chandigarh University, Mohali, Punjab, 140413 ,India.

Abstract
The forensic examination of petrol for adulteration by gas chromatography-mass spectrometry (GC-MS) is a highly specialized analytical method that involves the use of advanced instrumentation to detect and identify various compounds that may be present in gasoline. The primary aim of this analytical technique is to determine the purity of the petrol, detect any adulterants, and provide evidence that can be used in legal proceedings. In this study, petrol samples collected from different states were analysed using GC-MS to identify the presence of adulterants. The chromatographic separation of the components in the petrol samples was achieved using a fused silica capillary column. The mass spectrometry analysis provided information on the identity and quantity of the compounds present in the samples. The results of the analysis were compared to the standard petrol sample, and showed that some of the petrol samples were adulterated with kerosene and diesel. The abstract demonstrates the utility of GC-MS in forensic analysis of petrol adulteration and its potential applications in forensic investigations.

Keywords: Gas chromatography, Adulteration, petrol

1. Introduction

A petroleum derived volatile, flammable combination of hydrocarbons (such as hexane, heptane, and octane), mostly used as fuel in internal combustion engines is known as petrol. India is using more and more petroleum products as a result of population increase, urbanisation, and lifestyle changes. The price of the product rises along with the demand. Fuel sellers intentionally adulterate their product in order to maximise profits while ignoring the harm it does to human life and to vehicles. For example, kerosene that has been adulterated with petrol may be extremely dangerous since it may be highly flammable [1].

Due to their comparable physical and chemical qualities, kerosene and naphthalene (distillates of naphtha) are frequently added to petrol and diesel to adulterate it. It can be difficult to tell the difference between fuel and adulterants. Naphtha, Benzene, Toluene, Pentane, Hexane, SBP spirits, MTO, OCS 73, OCS 75, REMAX, SLOP OIL, C6 -C9 raffinates, Resolve 77, Kerosene, Rexon, Pyrolysis Gasoline, etc. are examples of frequent adulterants specially for petrol [2].

Although fuel adulteration is an attempt to lower the price by adding less expensive solvents by the beneficiary, the end effect is air pollution. The Indian government established the Bharat Stage Emission Standards to control air pollution from internal combustion engine equipment, including motor vehicles. The "Central Pollution Control Board," which is part of the "Ministry of Environment & Forests and climate change," establishes the requirements and the schedule for execution. The requirements are listed in Table 1 [3].

Table 1: Bharat Stage Emission Standards for petrol

Sl..no	Characteristics	Units	Requirements	
			Minimum	Maximum
1	Colour, Visual			Orange
2	Density at 15°C	Kg/m3	750	
3	Distillation (Recovery up to 70°C)	%by vol.	10	45
4	Research Octane Number		91	
5	Motor Octane number		81	
6	Existent gum	g/m3		40

7	Sulphur, total	Mg/m3	50
8	Lead content	g/l	0.005
9	Benzene content	% by vol.	1
10	Benzene content	% by vol.	1
11	Aromatic content	% by vol.	35
12	Oxygen content	% by mass	2.7

1.1. Forensic significance of examination of petrol for adulteration

Firstly, adulterating petrol is a crime in many nations, and forensic testing can provide proof in court that a specific batch of petrol has been altered. Second, altering with petrol can have detrimental effects on the efficiency and longevity of engines that utilize it. The presence of such adulterants can be detected through forensic analysis, which can also provide information that can be used to stop such instances from happening in the future. Thirdly, adulteration sources can be found via forensic analysis, which can help with investigations and the conviction of individuals involved. Overall, testing petrol for adulteration using forensic methods is crucial for protecting public safety, the integrity of the petroleum sector, and the ability to prosecute crimes.

1.2. Legal viewpoint

According to Section 3 of the Essential Commodities Act, adulteration is the illegal inclusion of any foreign element into motor petrol. This is stated by "THE MOTOR SPIRIT AND HIGH SPEED DIESEL" ORDER 1993.The Essential Commodities Act, section 420 of the IPC, and the Petroleum Act of 1934 all have penalties for adulteration related offences. Under Schedule III of Clause 8(5) of the EC Act 1955, all Central, State, and Regional Forensic Science Laboratories are allowed to test Petrol Samples [4].

1.3. Various Indian Petroleum Guidelines:

The IS 2796/2000 Indian Standard Specification for Motor Petrol confirmed in 1991 is used to test numerous technical characteristics in accordance with quality control and assurance. Adulteration in petrol is identified in several laboratories by examining the physical features of the fuel, including its colour and density, as well as its distillation, Research Octane Number, sulphur, lead, benzene, olefin, aromatic content, etc. In this study, a chromatographic method called gas chromatography is utilised to detect the adulteration [5].

2. Materials and methods

1.1. Samples

A representative set of 6 samples obtained from 6 different states and their conditions are given below in table 2. For each sample of petrol, one Chromatogram was acquired, therefore a total of 6 Chromatograms were recorded.

1.2. Instrumental method

A TRACE 1300 Gas chromatography (GC) with Xcalibur software is used for this study. This device is made up of three fundamental components: an injector, a column, and a detector. Three pressure gauges are present to regulate the flow of carrier gas, igniting gas, and supporting gas. The temperature of the column is maintained using an oven. The methods used for this study are mentioned in table 2.

Table 2: Condition of petrol samples before analysis.

Sample ID	Data file	States	Run time (min)	Injection volume(µl)	Scans	Low mass(m/z)	High mass(m/z)	Instrument Method
1	petrol_01	Odisha	22.09	1.00	6495	50	650	C:\Users\TSQ\Desktop\GCMS2023\testls_us_sn30
2	petrol_02	Punjab	22.11	1.00	6500	50	650	C:\Users\TSQ\Desktop\GCMS2023\testls_us_sn30
3	petrol_03	Chandigarh	22.10	1.00	6499	50	650	C:\Users\TSQ\Des

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								ktop\GCMS2023\testls_us_sn30.meth
4	petrol_04	Himachal Pradesh	22.10	1.00	6497	50	650	C:\Users\TSQ\Desktop\GCMS2023\testls_us_sn30.meth
5	Petrol_05	Haryana	21.09	1.00	6202	50	650	C:\Users\TSQ\Desktop\GCMS2023\testls_us_sn30
6	Petrol_06	Delhi	21.10	1.00	6204	50	650	C:\Users\TSQ\Desktop\GCMS2023\testls_us_sn30

2. Results and discussion

For this work Petrol samples from different states are taken. Then they are injected into the GC column one by one and the chromatograms (Fig. 1 – Fig. 6) are obtained. From the Chromatogram for Petrol sample from Odisha (Fig. 1) it is observed that peak height is maximum in RT 4.88 and minimum in RT 3.41 and Benzene is the main compound. From the chromatogram for Petrol sample from Punjab (Fig. 2) in which maximum peak height in RT 3.54 and minimum in RT 4.54 and Benzene is the main compound. The results obtained for the Chromatogram for Petrol sample from Chandigarh (Fig.3) in which maximum peak height is in RT 3.64 and minimum in RT 3.07 and Benzene is the main compound. The results obtained for the Chromatogram for Petrol sample from Himachal Pradesh (Fig.4) in which maximum peak height in RT 3.58 and minimum in RT 4.20 and Benzene is the main compound. There are no adulterant compounds found in the above sample. The results obtained from the Chromatogram for Petrol sample from Haryana (Fig.5) in which maximum peak height is in RT 18.60 and minimum in RT 6.14 and Tetrapentacontane is the main compound that is found in maximum peaks that means kerosene is mixed in the above sample. From the results obtained for the Chromatogram for Petrol sample from Delhi (Fig.6) in which maximum peak height in RT 18.58 and minimum in RT 6.49 and Tetrapentacontane, Benzene, pentatriacontane are the main compounds that were found in maximum peaks. That means kerosene is mixed in the above sample. After analysing the chromatograms, it was found that the chromatograms of sample number 5 and 6 are different from sample number 1-4. Sample 5,6 that have been collected from Haryana and Delhi state contain kerosene compounds i.e. Tetrapentacontane, pentatriacontane compound. The petrol sample collected from Himachal Pradesh is the purest petrol sample because it doesn't contain any adulterated compounds. From table 3 it has been stated that Benzene is the common compound in every sample. The common compounds and the sample specific compounds are given in table 3.

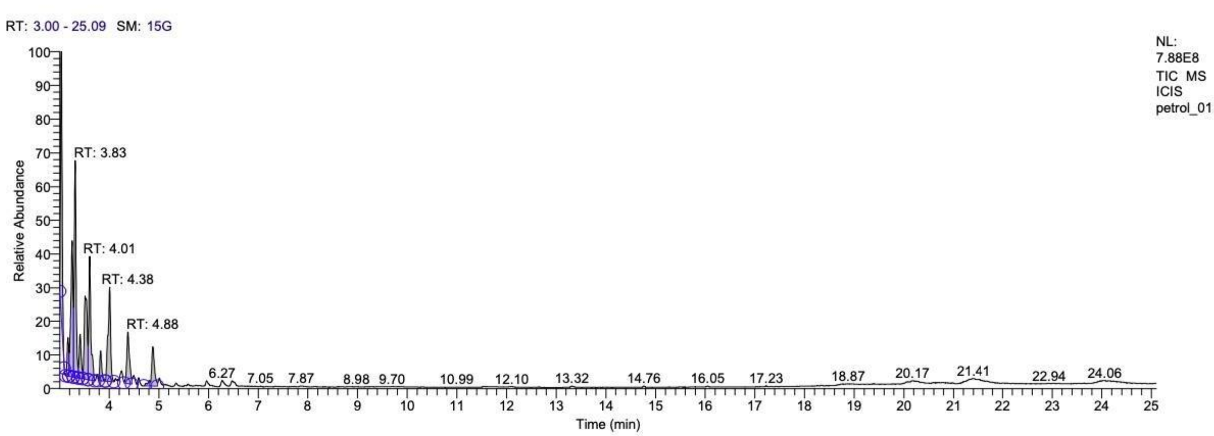

Fig 1: Chromatogram of petrol sample from Odisha

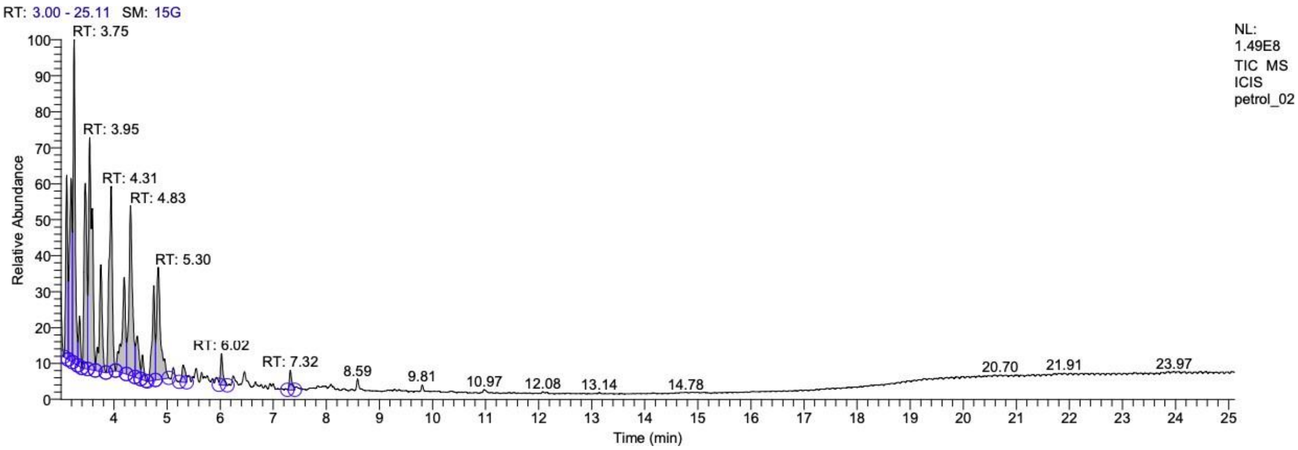

Fig 2: Chromatogram of petrol sample from Punjab State

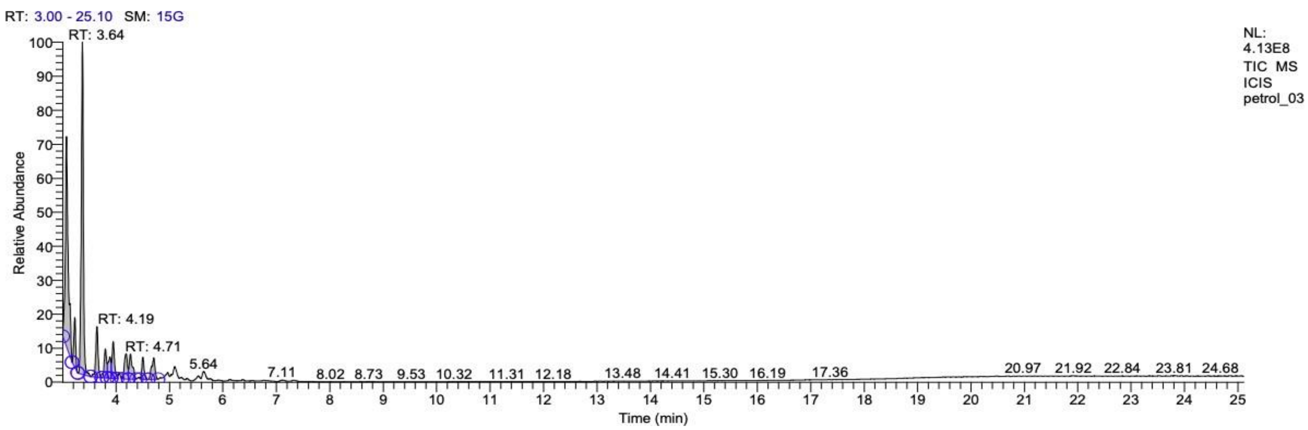

Fig 3: Chromatogram of petrol sample from Chandigarh state

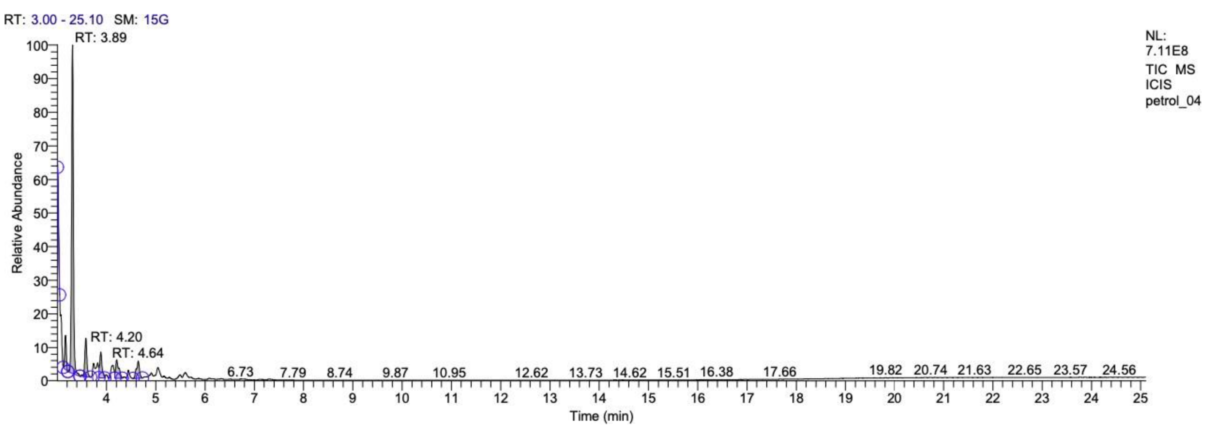

Figure 4: Chromatogram of petrol sample from Himachal Pradesh state

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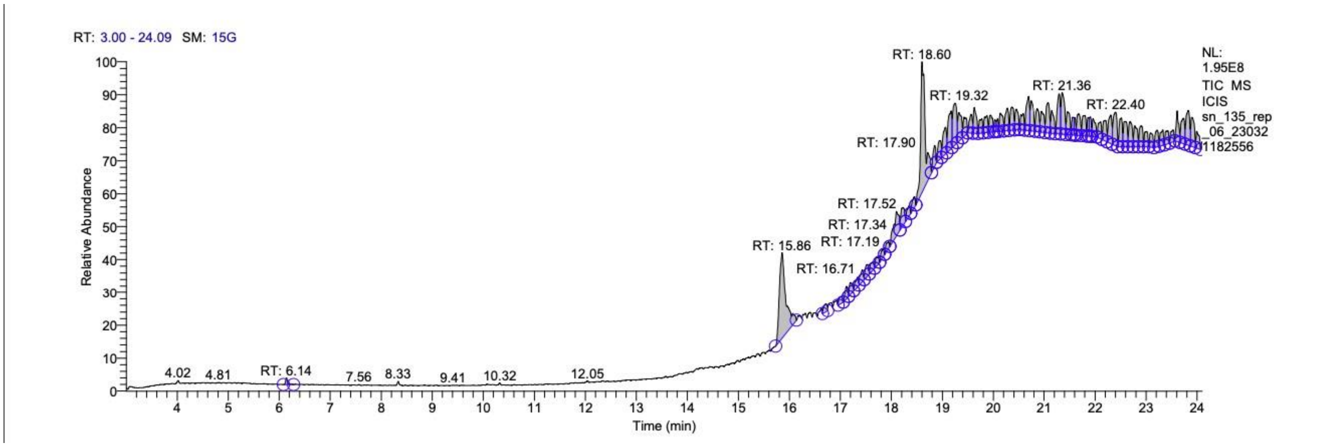

Figure 5: Chromatogram of petrol sample from Haryana State

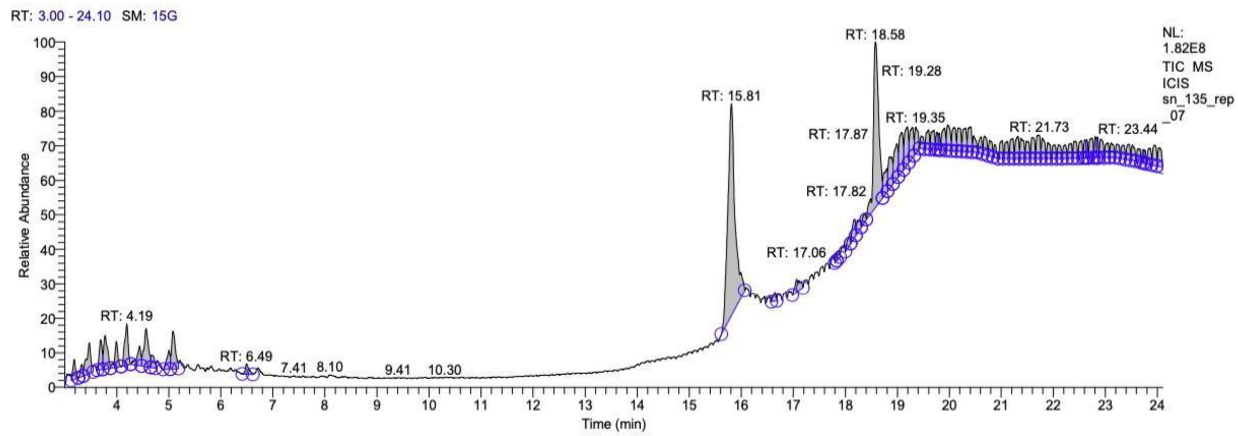

Figure 6: Chromatogram of petrol sample from Delhi State

Table 3. The common and sample specific compounds from different petrol samples.

State	Sample specific compounds	Common compounds
Odisha	Deltacyclene Bicyclo [4.2.0]octa-1,3,5-triene,7- methyl Tetracyclo [3.3.1.0(2,8).0(4,6)]-no n-2-ene Benzene, 1-methyl-3-propyl Benzene, (1-methylpropyl)- Benzene, (1-methylpropyl)- Benzene, 1-methyl-3-(1- methyl ethyl) 5,5-Dimethyltricyclo [6.2.1. 0(1,6)] undec-6-ene-9,9,10,10- tetra carbonitrile 1H-Indene, 1-methylene	Benzene, 1,4-diethyl Benzene,2-ethyl-1,4-dimethyl o-Cymene Benzene,1,2,4,5-tetramethyl Benzene, 1,4-diethyl Benzene, 1,3-diethyl Benzene,2-ethyl-1,4-dimethyl Benzene,1-ethyl-2,4-dimethyl Benzene,1-ethyl-2,3-dimethyl Benzene,4-ethyl-1,2-dimethyl Benzene,2-ethyl-1,4-dimethyl
Punjab	Bicyclo[4.2.0]octa-1,3,5-triene,7-methyl (Z)-1-Phenylpropene Benzene, (1-methylpropyl) 2-Tolyloxirane Benzene, 4-ethyl-1,2-dimethyl Benzene,1-methyl-3-(1-methylethyl)-Exo-tricyclo [5.2.1.0(2.6)]decane Endo-tricyclo[5.2.1.0(2.6)]decane	Benzene,1-ethyl-2,4-dimethyl Benzene,1,2,3,4-tetramethyl

	Tricyclo[4.4.0.0(3,9)]decane Benzene, 1-methyl-3-(1-methylethyl) Benzene,1-methyl-4-(2-propenyl)-3-Phenylbut-1-ene Benzene, 1-methyl-4-(2-propenyl)- Benzene, 1-methyl-2-(2-propenyl)- Benzene, 1-ethyl-4-(1-methylethyl)- Benzene,(1,1-dimethylpropyl)-2,4,4,6-Tetramethyl-6-phenyl-1-heptene 1H-Indene,1-ethyl-2,3-dihydro-1-methyl- Benzene,1-methyl-3-(1-methyl-2-propenyl) Benzene,(1,1-dimethyl-2-propenyl)- Benzene,1-methyl-4-(1-methyl-2-propenyl) 1H-Indene, 2,3-dihydro-4,7-dimethyl Pentadecane Tetradecane Tridecane Dodecane Pentadecane, 7-methyl- Nonane, 2-methyl-5-propyl- Dodecane, 2,5-dimethyl-
Chandigarh	Deltacyclene Benzene, (1-methylpropyl) Benzene,2-ethyl-1,4-dimethyl-2,6-Dimethyl-1,3,5,7-octatetraene,E,E-Endo-tricyclo[5.2.1.0(2.6)]decane Exo-tricyclo[5.2.1.0(2.6)]decane 1,2,3,4,4a,5,6,8a-Octahydro-naphthalene
Himachal Pradesh	N/A
Haryana	Cyclohexasiloxane, dodecamethyl- Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl-Silane,dimethyl(dimethyl(dimethyl(2-isopropylphenoxy)silyloxy)silyloxy)(2-isopropylphen)-3,3,5-Triethoxy-1,1,1,7,7,7-hexamethyl-5-(trimethyl silyloxy)tetrasiloxane Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecameth yl 9,12-Octadecadienoic acid (Z,Z)- 9-Octadecene,1,1'-[1,2-ethanediylbis(oxy)]bis-,(Z,Z)- 9,12,15-Octadecatrienoicacid, 2,3-dihydroxypropyl ester, (Z,Z,Z) Cyclopropane Octanoic Acid,2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]meth Yl]-,methylester Butyl 9,12,15-octadecatrienoate
Delhi	Bicyclo[4.3.0]nonane, 2-methylene-, cis- 1-Phenyl-1-butene Bicyclo[4.2.0]octa-1,3,5-triene, 2,4-dimethyl-2-Isopropylbenzaldehyde Benzene, 1-methyl-3-(1-methyl-2-propenyl Benzene,1-methyl-4-(1-methyl-2-propenyl)-5,5-Dimethyltricyclo[6.2.1.0(1,6)]undec-6-ene-9,9,1 0,10-

tetracarbonitrile Naphthalene, 2-methyl- Naphthalene, 1-methyl- Benzocycloheptatriene 1H-Indene, 1-ethylidene- 9,12-Octadecadienoic acid (Z,Z)-12-Methyl-E,E-2,13-octadecadien-1-ol Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester Hexadecanoicacid,1-[[[(2-aminoethoxy)hydroxyphosphinyl]oxy]methy l]-1,2-ethanediyl ester Docosanoic anhydride 15-Hydroxypentadecanoic acid 9-Octadecene, 1,1'-[1,2-ethanediylbis(oxy)]bis-, (Z,Z)-

3. Conclusion

The forensic examination of petrol for adulteration by GC-MS is an effective method for determining whether or not a fuel sample has been tampered with. GC-MS stands for Gas Chromatography-Mass Spectrometry, and it is a powerful analytical technique that allows for the separation, identification, and quantification of different compounds present in a sample. The analysis involves the extraction of hydrocarbons from the petrol sample, followed by separation using a gas chromatograph and detection by mass spectrometry. By comparing the chromatographic profiles and mass spectra of the sample to those of known standards, it is possible to determine whether or not the petrol has been adulterated with other compounds. The results of the GC-MS analysis can provide valuable information for law enforcement agencies, fuel industry regulators, and other stakeholders in the petroleum industry. They can help to identify fraudulent activities and protect consumers from substandard and potentially harmful fuels. In conclusion, the forensic examination of petrol for adulteration by GC-MS is a reliable and effective method for detecting fuel adulteration. Its accuracy and precision make it an essential tool for ensuring the quality and safety of petroleum products.

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