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CHARACTERISTICS OF PETROLEUM FUELS AND DETERMINATION OF (POSSIBLE) ADULTERANTS IN PETROL/GASOLINE BY USING GAS CHROMATOGRAPHY[1, 2] (PETROCOL COLUMN[3])

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ABSTRACT

This study explains a few aspects about the characteristics of the fuels like Motor gasoline, diesel and kerosene. Adulteration in the motor gasoline has been analyzed and methods to find the adulterants is explained here. Adulteration in the motor gasoline can be find out using "Gas Chromatography". This study also explains the role of the solvents as the adulterants.

Key words: Motor Gasoline, Gas Chromatography, Solvents, adulteration, Flame ionization detector, Suitable boiling point solvents, Retention time, Area %.

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Introduction

Petroleum is one of the most important liquid fuels in the world. Present say material civilization would have been impossible without it. Gasoline, Petrol and Diesel, the main product obtained from a naturally occurring crude oil, called petroleum, supply power to automobiles. The crude is otherwise called rock oil or mineral oil. It is highly colored viscous liquid and occurs below the surface of the earth below strata of shale, limestone and clay at a depth of 500-1500 ft at various places. It is generally present with water and the natural gas forms a middle layer. The biggest oil producing country of the world is U.S.A., which produces more than 60% of the total world output.

Origin

Opinions are divided regarding the formation of petroleum. Any theory put forward to explain the origin of petroleum must explain the following important properties associated with the petroleum.

i) The presence of chlorophyll, haemin and resins.

ii) The presence of nitrogen and sulphur compounds.

iii) The optical activity.

iv) Its association with sodium chloride (brine)

A theory called inorganic origin put forward by Mendeleeff (1876) had failed due to the insufficient explanations about the optically active compounds. Engler's Organic origin was unable to explain the presence of the chlorophyll.

According to the modern views, natural petroleum is formed due to the decomposition of animal as well as vegetable matter. At some places, the petroleum is of animal origin and other places, it is of vegetable origin. This theory readily accounts for the presence of chlorophyll and occurrence of coal deposits in the neighborhood of oil deposits. It also accounts for the presence of high percentage of resins in oils.

Composition of Petroleum

The composition of petroleum varies from place to place and crude petroleum is made up of hundreds of different individual chemicals, from methane to asphalt.

In general, most of the constituents are straight chain paraffins and aromatic hydrocarbons e.g. benzene, toluene etc. The ultimate analysis of petroleum indicates that in addition to hydrocarbons (83-87% of carbon and 11-15% of hydrogen) small quantities of nitrogen, sulphur, and oxygen are also present in it. Sulphur is present generally as alkylsulphides, hydrosulphides, hydrogen sulphide and thiophine and less frequently, combined oxygen is present as carboxylic acids (naphthalenic acids), ketones and phenols. The disagreeable odour of petroleum is due to the sulphur compounds present in it. The hydrocarbon present in the crude petroleum may be divided into two main classes.

Open chain or aliphatic compounds: n-paraffins series (C_nH_{2n-2}), isoparaffin series (C_nH_{2n+2}) and olefin series (C_nH_{2n}).

Ring Compounds: Naphthalene series (C_nH_{2n}) and aromatic series or benzene series.

In petroleum gaseous paraffins (hydrocarbons) from CH_4 to C_4H_{10} are present in dissolved state. The naphthenic hydrocarbons present in petroleum are mainly the derivatives of cyclopentane and cyclohexane.

Petroleum Fractions

S.No.	Petroleum Fraction	Boiling Range °C	Approximate no. of Carbon atoms
1	Petroleum Ether	30-70	C_5-C_7
2	Gasoline	40-140	C_5-C_9
3	Naphtha	140-180	C_9-C_{10}
4	Kerosene	180-250	C_{10}-C_{16}
5	Diesel	250-320	C_{10}-C_{18}

Characteristics of Fuels

Petrol

The petrol/gasoline has the boiling point range between 40 and 1400C. The density of the petrol may lie between 710-770 kg/m^3. The distillation[5]* range starts and ends within this range, but sometimes the final boiling point may rise due to the presence of the (light) naphtha. The octane number[6] is 88 for ordinary petrol and 93 for the premium petrol. The sulphur, benzene,[7] gum content, antiknocking[8] property and all the requirements are given below.

S.No.	Tests	Method No.	Requirement
1	Colour visual	IS 1448 (P: 16)	Orange
2	Density at 15°c kg/m^3		710 – 770
3	**Distillation:** a) Recovery up to 70°c (E70), % by Vol.	IS 1448 (P: 18)	10 - 45
	b) Recovery up to 100°c (E100), % by Vol.		40 – 70
	c) Recovery up to 180°c (E180), % by Vol.		90 Min
	d) Final Boiling Point (FBP) °c		215 Max
	e) Residue, % by Vol.		2 Max
4	Research Octane Number (RON)	IS 1448 (P: 26)	88 Min
5	Anti-Knock Index (AKI)	IS1448 (P: 26) & IS1448 (P: 27)	84 Min
6	Existent gum, g /m^3	IS 1448 (P: 29) Air jet solvent washed	40 Max
7	Potential gum, g/m^3	IS 1448 (P: 147)	50 Max
8	Sulphur, total, % by mass	IS 1448 (P: 34)	0.10 Max
9	Lead content (as Pb), g/l	ASTM D5059 or IP 352	0.013 Max

10	Reid Vapour Pressure (RVP), Kpa	IS 1448 (P: 39)	35–60
11	Vapour Lock Index, (VLI=10RVP+7E70)		950 Max
12	Benzene content, % by volume	ASTM D3606	3.0 Max
13	Copper strip corrosion for 3 hr at 50° C	IS 1448 (P: 15)	Not worse than number 1

Diesel

The Diesel is an important fuel for our day-to-day life. Its density is 810 to 870 kg/m^3. The distillation range starts from 150°C and ends around 380°C. This may be due to the presence of some amount of kerosene and some heavy oils. The flashpoint[9] is an important property to the diesel for the storage purpose; it should be greater than 35°C. It is found out by using Abel flashpoint apparatus. Flash point[10] 66°C is applicable for Naval applications only for high flash HSD including Merchant Navy and fishing vessels of 12 m in length. Pensky Marten's apparatus can determine it. The pour point[11] is a vital experiment to find the cease point of the fuel especially in the hilly places. The kinematic viscosity[12] is also a significant test for this fuel to test the quality of the diesel. It should be 2.0-5.0 CST. The cetane index is also important factor in the diesel. The percentage of carbon can be found out by the Rams bottom method, the carbon residue should be 0.30% by mass, and the acidity, ash limitations are given below.

S.No.	Tests	Method No.	Requirement
1	Acidity, inorganic	IS 1448 (P: 2)	Nil
2	Acidity, Total, mg of KOH/g	IS 1448 (P: 2)	0.20 Max
3	Ash, % by mass	IS 1448 (P: 4)	0.01 Max
4	Carbon residue (Rams bottom) on 10% Residue % by mass	IS 1448 (P:8)	0.30 Max
5	Cetane Index	ASTM D 4737	46 Min
6	Pour Point, °c	IS 1448 (P: 10)	15 Max
7	Copper strip corrosion for 3 h at 100 deg. c	IS 1448 (P: 15)	Not worse than No.1

8	Distillation, % v/v, recovered	IS 1448 (P: 18)	
	a) At 350°c b) At 370°c		85 Min 95 Min
9	Flash Point, Abel, °c	IS 1448 (P: 20)	35 Min
10	Kinematic viscosity at 40°c, cSt	IS 1448 (P: 25)	2.0 – 5.0
11	Sediment, % by mass	IS 1448 (P: 30)	0.05 Max
12	Density at 15°c, kg/m³	IS 1448 (P: 16) or (P: 32)	820 – 860
13	Total sulphur, percentage by mass	IP 336 or IS 1448 (P: 33)	0.25 Max
14	Water content, % by volume	IS 1448 (P: 40)	0.05 Max
15	Cold filter plugging point (CFPP), °c	IS 1448 (P: 110)	18 Max
16	Total sediments, mg/100 ml	ASTM D2274	1.5 Max

Kerosene

The kerosene's distillation range starts from the 150°C to 250°C. To avoid the adulteration of diesel using kerosene the dye is added with the colorless kerosene. The flash point of the kerosene may be greater than 35°C.

S.No.	Tests	Method No.	Requirement
1	Colour Say bolt	IS 1448 (P: 14)	Plus 10, Min
2	**Distillation** a) Percent recovered below 200°c b) Final boiling point °c	IS 1448 (P: 18)	20 Min300
3	Flash point, Abel, °c	IS 1448 (P: 20)	35 Min
4	Smoke point, mm	IS 1448 (P: 31)	18 Min

5	**Burning Quality** a) Char value, mg/kg of oil consumed b) Bloom on chimney, predominating colour c) Bloom on chimney, general appearance	IS 1448 (P: 5)	20 Max Not darker than gray Normal
6	Acidity, inorganic, KOH/gm	IS 1448 (P: 2)	Nil
7	Sulphur, total, % by mass	IS 1448 (P: 34)	0.25 Max
8	Copper strip corrosion for 3 hrs at 100°c	IS 1448 (P: 15)	Not worse than No.1
9	Density at 15°c, g/ml	IS 1448 (P: 16)	Report

The distillation procedure for petrol, diesel and kerosene, and the testing condition is different in each case. For petrol the distillation flask is cooled, the bath temperature is maintained at 0 to 4°C and the collecting jar temperature is maintained at 10-15°C. The tiles, which is used to fix the distillation flask, has 38mm diameter hole. In the case of kerosene the bath temperature is kept as ambient and the collecting jar is also maintained at ambient temperature. For diesel the bath temperature is increased and maintained at about 40-60°C and the collecting jar is at room/ ambient temperature.

Important Criteria of Fuel

Knocking is a "sharp metallic sound similar to ratting of hammer, which is produced in the internal combustion engine owing to immature ignition of the air gasoline mixture". Knocking tendency of paraffins increases with the increase in the length of the carbon chain. Branched chain paraffins have lower tendency to knock and so have higher octane numbers. The aromatic hydrocarbons have less knocking tendency than Naphthenes. Straight run gasoline has higher knocking properties. Knocking property is expressed as octane number or octane rating. Normally to increase the antiknocking property the oil companies add some compounds called antiknock compounds like Tetra Ethyl Lead (TEL). Usually a mixture called ethyl fluid (tetra ethyl lead 63%, ethylene bromide 26%, ethylene dichloride 9%, and a dye called methylene blue 2%) 1-3cc. of this mixture is added to one gallon of gasoline. Now Tetra Methyl Lead (TML) has been found better than TEL, new compound cyclopentadienyl manganese carbonyl is used, to avoid lead pollution.

Octane Number: "The percentage of iso-octane in a mixture of iso-octane and n-heptane that has the same knocking characteristics of the fuel under examination in a standard one cylinder engine operated under conditions. The higher the octane number of the fuel, the highest is its antiknocking property." For example, the fuel with octane number 60 would give the same knocking as a mixture by volume of 60%, iso-octane and 40% n-heptane. In other words, the gasoline having an octane number of 60, behaves like a mixture of 60% iso-octane and 40% n-heptane. Octane number decreases with increase in chain length. The hydrocarbon tripentane (2, 2, 3-trimethyl butane) is superior to iso-octane, because its octane number 124. Therefore, gasoline obtained by cracking has higher octane number because it contains higher percentage of alkenes. Thus octane number is related to molecular mass and structure. For example, octane numbers of propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane and n-nonane are 100, 92, 61, 25, 0, -27 and -45 respectively. Similarly octane numbers of n-heptane, 2-methyl hexane, 2, 3-dimethyl pentane and 2, 2, 3-trimethyl butane are 0, 45, 93 and 116 respectively.

Adulteration Possibilities

The government of India gives some specifications for the fuels like gasoline, diesel and kerosene etc. through the Bureau of Indian Standards (BIS). The adulteration in petrol due to the mixing of kerosene was found out by the Furfural test (using furfuraldehyde). Normally oil companies add furan-2-aldehyde in kerosene to avoid the adulteration of petrol. When petrol samples are tested with Furfural test (i.e., aniline acetate is added to petrol the presence of the red color shows the adulteration of kerosene in petrol). But sometimes the oil companies don't add furfural in kerosene and the adulteration of petrol by kerosene is also reduced. The crucial factor is the price of kerosene. Due to hike in the price, the utility of kerosene is highly reduced. Instead of kerosene they use the solvents as the adulterants. The physical tests like distillation and density show the kerosene adulteration. Though the gasoline is an adulterated one it also meets the specification given by the BIS. This is due to the adulteration of petrol by different solvents. The adulteration using kerosene is an old method. Now the adulteration done by proper technique, it is nothing but adulteration using solvents especially using Suitable Boiling Point (SBP) solvents.

There are so many SBP solvents which are readily available in the market. The SBP solvents are being used as the adulterants since the price is lower than kerosene.

Another important concept is the boiling point of the solvents; they have the similar boiling points as the petrol and its components, the price is also less than kerosene. The quantity of solvents especially paraffins reduce the octane number so they add

the octane boosters i.e., the least carbon paraffins and olefins have the higher octane number, so when it is mixed with petrol as the adulterants it boost the octane number. Usually olefin forms gum frequently so to avoid the gum formation refineries add antioxidants like N, N'-disecondary-butyl-paraphenylene diamine; 2,4-dimethyl-6-tertiary butyl phenol; 4-methyl-2, 6-ditertiary-butyl phenol; N, N'-isopropyl-paraphenylene diamine; N, -normal butyl-p-aminophenol. Generally oxygenates like methanol, ethanol, isopropanol, 2-butanol, tert-butanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), diisopropyl ether (DIPE) are added .

The excess of oxygenates, aromatics may create knocking in the engines but not good for engines and harmful for our health since it gives sooty smoke, (which cause breathing troubles and cancer). The oxygenates like 1,2-dichloro propane, isomers of hexane, heptane and pentane are in petrol.

The presence of the olefins form gum, which spoil the engines. We can find out the amount of the gum content by the BIS methods existent gum, g /m^3 - IS 1448 Air jet solvent washed and Potential gum, g/m^3 IS 1448. But the excess amount of the aromatics in petrol can only be find out by the Gas Chromatography method. By using proper column we can find out the percentage of the oxygenates, paraffins and aromatics like benzene, toluene, o-xylene, p-xylene, m-xylene, ethyl benzene, propyl benzene, 2-ethyl toluene.

Gas Chromatography Method

Gas Chromatography is a separation technique, using gas as a mobile phase, in a column with stationary phase being a solid support or inert solid support coated with liquid phase. Separation is due to the Differential Distribution Coefficients.

This method determines the majority of individual hydrocarbon components of gasoline with boiling ranges up to 250°C. Individual components or groups of co-eluting components are determined from 0.001-100 mass percent. Mixtures with C_4-C_8 olefins at concentrations up to thirty percent mass can be analyzed. This method is also applicable to mixtures containing alcohols or ethers.

Instrumentation

Gas chromatograph (GC) Chemito GC1000 equipped with a Flame Ionization Detector (FID), a split/splitless capillary injector, a 100 meter long and 0.25mmID Petrocol DH-100 (supelco) and a precolumn of 2-3 meters long analytical column

used. Micro syringe 2.0 micro liter for injection, only 0.2 μL is injected into the GC. From the injected sample, only a small amount gets into the column, to regulate this amount of sample use split ratio[13] normally we use 1:80 split ratio for this purpose. Chemitochrom 2000 software used for the detection of the components. DHA is an advanced software to find out the exact contents of the hydrocarbon mixture /MS.

But this study is based on the usage of the GC-FID[14-24] without the Detailed Hydrocarbon Analysis (DHA) software.

Principle and Application

The function is based on the principle that different components in a mixture are attracted differently and absorbed on solid absorbents.

There is a carrier gas (He) flowing at a particular speed through a column that is kept in oven.

The conditions for the GC is given as below

Column: 100 meter Petrocol DH

Injection Temperature: 250°C

Detection Temperature: 265°C

Oven Temperature: 40°C -200°C

Rate of heating: 3°C/min.

Ramping: 40-1.00min. -3°C /min.; 200-1.00min.

Oxidant: Zero air (99.999%)

Make up gas and Carrier gas: Helium (99.999%)

Fuel gas: Hydrogen (99.999%)

- The components of the sample are carried away by the carrier gas through the column.
- The adsorbent differently attracts and hence controls the speed of the components of the mixture.
- The components which is least attracted is to leave the column first and the most attracted component leaves the column last.

- The sample that enters the detector, Flame Ionization Detector (FID) where it is entirely vaporized. During combustion positive and negative ions are produced which are controlled over the respective electrodes and the current produced proportional to the ions collected in the form of analog signals, then converted into the digital signals and is monitored, detected in the form of chromatogram.

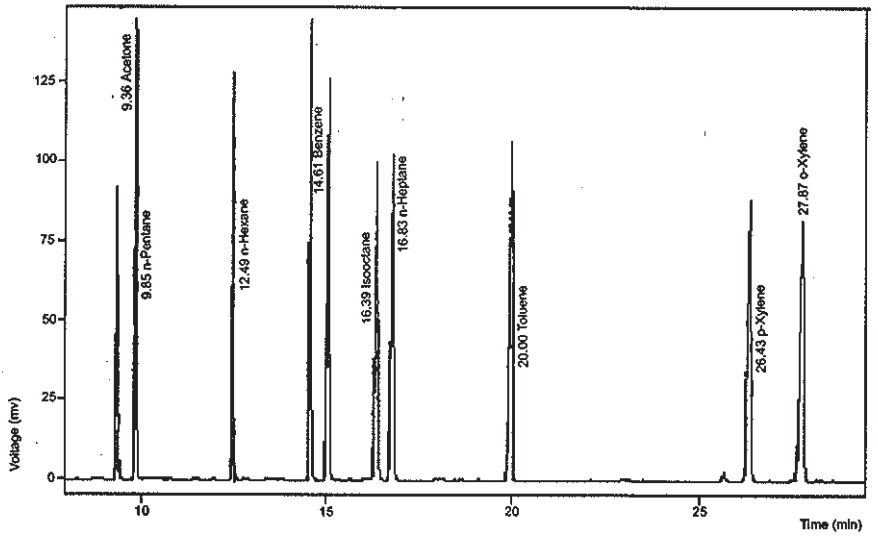
- The recorder plots the current produced for the combustion of each component possess its characteristic Retention Time (RT). The Chromatograms obtained by plotting retention time against area percent (in terms of mV). Retention Time is the time taken by the component to leave the column. The area percent is the amount of organic components present in the total mixture.

Interpretation and Conclusion

When inject some individual solvents we can get the chromatogram like Chromatogram 1. According to the Retention index, the components elute at different Retention Times. The given below is a mixture of solvents. Here the solvent mixture is injected that mixture contains acetone, pentane, hexane, benzene, cyclohexane, isooctane, heptane, toluene, p-xylene, o-xylene.

From this Chromatogram 1 we clearly identify the above-mentioned solvents, with their Retention time.

Chromatogram 1: The mixture of Solvents



This is the result table for the Chromatogram 1.

Peak. No	R.T	Area (mV.s)	Amount (ul)	Amount %	Peak Type	Component
1	9.360	233.8034	62.6357	26.8694	Ordnr	Acetone
2	9.847	343.1072	87.2323	37.4208	Ordnr	n-Pentane
3	12.493	378.0441	14.8247	6.3595	Ordnr	n-Hexane
4	14.607	544.4891	12.8811	5.5257	Ordnr	Benzene
5	15.060	457.9062	11.5381	4.9496	Ordnr	Cyclohexane
6	16.387	403.6193	10.3614	4.4448	Ordnr	Isooctane
7	16.827	421.2618	10.6976	4.589	Ordnr	n-Heptane
8	20.00	542.1897	7.8614	3.3724	Ordnr	Toluene
9	26.427	554.621	7.0829	3.0384	Ordnr	p-Xylene
10	27.873	511.2054	7.9964	3.4304	Ordnr	o-Xylene
-	Total	4390.2473	233.1117	100		

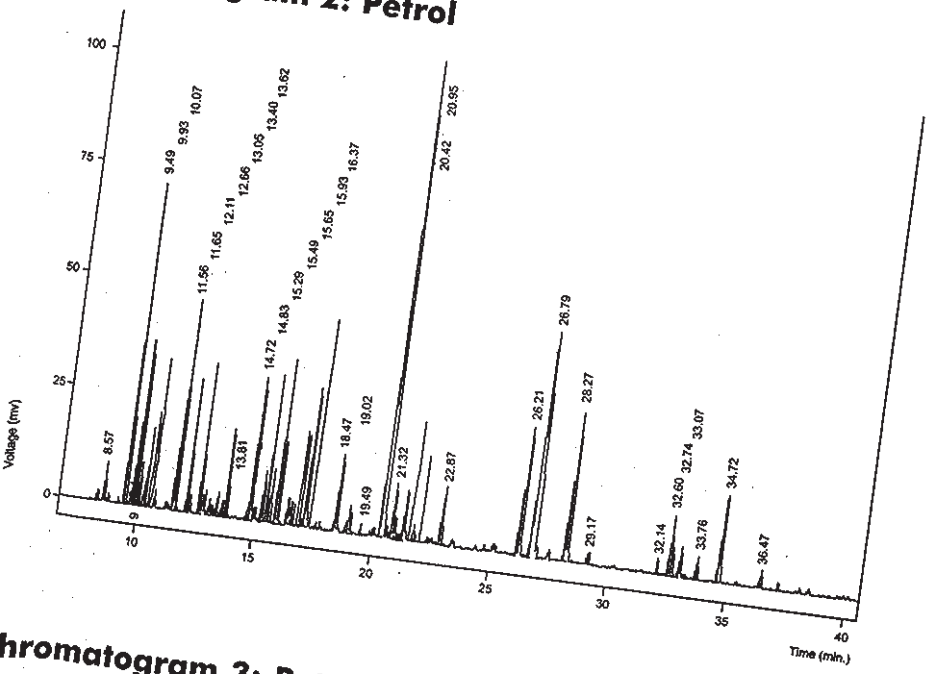
It is used to find out the volume percent theoretically. For example the amount of volume injected in the mixture is 10%, when calculate this using the theoretical calculation we get 9.96% as volume percentage, to avoid the disorder in the volume percentage we can use the auto sampler.

The second chromatogram shows the pure motor gasoline peaks and their retention Times, the result table given in annexure 1. This chromatogram represents all the components present in the motor gasoline.

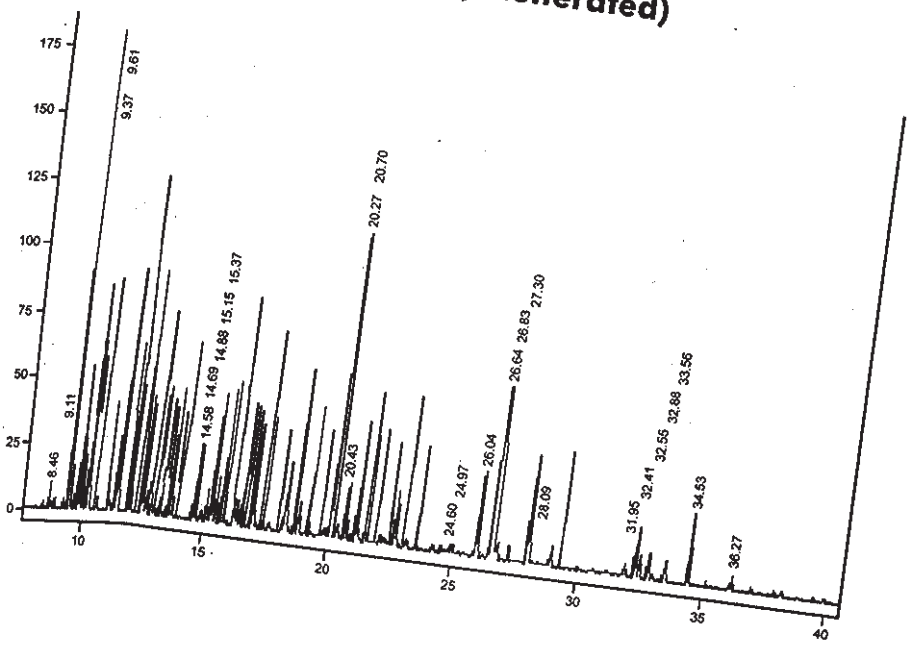
The third one (chromatogram 3) shows extra peaks other than the normal motor gasoline. It represents a few specific peaks arise at some places/Rt, they clearly show that this petrol is an adulterated one.

Normally the GC software itself gives the area and area%. Using the area and area% we can find the adulterated solvents, but it is impossible to find all the solvents/adulterants. But we can find out the possible adulterants.

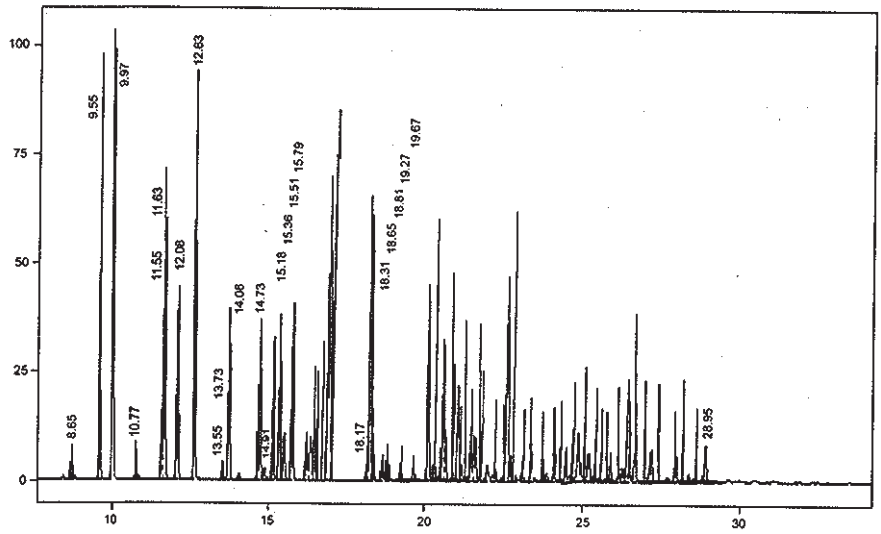
Chromatogram 2: Petrol



Chromatogram 3: Petrol (adulterated)

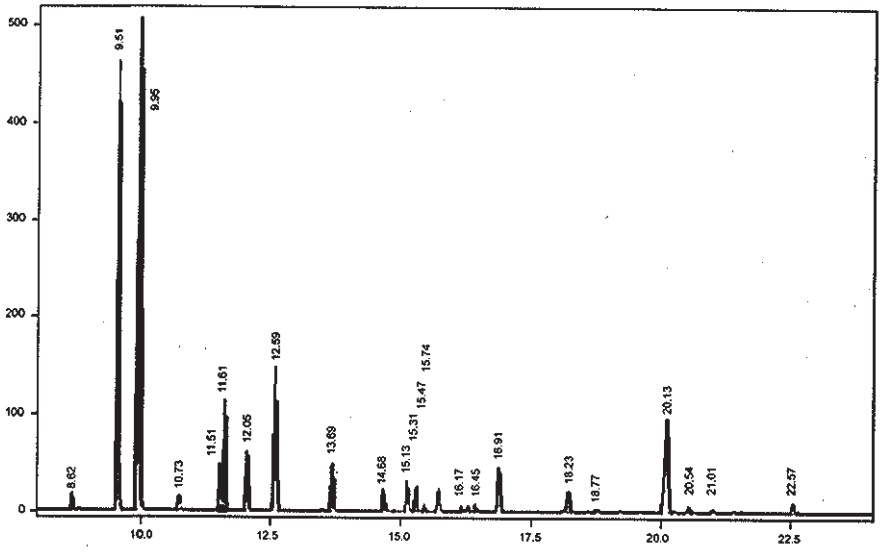


Chromatogram 4



The above chromatogram shows peaks of the light aromatic naphtha that is available in the market, this shows the similar peaks like in the motor gasoline. The refineries use this for the blending purpose. The aromatic components are less in this sample and in area percentage.

Chromatogram 5



This chromatogram represents one of the SBP solvents, which shows that the lower saturated hydrocarbons predominantly present in this compound. This is the major adulterant available in the market. Normally motor gasoline has all the above components, but when the SBP solvent are added to the motor gasoline, the adulterated motor gasoline shows the higher percentage of these components. This clearly indicates that the particular motor gasoline is adulterated.

Let us compare the retention times of the SBP solvents and light aromatic naphtha with the third chromatogram. SBP solvent present in the large amount shows that they are added as adulterant. The third chromatogram clearly shows that lower saturated hydrocarbons may be added as an adulterant. SBP solvents like n-butane, 1-butane, butene-2, n-pentane, 2-methylbutene-2, 2, 2-dimethyl butane, cyclopentane, 2, 3-dimethyl butane, 2-methyl pentane, 3-methyl pentane are present in higher amount in this sample. So adulteration may be possible using these solvents.

It is clear that the solvents are added as adulterants due to the cost factor, but they are not violating the specifications. This motor gasoline obeys all the specification given by the BIS. But the above chromatograms clearly show that the adulteration made using the solvents. Even though we find adulteration of few solvents it is impossible to find all the solvents, which are added in the least level. Without DHA we can find out a few possible solvents using the Gas Chromatography method.

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Annexure 1

The Result table for the Chromatogram 2.

Peak. No	R.T	Area (mV.s)	Height (mV)	WO5 (min.)	Area(%)
1	8.573	17.9410	8.3529	0.0400	0.5603
2	9.487	173.7524	71.5257	0.0467	5.4261
3	9.840	20.5574	8.5690	0.0400	0.6420
4	9.933	85.0234	36.4506	0.0400	2.6552
5	10.067	23.2638	9.6657	0.0400	0.7265
6	10.240	12.9611	5.2840	0.0467	0.4048
7	10.340	42.8650	17.3778	0.0467	1.3386
8	11.560	36.4280	13.6828	0.0467	1.1376
9	11.647	121.2280	46.9691	0.0467	3.7858
10	12.113	91.7811	29.4511	0.0467	2.8662
11	12.660	124.9940	33.3380	0.0467	3.9034
12	13.047	19.5279	3.3704	0.0600	0.6098

13	13.400	14.6400	5.2844	0.0467	0.4572
14	13.620	9.7864	3.3947	0.0467	0.3056
15	13.807	75.3293	19.5611	0.0667	2.3525
16	14.720	12.0049	3.6980	0.0533	0.3749
17	14.833	107.4656	31.8003	0.0533	3.3561
18	15.293	35.2237	11.3764	0.0533	1.1000
19	15.493	104.7933	32.6870	0.0533	3.2726
20	15.647	34.5168	11.7837	0.0467	1.0779
21	15.933	118.5377	36.3680	0.0533	3.7018
22	16.373	24.8666	5.6920	0.0533	0.7766
23	16.513	17.4356	5.0549	0.0600	0.5445
24	16.647	13.1224	4.5290	0.0533	0.4098
25	17.120	118.9117	31.0840	0.0533	3.7135
26	18.473	53.7591	16.4471	0.0600	1.6788
27	19.020	22.4109	5.9170	0.0600	0.6999
28	19.493	10.2429	2.4305	0.0667	0.3199
29	20.427	563.0202	106.3854	0.0867	17.5826
30	20.847	39.0147	12.1202	0.0600	1.2184
31	20.953	19.4414	4.8687	0.0667	0.6071
32	21.320	52.3014	11.1112	0.0600	1.6333
33	21.727	16.5143	3.5372	0.0600	0.5157
34	22.873	49.7522	12.8568	0.0600	1.5537
35	26.213	117.9056	28.5483	0.0667	3.6821
36	26.793	406.3812	50.3144	0.1400	12.6909
37	28.267	146.8873	33.2787	0.0733	4.5872
38	29.173	9.8805	2.6498	0.0600	0.3086
39	32.140	13.3822	3.3861	0.0600	0.4179
40	32.600	53.4595	13.5027	0.0667	1.6695
41	32.740	23.4666	6.2005	0.0600	0.7328
42	33.067	32.0973	6.7733	0.0667	1.0024
43	33.760	20.5071	5.0044	0.0733	0.6404
44	34.720	80.1263	19.0847	0.0733	2.5023
45	36.467	14.6366	3.7908	0.0667	0.4572
-	Total	3202.1447	834.5585		