

British Standard Methods of test for

Petroleum and its products

Part 107. Sulphur in petroleum products (lamp method)

(Identical with IP 107/73(80))

Méthodes d'essai pour le pétrole et les produits pétroliers

Partie 107. Soufre dans les produits pétroliers (méthode à la lampe)

Prüfmethoden für Erdöl und Erdölprodukte

Teil 107. Schwefel in Erdölprodukten (Lampentest)

Foreword

BS 2000 comprises a series of test methods for petroleum and its products that have been published previously by the Institute of Petroleum (IP) and have been accorded the status of British Standards. Each method should be read in conjunction with BS 2000 : Part 0 'General introduction' which gives details of the BSI/IP agreement for publication of the series, lists more than 50 methods scheduled to be published in this way in 1982, and provides general information on safety precautions, sampling and other matters.

The numbering of the other Parts follows that of the corresponding methods published in 'IP Standards for petroleum and its products, Part 1 Methods for analysis and testing'. BS 2000 : Part 107 is thus identical with IP 107/73, which was reapproved in 1980. IP 107/73 was previously published in A5 format as BS 4350* which has now been re-numbered and issued in the BS 2000 series. It is intended to issue further revisions when necessary in line with changes that may be made in subsequent editions of the IP method.

Caution. Attention is drawn to the safety precautions mentioned in Part 0 of this British Standard and also to the specific hazard indicated in 5.4.

NOTE. The titles of the standards publications referred to in this Part of this British Standard are listed on the inside back cover.

WITHDRAWN

*Now withdrawn.

Method (identical with IP 107/73 (80)¹)**1. SCOPE**

1.1. This method covers the determination of total sulphur in liquid petroleum products in concentrations above 0.002% by weight [Note 1]. A special sulphate analysis procedure is described in Appendix I that permits the determination of sulphur in concentrations as low as 5 ppm.

NOTE 1: The comparable lamp method for the determination of sulphur in fuel gases is described in ASTM Method D 1072. For the determination of sulphur in heavier petroleum products that cannot be burned in a lamp, see the bomb method (ASTM D 129-IP 61), the quartz tube method (ASTM D 1551 or IP 63), or the high-temperature method (ASTM D 1552).²

1.2. The direct burning procedure (Section 7) is applicable to the analysis of such materials as gasoline, kerosine, naphtha, and other liquids that can be burned completely in a wick lamp. The blending procedure (Section 8) is applicable to the analysis of some 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, bitumens, tars and other heavy residues **CANNOT** be analysed by this method.

1.3. Phosphorus compounds normally present in commercial gasoline do not interfere. A correction is given for the small amount of acid resulting from the combustion of the lead anti-knock fluids in gasolines. Appreciable concentrations 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. SUMMARY OF METHOD

2.1. The sample is burned in a closed system, using a suitable lamp (Fig. 1) and an artificial atmosphere composed of 70% carbon dioxide and 30% oxygen to prevent formation of nitrogen oxides. The oxides of sulphur are absorbed and oxidized to sulphuric acid by means of hydrogen peroxide solution which is then flushed with air to remove dissolved carbon dioxide. Sulphur as sulphate in the absorbent is determined acidimetrically by titration with standard sodium hydroxide solution, or gravimetrically by precipitation as barium sulphate (see Appendix II).

2.2. Alternatively, the sample may be burned in air, the sulphur as sulphate in the absorbent being determined by precipitation as barium sulphate for weighing (see Appendix II).

NOTE 2: In the absence of acid-forming or base-forming elements, other than sulphur, results by the volumetric and gravimetric finishes described are equivalent within the limits of precision of the method.

2.3. For sulphur contents below 0.002% by weight, it is necessary to determine the sulphate content in the absorber solution turbidimetrically as barium sulphate (see Appendix I).

3. APPARATUS

3.1. *Absorbers, Chimneys, Lamps, and Spray Traps* (Fig. 1) – as required are described in detail in Appendix III. The standard flask and burner (Fig. 4) as shown is not suitable for burning highly aromatic mixtures without blending, as described in Section 8. The flask and burner for aromatic samples (Fig. 4) permits burning these samples directly without blending and may also be used to burn non-aromatic samples; with this lamp, a second port with control valve in the burner manifold is required.

3.2. *Cotton Wicking* – Clean, unused, uniform, twisted white cotton yarn of good quality.³ For the burner to burn aromatic samples use long staple, fine spun, commercial 'fine' grade.⁴

3.3. *Manifold System* – consisting of a vacuum manifold with regulating device, valves, etc. (Fig. 2) and a dual manifold (burner and chimney) supplying a gas mixture of approximately 70% carbon dioxide (CO₂) and 30% oxygen (O₂) at regulated pressures. The vacuum manifold shall be connected to a pump of

NOTES to note 1. BS 2000 : Part 61 (formerly BS 4454) is identical with IP 61.

BS 4384 was published in 1969, identical with ASTM D 1551 - IP 63. However, in 1976 IP 63 was declared by the Institute of Petroleum to be obsolete and was therefore no longer published in 'IP Standards'. Accordingly the reference to IP 63 is to be deleted from IP 107 in the next (1982) edition of 'IP Standards'. It is also intended to withdraw BS 4384.

¹ Under the standardization procedure of ASTM, this method is under the jurisdiction of the ASTM Committee D-2 on Petroleum Products and Lubricants.

In the IP, this method is under the jurisdiction of the Standardization Committee.

² *Annual Book of ASTM Standards*, Part 23.

³ Lily Rug yarn, white, 4-strand (2–3 mg per cm per strand), manufactured by Lily Mills, Shelby, N.C., as Article 241, has been found satisfactory for this purpose, or the type marketed by various suppliers in the U.K. as 13s/14 ends, scoured and bleached.

⁴ Available from Arthur H. Thomas Co., West Washington Square, Philadelphia 6, Pa.

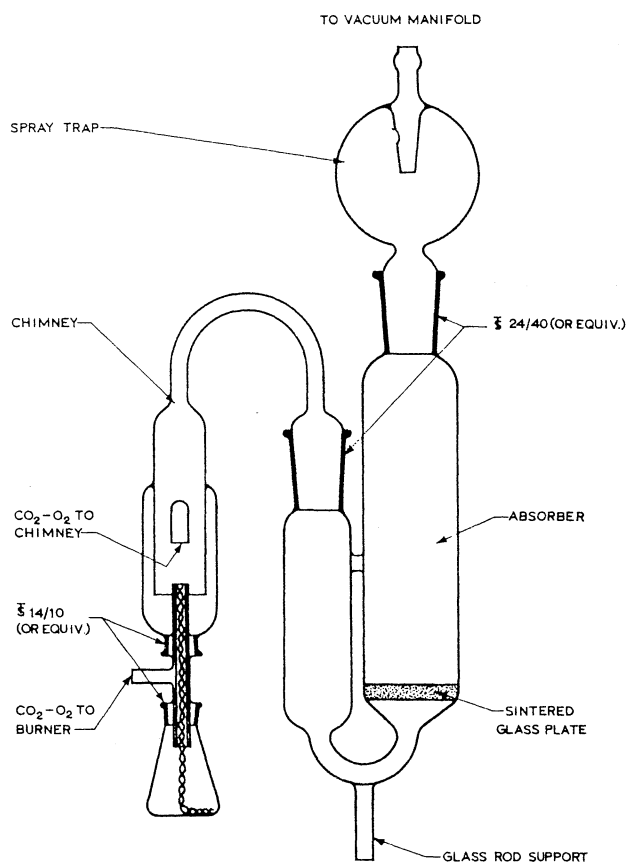
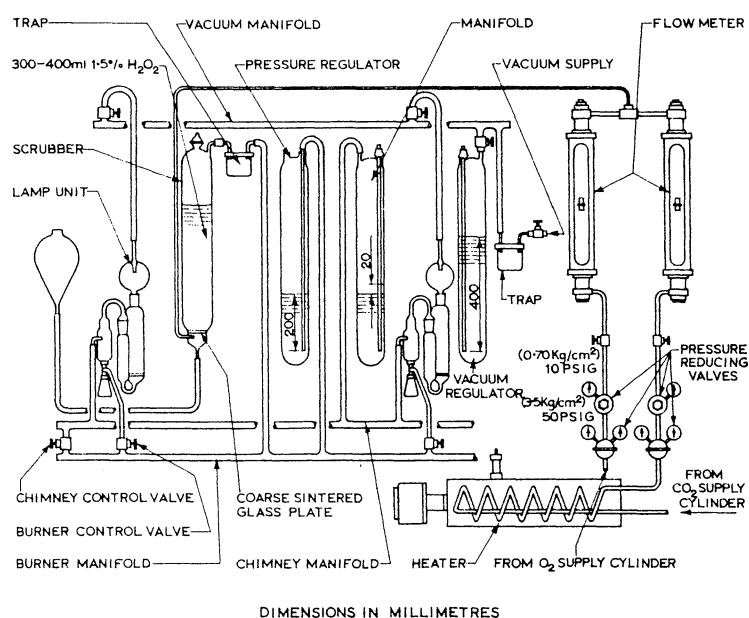


Fig. 1. Assembled lamp unit.

NOTE to Fig. 1. The symbol '§' indicates an interchangeable conical ground glass joint. The nearest equivalent conical joint sizes to 14/10 and 24/40, given in BS 572, are 14/15 and 24/29.

Fig. 2. CO₂-O₂ supply manifold and lamp system.

sufficient capacity to permit a steady gas flow of about 3 litres per min through each absorber and to maintain a constant manifold pressure of approximately 40 cm of water below atmospheric. The gas mixture in the chimney manifold shall be maintained at a nearly constant pressure of 1 to 2 cm of water and the burner manifold at approximately 20 cm of water. A suitable arrangement is shown in Fig. 2 and described in Appendix III, but any other similar system may be used. Modifications of the manifold and associated equipment for burning samples in air are shown in Fig. 3 and described in Appendix II.

4. REAGENTS AND MATERIALS

4.1. *Purity of Reagents* – Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications for analytical reagents of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available or to other such recognized standards for reagent chemicals.⁵ Other grades may be used, provided it is known or first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2. *Purity of Water* – Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

4.3. *Carbon Dioxide and Oxygen* – The carbon dioxide (CO₂) and the oxygen (O₂) shall each be at least 99.5% pure. These gases shall meet the requirements of Section 7.5.

4.4. *Diluent* – The diluent used shall have a sulphur content less than 0.001%, be completely miscible with the sample to be analysed, and permit burning at a moderate rate without smoking. *N*-heptane, isooctane, and absolute ethyl alcohol have been found suitable [Note 10].

4.5. *Hydrogen Peroxide Solution (1:19)* – Mix 1 vol of concentrated hydrogen peroxide (H₂O₂, 30%) with 19 vol of water. Store in a dark-coloured glass-stoppered bottle.

4.6. *Methyl Purple Indicator* – Aqueous solution containing approximately 0.1% active constituent.⁶ (Not methyl violet.)

4.7. *Sodium Hydroxide Solution (100 g per litre)* – Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 litre.

4.8. *Sodium Hydroxide, Standard Solution (0.05 N)* – Dilute 2.8 ml of saturated NaOH solution to 1 litre [Note 3], using for this purpose the clear saturated solution decanted after standing long enough to permit any precipitate to settle out. Standardize by titration against standard acid, using the methyl purple indicator. Store in an alkali-resistant glass bottle and protect to minimize contamination by CO₂ from the air. Use only pure gum rubber tubing for connexions between the storage bottles and burettes.

NOTE 3: The calculation of results may be simplified by adjusting the normality of the NaOH solution to 0.0624 ± 0.0001 . Then 1 ml of the NaOH solution will be equivalent to 0.0010 g of sulphur. In this case, the factor 16.03 *N* in the calculation (Section 10.1) becomes 1.000.

5. PREPARATION OF APPARATUS

5.1. When the apparatus is first assembled, charge the absorber with 30 ± 2 ml of water. Adjust the individual valves between the vacuum manifold and spray traps so that approximately 3 litres of air per min will be drawn through each absorber when the chimney outlets are open to the atmosphere, while maintaining the pressure in the vacuum manifold at approximately 40 cm of water below atmospheric. When all adjustments have been made, remove the water from the absorbers. The height of the liquids in the pressure and vacuum regulators is indicated in Fig. 2, and during operation a slow leak of gas through them should be maintained [Note 4].

NOTE 4: In use, place 300 to 400 ml of H₂O₂ solution (1.5%) in the scrubber. Since the manifold manometer also serves as a scrubber at the end of the test to remove CO₂ from the absorbent, use H₂O₂ solution (1.5%) as the manometric liquid. Replace weekly or whenever the volume becomes appreciably less than the original.

⁵ See 'Reagent Chemicals, American Chemical Society Specifications,' Am. Chemical Soc., Washington, D.C., or proprietary specifications for Analytical Grade Chemicals. For suggestions on the testing of reagents not listed by the American Chemical Society or in proprietary specifications, see 'Reagent Chemicals and Standards,' Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the 'United States Pharmacopoeia,' or 'British Pharmacopoeia.'

⁶ Fleisher Methyl Purple Indicator, U.S. Patent No. 2416619 may be obtained from Harry Fleisher Chemical Co., Benjamin Franklin Station, Washington 4, D.C., or from any chemical supply company handling Fleisher Methyl Purple.

NOTE to 4.2. Water complying with BS 3978 is suitable.

NOTE to 4.3. Carbon dioxide and oxygen, complying respectively with BS 4105 and BS 4364, are suitable.

NOTES to 4.4. The IP specifications for *n*-heptane and isooctane are given in BS 2000 : Part 0 : Addendum 1.

Ethanol complying with BS 507 is suitable.

5.2. Neutralize the H_2O_2 solution (1:19) immediately before use. As 30 ml of the solution is needed, transfer to a beaker multiples of 30 ml sufficient for the number of absorbers to be used simultaneously. Add 1 drop of methyl purple indicator solution for each 100 ml of H_2O_2 solution and then add 0.05 N NaOH solution dropwise until the colour changes from purple to light green.

5.3. Introduce 30 ± 2 ml of the freshly neutralized H_2O_2 solution (1:19) into the larger bulb of each absorber. In addition, for each set of samples burned, prepare an extra absorber for use as a control blank. Attach the spray traps and chimneys and connect them to their respective manifolds by means of sulphur-free rubber tubing. Close the chimney openings by means of corks.

5.4. With the burner control valves closed, the valve to the vacuum regulator fully open, and the pressure in the vacuum manifold adjusted to approximately 40 cm of water below atmospheric, turn on the CO_2 and O_2 supplies [CAUTION: see Note 5]. Adjust the chimney manifold control valve so that, at the required rate of flow through the absorbers, only a small stream of CO_2 - O_2 gas escapes at the pressure regulator, a small stream of air enters at the vacuum regulator, and the pressure in the chimney manifold is 1 to 2 cm of water. Minor adjustment of the vacuum regulator and vacuum control valve may be necessary to achieve this condition [Note 6].

NOTE 5: CAUTION – A hazardous (explosive) condition may result if the CO_2 supply is interrupted and the O_2 flow is continued while samples are being burned. The installation of suitable warning or control equipment is recommended.

NOTE 6: It is convenient to balance the gas flow system by regulating the pressure in the vacuum manifold. This is done by raising or lowering the air inlet tube in the vacuum regulator by sliding it in a rubber sleeve.

5.5. Cut the wicking to 30 cm lengths. Use the number of lengths dictated by the sample (see Section 6); fold the wicking once to give a 15 cm long bundle for threading the burners. Thread the required number of burners by inserting the looped ends into the top of the inner tube of the burner. Draw the wicking through by means of a metal hook. Trim the wick as close as possible to the top of the burner with a pair of sharp scissors. It is essential that thoroughly cleaned burners and new wicking be used for each test.

6. CONTROL OF COMBUSTION

6.1. Most types of liquid samples burn with a luminous yellow flame, the size and shape of which is dependent on 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. It is preferable that the latter two variables be fixed with relation to the first before burning is started so that the flame can be controlled by variation in the rate of CO_2 - O_2 flow.

6.2. Highly volatile samples require a tight-fitting wick, the top of which may need to be several mm below the top of the burner, and in extreme cases may have to be cooled in ice during the burning. Less volatile materials require a more loosely fitting wick and may require warming.

6.3. After trimming, draw the wick down until the trimmed edge is flush with or just a little below the top of the burner. With the burner for aromatic samples, the distance from the top of the burner to the top of the wicking should be 8 mm or more for benzene and 4 mm for toluene; a slight heating of the upper end of the burner will be helpful in starting vaporization of heavier materials.

6.4. To use the standard lamp, light the wick and then slowly admit combustion atmosphere to the burner to obtain a smoke-free flame. To use the burner for aromatic samples, introduce a small amount of combustion atmosphere into the flask to provide sufficient vapour 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 snuffed out, relight.

6.5. A short burning period (1 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. In 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. In any case, it is essential that the flame burn smoothly and symmetrically and without jets in the inner cone or smoke on the outer fringes.

6.6. Satisfactory combustion of materials difficult to burn can sometimes be obtained by increasing the O_2 content of the combustion atmosphere. Never increase the O_2 content of the combustion atmosphere to more than 40%.