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***भारतीय मानक***

***Indian Standard***

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 **पेट्रोलियम और उसके उत्पाद — परीक्षण पद्धतियाँ**

 **भाग 34 पेट्रोलियम उत्पादों में सल्फर का निर्धारण**

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 ***(तीसरा पुनरीक्षण)***

 **PETROLEUM AND ITS PRODUCTS —**

 **TEST METHODS**

 **PART 34 DETERMINATION OF SULPHUR IN**

 **PETROLEUM PRODUCTS (LAMP METHOD)**

**(Third Revision)**

 ICS 75.080

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**July 2024 Price Group X**

Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee, PCD 01

**FOREWORD**

This Indian Standard (Third Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

This standard was last revised in 1979 to align with the joint publication of ASTM D 1266-70, IP designation 107/73, and ISO 2192:1973.

This revision has been taken up to align with the joint publication of ASTM D 1266-18, IP designation 107/86. Test method for determination of Sulphur in liquefied petroleum gases (oxy-hydrogen burner or lamp) has been removed from joint publication of ASTM D 1266-18, and IP designation 107/86 due to withdrawal of ASTM D 2784-06 and ISO 2192:1973.

In this revision, Method D ‘Determination of sulphur in liquefied petroleum gases (LPG)’ has been deleted due to the withdrawal of ASTM D 2784 and accordingly, the scope has been modified.

The composition of the Committee and Subcommittee, responsible for the formulation of this standard is given at Annex A.

In reporting the results of a test analysis made in accordance with this standard, if the final Value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2:2022 ‘Rules for rounding off numerical values (*second revision*)’.

*Indian Standard*

**METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS**

**PART 34 DETERMINATION OF SULPHUR IN PETROLEUM PRODUCTS**

 **(LAMP METHOD)**

(*Third Revision*)

**1 SCOPE**

**1.1** The standard prescribes three methods of test for the determination of the concentration of total sulfur present in liquid petroleum products. Methods A and B are applicable for the determination of concentration above 0.002 percent by mass, while method C is applicable for the determination of trace quantities of total sulfur as low as 0.0005 percent by mass. However, this method cannot determine sulfur concentration less than 0.03 percent by mass in liquids that contain lead anti-knocking agents.

**1.2** The direct burning procedure (*see* **8.1**) is applicable for the analysis of such materials as gasoline, kerosene, naphtha, industrial aromatic hydrocarbons, and other liquids that can be burned completely in a wick lamp. The blending procedure (*see* **8.2**) is applicable for the analysis of materials that cannot be burned satisfactorily by the direct procedure, such as gas oils, distillate fuel oils, naphthenic acids, and alkyl phenols. Residual fuel oils, bitumen, tar, and other heavy residues cannot be analyzed by this method.

**1.3** Phosphorus compounds normally present in commercial gasoline do not interfere. A correction is given for small quantities of acid resulting from the combustion of lead anti-knocking agents. Appreciable concentration of acid forming or base forming elements from other sources interfere when the titration procedure is employed since no correction is provided in these cases.

**2 REFERENCE**

The following standards contain provisions which, through reference in the text constitute provisions of this standard. At the time of publication, the editions indicated were valid. All the standards are subject to revision, and parties to an agreement based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

|  |  |
| --- | --- |
| *IS No.* | *Title* |
| IS 256 : 2024 | Glauber Salt (Sodium Sulphate, Decahydrate), Technical — Specification *(second revision)* |
| IS 265 : 2021 | Hydrochloric Acid — Specification (*fifth revision*) |
| IS 1070: 2023 | Reagent Grade Water — Specification (*fourth revision*) |

**3** **PRINCIPLE**

**3.1** An adequate weight of the sample is burned in an artificial atmosphere of 70 percent carbon dioxide and 30 percent oxygen to convert sulfur compounds to oxides of sulfur. In method A, the oxides of sulfur are absorbed by hydrogen peroxide and oxidized to sulfuric acid. It is determined acidimetrically by titration with standard sodium hydroxide in presence of a methyl purple indicator.

**3.2** In method B, the oxides of sulfur are converted to sulfate in the absorbent and estimated gravimetrically as barium sulfate.

**3.3** For sulfur concentration below 0.002 mass percent, it is necessary to determine sulfur concentration by method C. Method C converts oxides of sulfur to sulfates in an absorber solution and Sulfur is determined turbidimetrically as barium sulfate. The suspension is stabilized by the addition of alcohol and glycerin, and its turbidity is measured by the use of a spectrophotometer or filter photometer.

**4 APPARATUS**

**4.1** **Combustion Apparatus**

**4.1.1** *Flask and Burner*

25 ml Erlenmeyer flask and burner are two integral parts of a lamp for burning aromatic and non-aromatic samples. The Erlenmeyer flask shall have glass hooks 180° apart. However, for burning high aromatic samples without blending, the flask shall have an additional side arm as shown in Fig 1. This flask may also be used to burn non-aromatic samples. The burner consists of concentric sealed glass tubes supported by three glass beads. The external tube has an arm with standard taper glass joints to connect with the chimney at the top and the flask at the bottom. The lamp shall be held in position between glass hooks on the flask and chimney with aid of rubber bands or metal springs. In order to equalize the pressure between the chimney and flask the burner shall have a 1 mm opening at its base for non-aromatic samples. For the aromatic samples, the burner shall have no opening and a second control valve is required in the burner manifold. The upper ends of both burner tubes shall be polished having a plane surface in the same horizontal plane.

**4.1.2** *Chimney*

Chimney shall be provided with standard taper glass joint so as to connect to burner and absorber.



All dimensions in millimeters

FIG. 1 DETAILED DIAGRAM OF COMBUSTION AND ABSORPTION APPARATUS

**4.2 Absorption Apparatus**

**4.2.1** *Absorber*

An absorber conforming to dimensions as per Fig 1 shall be with two bulbs and standard taper glass joint in order to connect with chimney and spray trap. A sintered disc shall be present in the larger bulb with an average pore diameter ranging from 150 µm to 200 µm and its porosity shall be in such a way that air should pass through it in the forward direction at the rate of 3.0 l/min when 50 ml water is present in the absorber. The difference in pressure across the absorber is between 15 cm to 23 cm of water with uniform dispersion of air.

**4.2.2** *Spray Trap*

The spray trap shall be conforming to the dimension as per Fig. 1 and shall be connected to the absorber with a standard taper glass joint.

**4.3** **Cotton Wick**

Unused, clean, uniform, and twisted white cotton yarn shall be used for burning. The wick should be rug yarned, 4-stranded, weighing 2-3 mg/cm per strand or equivalent material. To burn an aromatic sample, the wick shall be a lone staple, fine spun, and commercially fine graded.

**4.4** **Manifold System**

**4.4.1** A satisfactory vacuum and combustion atmosphere manifold and supply system for supplying the required carbon dioxide-oxygen mixture to the lamp assemblies is shown diagrammatically in Fig. 2. It consists of a vacuum manifold with regulating device, valves, etc., and a dual manifold (burner and chimney) supplying a gas mixture of approximately 70 percent (*v/v)* carbon dioxide and 30 percent (*v/v)* oxygen at regulated pressure. The gases are supplied from commercial cylinders, the pressure of each gas being adjusted to 0.70 ± 0.14 bar by means of two single stage regulating valve to ensure constant at the flow regulating needle valve. It is necessary to pass the carbon dioxide through a heat pressure exchanger installed ahead of the regulating valve to prevent freezing of the valves. The gases are passed through a metering system consisting of two calibrated rotameter flow meters, to indicate the proportion of the two gases mixed in the surge tank. Any number of lamp assemblies may be operated as a unit; the throughput of the flow meters being chosen accordingly. The tubing that connects that chimney manifold to the chimneys should have an internal diameter not smaller than 6.4 mm in order to prevent unnecessary restriction in gas flow. The scrubber should have a capacity of about l liter.

**4.4.2** The vacuum manifold shall be connected to a pump of sufficient capacity to permit a steady gas flow of about 3 liters per minute through each absorber and to maintain a constant manifold pressure of approximately 40 mbar below atmospheric. The gas mixture in the chimney manifold shall be maintained at nearly constant pressure of 1 mbar to 2 mbar and the burner manifold at approximately 20 mbar. Any other system similar to the one described here may also be used, Modifications of the manifold and associated equipment for burning samples in air are shown in Fig. 3 and described in Method B.

**5 REAGENTS AND MATERIALS**

Analytical reagent grade chemicals and distilled water (*see* IS 1070) shall be employed in tests.

**5.1 Gas**

**5.1.1 Carbon Dioxide, Purity 99.5 Percent**

**5.1.2 Oxygen, Purity 99.5 Percent**

**5.2** **Diluent**

Sulphur in the diluent shall be less than 0.001 percent. The diluent shall be completely miscible with the sample and allow burning without smoke at a moderate rate. *n*-heptane, *iso*-octane, and absolute ethyl alcohol are found suitable.

**5.3****Hydrochloric Acid (1:10**)

1 volume of concentrated hydrochloric acid (*see* IS 265) shall be mixed with 10 volumes of water.

**5.4 Hydrogen Peroxide Solution (1:19)**

1 volume of concentrated hydrogen peroxide (H2O2, 30 percent) shall be mixed with 19 volumes of water and shall be stored in a dark-colored glass-stoppered bottle.

**5.4.1 Naturalized Hydrogen Peroxide Solution**

The H2O2 solution (1:19) (*see* **5.4**) is neutralized immediately before use. Transfer multiples of 30 ml, sufficient for the number of absorbers to be used, in a beaker. 1 drop of methyl purple indicator is added to the solution for each 100 ml of H2O2 solution and add 0.05 NNaOH solution dropwise until the color changes from purple to a light green.

**5.5 Methyl Purple Indicator**

The indicator shall be an aqueous solution containing approximately 0.1 percent active constituent

**5.6 Sodium Hydroxide Solution (100 g/l)**

100 g of sodium hydroxide technical pellets are dissolved in water and diluted to 1 liter.

**5.7****Sodium Hydroxide, Standard Solution (0.05 N)**

A clear saturated solution of NaOH, obtained by decanting a long standing column, shall be used 2.8 ml of this saturated NaOH solution shall be diluted to 1 liter (*see* Note) and standardized by titration against standard acid, using the methyl purple indicator. The solution is stored in an alkali-resistant glass bottle and protected to minimize contamination by CO2 from the air. Only pure gum rubber tubing is used for connections between the storage bottles and burette.

NOTE — The calculation of results can be simplified by adjusting the molarity of the NaOH solution to 0.0624 ± 0.0001. Then 1 ml of the NaOH solution will be equivalent to 0.0010 g of sulfur. In this case, the factor 16.03 Nin the calculation becomes 1.000.

**6** **PREPARATION OF APPARATUS**

**6.1** The absorber is filled with (30 ± 2) ml of water when the apparatus is initially assembled. The individual valves between the vacuum manifold and spray traps are adjusted so that approximately 3 l/min air shall be drawn through each absorber when the chimney outlets are open to the atmosphere and when maintaining the pressure in the vacuum manifold at approximately 40 cm of water below atmospheric. The water is removed from the absorbers when all adjustments are carried out. The height of the liquids in the pressure and vacuum regulators shall be maintained as shown as Fig. 2. A slow flow of gas shall be maintained through them during operation.

NOTE — While burning, fill the scrubber with 300 ml to 400 ml of 1.5 percent H2O2 solution. H2O2 solution is used as manometric liquid, since the manifold manometer also serves as a scrubber at the end of the test to remove CO2 from the absorbent. The H2O2 is replaced weekly or whenever the volume becomes appreciably less.

 

FIG. 2 SCHEMATIC DIAGRAM OF CO2-O2 SUPPLY MANIFOLD AND LAMP SYSTEM

**6.2** (30 ± 2) ml of freshly neutralized Hydrogen Peroxide solution (*see* **5.4.1**) is taken in the larger bulb of each absorber. Also, an extra absorber as a control blank for each set of samples burned is prepared. The spray traps and chimneys are attached and connected to the respective manifolds by means of sulfur-free rubber tubing. The chimney openings are closed corks.

**6.3** The valve to the vacuum regulator is kept fully open, the burner control valves closed and the pressure in the vacuum manifold is adjusted to approximately 40 cm of water below atmospheric. The CO2 and O2 supplies are turned on in this condition. The chimney manifold control valve is adjusted so that only a small stream of CO2-O2 gas escapes at the pressure regulator, a small stream of air enters the vacuum regulator at the required rate of flow through the absorbers, while the pressure in the chimney manifold is 1 cm to 2 cm of water. Minor adjustments of the vacuum regulator and vacuum control valve may be necessary to achieve this condition.

*Warning* — A hazardous (explosive) condition may occur, if while burning the sample, the CO2 supply is interrupted and the O2 flow is continued. It is recommended to install suitable control equipment and provide warning

NOTE — The gas flow system can be conveniently balanced by regulating the pressure in the vacuum manifold. This is achieved by raising or lowering the air inlet tube in the vacuum regulator by sliding it in a rubber sleeve.

**6.4** Cut the wicking to 30 cm lengths and fold the wicking once to give a 15 cm long bundle for threading the burners. Different lengths can be used as per sample (*see* **7**).The required number of burners are threaded by inserting the looped ends into the top of the inner tube of the burner. The wick is drawn by means of a metal hook and trimmed as close as possible to the top of the burner with a pair of sharp scissors. Only thoroughly cleaned burners and new wicks shall be used for each test.



FIG. 3 SCHEMATIC DIAGRAM OF PURIFIED AIR SUPPLY MANIFOLD AND LAMP METHOD

**7 CONTROL OF COMBUSTION**

**7.1** Most of the liquid samples burn with a luminous yellow flame. The size and shape of the flame are guided by the gas flow to the burner, the volatility of the material, the tightness of the fit of the wick in the burner tube and the position of the top of the wick relative to the top of the burner. In order to control the flame by varying the rate of CO2-O2 flow, it is preferable that the last two variables be fixed with respect to the first.

**7.2** A tight-fitting wick is required for highly volatile samples, the top of which can be several millimeters below the top of the burner, and in extreme cases, it may have to be cooled in ice during the burning. On the other hand, less volatile materials require a more loosely fitting wick and may require warming.

**7.3** The wick is drawn down until the trimmed edge is flush with or just a little below the top of the burner after trimming. For aromatic samples, the distance from the top of the burner to the top of the wick shall be 8 mm or more for benzene, and 4 mm for toluene. A slight heating of the upper end of the burner may be required to vaporize heavier materials.

**7.4** To use the standard lamp, light the wick and then slowly allow combustion atmosphere to the burner to get a smoke-free flame. For aromatic samples, introduce a small amount of combustion atmosphere into the flask to provide sufficient vapor for lighting the burner. After lighting the burner, introduce combustion atmosphere directly into the burner to prevent smoking and to adjust the flame size. If the flame is accidentally turned off, relight.

**7.5** A short burning period of 1 min to 2 min is usually sufficient at low flame height is necessary to allow combustion to reach equilibrium before the flame size can be increased without causing a smoky flame. For adjusting the standard lamp, the entire control is at the burner. For the burner for aromatic samples, first adjust the flow of gas to the flask and then reduce the flow of gas to the burner as required. The flame burn shall be smooth and symmetrical and without jets in the inner cone or smoke on the outer fringes.

**7.6** For materials which are difficult to burn reasonably, proper burning can sometimes be obtained by increasing the O2 content of the combustion atmosphere. However, the O2 content of the combustion atmosphere shall not be increased to more than 40 percent.

**7.7** Allow the sample to burn until the flask and wick appear to be dry and the flame has reduced considerably in size, before extinguishing the flames. Frequently the flame continues to burn a short time after the flask appears dry because of the sample in the wick. For example, for gasoline samples, which burn with a high flame, the flame shall be extinguished when it is only 3 mm to 4 mm high. If the flame is allowed to burn until it goes out, partially oxidized substances (probably organic acids) are produced, which result in indistinct end points. When samples are not burned until the flask is apparently dry, erratic results may be obtained. In the case of volatile samples, any unburned sample will escape from the burner during weighing. When elemental sulfur is present, it is particularly important to burn the sample to apparent dryness and that the wick be maintained flush with the top of the burner to ensure complete combustion. With mixtures containing light and heavy hydrocarbons, the lighter materials seem to burn first, possibly leaving behind sulfur compounds in the material.

**8** **METHOD – A (ACIDIMETRICALLY DETERMINATION BY TITRATION METHOD)**

**8.1 Procedure for Direct Combustion of Liquid Samples**

**8.1.1** By means of an appropriate pipette, introduce into the flask of each lamp an approximate quantity of sample as indicated in Table 1.

**Table 1 Sample Size for Direct Combustion of Liquid Samples**

(*Clause* 8.1.1)

|  |  |  |
| --- | --- | --- |
| **SI. No.** **(1)** | **Sulfur Content, mass percent****(2)** | **Sample** |
| **Size, g****(3)** | **ml****(4)** |
| i) | Under 0.05 | 10 to 15 | 20 |
| ii)  | 0.05 – 0.3 | 5 to 10 | 10 |
| iii) | 0.3 – 1 | 3 to 5 | 5 |
| iv) | Over 1 | 2 to 3 | 3 |

Stopper the flasks with clean, corks and number them. Weigh each flask and its burner to the nearest 0.005 g.

NOTE — All the prepared burners shall be weighed separately while the flasks are stoppered. It is usually more convenient to place each flask and its burner on the balance pan and obtain the combined weight in a single weighing.

**8.1.2** Each lamp is handled individually and the burner is inserted in the flask. As soon as the sample has risen by capillary action to the top of the wick, the side tube of the burner is connected to the burner manifold by means of sulfur-free rubber tubing. The burner is lit with a sulfur-free flame (such as an alcohol lamp) and inserted into the chimney. The connection between the chimney and the chimney manifold during the insertion is pinched off if the flame tends to be blown out. The gas flow to the burner is adjusted at the same time so that the flame is maintained at a point just below smoking and has a steady symmetrical appearance. Continue the same action until all lamps have been placed in the chimneys. Any minor adjustment of the chimney manifold control valve can be made if necessary to maintain the required pressure (*see* **6**). While burning, particularly during the latter stages when the flame becomes small, decrease the CO2-O2 supply to the burners in order to prevent the extinction of flames.

NOTE —The absorber liquid will foam excessively if incomplete combustion occurs.

**8.1.3** When each sample is burnt completely and evidently the flame becomes small owing to depletion of the sample, remove the burner and flask from the chimney, and extinguish the flame. The CO2-O2 supply to the burner is shut off and the chimney opening is stoppered. Reweigh the flask, burner, and numbered cork immediately. Turn off the CO2 and the O2 supplies, close the chimney control valve, and close the connection to the vacuum regulator when all the combustions have been completed. This allows air to be drawn into the chimney manifold through the manometer. Allow air to be drawn through the absorbers in this manner for 5 min to remove dissolved CO2 from the absorbent; then close the vacuum control valve.

NOTE — If the combustion atmosphere would like to be conserved, the gas flow through each individual absorber can be turned off upon completion of the burning period. To obtain this, pinch off the rubber tubing connecting the spray trap to the vacuum manifold, reduce the flow of mixed gases at the Rota meters proportionately, and readjust the vacuum control valve and the chimney control valve. When the burning of all samples has been completed, the pinch clamps are removed and the vacuum control valve is readjusted in order to draw air at the required rate through the absorbers for the removal of dissolved CO2.

**8.1.4** Rinse the chimneys and spray traps three times with about 10 ml of water each time. If the sample contains lead anti-knock agents, use hot water to rinse the chimneys. Add the rinsing to the absorbers, and titrate as directedin **8.3**.

**8.1.5** *Blank*

Leave the chimney of the blank absorber (*see* **8.3**) stoppered, and allow the CO2-O2 stream to pass through that absorber until all samples started at one time have finished burning. Turn off the CO2 and the O2 supplies and aerate the blank absorber in the same manner as the sample absorbers (*see* **9.3**). Titrate the absorber liquid as directed in **8.3**. Normally, the combustion atmosphere blank will be small, but if the titration requires more than 0.1 ml of 0.05 *N* NaOH solution discard the determination and replace the CO2 cylinder

**8.2 Procedure for Blending and Combustion of Liquid Samples**

**8.2.1** 6 ml of sulfur-free diluent is added to each flask and the flasks are stoppered with numbered corks and weigh to the nearest 0.005 g. By means of a pipette, an approximate quantity of sample as indicated in Table 2 is introduced into the flask of each burner. The mixture is swirled thoroughly, and reweighed. Alternatively, 40 percent blend of the sample in sulfur-free diluent can be made and determined as described in clause **8.1**.

**Table 2 Sample Size for Testing Blended Liquid Samples**

(*Clause* 8.2.1)

|  |  |  |
| --- | --- | --- |
| **SI. No.****(1)**  | **Sulphur Content, mass percent****(2)** | **Sample** |
| **Size, g****(3)** | **ml****(4)** |
|  | 0.05 and under | 3 to 4 | 5 |
|  | Over 0.05 | 2 to 3 | 3 |

 **8.2.2** Insert the burner and burn as described in **8.1.2**. Remove each lamp from its chimney as the flame nears extinction and extinguish the flame. Add 2 ml of diluent, allowing the diluent to rinse down the walls of the flask. Burn the additional diluent and repeat the addition of the diluent one more time so that a total of 10 ml of diluent has been burned.

NOTE —In this case, it is desirable that a 10-ml diluent blank be run; the titration of the absorber solution from this blank, shall not exceed 0.1 ml of 0.05 mNaOH solution.

**8.2.3** After all lamps have been completely burnt, turn off the CO2 and O2 supplies. The connection to the vacuum regulator is closed, air is drawn through the absorbers for 5 min, and finally, the vacuum control valve is closed. Rinse the chimneys and spray traps three times, using about 10 ml of water each time. Add the rinsing’s to the absorbers, and titrate as directed in **8.3.**

**8.3 Titration of Absorbent Solution**

3 to 4 drops of methyl purple indicator solution are added to the liquid in each absorber and the absorbent solution is titrated by introducing 0.05 NNaOH solution from a burette into the smaller bulb of the absorber. A 10 ml micro burette can be used if less than 10 mg of sulfur is expected to be present in the absorber. Stir during the titration by applying suction intermittently to the top of the larger bulb.

*Caution*— Do not apply suction with the mouth.

NOTE — If incomplete combustion of the sample occurs, the air drawn through the absorber during the titration will have a characteristic taste or odor and the end point will be broad. Hence, discard the determination.

**8.4 Calculations**

**8.4.1** The sulfur content of liquid samples is calculated as follows

Sulfur content, mass percent (S) = (16.03 *A N*)/10 *M*

where

*A* = milliliters of NaOH solution required to titrate the acid in the absorbent solution from the burned sample,

*N* = Normality of the standard NaOH solution, and

*M =* grams of sample burned, and

**8.4.2** When it is necessary to correct the sulfur content for lead antiknock agents, the corrected values are calculated as follows

Corrected sulfur content, mass percent = *S* - *LF*

where

*F* = 0.0015 if the sample contains aviation lead antiknock agent or 0.0035 if the sample contains tetra ethyl lead, tetra methyl lead, or the mixed lead alkyl antiknock agent,

*L* = lead content, g per litre; and

*S* = sulfur content, mass percent.

NOTE **—** The above corrections are based on experiments of burning fuels blended with antiknock fluid containing tetraethyl lead and ethylene halide in commonly-used combinations. Tetra methyl lead and the mixed lead alkyl antiknock fluids contain the same ethylene halide combination as the tetraethyl lead fluid.

**8.5 Report**

Report the results of the test to the nearest 0.01 percent for sulfur at a level of 0.05 percent and higher.

**8.6 Precision**

The following criteria are applied to the direct burning of liquid samples in the range of 0.01 percent to 0.4 percent sulfur and shall be used for judging the acceptability of results. (95 percent confidence).

**8.6.1** *Repeatability*

The duplicate results obtained by the same operator with the same apparatus under constant operating conditions on identical test material shall not differ by more than 0.005 percent.

**8.6.2** *Reproducibility*

The results obtained by each of the two laboratories shall not differ by more than 0.010 + 0.025 S.

where

 *S* = The total sulfur content of the sample, mass percent.

**9 METHOD – B (AIR BURNING OF SAMPLE, GRAVIMETRIC FINISH)**

**9.1 Apparatus**

The manifold system described in **4.4** may be used with only a slight modification, i.e. by substituting filtered air for the CO2-O2 supply train and adding a second sintered-plate scrubber to the incoming airline as shown in Fig.3

**9.1 Additional Reagents** –Following reagents are required in addition to reagents given in **5**.

**9.1.1** *Barium Chloride Solution* (100 *g/l*)

Dissolve 100 g of barium chloride di-hydrate (BaCl2·2H2O) in water and dilute to 1 liter.

**9.1.2** *Hydrochloric Acid* (*relative density* 1.19)

Concentrated hydrochloric acid (HCl). (*see* IS 265)

**9.1.3** *Hydrogen Peroxide Solution* (30percent)

**9.1.4** *Sodium Hydroxide Solution* (100 *g/l*)

Dissolve 100 g of technical grade sodium hydroxide (NaOH) pellets in water and dilute to 1 liter.

**9.1.5** *Sulfuric Acid* (1:16)

Mix 60 ml of concentrated sulfuric acid (H2SO4, sp gr 1.84) with 960 ml of water.

**9.2 Preparation of Apparatus**

**9.2.1** 300 ml to 400 ml of NaOH solution (*see* **5.6**) is taken in the first scrubber (Fig. 3) and the same amount of H2O2-H2SO4 solution (300 ml of H2O, 30 ml of H2SO4 (1: 16), and 30 ml of H2O2 (30 percent)) is taken in the second scrubber. For daily use, these solutions are replaced twice a week or whenever the volume becomes less than two-thirds of the original.

**9.2.2** Make other preparations as described in Item 6, except that the H2O2 solution (30 percent) need not be neutralized.

**9.3 Procedure for Combustion**

**9.3.1** Burn the sample as described in clause **8.1**, controlling combustion as described in Item 7. Use a sample size as per Table 3.

**Table 3 Sample Size for Air Burning of Liquid Samples**

(*Clause* 9.3.1)

|  |  |  |
| --- | --- | --- |
| **SI. No.** **(1)** | **Sulphur Content, mass percent****(1)** | **Sample** |
| **Size, g****(2)** | **ml****(3)** |
|  | 0.05 and under | 3 to4 | 5 |
|  | Over 0.05 | 2 to 3 | 3 |

 Analyze the absorber solutions from the samples and blank as described in **9.5.**

**9.4 Procedure for Analysis of Absorber Solution**

**9.4.1** The absorber liquid is transferred to a 400 ml beaker. And the absorber and chimney are rinsed thoroughly with water. Add the rinsing to the beaker. The solution is filtered to remove any foreign material, receiving the filtrate in a 400 ml beaker having a mark to indicate 75 ml. 2 ml of HCl is added and boiled, followed by addition of 10 ml of BaCl2 solution, either in a fine stream or drop wise. Stir the solution during the addition and for 2 min thereafter.

**9.4.2** The beaker shall be covered with a fluted watch glass and continued to boil slowly until the solution is evaporated to a volume of approximately 75 ml, as indicated by the mark on the beaker. The beaker is removed from the hot plate (or another source of heat) and allowed to cool for 1 h before filtering.

**9.4.3** The supernatant liquid is filtered through a close-texture, ashless filter paper, and the precipitate is washed with water, first by decantation and then on the filter paper, until free of chloride ions. The paper and precipitates are transferred to a suitable weighed crucible and dried at low heat until the moisture has evaporated. The paper is charred completely without ignition and finally ignites at a bright red heat until the precipitate is burned white. After the complete ignition, the crucible is allowed to cool to room temperature and weigh.

NOTE —A satisfactory means to do these operations in the uncovered crucible containing the wet filter paper in a cold electric muffle furnace and turn on the current. Drying, charring, and ignition shall usually occur at the desired rate.

**9.5 CALCULATION**

**9.5.1** The sulfur content of the sample is calculated as follows:

Sulfur content, mass percent = (*m1* – *m2*) ×13.73/*M*

where

*m1* = barium sulfate precipitate in the absorber solution from the burned sample, in g;

*m2* = BaSO4 precipitate from the corresponding blank absorber solution, in g; and

*M* = sample burned, in g.

NOTE —The determination shall be discarded if the blank correction exceeds 1.5 mg of BaSO4. Frequently, impure reagents are the cause of this difficulty.

**9.6 REPORT**

Report the results of the test to the nearest 0.01 percent for sulfur at a level of 0.05 percent and higher.

**9.7 PRECISION**

The following criteria is applied to the direct burning of liquid sample in the range of 0.01 percent to 0.4 percent sulfur and shall be used for judging the acceptability of results (95 percent confidence).

**9.7.1** *Repeatability*

The duplicate results obtained by the same operator with the same apparatus under constant operating conditions on identical test material shall not differ by more than 0.005 percent.

**9.7.2** *Reproducibility*

The results obtained by each of two laboratories shall not differ by more than 0.010 + 0.025 S.

where

 *S* = The total sulfur content of the sample, in mass percent.

**10 METHOD - C (METHOD OF TEST FOR TRACE QUANTITIES OF SULFUR)**

**10.1 Additional Apparatus**

**10.1.1** *Photometer*

Preferably a spectrophotometer having an effective band width of about 50 nm and equipped with a blue-sensitive phototube for use at 450 nm, or alternatively a filter photometer equipped with a color filter having a maximum transmission at approximately 425 nm.

**10.1.2** *Absorption Cells*

Cells having optical path lengths of 50 mm are preferred. With use, the cells may become coated with a film. To remove this film, wash the cells with a detergent using a soft brush. Rinse thoroughly with deionized water following cleaning.

NOTE —The procedure as written assumes an absorbance change of about 0.100 for each 0.1 mg of sulfur in 50 ml of the solution measured in a 5 cm cell. Photometers employing cells of shorter optical paths give proportionately poorer precision.

**10.1.3** *Scoop*, capable of dispensing (0.30 ± 0.01) g of barium chloride dehydrate (500 µm – 850 µm size)

**10.1.4** *Magnetic Stirrer*, shall be equipped with tetra fluoro ethylene covered stirring bars about 32 mm (11⁄4 inch) long.

**10.1.5** *Lamp Assembly*, as described in **4**.

NOTE— Reserve complete units consisting of flask, burner, chimney, absorber, and spray trap for use in this procedure only.

**10.2 Additional Reagents:**

**10.2.1** *Alcohol- Glycerin Mixture,*

2 volumes of denatured ethyl alcohol (95 percent by volume) with 1 volume of glycerin.

**10.2.2** *Barium Chloride Di-hydrate* (BaCl2·2H2O)*,* 500 µm to 850 µm size crystals

NOTE —The crystal size of the BaCl2·2H2O is an important variable that affects the development of turbidity.

 **10.2.3** *Hydrochloric Acid* (1:12)

Add 77 ml of concentrated hydrochloric acid (*see* IS 265) to a 1liter volumetric flask and dilute to the mark with deionized water.

**10.2.4** *Hydrochloric Acid* (1: 215)

Add 60 ml of 1: 12 HCl (*see* **10.2.3**) to a 1liter volumetric flask and dilute to the mark with deionized water.

**10.2.5** *Sulfuric Acid* (*1 ml = 0.100 mg S*)

Dilute (6.246 ± 0.01) ml of 1 *N* sulfuric acid (H2SO4) to exactly 1 literwith deionized water. Check the dilution by titration against standard NaOH solution of about the same normality and adjust the concentration, if necessary, so that each milliliter of this solution is equivalent to 0.100 mg of S.

**10.2.6** *Water, Deionized Distilled*

Percolate water through a column of mixed anion and cation exchange resins.

NOTE —A means for determining when to replace the exchange resins should be supplied. Use of a simple electrical conductivity meter has been found satisfactory for this purpose.

**10.3 Calibration**

**10.3.1** Into 50 ml volumetric flasks introduce, by means of a burette, 0.25 ml, 0.50 ml, 0.75 ml, 1.00 ml, 1.50 ml, 2.00 ml, 3.00 ml, and 5.00 ml of H2SO4 (1 ml = 0.100 mg S). Add 3.0 ml of HCl (1 :12) to each flask, dilute to volume with water, and mix thoroughly. A reagent blank standard is prepared in a similar way, omitting the H2SO4.

**10.3.2** The entire contents of each flask is to be poured into a 100 ml beaker, add by means of a pipette (10 ± 0.1) ml of alcohol glycerin mixture, and mix for 3 min on the magnetic stirrer.

Select a stirring speed just below that which might cause loss of sample through splashing. Maintain this speed throughout the entire procedure.

**10.3.3** The solution is allowed to stand undisturbed for 4 min and transferred in the absorption cell and the initial absorbance is measured using water as reference.

**10.3.4** The solution is returned into the beaker and (0.30 ± 0.01) g of BaCl2·2H2O crystals is added, either by weighing this amount or by use of the scoop and stirred with the magnetic stirrer for exactly 3 minutes. the solution is allowed to stand for an additional 4 min, transferred to the cell, and again the absorbance relative to water is measured.

**10.3.5** A reagent blank is obtained by following the steps described in **10.3.2** to **10.3.4** and the reagent blank reading is obtained by subtracting the initial absorbance of the reagent blank standard from that obtained after the addition of BaCl2·2H2O. This reading shall not exceed 0.005.

**10.3.6** Net absorbance is obtained for each standard by subtracting the initial absorbance and reagent blank reading from the absorbance obtained in accordance with **10.3.4**. The net absorbance is plotted for each standard against milligrams of sulfur contained in 50 ml of solution, and a smooth curve is drawn through the points.

**10.3.7** The calibration curve is checked daily by making single determinations to detect possible shifts.

**10.4 Procedure for Combustion of Samples**

**10.4.1** Prepare the combustion apparatus and burn between 5 g and 30 g of sample depending on the expected sulfur level. Follow the general procedures described in item **6, 7,** and **8.1** of the main method. The requirements for initial neutralization of the H2O2 solution (*see* **5.4**) and for final removal of dissolved CO2 from this solution (*see* **8.1.3** and **8.2.3**), may be omitted. Draw combustion atmosphere through one absorber of a set to serve as a blank on the purity of this atmosphere. Reserve all glassware exclusively for use with this trace procedure to avoid any possible contamination from other sources. The absorber solution, containing rinsing from the spray trap and chimney (*see* **8.1.4**) shall be transferred to a 250 ml beaker. The absorber shall be two or three times with 10 ml portions of water, and add the rinsing to the solution in the beaker.

NOTE— A sample size that will yield between 0.15 and 2.5 mg of sulfur in the absorber shall be selected. This will then allow subsequent direct application of the procedures described in **10.5.3** and **9.6** and will avoid the necessity for using less than a one-fifth aliquot of the absorber solution for analysis. When the sulfur level of the sample is about 15 mg/kg or less, at least 30 g of sample shall be burned. To accommodate the large sample sizes, a burner flask of suitable size shall be fabricated to replace the standard 25 ml flask. In recognition of the larger size of the flask, it is preferable to use 18 cm of wicking rather than the 15 cm specified in **8.5**. To avoid excessive depletion of absorber liquid caused by the longer burning time for larger samples, it is preferable to charge the absorbers with 50 ml of the hydrogen peroxide solution instead of the 30 ml specified in **6.2**.

**10.4.2** The volume of the absorber solution is to be reduced to about 20 ml by evaporation on a hot plate. Quantitatively transfer the resulting solution to a 50 ml volumetric flask, rinsing the beaker with several small portions of water. Add 3 ml of HCl (1: 12) to the flask, make up to volume with water, and mix thoroughly.

**10.4.3** If the sulfur content of the absorber solution is known to be less than 0.5 mg, use the entire contents of the volumetric flask for analysis. If the approximate sulfur content is unknown or is expected to exceed 0.5 mg, transfer a 10 ml aliquot to a second 50 ml volumetric flask and dilute the solution in both flasks to volume with HCl (1: 215). Use the more dilute solution first and, if less than 0.05 mg of sulfur is found, then use the more concentrated solution. Prepare a dilution of the combustion atmosphere blank similar to the solution used for analysis. Analyze the solutions as described in **10.4**.

**10.5 Procedure for Analysis of Solutions**

**10.5.1** The entire contents of the 50 ml volumetric flask containing the solution to be analyzed are to be poured into 100 ml beaker and proceed as directed in **10.3.2, 10.3.3, and 10.3.4.** Treat the combustion atmosphere blank in the same way and obtain a combustion atmosphere-reagent blank reading by subtracting its initial absorbance from that obtained after the addition of BaCl2 ·2H2O.

NOTE— If the blank reading exceeds 0.020, the precision obtainable will be impaired. In this event, make an analysis of the reagents alone to determine whether the atmosphere or reagents are at fault. Take 30 ml of the H2O2 (1.5 percent) in the 50 ml volumetric flask, dilute to the mark with HCl (1: 215), and proceed as described in **10.3.5**. If the reagent blank reading exceeds 0.010, results shall not be considerable reliable.

**10.5.2** The net absorbance of the analyzing solution is to be obtained by subtracting the initial absorbance and the combustion atmosphere-reagent blank reading from that obtained after the addition of BaCl2·2H2O.

**10.5.3** Convert net absorbance to milligrams of sulfur by using the calibration curve.

**10.6 Calculation**

**10.6.1** The amount of sulfur in the sample is calculated as follows

Sulfur content, ppm = (*A*/*WF*) x 1000

where

*A* = sulfur read from the calibration curve, in mg;

*W* = sample burned, in g; and

*F* = aliquot fraction of the sample solution used for analysis.

**10.7 Precision**

The following criteria shall be used for judging the acceptability of results (95 percent confidence)

**10.7.1** *Repeatability*

 Duplicate results obtained by the same operator shall not differ by more than the following amounts

|  |  |
| --- | --- |
| *Sulfur Content, percent by mass* | *Repeatability* |
| 0.0005 to 0.008 | 0.0000116  |
| Over 0.008 to 0.028 | (0.000001 ) + 0.00085 |

 **10.7.2** *Reproducibility*

The results submitted by each of two laboratories shall be considered suspect if the two results differ by more than the following amounts

|  |  |
| --- | --- |
| *Sulfur Content, percent by mass* | *Repeatability* |
| 0.0005 to 0.0125 | 0.0000145  |
| Over 0.0125 to 0.0280 | 0.0000508 − 000045.4 |

**ANNEX A**

(*Foreword*)

**COMMITTEE COMPOSITION**

**Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee, PCD 01**

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| Bharat Petroleum Corporation Limited, Mumbai | Shri R. Subramanian Shri C. Shanmuganathan *(Alternate*) |
| CSIR - Central Institute for Mining and Fuel Research, Dhanbad | Shri S. R. K. Rao  Shri P. K. Singh (*Alternate* I) Shri S. Dutta (*Alternate* II) |
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| Oil and Natural Gas Corporation Limited, New Delhi | Shri Gour Mohan Dass Shrimati Leena John (*Alternate* I)SHRI DINESH S R REDDY KAKUTURI *(Alternate II)* |
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| Reliance Industries Limited, Mumbai | Shri Pramod Mall |
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**Physico-chemical Test Methods for Petroleum and related products of synthetic or biological origin (excluding bitumen, lubricants, greases and gaseous fuels) Subcommittee, PCD 1:3**

|  |  |
| --- | --- |
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