

SECTION - 1

PETROLEUM PRODUCTS

- 1.1 **Title:** Analysis of Petroleum Products
- 1.2 **Scope:** Analysis of Various Petroleum Products like Petrol, Kerosene, Diesel, Aviation Turbine Fuel (ATF-Kerosene) Lubricating oil, Furnace oil, etc., in the Crime Cases.
- 1.3 **Purpose:** To know the precise characteristic of **Petroleum Products** as per **Bureau of Indian Standards** and also other relevant **Scientific methods** to find out any possible adulterants and to assist the investigating agencies and law enforcement bodies.
- 1.4 **Responsibility of Examination & Report:** Jr. Scientific Officer, Senior Scientific Officer, Assistant Director, Deputy Director and Director with relevant field of specialization or any gazetted officer authorized by the Director.
- 1.5 **Introduction:** Petroleum Products most frequently referred to any Forensic Science Laboratories for examination are Petrol, Kerosene (White and PDS), Diesel (Light Diesel Oil (LDO) and High Speed Diesel (HSD)), Aviation Turbine Fuel (ATF) -Kerosene, Lubricating oil, furnace oil, waste oil, etc., These samples are forwarded to FSL for their purity, detection of adulteration if any or under the **Essential Commodities Act** or under section 420 IPC and also under Petroleum Act, unlawful possession, breach of contract, pilferage, etc., The analysis of these Petroleum Products is prima-facie, a complex task as these are complex mixtures of hydrocarbons obtained by fractional distillation of crude oil of variable nature, yet broadly falling in well recognizable boiling/distillation ranges and having other Physico-Chemical parameters, as for instance laid down by Indian Standard Specification for **Motor Gasoline / Petrol (IS 2796/2000)** includes amongst other parameters, the distillation recovery criteria which is very helpful in assessing these samples, notwithstanding the fact that the final boiling point Max;215°C as prescribed therein, appears to be relaxed too much on the higher side. The density at 15°C in Kg/m³ is 710 - 770 which is very wide range and allows normally 40 - 50% adulteration using any solvent or middle distillate etc., The situation is unfortunately not the same as in the case of Kerosene and Diesel which may also be termed as middle distillates. As stated therein, these Specifications **Kerosene IS (1459/1974 reaffirmed in 1991)** and **Diesel IS (1460/2000)** are formulated by keeping in view the difficulties in importing the crude oil and also with a view to increase the availability of middle distillate as much as possible.

1.6 Definitions: As per “THE MOTOR SPIRIT AND HIGH SPEED DIESEL (PREVENTION OF MALPRACTICES IN SUPPLY AND DISTRIBUTION) ORDER 1993 by Section 3 of Essential Commodities Act (E.C. Act) (Central Act 10 of 1955)

- **Adulteration:** Means the introduction of any foreign substance into motor spirit / high speed diesel illegally / unauthorizedly.
- **Malpractices:** it shall include the following acts of omission, commission in respect of motor spirit and high speed diesel:
 - **Adulteration**
 - **Pilferage**
 - **Stock variation**
 - **Unauthorised exchange**
 - **Unauthorised purchase**
 - **Unauthorised sale**

- **Motor spirit:** Means any hydrocarbon oil (excluding crude mineral oil) which has a minimum RON 88, which either by itself or in admixture with any other substance, is suitable for use as a fuel in spark ignition engines.

- **High Speed Diesel:** Means any hydrocarbon oil (excluding mineral colza oil and turpentine substitute), which has its flash point at or above 35 degree Celsius & Cetane 48 minimum and is suitable for use as a fuel in compression ignition engines.

- **Kerosene:** Means middle distillate mixture of hydrocarbons meeting BIS Specification (IS 1459/1974) with important characteristics of flash point at a minimum of 35 °C and a smoke point at minimum of 18 mm.

- **Petroleum Products: Includes**
 - **LPG and CNG etc.**
 - **Motor spirit all grades and naphtha**
 - **Aviation spirit**
 - **Solvents of all types**
 - **Aviation turbine fuel**
 - **Kerosene**
 - **Light Diesel Oil**
 - **High Speed Diesel Oil**
 - **Fuel oil of all grades**
 - **Lubricating oils and greases including base oil**
 - **Wax of all grades**
 - **Bitumen**

1.7 Sampling of Products by Sample Drawing Authority (EC ACT 1955)

- **Power of Search and Seizure:** Any officer of the **State Government**, not below the rank of an Inspector, in the department of Food and Civil Supplies duly authorized and notified in the Official Gazette by such State Government, or any officer of an Oil Company not below the rank of a Sales officer may, with a view to securing compliance with the Provisions of this order, or for the purpose satisfying himself that this order or any order made there under has been complied with.
- **Sampling:** The Officer authorized shall draw the sample from the tank, nozzle vehicle or receptacle as the case may be to check whether density of the product confirms to the requirements indicated in Schedule.
- The officer authorized shall take, sign and seal **three samples** of 1 litre each of the product, one to be given to the dealer, transporter or concerned person under acknowledgement with instructions to preserve the sample in a safe custody till the testing/investigations are completed, the second sample to be kept by the concerned Department and the third for **laboratory analysis**.
- Samples shall be taken in clean **glass or aluminium containers**. (Plastic containers shall not be used for drawing samples.)
- The authorized officer shall send the third sample of the product within **10 days** to the laboratories.
- All **Forensic Science Laboratories in Central/States/UTs** are authorized under Schedule III of Clause 8(5) of EC Act 1955 for testing of Petroleum Product Samples.

1.8: Policy for Accepting, Reporting and disposal of samples:

REFERENCES

1. Petroleum Laws and Essential Commodities Act (E.C. Act) 1955
2. The ISI Specification for Motor Gasoline (IS: 2796/2000)
3. The ISI Specification for Kerosene (IS: 1459/1974)
4. The ISI Specification for Diesel (IS: 1460/2000)

SECTION – 2

MOTOR GASOLINE / MOTOR SPIRIT / PETROL

2.1 Introduction

Petrol, which is a highly inflammable liquid, used as a fuel in the Spark Ignition Engines. It consists essentially of C₅ to C₁₀ hydrocarbons. Commercial Motor Gasoline is a blend of Paraffins, Iso-Paraffins, Olefins, Naphthenes and Aromatics (PIONA) along with additives which are normally added to enhance various performance features related to the satisfactory operation of engines as well as to minimize fuel handling and storage. Dyes are usually added for identification in solid or liquid form. Orange dyes are added for regular Petrol, red dyes are added for Premium Petrol and green dyes are added for aviation gasoline.

The most important characteristics given in IS 2796 are Colour, Density, Distillation, Research Octane Number (RON), Anti-Knock Index (AKI), Gum Content, Reid Vapour Pressure, Benzene Content, etc.,

2.2 Test Methods and their Significance (As Per IS 2796/2000 – Motor Gasoline)

2.2.1 Density : Experimental (P:16-IS 1448 Methods of Test)

It is a measure of mass per unit volume. Density can be measured by using hydrometer or by the automatic Density Meter method. Take the sample (Petrol) in open mouth cylinder and note its temperature, then dip a hydrometer in it. And read its lower meniscus. By using conversion table, the density can be corrected to 15°C.

In Automatic Density Meter Method (ASTM D 4052/ IP 365), follow the instructions given in the working manual and inject the sample (the quantity required is about 1ml) and set the temperature to 15°C. When the conditions are valid, it gives three measurements namely density, specific gravity and API gravity (American Petroleum Institute) at 15°C. API gravity is an arbitrary scale and is related to specific gravity by the formulae,

$$\text{API Gravity (Degrees)} = \frac{141.5}{\text{Sp.Gr @ } 15.6^{\circ}\text{C}} - 131.5$$

The density at 15°C of a typical standard Petrol (Motor Gasoline) is **710-770 (Kg/m³)**.

Significance:

- Aromatics have the highest density.
- Paraffins have the lowest density.
- Cycloparaffins and Olefins have the intermediate density.
- Increase in density (above 770 Kg/M³) indicates the presence of possible adulterants like Kerosene, Diesel, High Aromatic Naphtha (HAN) and narrow cut aromatics like Benzene, Toluene, etc.,
- Decrease in density (below 710 Kg/M³) indicates the presence of possible adulterants like SBP solvents, narrow cut solvents mainly aliphatics.
- Intermediate density (between 750 – 770 Kg/M³) indicates the presence of possible adulterants like HAN, BTX (C₆, C₇ & C₉ aromatics), etc.,

2.2.2 Distillation: Experimental(P:18-IS 1448 Methods of Test/ IP123/ASTM D 86)

It gives an idea of volatility characteristics of the fuel. It can be determined by

- **Non-fractionating type ASTM – Manual**
- **Non-fractionating type ASTM – Automatic**

100 ml of the sample is taken in a standard distillation flask of 125 ml for manual distillation. The sample is distilled under standard condition either manually or automatically. Initial boiling Point (**IBP**) at which the first drop falls in the measuring cylinder is noted and after that every 10% volume, the distillation temperature is recorded. Adjust the flow rate around 4 to 5 ml per minute. The highest temperature reached during the distillation is known as Final boiling Point (**FBP**), the residue left and loss during distillation are also reported. It is important that recovery at 70°C, 100°C & 180°C are also noted. IBP shows the ease of starting, 10% to 90% gives the idea rate of acceleration, smooth running and complete combustion of fuel respectively.

The distillation criteria of standard Petrol will be

<u>Temp °C</u>	<u>Distillate % by volume</u>
IBP	to report
70 °C	10 - 45
100 °C	40 - 70
180 °C	90 (minimum)
FBP	215°C (maximum)
Residue % by volume	2 (maximum)

Significance:

- Depending upon the nature of adulterant the IBP and FBP will vary.
- Depending upon the nature of adulterant the E₇₀, E₁₀₀ and E₁₈₀ will vary.

- Residue percent by volume depends upon the volatility of the solvent. High boiling compound normally leaves more residue than low boiling compound (eg: Kerosene, Diesel and High Aromatics)
- Constant boiling temperature shows the possible presence of adulterants like narrow cut solvents (aliphatic, aromatic or cyclic) like Benzene, Hexane, etc.,

Hexane (64°C -- 70°C)

Benzene (80°C -- 82°C)

Note:

As per IS 2796/2000 a wide range is given for density (**710 – 770 Kg/M³**), which shows that petrol can be adulterated by significant amount of kerosene, naphtha and other middle boiling solvents in petrol. If petrol is adulterated with Naphtha, the density will not vary much and lies well within the limit. In case of simulation also, it is difficult to opine based on density. The same holds good for distillation criteria. Based on these two parameters, it is difficult to determine the quality of the fuel.

Although different methods have been incorporated in BIS, the methods mentioned below are developed and validated used in analysing any type of Petrol adulteration.

2.2.3 Colour: (orange/red) as per IS 2796/2000

Normally oil orange dye (Phenyl azo 2-naphthol) is used for colouring Motor Gasoline (Petrol). It is an azo dye.

- **Visual:** Note down the colour of the sample visually
- **UV – Visible Spectrophotometry:** Note down the wavelength for maximum absorption for orange and red using visible spectrophotometer.

Equipment	: UV-VIS Spectrophotometer
Method	: Scan - Ordinate mode
Scan Speed	: 120 nm / min
Lamp	: Visible
Wavelength	: 400 nm – 700 nm
Peak threshold	: 0.02

Oil Orange dye : λ_{max} -- 470 nm

Oil yellow dye : λ_{max} -- 460 nm

Oil red dye : λ_{max} -- 505nm

- **Thin Layer Chromatographic methods for the detection of oil soluble dyes.**

The standard Petrol sample (2 μ l), reference standard dyes namely oil orange, oil red in solvent ether (2 μ l) and case samples were spotted on TLC (Silica Gel – 60G) plates or Silica Gel (60F 254) Alumina pre-coated plates. The plates were developed in Hexane: Toluene: Acetic Acid [50 : 50 : 2] as solvent systems after the chambers are well saturated. The plates were run upto 10 cm. Remove the plate from the chamber and dry it. Spray the plate with dilute sulphuric acid.

Observation: Orange dye from Petrol (Standard) sample shows two spots. The following observations were made:

Spot	Rf	Before Spraying	After Spraying
1	0.49	Pink	Pink
2	0.51	Orange	Orange

If any other dye is used there will be a perceptible change after spraying with dilute sulphuric acid due to dye characteristics.

2.2.4 Filter Paper Test for detecting Adulteration of Petrol with Kerosene/Diesel:

Petrol is highly volatile liquid fuel. It is a clean fuel. Hence drops of Petrol vaporize extremely fast and they vanish without leaving any trace behind. Kerosene and other high boiling compound is very much less volatile as compared to Petrol and hence it does not vapourise quickly.

Hence if Petrol containing Kerosene or Diesel are placed on any filter paper, Petrol will evaporate leaving behind Kerosene/Diesel, which looks like oily, patch with characteristic smell of kerosene or diesel.

Test Procedure:

Put two drops of Petrol on a filter paper. Wait for few minutes.

- If the Petrol is *unadulterated*, then there will be no patch or mark left on the filter paper.
- If the Petrol is *adulterated with Kerosene and Diesel*, it will leave an oily patch on the paper within minutes.

Note:

If Petrol is *adulterated with volatile hydrocarbon solvents like narrow cut aliphatics, aromatics, naphtha*, etc., then this test **may not** detect the adulteration.

2.2.5 Tests for presence of Gum Contents:

Olefins present in Gasoline form a gummy deposit resulting the choking of nozzle. This can be carried out by Existent Gum test.

Test Procedure

A known amount of the sample i.e. 50 ml in a standard beaker is evaporated at 150⁰ C by passing heated air for 30 minutes. The beaker is taken out, cool and weigh. Again give n-heptane washing to the beaker, dry it & weigh. This weight gives the indicative of Gummy material where as before washing if the quantity is more, it shows that it is contaminated/ adulterated with kerosene or other high boiling liquid.

- Other tests are oxidation stability test and potential Gum.

2.3 Methods for Detection of Adulteration

2.3.1 TLC / HPTLC Planar Chromatographic Methods for the determination of Adulteration in Petrol with Kerosene.

The Petrol (P), Kerosene (K) and various (P+K) admixtures were prepared. About 2 µl volumes of each were spotted either on TLC (Silica Gel-G) plates or HPTLC (Silica Gel-60F-254) plates along with the respective case work samples. The Plates were separately developed in the saturated chambers with any of the following system

- (i) n-heptane.,
- (ii) iso-octane
- (iii) iso-octane: Carbon tetrachloride (8:2)
- (iv) n-heptane : Carbon tetrachloride (8:2)

Detection:

No prominent spots were observed for Petrol however, three different spots at Rf 0.78, 0.68 and 0.54 showing increasing intensities, sizes / areas of the spots / peaks were observed in either n-heptane or iso-octane using single solvent systems, the percentage of Kerosene in P:K admixtures increase, by using various detection methods such as:

UV Lamp:

After development the dried plates were first observed under UV lamps having both 254 nm and 366 nm wavelength.

Chloranil spray reagent:

The developed TLC / HPTLC plates from the solvent chamber were sprayed with chloranil spray reagent (10% w/v of chloranil in benzene followed by double diluted sulphuric acid), then heated in oven at 105°C for 10minutes, brick-red addition compounds/spots were observed.

Rhodamine Spray reagent:

Another sets of developed TLC/HPTLC plates were taken out from the chamber were sprayed with chromic acid [5g of pot. dichromate dissolved in sulphuric acid (40%v/v) made to 100ml]. The plate was air dried till greenish coloured spots were developed. Then the plate was sprayed with saturated aqueous solution of Rhodamine followed by 50%v/v of conc. aq. ammonia. Greenish blue / violet coloured spots were observed.

2.3.2 Densitometric method

Another sets of developed HPTLC plates were taken out from the solvent chamber were subjected to HPTLC instrumental scanner / densitometric UV detection at 250nm characteristic peaks were observed.

2.3.3 Thin Layer Chromatographic Methods for the detection of Petrol, Kerosene and Diesel.

About (2 µl) volumes of each of Petrol (P), Kerosene (K) and Diesel were spotted either on TLC (Silica Gel-G) plates or HPTLC (SilicaGel-60F-254) plates along with the respective case work samples. The Plates were separately developed in the saturated chambers containing Hexane: Toluene: Acetic Acid [50:50:2] as solvent system. Run the chromatogram up to 10cm distance. After development the dried plates were first observed under UV lamps (254 nm).

Detection

The developed TLC / HPTLC plates from the chamber is air dried and sprayed with Rhodamine solution (1% v/v in alcohol) followed by bromination. Then the plates were observed under UV (366 nm)

- Pinkish orange fluorescence for Petrol
- Bluish violet fluorescence for Kerosene
- Violet fluorescence for Diesel

2.3.4 High-Performance Liquid Chromatographic method (HPLC)

Equipment: HPLC unit with RP– C-18 column or any equivalent column variable wavelength UV detector fitted with integrator recorder.

Chromatographic Conditions:

Quantity of injection: 10µl of Petrol (P), Kerosene (K) and various (P:K) admixtures (liquid) samples each separately diluted 100times with methanol.

Mobile phase: Isocratic solvent system of acetonitrile : water (8:2)

Flow rate: 1ml / min at ambient temperature

UV detection: 275nm, 285nm and 220nm wavelength

Characteristic peaks at Rt 4.9, 6.2 and 8.0 \pm 0.1 min were observed for naphthalene, 1methyl naphthalene and 2,6 dimethyl naphthalene. The peak height increased with the increasing percentage of kerosene in the (P: K) admixtures.
(As Kerosene is rich in Naphthalene concentration)

2.3.5 Gas Chromatography

It is an analytical technique is used to identify Petrol, Kerosene, Petroleum Hydrocarbon Solvents, Petrol: Kerosene admixtures and Petrol Solvent admixtures.

Experimental Conditions – Petrol and low boiling hydrocarbon solvents

METHOD: 1

- Column : SP 2100 5% on Chromosorb 80 – 100 mesh
2m X 1/8” x 2.0mm SS
- Carrier gas : Nitrogen Flow rate : 10ml / min)
- Fuel gas : Hydrogen Flow rate : 25ml / min
- Air : Flow rate :250ml / min
- Injector Temperature : 280°C
- Detector Temperature : Flame Ionisation Detector 300°C
- Oven
 - Initial Temperature : 40°C Hold 2 mts
 - Ramp 1 : 70°C Rate 5°C/min Hold 2 mts
 - Ramp 2 : 150°C Rate 5°C/min Hold 2 mts
 - Ramp 3 : 220°C Rate 5°C/min Hold 2 mts
 - Ramp 4 : 250 °C Rate 5°C/min Hold Infinite

METHOD: 2

- Column : Apiezon L 10% 2m X 1/8" X 2.0mm SS
- Carrier Gas : Nitrogen Flow Rate 30 ml/min
- Fuel Gas : Hydrogen Flow Rate 25 ml/min
: Air Flow Rate 250 ml/min
- Injector Temperature : 200°C
- Detector Temperature : Flame Ionisation Detector 250 °C
- Oven :
Initial Temperature : 40°C Hold 8 min
Final Temperature : 150°C
Rate : 10°C/min
Hold : 20 min

Procedure:

1 µl of each Petrol, Kerosene and Petrol & Kerosene admixture (9:1, 8:2, 7:3, 6:4, & 5:5) and adulterated sample are injected and the chromatograms are compared with that of adulterated sample (Kerosene as an adulterant) under identical conditions. Retention time and peak areas from 10.0 min onwards in the chromatogram of adulterated sample is compared respectively with the peak area of Petrol and Petrol + Kerosene samples at same retention time. Hence by comparing the area of adulterated sample with the mixture of Petrol + Kerosene samples quantitative estimation of the adulterant Kerosene in Petrol is studied.

Significance:

- It is an excellent analytical tool for kerosene and other medium boiling hydrocarbon solvents like Mineral Turpentine oil, ATF, oil as an adulterant to Petrol
- Individual characterization of Petrol (but not the groups) and other low boiling hydrocarbon solvents namely SBP solvents, Naphtha are possible

Note 1:

Gas chromatograph is an excellent analytical technique for separation of individual hydrocarbons in a mixture. But GC alone fails

- When Petrol is adulterated with similar boiling range solvents like LAN and HAN in lower concentrations, it is very difficult to characterize the type of hydrocarbon solvents
- Fingerprinting of hydrocarbon based on their group and carbon number becomes very critical

Note 2:

All the methods mentioned earlier have certain Note especially when Naphtha or other low boiling hydrocarbon solvents have been used as an adulterant. The hydrocarbon distribution of Naphtha and Petrol are almost similar except for the most important component – **Olefin**. This is a component absent in solvents like LAN, HAN, SBP, aliphatic narrow cut solvents, aromatic narrow cut solvents, kerosene etc.

The above facts necessitate employment of a special analyser (GC-DHA), which is able to separate, and detail the presence of various hydrocarbons and their amount becomes essential to pinpoint any sort of adulteration. This method is detailed below.

2.3.6 Detailed Hydrocarbon Analyser (GC-DHA)-ASTM D 6730 / 6733 for calculation of RON (Though not included in BIS Specifications but is useful for Forensic Laboratories)

Capillary Gas Chromatograph is an indispensable tool for the evaluation of compositional analysis of light hydrocarbons, which has led to the complete understanding of each of the hydrocarbons present in the gasoline. The detailed evaluation of each of the component and its quantity in Gasoline has made easier to obtain RON by calculation approach. The capillary gas chromatographic method is used in the identification of the common adulterants in Motor Gasoline such as **Naphtha, Special Boiling Point Solvents and other industrial Solvents**, which invariably lead to lowering of RON. The Capillary Gas Chromatographic method of analysis for understanding the chemical composition of the adulterated petrol is explained in detail with equipment configuration and operating procedures.

Motor Gasoline commercially known as Petrol is a mixture of volatile hydrocarbons namely Paraffins, iso-paraffins, olefins, Naphthenes and Aromatics with their carbon number ranging from C₄ to C₁₀. Indian refineries ensure that the mixture of hydrocarbons they market as **Finished Gasoline** is marketed only when it meets all the statutory Bureau of Indian Standard (BIS) requirements including the value of 88 minimum for Research Octane Number (RON). The adulterants if any in Petrol is difficult for detection by any simple conventional Petroleum testing method and RON value determination can only be taken as conclusive test. *The RON value determination requires a huge investment for CFR (Committee on Fuel Research) engine and the method is tedious, expensive and also time consuming.*

The hydrocarbon type analysis is important in determining the composition as well as **RON** of naphtha, gasoline and other solvents. The major hydrocarbon type constituents of naphtha and gasoline are determined by using the Standard ASTM

method of **Fluorescent Indicators Adsorption (FIA)** or non-standardized chromatographic techniques. The later includes methods based on the complete separation of components by single capillary column or group type separation according to Carbon numbers using valve switching multiple packed columns – ASTM method of hydrocarbon types by **Multi dimensional Gas Chromatography**.

Recent development of compositional analysis of light hydrocarbons by high-resolution **capillary gas chromatograph coupled with detailed hydrocarbon analyser (GC-DHA)** has led to the complete understanding of each of the hydrocarbon present in the gasoline mixture. The RON value can easily be calculated by the contributions of each of the hydrocarbon types based on calculation approach.

Experimental

Material

- Carrier gas, helium 99.9% pure (warning - compressed gas under high pressure)
- Fuel gas, hydrogen 99.99% pure (warning – extremely flammable gas under high pressure)
- Oxidant – Air 99.9% pure (warning – compressed gas under high pressure)
- Make-up gas – Helium or Nitrogen 99.9% pure (warning – compressed gases under high pressure)
- Reference standards – Gravimetric standards of individual hydrocarbons of interest. Mainly n-alkanes like hexane, heptane and nonane are used. Quantitative synthetic mixtures of many of the hydrocarbon listed in the data base are also available
- **Reference Gasoline** – Finished gasoline from the refinery as a standard
- **Reference Naphtha** – both Low Aromatic Naphtha (**LAN**) and High Aromatic Naphtha (**HAN**) from the refinery stream used as a standard
- **Narrow cut aliphatic**– commercial Hexane available from the market
- **Narrow cut aromatic**– commercial Benzene & Toluene available from the market
- **Special Boiling Point (SBP) solvents available from the market.**

Instrument

Detailed Hydrocarbon analyzer- DHA (AC-DHA) consists of analytical gas chromatograph to perform component separation and computer software to perform component separation, identification, Quantitation and reporting within the gasoline boiling point range.

Detailed Hydrocarbon analysis was performed on a gas chromatograph interfaced with analytical control software system. Extra memory provided by the computer is needed to process post-run calculations for 225 saturates, aromatics and olefins peak listed in the DHA data base. This method determines the hydrocarbon types in petroleum distillates to a final boiling point of 215°C as defined by **ASTM D 2887**.

The DHA system consists of Gas chromatograph with capillary split liquid sample inlet, high-pressure capillary back-pressure regulator, Flame Ionisation Detector (FID), Supelco Petrocol DH 100mt X 0.25mm ID X 0.5 m column. Computer with a minimum of 4 megabytes RAM, math co-processor (internal to processor or external) hard disk software. GC auto injector provides optional system automation.

The Software controls all of the System components, performs signal integration and stores the integration reports on hard disk. DHA Software processes these integration reports and produces the finished test reports. The separation of Complex hydrocarbon samples depends on the complete system: a properly functioning analytical gas chromatograph and properly calibrated Software.

This technique is used in order to provide easiest way in which to predict the performance of individual analytes while optimizing analysis time. As the Carbon number increases the number of potential analytes increases and the boiling point differences between the analytes decreases. DHA Software reads the area % integration report for the sample as generated by the Chemstation. The Chromatographic operating conditions employed are shown in Table;2.2. Two GC methods are utilized, a method starting at ambient oven temperature for non-oxygenated samples (DHA method) and 5°C oven starting temperature for oxygenated gasolines (DHAX method)

Method

Install and condition the *column* as per the instructions given in the manual. After conditioning, attach column outlet to Flame Ionisation Detector inlet and check for leaks throughout the system. If leaks are found, tighten or replace fittings before proceeding. Flow rate adjustment is made by raising or lowering the carrier gas pressure to the injector. After final adjustment of the carrier gas flow rate, note the carrier gas pressure and adjust the injector split flow rate to give the specified split ratio.

Set the *oven* temperature to 35°C and allow oven to equilibrate for atleast 15minutes, and then observe the temperature reading. Adjust the operating conditions to conform to the list in **Table:2**. Turn on the detector, ignite flame and allow the system to equilibrate.

Correct sample split must be established to ensure optimal sample quantitation. The split ratio used is dependent upon the split linearity characteristic of the particular injector and the sample capacity of the column. The capacity of a particular column for a sample component is proportional to the amount of liquid phase and the ratio of column temperature to the component boiling point. The Split ratio used is 200:1.

TABLE: 2.2 Capillary Column Gas Chromatographic operating Conditions

Instrument	: Any gas chromatograph Integrated with computer –Software & DHA System Software		
Detector	: Flame Ionisation Detector		
Column	: 100mt X 0.25mm ID X 0.5µm on fused silica		
Stationary Phase	: Cross linked methyl silicone		
Carrier gas	: Helium		
Average linear velocity	: 24cm/s @ 35°C		
Flow rates ml/min	: Air : 370	Hydrogen : 35	Helium : 30
Split ratio	: 200 : 1		
Injection Volume	: 0.4 µl		
Injection port temperature	: 200°C		
Detector temperature	: 250°C		
Oven temperature programming			
Initial temperature	: 35°C		
Initial time	: 13 min		
First program rate	: 10.0°C/min		
First hold temperature	: 45°C		
First hold time	: 15min		
Second Program rate	: 1.0°C/min		
Second hold temperature	: 60°C		
Second hold time	: 15min		
Third program rate	: 1.9°C/min		
Third hold temperature	: 200°C		
Third hold time	: 5min		

Automatic liquid syringe sample injection to the splitting injector may be employed. Normal injection volume is 0.2 µl to 1.0 µl. It should be noted that inadequate splitter design or poor injection technique or both can result in sample fractionation.

Set the Chemstation ready to properly detect integrate and store the signal file generated by the sample. Make a **blank** analysis run to insure proper instrument operation and further condition the column. Check for steady base line.

Set the analysis by injecting 0.4µl of the standard reference GC-DHA test sample namely n-hexane. The windows used for reference peak identification should be as large as necessary to include normal retention time variation. The n-alkane peaks are always the largest components the only constraint is that they do not overlap. Other samples namely naphtha (both LAN & HAN), regular grade motor gasoline, hexane, benzene, toluene, SBP Solvents were also analysed by this technique and

individual component assay are tabulated. Prior to this analysis, the samples are properly identified by conventional methods. (Table:2.3)

Calculation of results

Identify each peak by matching retention times with known components (standard). Examine the report to insure that the peaks are properly identified. Calculate the areas for each peak. Multiply each area by its appropriate response factor, taken from the Table, obtains corrected weight percent areas.

$$\text{Wt \% Component} = 100 \times \frac{\text{Corrected peak area}}{\text{Total corrected peak area}}$$

Each peak can be identified by retention index. Retention indices of all other components are calculated using the equation of linear indices. The Kovats retention indices are used for calibration of each analysis and peak identification. N-alkanes generally presenting abundance and these are the primary reference peaks and become the basis for calculation of the retention index for the remaining peaks in the samples. DHA uses variable windows to perform analyte identification. These windows vary depending on the calculated retention index.

HP-Chemstation Software system stores all the data and the analytical control software identifies each peak based on Relative Retention Indices and these will have abbreviation like P, I, O, N & A. The abbreviation indicates the type of component whether **Paraffins, iso-paraffins, Olefins, Naphthenes and Aromatics** that it is believed to be and any other characteristics that are estimated to be associated with the component. This Software has been updated according to the many opportunities given by a detailed analysis. Data handling after identification consists in classifying the compounds by hydrocarbons group type. Carbon numbers, fractions of distillation and giving the results in weight %, mole %, volume % and in the elementary analysis & major Physical property **Research Octane Number (RON)**

The GC-DHA report gives complete profile of hydrocarbon types (C₄ to C₁₂) and now extended upto C₂₀ hydrocarbon. RON was calculated from the individual component contributions based on mathematical calculation. The detailed profile of the standard samples is shown in **Table: 2.4**

Results

Based on the hydrocarbon distribution and their contribution towards Octane Number serves to find out the purity, adulteration or simulation. The conventional testing methods are not sufficient for complete fuel analysis. All types of Petroleum Naphthas are easily characterized by this technique (**Table:2.4**)

The common adulterant such as LAN, SBP solvents, narrow cut aliphatics invariably lead to lowering of RON from 88 (minimum) as per IS 2796/2000. The other adulterant such as HAN, narrow cut aromatics and other higher aromatics like C₉ aromatics lead to increase in RON from 88 depending upon the type and amount. RON is not considered as a mere number. RON by GC-DHA method is based on the contribution of all the types of hydrocarbons, which in turn indicates the type of blending. Aromatics will have maximum contribution towards RON. Next come the Olefins, than iso-paraffins, than cyclo-paraffins (naphthenes) and finally the paraffins. Motor Gasoline is a complex mixture of hydrocarbons of all the types (PIONA) and the RON depends upon the contribution from **Aromatics** and **Olefins**, especially from Olefins, which is almost negligible in all other types of solvent. (Table: 2.4)

Note:

All the conventional petroleum-testing methods have certain limitations especially when Naphtha has been used as an adulterant. The hydrocarbon distribution of Naphtha and motor Gasoline are almost similar except the most significant component – **Olefin**. This component is highly characteristic and it has got Forensic Significance. Based on the above fact that the GC-DHA method of evaluation of RON is a quick reliable indicator to fix the quality of the fuel. The degree of information increases from Fluorescent Indicator Adsorption (FIA) to Multivalve Switching gas chromatography to Capillary gas chromatography-DHA. As per IS Specification, the RON values of unleaded regular and unleaded premium are 88 and 93. This determination needs CFR engine as per IS 2796. This method has several Notes. It is very expensive and takes longer analysis time and more operator attention than GC-DHA method. Individual component analysis and Carbon number distribution and their contribution cannot be achieved by this engine method.

The advantages of this approach to the analytical laboratory is that one GC-DHA analysis and some calculations could replace the determination of six properties, namely the Research Octane Number (RON), the Motor Octane Number (MON), the distillate octane number, the boiling point distribution, the Reid Vapour Pressure and Vapour-liquid ratio.

The advantage of GC-DHA is that it uses a single column to separate all the components. The special analyzer system with dedicated Software should be able

to perform the analysis, separation and reporting of detailed hydrocarbon with facility to perform RON calculation for Gasoline sample. The equipment is simpler and requires less maintenance than CFR Engine and Multi Valve System. The bias between GC-DHA method and CFR-engine method was found to be ± 1.00 .

TABLE: PHYSICO – CHEMICAL CHARACTERISTICS OF STANDARD SAMPLES - CONVENTIONAL METHOD

S.No.	Sample	Density at 15°C	RI 30°C	Distillation D-86					Residue % / V
				IBP °C	E 70 Vol. %	E 100 Vol.%	E 180 Vol.%	FBP °C	
1.	Petrol	0.7316	1.412	38	34	62	97	182	1.5
2.	Petrol	0.7308	1.413	40	35	63	97	180	1.5
3.	Petrol	0.7312	1.412	40	34	63	97	182	1.5
4.	Hexane	0.6605	1.375	64	99	--	--	70	0.5
5.	Benzene	0.8792	1.500	80	--	99	--	82	0.5
6.	Toluene	0.8678	1.496	109	--	99	--	113	0.5
7.	LAN	0.7026	1.404	40	18	47	97	170	1.5
8.	HAN	0.7508	1.434	44	16	49	97	172	2.0
9.	SBP-1	0.6685	1.374	38	75	90	98	115	0.5
10.	SBP-2	0.6966	1.380	46	20	60	98	160	1.0

TABLE: COMPOSITE ANALYSIS & RON OF STANDARD SAMPLE- CAPILLARY GC – DHA

S.No.	Sample	Hydrocarbon Type (Mass Percent)					RON
		n-paraffin	i-paraffin	Olefins	Naphthenes	Aromatics	
1.	Petrol	12.10	37.16	22.56	9.50	24.26	88.00
2.	Petrol	12.52	37.00	22.14	9.75	24.78	88.00
3.	Petrol	12.46	37.24	22.76	9.88	24.18	89.00
4.	Hexane	44.36	55.56	-	-	-	19.80
5.	Benzene	-	-	-	-	99.96	98.00
6.	Toluene	-	-	-	-	99.95	124.00
7.	LAN	24.39	28.06	1.00	20.16	25.50	66.00
8.	HAN	6.87	20.68	0.63	11.88	37.86	77.63
9.	SBP – 1	42.20	37.00	-	16.10	4.56	59.62
10.	SBP -- 2	31.08	38.76	0.30	15.07	9.18	69.20

(CFR Engine value to be given)

Significance

- The conventional testing methods are not sufficient for complete fuel analysis

- All types of Petroleum Naphtha are easily characterized by this technique
- The most significant property “RON” can easily be done and it is quite comparable with Engine method
- This method is approved by ASTM (D-5134, 6730 & 6733)
- This method will solve almost all Forensic Problems related to novel fuel adulteration
- It gives a detailed hydrocarbon profile with respect to hydrocarbon group and Carbon Number in particular.
 - ❖ When Petrol is admixed with LAN
 - Decrease in olefinic content
 - Lowering of RON
 - ❖ When Petrol is admixed with HAN
 - Decrease in olefinic content
 - Increase in Aromatics
 - Increase in RON

When Petrol is admixed with SBP solvents

- Decrease in olefinic content
- Decrease in Aromatics
- Lowering of RON

2.3.7 Calculation of Research Octane Number (RON) by MID-FTIR (ASTM 6277/D 5845)

FTIR is an useful technique for the analysis of concentration of oxygenates, aromatics and olefins in petrol and petrol-oxygenates blends and for the prediction of octane numbers, the vapour pressure and the distribution properties. It also tells about distillation characteristics of petrol. Equipment available in MID IR range measurements is based on interferometry. Automatic FTIR analysers from many companies are available. The technique is fast giving indication of adulteration. The operational procedure differs from manufacturers to manufacturers. For detailed operations of a particular analyzer see the operation manual of the respective analyzer.

REFERENCE

- 1) The ISI Specification for Motor Gasoline (IS: 2796/2000)
- 2) The Indian Standard Methods of Test for Petroleum Products IS: 1448 [P: 16]
- 3) ASTM D 4052 / IP 365 Test Method for Density and Relative Density of liquids Digital Density Meter.
- 4) The Indian Standard Methods of Test for Petroleum Products IS: 1448 [P: 18]
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- 6) Working Procedure Manual - Indian Oil Corporation, Karnataka, Bangalore
- 7) ASTM D 1218 Refractive Index and Refractive Dispersion of Hydrocarbon liquids.
- 8) ASTM D 6623 “ Determination of individual components in Spark ignition
- 9) Engine Fuels by High Resolution Gas Chromatography.
- 10) George V. Dyroff, “ Manual on Significance of Petroleum Products” 6th edition, ASTM Manual, Series 1, 1993.
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- 15) V.R.Dhole and G.K.Ghosal, Journal of Liquid Chromatography, 18(12) (1995) 2475-2488
- 16) A.Visalakshi, D.KasthuriBai, L.C.Amutha, Kalyani Kannan, “Forensic Significance of Evaluation of Research Octane Number (RON) by Capillary Gas Chromatography” Forensic Science Congress, Mumbai January 2003.

SECTION - 3

PETROLEUM HYDROCARBON SOLVENTS

3.1 Introduction

The term **PETROLEUM SOLVENTS** described the Special Liquid hydrocarbon fractions obtained from Petroleum for use in Industrial processes and commercial formulations to dissolve, suspend or transport the other ingredients of the process or formulations. In recent years, the variety of Petroleum Solvents has been increased considerably due to the development of refining processes designed primarily for the transformation of low-octane feedstocks to high-octane fuels. Solvents are used extensively by industry in manufacturing processes for such diverse products as paint, printing ink, polish, adhesives, perfumes, glues, fats, etc., Further uses are found in the dry cleaning, leather and fur industries and the pesticide field. The hydrocarbon types present determine solvent properties. In general **aromatic hydrocarbons** have highest solvent power and **straight-chain aliphatics** the lowest.

3.2 Solvent types

The commercial classification of hydrocarbon solvents is

- Narrow cut aliphatics
- Special Boiling Point Solvents (SBP)
- Mineral spirit types
- Aromatics
- Kerosenes

3.3 Analysis and Test methods of low boiling Petroleum Hydrocarbon Solvents

The low boiling Petroleum Hydrocarbon Solvents such as Naphtha, SBP solvents, Mineral Spirits, raffinates, etc., are sent to this laboratory as such in context of illegal possession or sometimes coloured orange or red as simulated Petrol. The analysis of such low boiling hydrocarbon solvents involve measurements like density/relative density (Specific Gravity) refractive index, flash point, distillation range and aniline point.

3.3.1 Density / Specific gravity: Experimental (IP- 160/ ASTM D-1298)

Specific Gravity is defined as the ratio of a weight of a given volume of material to the weight of an equal volume of water under specified conditions. Specific gravity is usually determined by ASTM Test Methods for Specific Gravity of liquid Industrial Chemicals (**D 891**) or ASTM (**D 1298**). A glass hydrometer is used for this purpose. By using conversion tables temperature correction is made and Specific Gravity is measured at 15°C. API gravity is calculated (formula as mentioned in Section: 2) and the results are recorded. Automatic Density Meter can also be used to calculate the density, Specific Gravity and API Gravity.

3.3.2 Flash Point : (ASTM D56 : D 92 : D 93 : D 1310 : D 6450)

The flash point of a liquid is a lowest temperature at which application of flame causes the vapour above the sample to ignite. There are three types of apparatus used for the determination of Flash point namely Cleveland open cup, Pensky Marten closed cup (PMCC) and Abel. Abel is used for those liquids having flash point up to 70⁰ C. PMCC is used for the determination of flash point of fuels and lubricant whereas COC is mainly for lubricants. ASTM D 6450 determine the flash point of all the products from 10 – 250⁰ C. Flash points indicate comparatively the degree of safety in storage, transportation and use of liquid Petroleum hydrocarbon products either in closed or open containers.

3.3.3 Distillation: (ASTM D 86:D 850:D 1078: P18 IS 1448 Methods of Test: IP123)

The significance of distillation results is based on the close relationship to volatility, which in turn, largely govern evaporation rate. The same procedure (ASTM D 86) as mentioned for petrol is followed. The values are recorded. The distillation range gives an idea regarding the nature of the solvent whether narrow cut solvents or wide range solvents.

3.3.4 Aniline Point : (ASTM D 611: P 3 IS 1448 Methods of Test: IP2)

It is the lowest temperature at which the sample is completely miscible with an equal volume of aniline. Aromatics are more soluble in Aniline therefore have the lowest values whereas the Parraffins have the highest. It gives an idea whether the product is aromatic, naphthenic or paraffinic in nature.

3.3.5 Method

The test sample of the petroleum Product was dehydrated by using anhydrous sodium sulphate. The apparatus was cleaned and dried thoroughly. 5 ml / 10 ml of the dehydrated sample and 5 ml / 10 ml of freshly distilled aniline (while distilling Aniline the Ist and the last 10 % portion is to be discarded and the middle one is to be taken for experimental purposes). Equal volumes of test sample and aniline were taken in a sample tube. The cork stirrer and thermometer were assembled so that the bottom of the thermometer bulb was 5 mm from the bottom of the test tube and central with respect to the ring of the stirrer. The sample tube was concentrically supported in the jacket containing white oil bath, so that it was approximately 20 mm above the bottom of the jacket. The mixture was stirred rapidly but taking care to avoid splashing and inclusion of any air bubbles as much as possible. Aniline and test petroleum sample was not miscible at room temperature. When the solution was slowly heated in the glycerol bath in the jacket with constant stirring until complete miscibility was obtained. The temperature at which the two liquids are completely miscible is known as the aniline point. The apparatus was then removed from the bath and allowed the solution to cool, with

constant stirring at the rate not exceeding 1°C / min. The approximate aniline point was noted as the temperature at which the mixture becomes so cloudy as to obscure the thermometer bulb by reflected light.

Automatic digital aniline point apparatus can also be used for this purpose.

3.3.6 Gas Chromatography

It is an analytical technique used to identify hydrocarbon solvents.

3.3.7 Experimental Conditions – Low boiling hydrocarbon solvents like Naphtha (LAN & HAN), SBP Solvents etc.,

- Column : SP 2100 (packed)
- Carrier gas : Nitrogen (25ml / min)
- Hydrogen : Flow (25ml / min)
- Air : Flow (250ml / min)
- Injector : 200°C
- Detector : Flame Ionisation Detector 220°C
- Programming mode : Initial temp 40°C hold 2mts
Ramp rate 5°C/min Ramp 1 : 60°C Ramp 2 : 90°C
Ramp 3 : 150°C Ramp 4 : 180°C

3.3.8 Experimental Conditions – Kerosene and medium boiling hydrocarbon solvents like Mineral Spirits, ATF, etc.,

- Column : 5% SP 2100 on Chromosorb (packed)
- Carrier gas : Nitrogen (25ml / min)
- Hydrogen : Flow (25ml / min)
- Air : Flow (250ml / min)
- Injector : 280°C
- Detector : Flame Ionisation Detector 300°C
- Programming mode : Initial temp 70°C hold 2mts
Ramp rate 5°C/min Ramp 1 : 100°C Ramp 2 : 150°C
Ramp 3 : 200°C Ramp 4 : 250°C

3.3.9 Hydrocarbon characterization of Petroleum Hydrocarbon solvents by GC-DHA.

Detailed Experimental Procedure and Hydrocarbon Profile is given in Section 2.

REFERENCE:

1. ASTM D 1298 /IP 160 “ Density, Relative density or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer method.
2. ASTM D 4052 / IP 365 Test Method for Density and Relative Density of liquids Digital Density Meter.
3. ASTM D 1218 “Refractive Index and Refractive Dispersion of Hydrocarbon Liquids.
4. ASTM D 92 / IP 36 “Flash and Fire Points by Cleveland Open Cup
5. ASTM D 93 /IP 34 “ Flash Point Pensky Marten Closed Tester”
6. ASTM D 1310 “ Flash Point and Fire Points of Liquids by Tag open-cup Apparatus.
7. ASTM D 86 / IP 123 “Distillation of Petroleum Products”
8. ASTM D 5134 “Detailed Analysis of Petroleum Naphthas through n-nonane By Capillary Gas Chromatography.
9. ASTM D 6450 – 99 “ Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester

SECTION - 4

KEROSENE / SUPERIOR KEROSENE OIL (SKO)

4.1 Introduction

Fuel oils are complex mixtures of compounds of Carbon and Hydrogen, they cannot be classified rigidly or defined exactly by chemical formulae or definite physical properties. Two broad classifications are generally recognized:

1. “distillate fuel oils” & 2. “Residual fuel oils”. The latter are often referred to as heavy fuel oils and may contain cutter stock or distillates. eg., furnace oil. Distillate fuel oils are Petroleum fractions that have been vaporized and condensed. They are produced by distillation process in which petroleum is separated into fractions according to their boiling range. Distillate fuel oils may be produced not only from “straight run” crude oils but also from subsequent refinery process such as thermal or catalytic cracking. Kerosene and Diesel (gas oil) are typical examples of distillate fuels. Kerosene normally boils in the range of 150°C – 250°C (max: 300°C) and consists of C₁₁ – C₁₈ hydrocarbons. Kerosene is a blend of Paraffins, Naphthenes and Aromatics wherein Paraffins and Napthenes as major components and aromatics as minor components. The most important characteristics governed by **IS 1459/1974 (reaffirmed 1996)** are distillation, colour, flash point, smoke point and burning quality.

Two types of Kerosene are normally available commercially .

- ***Kerosene (colourless)***
- ***Regular Blue dyed Kerosene for Public Distribution Supply (PDS)***

(Blue dye is Di-alkyl amino anthraquinone)

4.2 Test Methods as per IS 1459/1974

4.2.1 Density: (P: 16 IS 1448 Methods of Test)

Methods are same as described in Petrol. This parameter is not included in Bureau of Indian Standard Specifications. A typical Standard Kerosene is having density (gm/cm³) at 15°C **0.78 – 0.82**.

4.2.2 Distillation: (ASTM D 86, IP 123, P: 18 IS 1448 Methods of test)

It gives an idea of volatility characteristics of the fuel. It can be determined by

- **Non-fractionating type ASTM – Manual**
- **Non-fractionating type ASTM – Automatic**

Procedure is similar to that of Petrol. The entire sample should distill below 300°C.

4.2.3 Flash Point : (P 20 IS 1448 methods of test : ASTM D 56 & D 6450)

Test method is similar as mentioned in Section 3.

4.2.4 Viscosity: (P: 25 IS 1448 methods of test: IP 71 : ASTM D 445)

The Viscosity is the property of its resistance to flow. Different units of viscosity are in use, based on a number of seconds taken for a specific and measured quantity of oil to flow in a standard apparatus at a fixed temperature.

The universally accepted method is Kinematic Viscosity and is a measure of resistance to gravity flow of fluid, the pressure head being proportional to density. For the determination of Kinematic Viscosity, the time is measured in seconds for a fixed volume of liquid flow under gravity, through a standard capillary of a calibrated viscometer at a closely controlled temperature. The Kinematic Viscosity is the product of time in seconds and calibration constant of the viscometer and is measured in centistokes at 40°C for Kerosene and Diesel.

- Canon Penske Viscometer – routine
- BS/IP U tube or any equivalent calibrated Viscometer

4.2.5 Method

The sample is put in a viscometer and kept in a viscosity bath to attain the temperature. Sample is sucked with the help of rubber sucker (bellow) & time of flow is noted. The time of flow in seconds multiplying with the constant of viscometer will give viscosity in cst.

4.2.6 Smoke point –(IP 57 : P 31 IS 1448 methods of test : ASTM D 1322):

It is the maximum height in mm at which Kerosene will burn without smoke in a smoke point lamp. It is an indication of degree of refinement. Higher the smoke point the larger will be smoke free flame therefore better illumination and degree of refinement of kerosene. Paraffins have the highest smoke point, aromatics the lowest and naphthenes the intermediate.

4.2.7 Method

Smoke point is an indicator of the combustion qualities of Aviation Turbine Fuels and Kerosene. The fuel sample is burned in the Smoke Point lamp and the maximum flame height obtainable without smoking is measured.

The Smoke point of a typical standard Kerosene is **18 mm to 22 mm**

4.2.8 Colour: (Blue dyed Kerosene) as per IS 1459 (second revision reaffirmed in 1991)

- *Visual : Note down the colour of the sample visually*

- **UV – Visible Spectrophotometry** : Note down the wavelength for maximum absorption for **BLUE** using visible spectrophotometer.

Equipment	: Spectrophotometer
Method	: Scan - Ordinate mode
Scan Speed	: 120nm / min
Lamp	: Tungston (Visible region)
Wavelength	: 600 nm – 700 nm
Peak threshold	: 0.02
Oil Blue dye	: λ_{max} -- 645nm – 655 nm (Di alkyl amino anthroquinone dye is normally used for colouring PDS kerosene)

Thin Layer Chromatographic methods for the detection of oil soluble dyes.

The standard Kerosene sample (2 μl), reference standard dyes namely oil blue in solvent ether (2 μl) each were spotted on TLC (Silica Gel 60 G) plates or Silica Gel (60 F 254) Alumina pre-coated plates along with case samples. The plates were developed in the saturated chambers containing **Hexane:Toluene: Acetic Acid [50 : 50 : 2]** as solvent systems and run the plate upto 10 cm distance and remove the plate from the chamber and dry it.

Detection: Blue dye from Kerosene (Standard) sample shows one blue colour spot at Rf around 0.4. This blue dye was found to be oil blue dye used for colouring Kerosene (**PDS - Kerosene**).

4.3 Gas Chromatograph

Refer Section 2 for details.

4.3.1 Conclusion

SKO is normally used as a domestic fuel for illumination and cooking. This may also be used for the industrial and the commercial application.

SKO may be misused by the transporters etc for adulterating Petrol and High Speed Diesel. Also there is every chance of the subsidized SKO being given to commercial applications by the dealers. To avoid misuse and adulteration using SKO, it is doped with blue dye.

SECTION - 5

DIESEL (LIGHT DIESEL OIL & HIGH SPEED DIESEL)

5.1 Introduction

Diesel and non-aviation gas turbine fuels were originally straight run products obtained from the distillation of crude oil. Today with the various refinery-cracking processes, these fuels may contain varying amounts of selected cracked distillates. This permits an increase in the volume of available fuel at a minimum cost. The boiling range of distillate fuel (Diesel) is approximately 150°C to 400°C. It consists of C₁₈ to C₂₈ hydrocarbons. It is a blend of Saturates and aromatics (mainly polyaromatics). The relative merits of the fuel types to be considered will depend upon the refining practices employed, the nature of crude oils from which they are produced, and the additive package if (any) used. The broad definition of fuels for land and marine diesel engines and non-aviation gas turbines covers many possible combinations of volatility, ignition quality, Viscosity, gravity, stability and other properties. The most important characteristics governed by IS 1460/2000 are density at 15°C, Flash Point, Pour Point, distillation and Kinematic Viscosity at 40°C, Cetane No, Cetane Index and Sulphur. Two types of Diesel namely Light Diesel Oil (LDO) and High Speed Diesel Oil (HSD) are normally referred for analysis.

5.2 Test Method (Required as per IS 1460/2000 – Diesel Fuels)

5.2.1 Density: (P: 16 IS 1448 Methods of Test)

Methods are same as described in Petrol. A typical Standard HSD is having density (Kg/m³) at 15°C **820 – 870**

Note:

- Increase in density (above 870 Kg/M³) indicates the presence of possible adulterants like Hi-Flash Heavy Aromatic Naphtha, light viscous oil, etc.,
- Decrease in density (below 810 Kg/M³) indicates the presence of possible adulterants like Kerosene and middle distillates.

5.2.2 Distillation: (ASTM D 86/ IP 123, P:18 IS 1448 Methods of Test)

It gives an idea of volatility characteristics of the fuel. It can be determined by

- **Non-fractionating type ASTM – Manual**
- **Non-fractionating type ASTM – Automatic**

Procedure is similar to that of Petrol. The entire sample should distill below 400°C. 85% volume recovery should be below 350°C and 95% volume recovery should be below 370°C. The distillation range of typical standard Diesel is **150°C to 380°C**.

5.2.4 Flash Point : (ASTM D 56 & 6450 : P 20 IS 1448 methods of test)

Test method is similar as mentioned in Section 3. The flash point of typical standard Diesel is 35°C -- 40°C.

5.2.5 Viscosity : (P:25 IS 1448 methods of test : IP 71 : ASTM D 445)

The Viscosity is the property of its resistance to flow. Different units of viscosity are in use, based on a number of seconds taken for a specific and measured quantity of oil to flow in a standard apparatus at a fixed temperature.

The universally accepted method is Kinematic Viscosity and is a measure of resistance to gravity flow of fluid, the pressure head being proportional to density. For the determination of Kinematic Viscosity, the time is measured in seconds for a fixed volume of liquid flow under gravity, through a standard capillary of a calibrated viscometer at a closely controlled temperature. The Kinematic Viscosity is the product of time in seconds and calibration constant of the viscometer and is measured in centistokes at 40°C for Kerosene and Diesel.

- Canon Penske Viscometer – routine
- BS/IP U tube or any equivalent calibrated Viscometer

5.2.6 Method

Already discussed in 4.2.5

Constant temperature Kinematic Viscosity bath can be utilized to maintain at a specified temperature. (KV Bath)

Note:

- Decrease in Kinematic Viscosity indicates the presence of possible adulterants like Kerosene and Heavy aromatic Naphtha
- Increase in Kinematic Viscosity indicates the presence of possible adulterant like low viscosity grade oil.

5.2.7 Pour Point (IP 15 : P 10 IS 1448 Methods of Test : ASTM D 97 / D 2500)

Petroleum oils do not have any freezing points as they contain compounds of large molecular size and configuration. They become only semi/plastic solid when cooled to sufficient low temperature under standard conditions. Pour point is the lowest temperature which is multiple of 3°C at which the oil ceased to flow under prescribed conditions and is reported 3°C higher than it. Manual / Automatic Pour point Apparatus can be used.

Note:

- Adulteration with low viscous oil will raise the Pour Point and some times this parameter becomes not characteristic.

Although different methods have been incorporated in BIS, the methods mentioned below will be very authentic and effective in analysing any type of Diesel adulteration.

5.2.8 Sulphur (IP 61 or P:33)

5.3 Calculated Cetane Index (CCI)

It is an indicative of ignition quality and can be calculated from density and distillation data. ASTM D 86 using ASTM D 4737 Method given below:

A correlation in SI units has been established between the ASTM cetane number and density and 10%, 50% and 90% recovery temperatures of the fuel. The relationship is given by the following equations:

$$\begin{aligned} \text{CCI} = & 45.2 \\ & + (0.0892)(T_{10N}) \\ & + (0.131 + (0.901)(B)) (T_{50N}) \\ & + (0.0523 - (0.420)(B)) (T_{90N}) \\ & + (0.00049)((T_{10N})^2 - (T_{90N})^2) \\ & + (107)(B) + (60)(B)^2 \end{aligned}$$

Where:

CCI = Calculated Cetane Index by four variable equation

D = Density at 15° C, determined test method D 1298

DN = D-0.85

B = $(e^{(-3.5)(DN)}) - 1$

T₁₀ = 10% recovery temperature, °C, determined by test method D 86 and corrected to Standard barometric pressure

T_{10N} = T₁₀ - 215

T₅₀ = 50% recovery temperature, °C, determined by test method 86 and corrected to Standard barometric pressure

T_{50N} = T₅₀ - 260

T₉₀ = 90% recovery temperature, °C, determined by test method 86 and corrected to Standard barometric pressure

T_{90N} = T₉₀ - 310

5.3.1 Calculated Cetane Index (ASTM D976-91)

$$\text{CCI} = 454.74 - 1641.416 D + 774.74 D^2 - 0.554 B + 97.803 (\text{Log}B)^2$$

Where D= Density at 15°C g/ml and B= Mid – boiling Temperature°C

5.4 Gas liquid Chromatography for quantitative determination of adulteration in Diesel with Kerosene

5.4.1 Equipment : Gas Chromatograph with FID and temperature programmer.

Operating Conditions:

- Column : Dual columns of 15% Apizeon on CHW Aw, ¼ inch OD, 8'length SS, max temp 300°C
- Nitrogen : 60ml/min Hydrogen/air : 40ml/min
- Sensitivity range : back off: 10^{-9} A
- Attenuation : 2
- sample for injection : 0.3 to 0.4µl
- 10% solutions of Diesel (D), Kerosene (K) and different admixtures (D-K) derived from D and K in moisture free solvent ether.
- Programming : Isothermal at 90°C for 3min then continued at 10°C/min between 90°C to 230°C and isothermal at 230°C for 8min.

5.4.2 Preparation of Samples

Pure Diesel, Kerosene and various admixtures (9D:1K, 8D:2K, 7D:3K...) were prepared in moisture free solvent ether. About 0.5µl was injected and the chromatograms were compared.

5.4.3 Observations and Calculations

A characteristic pattern of chromatogram for diesel samples indicate less amplitudes of earlier peaks (between 100C and 180C) and more amplitudes of later peaks (between 180C and 230C including 8 min final isothermal hold) [Fig]. The reverse is true for Kerosene samples [Fig 3.11 & 3.12]] similarly a gradual change in the chromatogram pattern was observed in the experimental admixtures [Fig 3.13 to 3.17]. The area of the earlier peaks, between the cut off points 1 to 2 (100C to 180C) was recorded as A and the area of the later peaks between the cut off points 2 to 3 [between 180C and 230C including 8 min final isothermal hold] was recorded as B. $\log (10X A/B)$ values were calculated for different D-K compositions in all the samples. A simple ratio of A/B Vs D-K composition would give a non-linear curve. Hence, with a view to have a linear plot log of this ratio was found to be necessary. Any adulteration of Diesel with Kerosene will change this value within the limits of standards.

5.4.4 Conclusion

Kerosene adulterant can easily be detected by Pour Point determination and also Instrumental technique like GC and HPLC.

5.5 Light Diesel Oil

As per IS 1450, the analysis of light diesel oil involves measurement of density, flash point, distillation, pour point, Kinematic viscosity at 40°C

5.5.1 Density: (P: 16 IS 1448 Methods of Test)

Methods are same as described in Petrol. A typical Standard LDO is having density (gm/cm³) at 15°C **0.850 – 0.890**

5.5.2. Flash Point –Pensky-Martens closed cup (P: 21 IS 1448 Methods of Test)

The Pensky-Martens closed cup (PMC) is used for the measurement of flash point of light diesel oil. In general, the flash Point of LDO is 66°C (minimum)

5.5.3 Method

Clean and dry all parts of cup and its accessories before starting the test. Fill the cup with the sample to be tested to the level indicated by the filling mark place the lid on the cup. Insert the thermometer in the sample cup. Light the test flame placed on the top of cup and adjust it to 4.0mm diameter. Heat the Pensky – martens apparatus with Bunsen burner and keep the rate of heating *as 5°C to 6°C per minute*. Turn the stirrer in the apparatus at the rate of 90 to 120rev/min. Stirring in downward direction measure the flash point with the help of test flame and measure the flash point of LDO.

5.5.4 Viscosity: (P: 25 IS 1448 methods of test: IP 71: ASTM D 445)

Test method is similar to HSD, Kerosene. The experimental procedure is identical to that for measurement of Kinematic Viscosity in High Speed Diesel and Kerosene.

5.5.5 Pour Point (IP 15: P 10 IS 1448 Methods of Test: ASTM D 97 / D 2500)

Experimental procedures and methods are similar to that of HSD. The values are recorded. The minimum value of pour point for summer is +12 and for winter +21.

SECTION - 6

AVIATION TURBINE FUELS (ATF – KEROSENE)

6.1 Introduction

Aviation Turbine Fuels (ATF) are manufactured predominantly from straight run Kerosenes or Kerosene/naphtha blends which are obtained from the atmospheric distillation of crude oil. Previously, jet fuels were manufactured from straight run kerosene which were produced from thermally cracking or catalytic cracked stocks. These jet fuels does not conform to IS specification. In recent years however hydro cracking processes have been introduced which produce high quality kerosene fractions ideal for jet fuel. The most important characteristics governed by IS: 1571 are chemical composition, volatility namely distillation, flash point, etc., density, smoke point and the most important property **Freezing point**. Normally, Forensic Science Laboratory receives ATF as a case of pilferage or some times as a case of adulteration.

6.2 Test Methods as per IS 1571/1985

6.2.1 Density: (P:16 IS 1448 Methods of Test)

Methods are same as described in Petrol. A typical Standard ATF-Kerosene is having density (gm/cm³) at 15°C **0.775 – 0.830**

6.2.2 Distillation: (P:18 IS 1448 Methods of Test : IP 123 :ASTM D 86)

It gives an idea of volatility characteristics of the fuel. It can be determined by

- **Non-fractionating type ASTM – Manual**
- **Non-fractionating type ASTM – Automatic**

Procedure is similar to that of Petrol is followed. The entire sample should distill below 300°C. Distillation points of 10, 20, 50 and 90 percent specified in IS are characteristic of this fuel.

The distillation range of typical ATF is **150°C to 240°C**.

6.2.3 Flash Point : (P 20 IS 1448 Methods of Test : ASTM D 56 & 6450)

Test method is similar as mentioned in Section 3. The flash point of typical standard ATF is **40°C -- 45°C**.

6.2.4 Viscosity: (P: 25 IS 1448 methods of test: IP 71: ASTM D 445 and 2170)

The Viscosity is the property of its resistance to flow. Different units of viscosity are in use, based on a number of seconds taken for a specific and measured quantity of oil to flow in a standard apparatus at a fixed temperature.

The universally accepted method is Kinematic Viscosity and is a measure of resistance to gravity flow of fluid, the pressure head being proportional to density. For the determination of Kinematic Viscosity, the time is measured in seconds for a fixed volume of liquid flow under gravity, through a standard capillary of a calibrated viscometer at a closely controlled temperature. The Kinematic Viscosity is the product of time in seconds and calibration constant of the viscometer and is measured in centistokes at 40°C for Kerosene and Diesel.

- Canon Penske Viscometer – routine
- BS/IP U tube or any equivalent calibrated Viscometer

6.2.5 Method

The specific details of operation vary for the different types of viscometers. In all cases, the following procedure is followed:

Select a clean dry, calibrated viscometer having a range covering the estimated viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time should not be less than 200 seconds. Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity with that employed when the instrument was calibrated. Should the sample contain solid particles, filter during charging through a 75-micron IS Sieve. Constant temperature Viscometer bath can be utilized for measuring KV at a particular temperature. Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Because this time will vary for the different instruments and for different temperatures, establish a safe temperature equilibrium time by trial (30 minutes should be sufficient). Use suction or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 5 mm ahead of the first timing mark. With the sample flowing freely, measure in seconds, to within 0.2 seconds and the time required for the meniscus to pass from the first timing mark to the second. If this flow time is less than the specified minimum select a viscometer with a capillary of smaller diameter and repeat the operation.

CALCULATION

Calculate the Kinematic Viscosity “ ν ” from the measured flow time ‘t’ and the instrument constant “C” by means of the following equation

$\nu = C \times t$, Where,

ν = Kinematic Viscosity in centistokes,

C = Calibration constant of the Viscometer in centistokes per second and

t = flow time in seconds

6.2.6 Freezing Point (P11 IS 1448 Methods of Test : IP 16 : ASTM 2386)

Aviation fuels must have acceptable freezing points and low-temperature pumpability characteristics so that adequate fuel flow to the engine is maintained during long cruise periods at high altitude. ASTM test for Freezing-Point of Aviation fuels (D 2386 / IP 16) and its associated specification limits guard against the possibility of solidified hydrocarbons separating from chilled fuel and blocking fuel lines, filter, nozzles, etc.,

Method

The automatic freezing point detection system provides automated sample testing with the accuracy and repeatability in accordance with ASTM D 2386. The sample is cooled in the test chamber with constant stirring. The sophisticated dynamic measurement system emits a light pulse every 0.5°C from a coaxial fiber optic cable positioned above the test sample. The light pulse is then reflected off the silvered bottom test jar to an optical sensor. The advanced software package analyzes the response of light pulse. The initial appearance of crystallization is monitored by light scattering. The sample is then warmed up and the temperature at which the hydrocarbon crystals disappear is recorded as the freezing point. All clear and transparent fuels are readily measured by the detection system, regardless of sample colour. The rapid cooling feature combined with a consistent cooling profile system provides repeatable results with high-test reproducibility.

The freezing point of a typical standard ATF is **--40°C to -55°C**

6.2.7 Smoke point (P 31 IS 1448 Methods of Test: IP 57 : ASTM D 1322)

It is the maximum height in mm at which kerosene will burn without smoke in a smoke point lamp. It is an indication of degree of illumination of sample. Higher the smoke point the large will be smoke free flame therefore better illumination.

Method

Smoke point is an indicator of the combustion qualities of aviation turbine fuels and kerosene. The fuel sample is burned in the Smoke Point lamp and the maximum flame height obtainable without smoking is measured.

The Smoke point of a typical standard ATF is **20 mm to 25mm**

6.3 Gas Chromatograph

Detailed explanation and experimental conditions etc., are given in **Section 2**.

6.4 Hydrocarbon composition (P: 23 IS 1448 methods of test)

GC-DHA method gives an entire profile of hydrocarbon composition of ATF, which is very much useful to fix the quality of the fuel. Detailed explanation and experimental procedures are given in Section 2.

Aromatics % by volume	22 (max)
Olefins % by Volume	5 (max)

ENGINE LUBRICATING OIL

7.1 Introduction

The major functions of lubricating oils is the reduction of friction and wear by the separation of surfaces, metallic or plastic, which are moving with respect to each other. Petroleum base lubricating oils are present in the residual fraction boiling above 370°C from the atmospheric distillation of selected crude oils of both Paraffinic and Naphthenic types. This residue is further distilled, under conditions of high vacuum, into series of fractions to provide light to heavy lubricating oil stocks. The number of fractions depends on the type of crude oil and the requirements of the refiner but 4 to 5 is a typical number. In the majority of cases to meet Specification requirements with respect to properties of base oils.

Petroleum based lubricating oils mainly consist of Paraffins, Naphthenes and Aromatics. The lubrication property of the particular lubricant depends on the distribution of these hydrocarbons. It consists of C₂₈ to C₄₀ hydrocarbons. The most important characteristics governed by **IS 13696** are **Specific** gravity, Flash point, Kinematic viscosity at 40°C and 100°C & Viscosity Index.

Apart from the above methods, the most significant parameter is **Total Base Number (TBN)**, which gives an indication of additive treatment in oil. The basic characteristics of this are to neutralize the acidic constituents formed during use. This parameter is very important to predict a sample is adulterated or simulated.

7.2 Test methods and their Significance

7.2.1 Relative density / Specific gravity –(P 32 IS 1448 Methods of Test : ASTM D1298)

It is defined as a ratio of the mass of a given volume of substance at t°C to the mass of the equal volume of water at the same temperature and is determined at 15°C.

The Specific Gravity is determined by using

- Hydrometer
- Specific Gravity Bottle
- Automatic density meter method

Specific gravity in many cases indicates the type or crude from which the product is made. Aromatics have the highest specific gravity where as paraffins the lowest. API gravity can be calculated from specific gravity (Section 2)

Significance

In case of used/reclaimed oils, lowering of specific gravity indicates

- Presence of high boiling solvents or admixture of lower gravity oils
- If the Specific Gravity of the used/reclaimed oil is heavier than the original it indicates one or more of the following
 - Oxidation of the oil charge
 - Presence of insolubles
 - Contamination with water
 - Addition of higher specific gravity oil.

The Specific Gravity of engine lubricating oil at 15°C normally varies from **0.85 to 0.90**

7.2.2 Viscosity: I (P: 25 IS 1448 methods of test: IP 71: ASTM D 445 and 2170)

The Viscosity is the property of its resistance to flow. Different units of viscosity are in use, based on a number of seconds taken for a specific and measured quantity of oil to flow in a standard apparatus at a fixed temperature.

The universally accepted method is Kinematic Viscosity and is a measure of resistance to gravity flow of fluid, the pressure head being proportional to density. For the determination of Kinematic Viscosity, the time is measured in seconds for a fixed volume of liquid flow under gravity, through a standard capillary of a calibrated viscometer at a closely controlled temperature. The Kinematic Viscosity is the product of time in seconds and calibration constant of the viscometer and is measured in centistokes at 40°C for Kerosene and Diesel.

- Canon Penske Viscometer – routine
- BS/IP U tube or any equivalent calibrated Viscometer

7.2.3 Method

The specific details of operation vary for the different types of viscometers. In all cases, the following procedure is followed:

Select a clean dry, calibrated viscometer having a range covering the estimated viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time should not be less than 200 seconds. Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity with that employed when the instrument was calibrated. Should

the sample contain solid particles, filter during charging through a 75-micron IS Sieve. Constant temperature Viscometer bath can be utilized for measuring KV at a particular temperature. Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Because this time will vary for the different instruments and for different temperatures, establish a safe temperature equilibrium time by trial (30 minutes should be sufficient). Use suction or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 5mm ahead of the first timing mark. With the sample flowing freely, measure in seconds, to within 0.2 seconds and the time required for the meniscus to pass from the first timing mark to the second. If this flow time is less than the specified minimum select a viscometer with a capillary of smaller diameter and repeat the operation.

CALCULATION

Calculate the Kinematic Viscosity “ ν ” from the measured flow time ‘t’ and the instrument constant “C” by means of the following equation

$$\nu = C \times t$$

Where,

ν = Kinematic Viscosity in centistokes,

C = Calibration constant of the Viscometer in centistokes per second and

t = flow time in seconds

The Kinematic Viscosity can be measured in centistokes at two different temperatures **40°C and 100°C** in order to find out the Index. Different grades of oil (SAE 5W, 10W, 20W and SAE 20,30,40,50) are available based on their viscosity at 100°C. Low viscosity oil is required for high-speed bearings. High viscosity oil is required for heavily loaded and slow speed bearings.

Note:

- Viscosity is the most important single property of a lubricating oil
- In case of used oils if viscosity is lower than the original it indicates fuel dilution or admixture with low viscosity oils

7.2.4 Viscosity Index (P 56 IS 1448 Methods of Test : IP 226)

Viscosity Index (VI) is the rate of change of viscosity with respect to temperature. During the engine operation the moving parts get heated resulting the thinning of the oil layer between the mating surfaces resulting the poor lubrication. Since most of the oils have to be operated over a range of temperature.

Dean and Davis introduced a scheme by which a single number called Viscosity Index classified oil according to its viscosity temperature characteristics. They took

two oil, one Paraffinic from Pennsylvanian crude and other Naphthenic oil from Gulf crude and determined viscosity at two different temperatures 100°F & 210°F (presently temperature followed are 40°C & 100°C). The Paraffinic oil which was assigned viscosity arbitrary number 100 and the Naphthenic oil which was assigned viscosity arbitrary number 0 were taken for calculating Viscosity Index by the following formula

$$\text{Viscosity Index (VI)} = \frac{L - U}{L - H} \times 100$$

Where,

L = low VI oil (zero) but having the same viscosity at 100°C as of the unknown oil (oil in question)

H = high VI oil (100) having the same viscosity at 100C as of the Unknown oil

U = Kinematic Viscosity of unknown oil at 40°C

**The values of L and H can be obtained from table given in IS 1448 P: 56
It shows that L, H & U have the same viscosity at 100°C but different at 40°C**

Note

- A genuine oil will have higher Viscosity Index
- Decrease in VI indicates the possible adulteration with high boiling compound or admixture of low viscosity oils
- Blending lubricating oil shall have Viscosity Index 90 minimum
- Presence of diluents may result in the high viscosity index & in this case the oil should be checked for flash point. Lowering of the flash point is an indication of contamination/ adulteration.

7.2.5 Flash Point : (P 20 IS 1448 Methods of Test : ASTM D56 : D 92: D 93: D 1310 & 6450)

: The flash point of a liquid is a lowest temperature at which application of flame causes the vapour above the sample to ignite. There are three types of apparatus used for the determination of Flash point namely Cleveland open cup, Pensky Marten closed cup (PMCC) and Abel. Abel is used for those liquids having flash point up to 70°C. Flash points indicate comparatively the degree of safety in storage, transportation and use of liquid Petroleum hydrocarbon products either in closed or open containers.

The flash point of lubricating oil is carried out by Cleveland open cup/ Pensky Marten closed cup (Automatic) and Cleveland open cup (Automatic). About 75ml

of the sample is taken in a flash point cup and set all the parameters mentioned in the procedure manual are followed and their flash point is observed.

7.2.6 Carbon Residue (P8 IS 1448 Methods of Test: IP 13, 14)

It is an amount of carbonaceous material formed when a sample is evaporated and pyrolysed under specified conditions. The lighter will evaporate but the heavier more complex compounds will decompose forming carbonaceous deposits. There are three methods for its determination.

- Conradson
- Ramsbottom
- Micro carbon residue

In the Conradson method sample is heated in a crucible under controlled conditions in absence of air and the residue left is weighed. Whereas, in Ramsbottom test the sample is placed in the tube with the capillary at the top and heated to 550⁰ C in a bath of molten metal.

Micro carbon residue ?

-

7.2.7 Neutralisation Value –(P: 1 IS 1448 Methods of Test:IP 177 ASTM D 974/97)

It is a measure of Acidity and Alkalinity of an oil. In order to improve the quality and life of an oil different types of additives are blended to it. The presence of acid and base number is an indication of additive treatment in a new oil. In new and used oils, the constituents considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals and addition agents such as inhibitors and detergents. Similarly, constituents considered to have basic properties include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, salts of heavy metals and addition agents such as inhibitors and detergents.

Summary of Test Method

To determine the acid or base number, the sample is dissolved in a titrating solvent consists of toluene and isopropyl alcohol containing small amount of water and the resulting acid-phase solution is titrated at room temperature with standard non aqueous alcoholic KOH or isopropyl alcoholic acid solution, respectively, to the end point indicated by the colour change of the added p-naphtholbenzein solution (orange in acid and green-brown in base)

Procedure for Acid Number

- Weigh a suitable quantity of the sample (about 2.0 gm) in a 250ml flask.

- Add 100ml of the titration solvent (500 ml toluene = 5ml water to 495ml of anhydrous isopropyl alcohol)
- Add 0.5 ml of the indicator (p-naphtholbenzein in a titration solvent – 10 gm/lit)
- If the mixture assumes yellow-orange coloration it is titrated against 0.1M KOH.
- The end point is the colour change from orange to green or green-brown.
- Repeat for concordant values
- Run blank determination by taking 100ml of the titrating solvent and 0.5 ml of indicator solution.

Calculation:

$$\text{Acid number, mg of KOH/g} = \frac{[(A-B)M \times 56.1]}{W}$$

Where,

A = KOH solution required for titration of the sample, ml

B = KOH solution required for titration for blank, ml

M = Molarity of KOH solution

W = Sample used in grams

7.2.8 Procedure for Base Number

- Weigh a suitable quantity of the sample (about 2.0 gm) in a 250ml flask.
- Add 100 ml of the titration solvent (500 ml toluene = 5ml water to 495ml of anhydrous isopropyl alcohol)
- Add 0.5 ml of the indicator (p-naphtholbenzein in a titration solvent – 10 gm/lit)
- If the mixture assumes green or green-brown coloration it is titrated against 0.1M HCl.
- The end point is the colour change from green-brown to orange.
- Repeat for concordant values
- Run blank determination by taking 100 ml of the titrating solvent and 0.5 ml of indicator solution. (same as in Acid Number)

Calculation

$$\text{Base number, mg of KOH/g} = \frac{[(Em + FM)] \times 56.1}{W}$$

Where,

E = HCl solution required for titration of the sample, ml

m = molarity of HCl

M = Molarity of KOH solution

W = Sample used in grams

F = KOH required for titration of the acid number blank, ml

7.2.9 Total Base Number of New and Used Lubricating oils (Mobil Lubricants)

Scope: A colour indicator titration test for TBN has been developed by MOBIL. This is applicable to oils containing Methyl and Amine type of additives. The sample is mixed with indicator solution and the solution titrated with perchloric acid to the end point, indicated by the colour change.

- **PURPLE : When BASIC**
- **GREEN : When NEUTRAL**
- **AMBER : When ACIDIC**

Reagents

1. Crystal Violet Indicator : 50 mgs of Crystal Violet Indicator is dissolved in glacial Acetic Acid and transferred to a one litre flask. Add 125 ml of Iso Octane. Make the volume to one litre with Glacial Acetic Acid and shake. Keep the contents in a glass bottle.
2. Glacial Acetic Acid (AR grade)
3. Perchloric acid : Dilute 27.5 ml of Perchloric acid to one litre with Glacial Acetic Acid.
4. Weigh 400mgs of Pot. Phthalate in a 100 ml flask and make up with glacial acetic acid

Procedure

Standardisation of Acid

- Titrate 25 ml of Pot. Phthalate solution with Perchloric acid using 15 ml of indicator solution to a green end point. Record the Volume of Acid used (v)
- Titrate a Blank (15ml of indicator solution with 25ml Glacial acetic acid) with Perchloric acid. Record the volume of Acid used. (b)
- Calculate the Titre (T) of the acid as follows:

$$T = \frac{0.06869 \times W}{(v-b)} \quad W = \text{Wt. Of Pot. Phthalate in mg.}$$

Total Base Number (TBN)

- Weigh about 2 g of the oil in a 50 ml beaker and warm gently at 50°C
- Transfer to a tarred graduated (30 ml capacity) clean centrifuge tube upto 2 ml.
- Reweigh the tube.
- Add the indicator solution into the tube so that the total volume reach 10ml
- Stopper the tube with a clean dry Teflon cork and shake it for 5 seconds.
- Allow the contents of the tube to settle
- Add perchloric acid from the burette, till the colour of the tip becomes purple and allow to settle and note down the volume of acid used.(V)
- Titrate a blank similarly.
- Note down the volume of acid used (B)

$$\text{Total Base Number (TBN) mg of TBN KOH / mg} = \frac{\mathbf{T(V-B)}}{\mathbf{S}}$$

Where T = Titre of Acid as determined above
S = weight of the sample used.

TBN can also be determined by Potentiometric method as per ASTM D 2896/98

Note:

- **The finished genuine blended Engine Lubricating oils will have a required TBN as per Company Specifications.**
- **In general, the TBN of finished blended Engine Lubricating oil is 5 (minimum)**
- **Decrease in TBN (as per company specification) indicates the presence of possible adulterants preferably reclaimed / re-refined used engine oil.**
- **Negligible TBN indicates the possible simulation with reclaimed / re-refined engine oil.**
- **TBN is an excellent parameter to find out the quality of an oil whether adulterated / simulated.**

SECTION - 8

LUBRICATING GREASES

8.1 Introduction

Greases were well known from ancient time. Lime mixed in olive oil was in use to lubricate the axles of wooden carriage by Egyptians in 1400 B.C. The development of modern grease has followed the development of modern industrial age. Grease is nothing but dispersion of thickening agent in liquid lubricant making it Semi lucid to lucid product. In order to improve its quantities to meet the requirements of particular machine / machinery certain additives are incorporated which improves not only the performance but also the stability and life. In brief greases must fulfill the following tasks in lubrication Technology.

- By slow separation of it, they must release a quantity of liquid lubricant sufficient to reduce friction and wear in the bearings over a wide range of temperature and long period of time.
- They must act as barrier against water and abrasive substances.

8.2 Classification of Greases

Greases are primarily classified by their thickness. The most common are metallic soaps. Other includes, poly-urea and inorganic thickeners, polymers, clay, lime etc. The grease manufactured/formulated must meet the respective specification laid down by Bureau of Indian Standard. Some of the important common and special types are covered as per the following specifications.

Graphite type IS 508
Automotive IS 506
General purpose IS 507
Grease low temperature 7514
Antifriction bearing IS 712
Locomotive IS 720
Lithium base IS 7623
Calcium Complex IS 9136
Calcium base heat resistance IS 9917
Wheel bearing IS 10647
Calcium base P IS 11637
Lithium Base IS 12203
Non soap IS 12790
Silicon IS 14383 - and many more

The most important properties in all the above greases are Acidity and Alkalinity, Drop Point, Evaporation Loss, Corrosion, Oil Separation during storage, Cone penetration (Consistency), Viscosity of Mineral Oil, Heat stability, Sulphated ash, Oxidation stability etc.

8.3 Acidity and Alkalinity of Greases (P 53 IS 1448 Methods of Test)

This method describes the procedure for the determination of free acid, free alkali and insoluble carbonates in Calcium, Sodium and lithium in greases of conventional type. A known quantity of sample is dissolved in n-hexane and to it alcohol is also added. Put few drops of indicator (Phenolphthalein). If the alcoholic layer after shaking becomes pink add known quantity of 0.5N Hcl solution and titrate the excess acid back with 0.5N alcoholic KOH solution and calculate the free alkalinity in term of Sodium Hydroxide. If the original alcoholic layer is not pink titrate the unheated solution with 0.5N alcoholic KOH and calculate for acidity in term of Oleic acid

8.4 Drop Point (ASTM D 2265 : P 52 IS 1448 Methods of Test)

Dropping point is the temperature at which the first drop of the material falls from the cup.

NOTE:

Dropping Point is a temperature at which the grease passes from semi solid to a liquid state under the conditions of tests. Greases containing thickness other than conventional type may, without in state may separate oil. This temperature is useful to assist in identifying the grease and maintaining bench mark for quality control.

8.5 Evaporation Loss (ASTM D 972 : P 61 & 68 IS 1448 Methods of tests)

This method covers the determination of evaporation loss of lubricating greases and oils for applications where evaporation loss is a factor in the range of 99 to 149C. The sample is placed in the evaporation cell kept in the bath at desired temperature. Heated air is passed over its surface for 22hours. The evaporation loss is calculated from the loss in weight of the sample.

NOTE:

The evaporation loss method can be used to determine the loss of volatile material from greases but it does not correlate with the service performance.

8.6 Corrosion (Copper Strip) ASTM D 4048 : P51 IS 1448 Methods of Tests

The method covers the detection of the corrosiveness to copper. The standard copper strip is immersed in a sample of grease and normally heated at 100C for 24 hours. At the end of the period the strip is removed, washed and compared with ASTM Copper Strip corrosion Standard.

NOTE:

Test method measures the tendency of lubricating grease to corrode Copper under specific conditions. Predicting of possible chemical attack on lubricated parts such as bearing. Such corrosion for example may cause premature bearing failures.

8.7 Oxidation Stability (ASTM D 942 : P 94 IS 1448 Methods of Tests)

It determines the resistance of lubricating greases to oxidation when stored in an oxygen atmosphere in a sealed system at an elevated temperatures under conditions of test. A sample of greases is taken in a Bomb and to it 110 PSI oxygen is charged. The Pressure is observed on the pressure gauge. The Bomb is immersed in the bath at 99C. The degree of oxidation after a given period of time is determined by the corresponding decrease in oxygen pressure.

NOTE:

This method may be used for quality control to indicate batch to batch uniformity.

8.8 Oil Separation from Lubricating Greases During Storage (ASTM D 1742: P 85 IS 1448 Methods of Tests)

This method covers the determination of the tendency of lubricating greases to separate oil during storage in either normally filled or partially filled containers.

The sample of grease support on 75mm is subjected to 0.25 PSI air pressure for 24 hours at 25°C. Any oil seepage that occurs draings into a beaker and weighed.

NOTE:

The results correlate directly with oil separation which occurs in 35 lbs pails of greases during storage. It is not intended to predict oil separation tendencies of greases under dynamic service conditions.

8.9 Thermal Stability (P 89 IS 1448 Methods of Test)

This method describes the procedure for measuring the tendency of lubricating grease to separate oils at elevated temperature under static conditions. Suspend the cone containing known quantity of grease well exposed on its surface in a clean weighed beaker. Keep the beaker at 100°C in an oven for 30hours. After the test, weigh the beaker and report the percent oil separated.

8.10 Cone Penetration (ASTM D 217 : P 60 IS 1448 Methods of Tests)

The depth, in tenths of a millimeter that the standard cone penetrates the sample under the prescribed conditions of weight, time and temperature. The test procedures include for the measurement of penetration on unworked, worked, prolonged worked and block. Penetration upto 475 may be measured. Unworked penetrations do not generally represented the consistency of grease in use as effectively as do worked penetrations. The latter are usually preferred for inspecting greases.

Penetration of blocked greases can be obtained on those products that are sufficiently hard to hold their shape. These greases have penetration below 85 (working on the subjection of lubricating greases to the shearing of standard grease worker.

Worked Penetration

Penetration of a lubricating grease that has been subjected to 60 double strokes in a standard grease worker and penetrated without delay.

Prolonged Worked Penetration

Where the penetration has been subjected to more than 60 double strokes.

Block Penetration

Penetration of the grease, that is sufficiently hard to hold its shape, determined on the freshly prepared face of cube cut from a block of the grease. Penetration is determined

SECTION - 9

FURNACE OIL/BLACK OIL

9.1 Introduction

The furnace oil or the black oil is the residual oil left after separating residual fuel distillate. It is brownish black in colour and consists of hydrocarbons above C₄₀. Based on Kinematic Viscosity different grades of furnace oil namely low viscous (LV), medium viscous (MV) and high viscous (HV) are available. It is normally used for heating furnaces. Forensic Sciences laboratory receives furnace oil related to Pilferage, Adulteration and Simulation cases.

The important characteristics governed by IS specifications (IS 1593) are Specific gravity, Flash point and Kinematic Viscosity.

9.2 Test methods and their Significance

1.2.1 Relative density / Specific gravity – Experimental (P 32 IS 1448 Methods of Test: ASTM D1298)

Procedure is similar to that of Engine Lubricating Oil. The specific gravity of a typical standard Furnace oil falls within the range of **0.900 to 0.950**.

9.2.2 Viscosity: Experimental (P: 25 IS 1448 methods of test: IP 71: ASTM D 445 and 2170)

Test methods and Experimental Procedure is similar to that explained in Section - 4 (Kerosene). The Kinematic Viscosity can be measured in centistokes at 50°C Different grades of oil (LV, MV1, MV2 & HV) are available based on their viscosity.

Significance

- Viscosity is the most important single property of a furnace oil
- Incase of used oils if viscosity is lower than the original it indicates fuel dilution or admixture with low viscosity oils

9.2.3 Flash Point : Experimental (P 20 IS 1448 Methods of Test : ASTM D56 : D 92: D 93: D 1310)

The flash point of lubricating oil is carried out by Fensky Marten closed cup (Automatic) and Cleveland open cup (Automatic) as the procedure given for lubricating oil.

Significance

- Genuinity of the sample can be found by Flash point

9.2.4 Carbon Residue (P8 IS 1448 Methods of Test : IP 13, 14)

It is an amount of carbonaceous material formed when a sample is evaporated and paralyzed under specified conditions. The lighter will evaporate but the heavier more complex compounds will decompose forming carbonaceous deposits. There are two methods for its determination.

- Conradson
- Ramsbottom

In the Conradson method sample is heated in a crucible under controlled conditions in absence of air and the residue left is weighed. Whereas, in Ramsbottom test the sample is placed in the tube with the capillary at the top and heated to 550°C in a bath of molten metal.

Significance

- Carbon residue/ High carbon content indicates the possible presence of bitumen + Kerosene(Simulation)

9.2.5 Water Content (IP74: P40 IS 1448 Methods of Test)

Petroleum products as marketed should be free from water. However products may pick up water during storage, handling or through condensation from atmosphere. The presence of water is undesirable in many cases.

Traces of water can be detected by means of crackle test. When a sample of oil is heated on a silent flame, crackling noise is heard, if any moisture is present in the oil. Water in percentage is estimated in special distillation apparatus known as Dean & Stark using toluene as a solvent.

Significance

Presence of water in lubricating oil is undesirable as it will tend to form emulsion and sludge in use.

APPENDIX-1 : BIS SPECIFICATIONS OF PERTOLEUM PRODUCTS

