BS 2000 :
Part 107 : 1993

Methods of test for

Petroleum and its products

Part 107. Determination of sulphur – Lamp combustion method

(Identical with IP 107/86)

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British Standards

Foreword

This British Standard, having been prepared under the direction of the Petroleum Standards Policy Committee, was published under the authority of the Standards Board and comes into effect on 28 February 1993.

This British Standard supersedes BS 2000 : Part 107 : 1991, which is withdrawn.

BS 2000 comprises a series of test methods for petroleum and its products that are published by the Institute of Petroleum (IP) and have been accorded the status of a British Standard. Each method should be read in conjunction with the preliminary pages of `IP Standard methods for analysis and testing of petroleum and related products' which gives details of the BSI/IP agreement for publication of the series, provides general information on safety precautions, sampling and other matters, and lists the methods published as Parts of BS 2000.

The numbering of the Parts of BS 2000 follows that of the corresponding methods published in `IP Standard methods for analysis and testing of petroleum and related products'. Under the terms of the agreement between BSI and the Institute of Petroleum, the revised version of BS 2000 : Part 107 will be published by the IP (in `Standard methods for analysis and testing of petroleum and related products' and as a separate publication). BS 2000 : Part 107 : 1993 is thus identical with IP 107/86. Square brackets marked in the margin of this IP Standard indicate text that differs from the previous edition.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Committee reference PTC/13

IP 107/86 ASTM D1266–87 BS 2000: Part 107: 1993

Determination of sulphur – Lamp combustion method

This method was adopted as a joint ASTM–IP Method in 1964.

This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations.

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 D129–IP 61), or the high-temperature method (ASTM D1552).[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 (CO_2) and 30% oxygen (O_2) at regulated pressures.

[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*, Vol. 05.01.

[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.

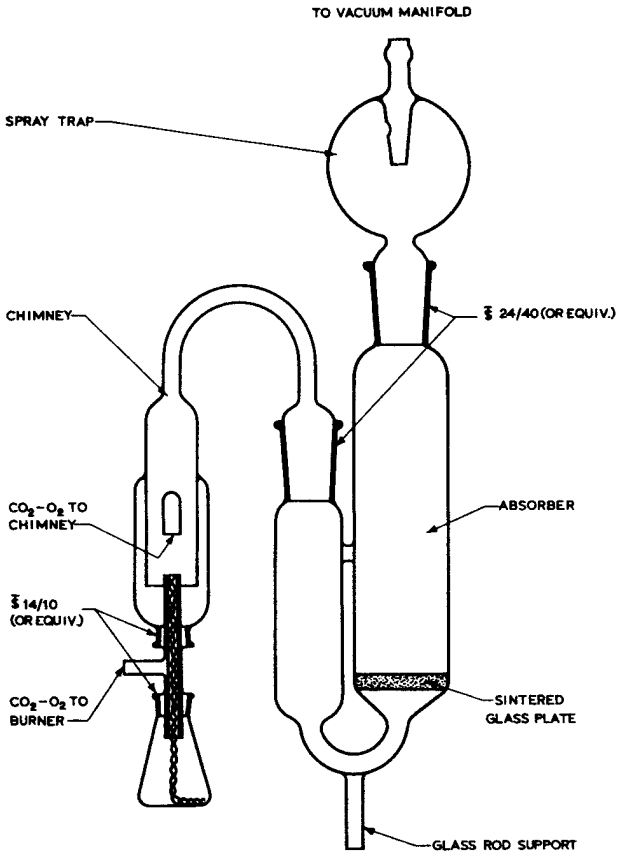

Fig. 1. Assembled lamp unit.

The vacuum manifold shall be connected to a pump of 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 (CO_2) and the oxygen (O_2) 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].

[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'.

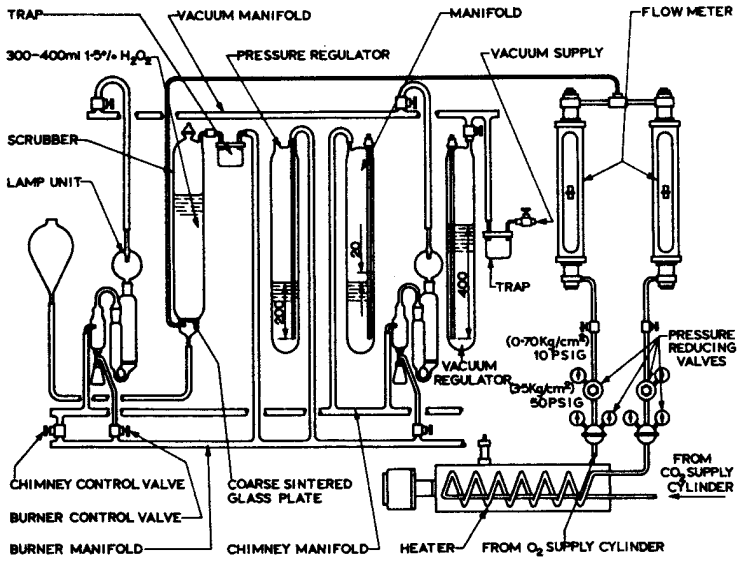

Fig. 2. CO_2–O_2 supply manifold and lamp system.

4.5. *Hydrogen Peroxide Solution* (1 : 19) – Mix 1 vol of concentrated hydrogen peroxide (H_2O_2, 30%) with 19 vol of water. Store in a dark-coloured glass-stoppered bottle. **CAUTION:** Hydrogen peroxide is a powerful oxidizing agent and should not be allowed to come into contact with the skin.

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. **CAUTION:** Sodium hydroxide is corrosive and can cause severe burns.

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 CO_2 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 H_2O_2 solution (1.5%) in the scrubber. Since the manifold manometer also serves as a scrubber at the end of the test to remove CO_2 from the absorbent, use H_2O_2 solution (1.5%) as the manometric liquid. Replace weekly or whenever the volume becomes appreciably less than the original.

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]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.

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%.

6.7. Before extinguishing the flames, the samples shall be burned until the flask and wicking appear to be dry and the flame has reduced considerably in size; 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 should be extinguished when it is only 3 to 4 mm high. If the flame is permitted to burn until it goes out, partially oxidized substances (probably organic acids) are produced; as a result broad, indistinct end points are obtained. 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 sulphur is present, it is particularly important that the sample be burned 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 more volatile materials seem to burn first, possibly concentrating sulphur compounds in the material remaining behind.

7. PROCEDURE FOR DIRECT COMBUSTION OF LIQUID SAMPLES

(see also Appendix II)

7.1. By means of an appropriate pipette, introduce into the flask of each lamp an approximate quantity of sample as indicated in Table 1. Stopper the flasks with clean, numbered corks. Weigh each flask and its burner to the nearest 0.005 g [Note 7].

NOTE 7: While the stoppered flasks and prepared burners may all be weighed separately, 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.

7.2. Handling each lamp individually, insert the burner in the flask. As soon as the sample has risen by capillary action to the top of the wick, connect the side tube of the burner to the burner manifold by means of suphur-free rubber tubing. Light the burner with a sulphur-free flame (such as an alcohol lamp) and insert into the chimney, pinching off the connexion between the chimney and the chimney manifold during the insertion if the flame tends to be blown out. At the same time, adjust the gas flow to the burner so that the flame is maintained at a point just below smoking and has a steady symmetrical appearance. Continue in this manner until all lamps have been placed in the chimneys. Make any minor adjustment of the chimney manifold control valve necessary to maintain the required pressure (see Section 5). During the burning, and particularly during the latter stages when the flame becomes small, decrease the CO_2–O_2 supply to the burners in order to prevent extinction of the flames [Note 8].

TABLE 1. Sample size for direct combustion of liquid samples

Sulphur content, per cent by weight	Sample size	
	g	ml
Under 0.05	10 to 15	20
0.05 to 0.3	5 to 10	10
0.3 to 1	3 to 5	5
Over 1	2 to 3	3

NOTE 8: When incomplete combustion occurs, the absorber liquid will foam excessively.

7.3. When the burning of each sample is complete, as evidenced by the flame becoming small owing to depletion of the sample, remove the burner and flask from the chimney, extinguish the flame, shut off the CO_2–O_2 supply to the burner and stopper the chimney opening. Immediately reweigh the flask, burner, and numbered cork. When all combustions have been completed, turn off the CO_2 and the O_2 supplies, close the chimney control valve, and close the connexion to the vacuum regulator; this will cause 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 CO_2 from the absorbent; then close the vacuum control valve [Note 9].

NOTE 9: If it is desired to conserve the combustion atmosphere, the gas flow through each individual absorber may be turned off upon completion of the burning period. To accomplish this, pinch off the rubber tubing connecting the spray trap to the vacuum manifold, reduce the flow of mixed gases at the rotameters proportionately, and readjust the vacuum control valve and the chimney control valve. When the burning of all samples has been completed, it is necessary to remove the pinch clamps and readjust the vacuum control valve in order to draw air at the required rate through the absorbers for removal of dissolved CO_2.

7.4. Rinse the chimneys and spray traps three times, using about 10 ml of water each time. When the sample contains lead anti-knock fluids, use hot water to rinse the chimneys. Add the rinsings to the absorbers, and titrate as directed in Section 9.

7.5. *Blank* – Leave the chimney of the blank absorber (Section 5.3) stoppered, and allow the CO_2–O_2 stream to pass through that absorber until all samples started at one time have finished burning. Turn off the CO_2 and the O_2 supplies and aerate the

TABLE 2. Sample size for testing blended liquid samples

Sulphur content, per cent by weight	Sample size	
	g	ml
0.5 and under	3 to 4	5
Over 0.5	2 to 3	3

blank absorber in the same manner as the sample absorbers (Section 7.3). Titrate the absorber liquid as directed in Section 9. 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 CO_2 cylinder.

8. PROCEDURE FOR BLENDING AND COMBUSTION OF LIQUID SAMPLES

8.1. Add 6 ml of sulphur-free diluent to each flask. Stopper the flasks with numbered corks and weigh to the nearest 0.005 g. By means of a pipette, introduce into the flask of each burner an approximate quantity of sample as indicated in Table 2; swirl to mix thoroughly, and reweigh [Note 10].

NOTE 10: Alternatively, make a quantitative 40% blend of the sample in sulphur-free diluent and proceed as described in Section 7.

8.2. Insert the burner and burn as described in Section 7.2. 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 diluent and burning so that a total of 10 ml of diluent has been burned [Note 11].

NOTE 11: 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 *N* NaOH solution.

8.3. After all lamps have completed burning, turn off the CO_2 and O_2 supplies, close the connexion to the vacuum regulator, draw air through the absorbers for 5 min, and finally close the vacuum control valve. Rinse the chimneys and spray traps three times, using about 10 ml of water each time. Add the rinsings to the absorbers, and titrate as directed in Section 9.

9. TITRATION OF ABSORBENT SOLUTION

9.1. Add 3 to 4 drops of methyl purple indicator solution to the liquid in each absorber. Titrate the absorbent solution by introducing 0.05 *N* NaOH solution from a burette into the smaller bulb of the absorber. Use a 10 ml microburette if less than 10 mg of sulphur 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 by mouth [Note 12].

NOTE 12: When incomplete combustion of the sample occurs the resultant solution may be discoloured and the end point will not be sharp. In these cases, discard the determination.

10. CALCULATIONS

10.1. Calculate the sulphur content of liquid samples as follows:

Sulphur content, per cent by weight =

$$16.03\,N \times \frac{A}{10W}$$

where

A = millilitres of NaOH solution required to titrate the acid in the absorbent solution from the burned sample;
N = normality of the NaOH solution [see Note 3]; and
W = grams of sample burned.

When it is required by specifications to correct the sulphur content [Note 13] for lead anti-knock fluids, calculate the corrected values as follows:

Corrected sulphur content, per cent by weight $= S - LF$

where

F = 0.0015 if the sample contains aviation lead anti-knock fluid or 0.0035 if the sample contains tetraethyllead, tetramethyllead, or the mixed lead alkyl anti-knock fluid;
L = lead content in g per USG [Note 14]; and
S = sulphur content, per cent by weight.

NOTE 13: These corrections are based on experiments of burning fuels blended with anti-knock fluid containing tetraethyllead and ethylene halide in commonly-used combinations. Tetramethyllead and the mixed lead alkyl anti-knock fluids contain the same ethylene halide combination as the tetraethyllead fluid.

NOTE 14: To convert grams of lead per IG into grams per USG, multiply by 0.8326. Multiply by 3.7853 to convert grams of lead per litre into grams per USG.

11. REPORT

11.1. Report the result of the test to the nearest 0.01% for sulphur at a level of 0.05% and higher.

12. PRECISION

12.1. The following criteria should be used for judging the acceptability of results (95% confidence) as applied to the direct burning of liquid samples in the range of 0.01 to 0.4% sulphur.

12.1.1. *Repeatability* – Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

	Repeatability
Sulphur content	0.005

12.1.2. *Reproducibility* – The results submitted by each of two laboratories should not be considered suspect unless the two results differ by more than the following amounts:

	Reproducibility
Sulphur content	$0.010 + 0.025\,S$

where

S = the total sulphur content, per cent by weight, of the sample.

APPENDIX I

METHOD OF TEST FOR TRACE QUANTITIES OF SULPHUR

SCOPE

A1. This appendix describes a procedure for extending the lamp method of test for sulphur to the analysis of samples having sulphur contents as low as 5 ppm [Note 16]. The procedure is not applicable for the determination of less than 300 ppm of sulphur in liquids containing lead anti-knock compounds.

NOTE 15: Only by the exercise of the most scrupulous care and attention to details may reliable results be obtained by this method. Before placing new glassware into use and thereafter as required, wash the glassware with concentrated nitric acid. Rinse three times with tap water, followed by three rinsings with de-ionized distilled water. Reserve units of glassware for use in this method alone.

SUMMARY OF METHOD

A2. A sample of suitable size is burned as described in the main method. Sulphate ion in the absorber solution is determined by precipitation as barium sulphate and measurement of the turbidity of a suspension of the precipitate. The suspension is stabilized by the addition of alcohol and glycerin, and its turbidity is measured by use of a spectrophotometer or filter photometer.

ADDITIONAL APPARATUS

A3. (*a*) *Photometer* – Preferably a spectrophotometer having an effective band width of about 50 mμ and equipped with a blue-sensitive phototube for use at 450 mμ, or alternatively, a filter photometer equipped with a colour filter having a maximum transmission at approximately 425 mμ.

(*b*) *Absorption Cells* – Cells having optical path lengths of 5 cm 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 de-ionized water following cleaning.

NOTE 16: The procedure as written assumes an absorbance change of about 0.100 for each 0.1 mg of sulphur in 50 ml of solution measured in a 5 cm cell. Photometers employing cells of shorter optical paths give proportionately poorer precision.

(*c*) *Scoop* – capable of dispensing 0.30 ± 0.01 g of barium chloride dihydrate specified in Section A4 (*b*).

(*d*) *Magnetic Stirrer* – equipped with tetrafluoroethylene-covered stirring bars about 1¼ in (32 mm) long.

(*e*) *Lamp Assembly* – as described in Appendix III. Reserve complete units consisting of flask, burner, chimney, absorber, and spray trap for use in this procedure only.

ADDITIONAL REAGENTS[7]

A4. (*a*) *Alcohol–Glycerin Mixture* – Mix 2 vol of denatured ethyl alcohol conforming to Formula No. 3A of the U.S. Bureau of Internal Revenue, or ethyl alcohol (95% v/v) with 1 vol of glycerin.[7]

[7]For Purity of Reagents, see Section 4.1.

(*b*) *Barium Chloride Dihydrate* ($BaCl_2.2H_2O$) – Crystals passing a ASTM E11 20 mesh or BS 18 mesh (850 μm) sieve and retained on a ASTM E11 30 mesh or BS 30 mesh (500 μm) sieve.

NOTE 17: The crystal size of the $BaCl_2.2H_2O$ is an important variable that affects the development of turbidity.

(*c*) *Hydrochloric Acid* (1 : 12) – Add 77 ml of concentrated hydrochloric acid (HCl, rel d 1.19) to a 1 litre volumetric flask and dilute to the mark with de-ionized water.

(*d*) *Hydrochloric Acid* (1 : 215) – Add 60 ml of 1 : 12 HCl to a 1 litre volumetric flask and dilute to the mark with de-ionized water.

(*e*) *Sulphuric Acid* (1 ml = 0.100 mg S) – Dilute 6.24 ± 0.01 ml of 1 *N* sulphuric acid (H_2SO_4) to exactly 1 litre with de-ionized water. Check the dilution by titration against standard NaOH solution of about the same normality and adjust the concentration, if necessary, so that each ml of this solution is equivalent to 0.100 mg of S.

(*f*) *Water, De-ionized Distilled* – Percolate water through a column of mixed anion and cation exchange resins.

NOTE 18: 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.

CALIBRATION

A5. (*a*) Into 50 ml volumetric flasks introduce, by means of a burette, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, and 5.00 ml of H_2SO_4 (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. Prepare a reagent blank standard in a similar way, omitting the H_2SO_4.

(*b*) Pour the entire contents of each flask 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.

(*c*) Allow the solution to stand undisturbed for 4 min. Transfer to an absorption cell and measure the initial absorbance, using water as reference.

(*d*) Return the solution to the beaker and add 0.30 ± 0.01 g of $BaCl_2.2H_2O$ crystals, either by weighing this amount or by use of the scoop. Stir with the magnetic stirrer for exactly 3 min. Allow to stand for an additional 4 min, transfer to the cell, and again measure the absorbance relative to water.

(*e*) Following steps described in Paragraphs (*b*), (*c*), and (*d*), obtain a reagent blank reading by subtracting the initial absorbance of the reagent blank standard from that obtained after addition of $BaCl_2.2H_2O$. This reading should not exceed 0.005.

(*f*) Obtain the net absorbance for each standard by subtracting the initial absorbance and reagent blank reading from the absorbance obtained in accordance with Paragraph (*d*). Plot the net absorbance of each standard against milligrams of sulphur contained in 50 ml of solution, and draw a smooth curve through the points.

(*g*) Check the calibration curve daily by making single determinations to detect possible shifts.

PROCEDURE FOR COMBUSTION OF SAMPLES

A6. (*a*) Prepare the combustion apparatus and burn between 5 and 30 g of sample depending on the expected sulphur level [Note 19]. Follow the general procedures described in Sections 5, 6, and 7 of the main method. The requirements for initial neutralization of the H_2O_2 solution (Section 5.2) and for final removal of dissolved CO_2 from this solution (Sections 7.3 and 8.3) 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. Transfer the absorber solution, containing rinsings from the spray trap and chimney (Section 7.4), to a 250 ml beaker, rinse the absorber two or three times with 10 ml portions of water, and add the rinsings to the solution in the beaker.

NOTE 19: A sample size that will yield between 0.15 and 2.5 mg of sulphur in the absorber must be selected. This will then allow subsequent direct application of the procedures described in Sections A6 (*c*) and A7 and will avoid the necessity for using less than a one-fifth aliquot of the absorber solution for analysis. When the sulphur level of the sample is about 15 ppm or less, at least 30 g of sample must be burned. To accommodate the large sample sizes, a burner flask of suitable size must 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 Section 5.5. 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 Section 5.3.

(*b*) Reduce the volume of the absorber solution 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.

(*c*) If the sulphur 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 sulphur 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 sulphur is found, then use the more concentrated solution. Prepare a dilution of the combustion atmosphere blank similar to the solution used for analysis. Analyse the solutions as described in Section A7.

PROCEDURE FOR ANALYSIS OF SOLUTIONS

A7. (*a*) Pour the entire contents of the 50 ml volumetric flask containing the solution to be analysed into a 100 ml beaker and proceed as directed in Sections A5 (*b*), (*c*), and (*d*). 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 addition of $BaCl_2 . 2H_2O$.

NOTE 20: Should the blank reading exceed 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. Place 30 ml of the H_2O_2 (1.5%) in the 50 ml volumetric flask, dilute to the mark with HCl (1 : 215), and proceed as described in Section A5 (*e*). If this reagent blank reading exceeds 0.010, results should not be considered reliable.

(*b*) Obtain the net absorbance of the analysis solution by subtracting the initial absorbance and the combustion atmosphere-reagent blank reading from that obtained after addition of $BaCl_2 . 2H_2O$.

(*c*) Convert net absorbance to milligrams of sulphur by using the calibration curve.

CALCULATION

A8. Calculate the amount of sulphur in the sample as follows:

$$\text{Sulphur content, ppm} = \frac{A}{WF} \times 1000$$

where

A = milligrams of sulphur read from the calibration curve;
W = grams of sample burned;
F = aliquot fraction of the sample solution used for analysis.

PRECISION

A9. The following criteria should be used for judging the acceptability of results (95% confidence):

(*a*) *Repeatability* – Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

Sulphur content, ppm	Repeatability
5 to 80	0.116 × ppm S
Over 80 to 280	(0.01 × ppm S) + 8.5

(*b*) *Reproducibility* – The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts:

Sulphur content, ppm	Reproducibility
5 to 125	0.145 × ppm S
Over 125 to 280	(0.508 × ppm S) − 45.4

APPENDIX II

AIR BURNING OF SAMPLE, GRAVIMETRIC FINISH

(Abstracted from former ASTM Method D90–55T)

SCOPE

B1. This procedure is recommended only for analysing liquid petroleum samples that can be burned with a wick lamp; it is not recommended for analysis of liquefied petroleum gas samples.

APPARATUS

B2. The manifold system described in Section 3.3 may be used with only a slight modification.

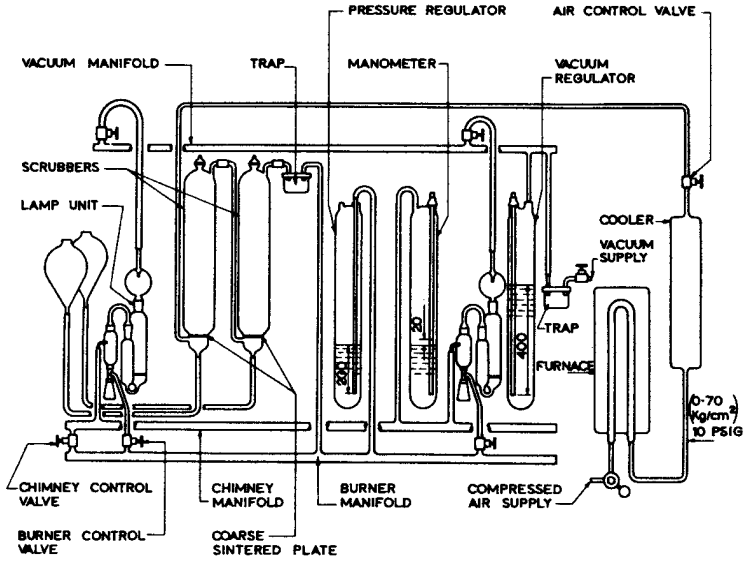

Fig. 3. Schematic diagram of purified air supply manifold and lamp system.

Substitute filtered air for the CO_2–O_2 supply train and add a second sintered-plate scrubber to the incoming air line as shown in Fig. 3.

ADDITIONAL REAGENTS[7]

B3. (*a*) *Barium Chloride Solution* (100 g per litre) – Dissolve 100 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in water and dilute to 1 litre.

(*b*) *Hydrochloric Acid* (rel d 1.19) – Concentrated hydrochloric acid (HCl).

(*c*) *Hydrogen Peroxide Solution* (30%) – Concentrated hydrogen peroxide (H_2O_2).

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

(*e*) *Sulphuric Acid* (1 : 16) – Mix 60 ml of concentrated sulphuric acid (H_2SO_4, rel d 1.84) with 960 ml of water.

PREPARATION OF APPARATUS

B4. (*a*) Place 300 to 400 ml of NaOH solution in the first scrubber (Fig. 3) and the same amount of H_2O_2–H_2SO_4 solution (300 ml of H_2O, 30 ml of H_2SO_4 (1 : 16), and 30 ml of H_2O_2 (30%)) in the second scrubber. For apparatus in daily use, replace these solutions twice each week or whenever the volume becomes less than two thirds of the original.

(*b*) Make other preparations as described in Section 5, except that the H_2O_2 solution (1.5%) need not be neutralized.

PROCEDURE FOR COMBUSTION

B5. Burn the sample as described in Section 7, controlling combustion as described in Section 6. Use a sample size as prescribed in Table 3. Analyse the absorber solutions from the samples and blank as described in Section B6.

PROCEDURE FOR ANALYSIS OF ABSORBER SOLUTION

B6. (*a*) Transfer the absorber liquid to a 400 ml beaker. Rinse the absorber and chimney thoroughly with water and add the rinsings to the beaker. Filter the solution to remove any foreign material, receiving the filtrate in a 400 ml beaker [Note 21] having a mark to indicate 75 ml. Add 2 ml of HCl, heat to boiling, and add 10 ml of $BaCl_2$ solution, either in a fine stream or dropwise. Stir the solution during the addition and for 2 min thereafter.

NOTE 21: Studies are in progress to ascertain if the procedure specified for washing the chimney quantitatively recovers the sulphur compounds deposited thereon.

(*b*) Cover the beaker with a fluted watch glass and continue boiling slowly until the solution has evaporated to a volume of approximately 75 ml, as indicated by the mark on the beaker. Remove the beaker from the hot plate (or other source of heat) and allow to cool 1 h before filtering.

(*c*) Filter the supernatant liquid through a close-texture, ashless filter paper. Wash the precipitate with water, first by decantation and then on the filter paper, until free of chloride ion. Transfer the paper and precipitate to a suitable weighed crucible, and dry at low heat until the moisture has evaporated. Char the paper completely without igniting it, and finally ignite at a bright red heat until the precipitate is burned white [Note 22]. After ignition is complete, allow the crucible to cool to room temperature and weigh.

TABLE 3. Sample size for air burning of liquid samples

Sulphur content, per cent by weight	Sample size	
	g	ml
0.5 and under	5 to 10	10
Over 0.5	3 to 5	5

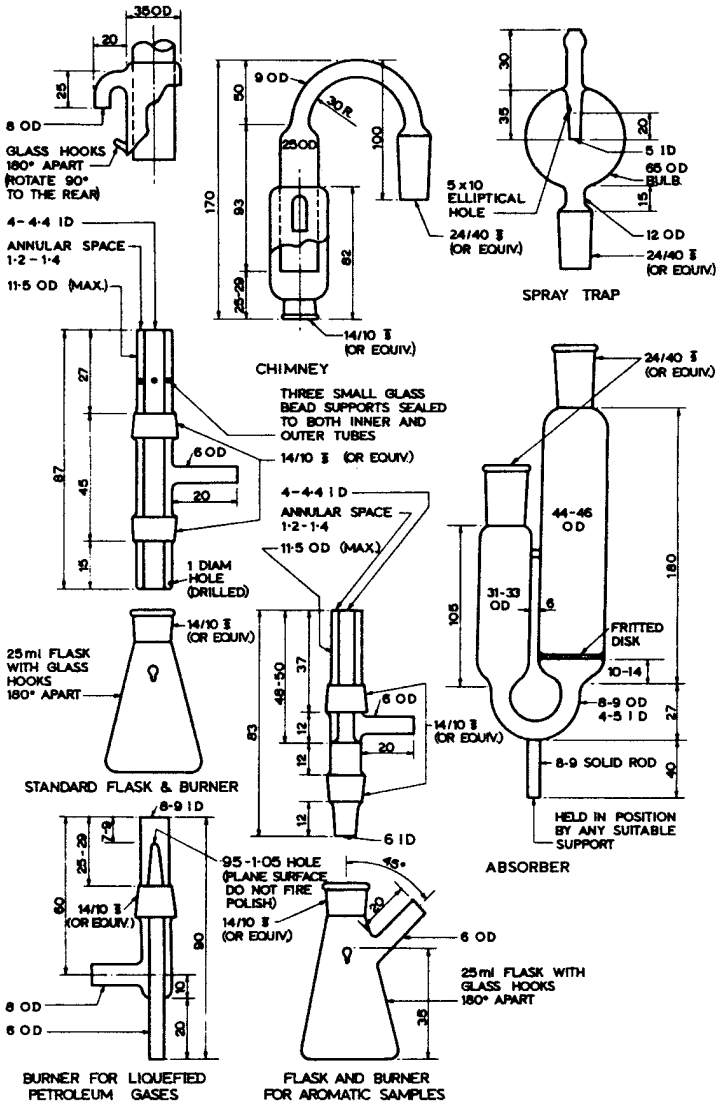

Fig. 4. Detailed drawing of combustion and absorption apparatus.

NOTE 22: A satisfactory means of accomplishing these operations is to place the uncovered crucible containing the wet filter paper in a cold electric muffle furnace and turn on the current. Drying, charring, and ignition usually occur at the desired rate.

CALCULATION

B7. Calculate the sulphur content of the sample as follows:

$$\text{Sulphur content, per cent by weight} = \frac{(w-b)\times 13.73}{W}$$

where

w = grams of barium sulphate ($BaSO_4$) precipitate in the absorber solution from the burned sample;

b = grams of $BaSO_4$ precipitate from the corresponding blank absorber solution [Note 23];

W = grams of sample burned.

NOTE 23: The determination should be discarded if the blank correction used in the calculation exceeds 1.5 mg of $BaSO_4$. Frequently, impure reagents are the cause of this difficulty.

PRECISION

B8. See Section 12 for recommended data.

APPENDIX III

APPARATUS DETAIL

FLASK AND BURNER FOR NON-AROMATIC SAMPLES

C1. A lamp of chemically resistant glass, consisting of a 25 ml Erlenmeyer flask and a burner that conforms to the dimensions shown in Fig. 4, shall be used. The burner consists of two concentric glass tubes, the external tube having an arm, provided with standard-taper glass joints for connexion with the flask and the chimney. The upper ends of both burner tubes shall be polished and shall have plane surfaces that are in the same horizontal plane. The burner shall have a 1 mm opening near its base to allow equalization of pressure between the chimney and the flask. When connected with the

chimney, the lamp shall be held in position by rubber bands or metal springs stretched between glass hooks on the flask and chimney.

FLASK AND BURNER FOR AROMATIC SAMPLES

C2. A lamp of chemically resistant glass, consisting of a 25 ml Erlenmeyer flask with a side-arm and a burner that conforms to the dimensions shown in Fig. 4, shall be used. The burner consists of two concentric glass tubes, the external tube having an arm, provided with standard-taper glass joints for connecting the burner with the flask and the chimney. The upper ends of both burner tubes shall be polished and shall have plane surfaces that are in the same horizontal plane. When connected with the chimney, the lamps shall be held in position by rubber bands or metal springs stretched between glass hooks on the flask and chimney.

CHIMNEY

C3. A chimney of chemically resistant glass conforming to the dimensions shown in Fig. 4 provided with standard-taper glass joints for connexion with the burner and absorber, shall be used.

ABSORBER

C4. An absorber of chemically resistant glass conforming to the dimensions shown in Fig. 4, provided with standard-taper glass joints for connexion with the chimney and spray trap, shall be used. A fritted (sintered) disk with average pore diameter from 150 to 200 μm (porosity P160) shall be sealed in the larger of two bulbs of the absorber. The fritted disk should be of such a porosity that, when 50 ml of water is placed in the absorber and air is passed through at the rate of 3.0 litres per min in the forward direction, the pressure differential between the two sides of the absorber is between 15 and 23 cm of water and the air is dispersed uniformly.

SPRAY TRAP

C5. A spray trap of chemically resistant glass conforming to the dimensions shown in Fig. 4, provided with a standard-taper glass joint for connexion with the absorber, shall be used.

MANIFOLD SYSTEM

C6. A satisfactory vacuum and combustion atmosphere manifold and supply system for supplying the required CO_2–O_2 mixture to the lamp assemblies is shown diagrammatically in Fig. 2. The gases are supplied from commercial cylinders, the pressure of each gas being adjusted to 10 ± 2 psi (0.70 ± 0.14 bar) by means of two single-stage regulating valves to ensure constant pressure at the flow-regulating needle valves. It is necessary to pass the CO_2 through a heat exchanger installed ahead of the regulating valves 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 can be operated as a unit, the throughput of the flow meters being chosen accordingly. The tubing that connects the chimney manifold to the chimneys should have an internal diameter not smaller than $\frac{1}{4}$ in (6.4 mm) in order to prevent unnecessary restriction in gas flow. The scrubber should have a capacity of about 1 litre.