

# SULPHUR BY THE LAMP METHOD

(Using Fast-Burning Lamp)

I.P.—107/45 (Tentative)

## SCOPE

1. (a) These methods are suitable for the determination of the total sulphur content of petroleum products such as gases, liquefiable gases, light distillates, kerosines, and gas oils. Gas oils require dilution with a volatile combustible solvent of known low-sulphur content. The method can also be applied to combustible materials not of petroleum origin, but coming within the volatility range covered by the above petroleum products.

NOTE 1.—The method has the following advantages:

- (i) The lamp specified for use with liquid products enables samples to be burned more rapidly than that prescribed in I.P.—62.
- (ii) The lamp facilitates the combustion of highly aromatic materials without smoking. In exceptional cases a small amount of aromatic free diluent of known low sulphur content may be required.
- (iii) Provision is made for carrying out the combustion in purified air.
- (iv) Sulphur present as carbon disulphide can be estimated satisfactorily.

(b) The test solutions from the absorber can be examined by volumetric, gravimetric or turbidimetric methods according to need. These are designated A, B and C respectively.

(c) The results obtained by the volumetric method (A) are slightly high, owing to formation of nitric acid during combustion. For petroleum products, the error is usually of the order of 0.01 per cent. sulphur, but it varies with the nature of the sample and the conditions of burning. The results obtained by the gravimetric method (B) and the turbidimetric method (C) are not affected by nitric acid formation, and are thus more accurate. Method B is suitable for sulphur contents down to 0.001 per cent., and Method C for sulphur contents down to 0.0001 per cent. Method C has a normal upper limit of 0.005 per cent. sulphur, but this can be considerably extended by burning small quantities of sample or by working with aliquot portions of the test solutions.

## APPARATUS

2. The apparatus (Fig. 1) shall consist of the following:

(a) *Burner for Gases*, of heat-resistant glass and of the form and dimensions shown in Fig. 2.

(b) *Lamp for Liquids*, of heat-resistant glass and of the form and dimensions shown in Fig. 3.

(c) *Chimney*, of heat-resistant glass and of the form and dimensions shown in Fig. 4. The neck of the chimney is fitted with two inlets for secondary air, and with a water-jacketed outlet (see Note 2).

NOTE 2.—The upper rubber stopper (see Fig. 4), which should be at least 15 mm. from the upper bend of the chimney, is fitted before the water-jacket is

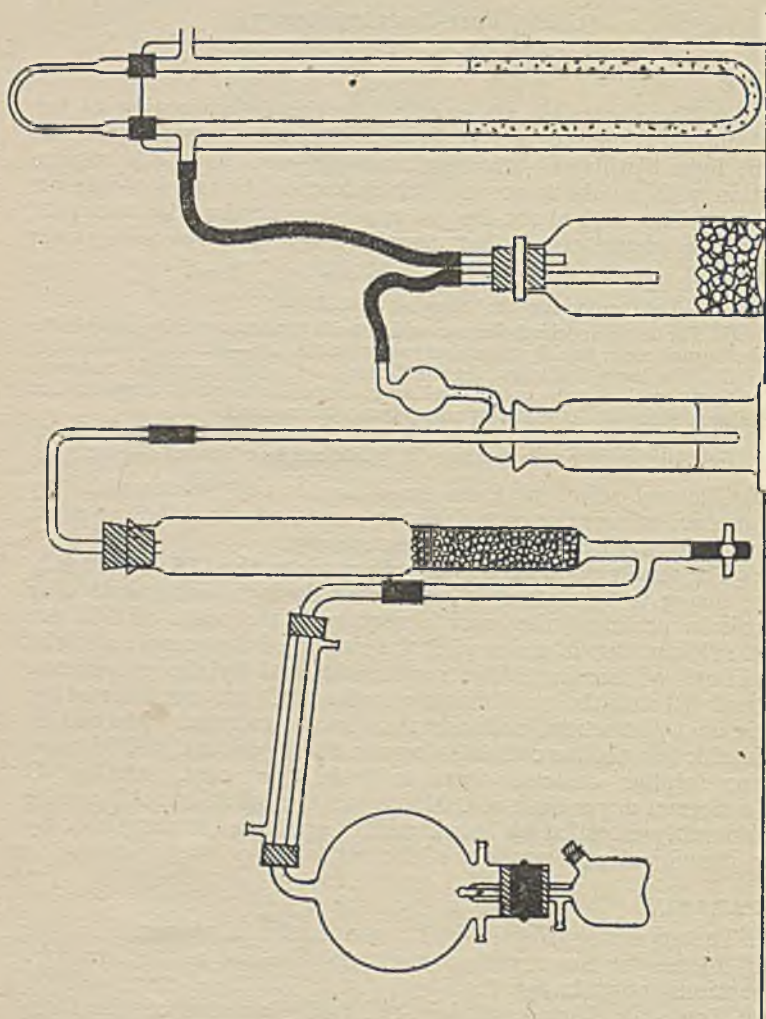


FIG. 1.  
ASSEMBLY.

added. The lower end of the outlet tube is bent when the water-jacket is in position and the lower rubber stopper is then fitted.

Alternatively, sealed glass joints may be used instead of rubber stoppers.

(d) *Absorber*, of chemically resistant glass and of the form and dimensions shown in Fig. 5, packed to a depth of 120 mm. with chemically resistant glass beads of 4–6 mm. diameter, supported on a perforated porcelain filter plate of approximately 20 mm. diameter. The drainage tube at the bottom of the absorber shall be closed by a screw clip on a short length of rubber tubing.

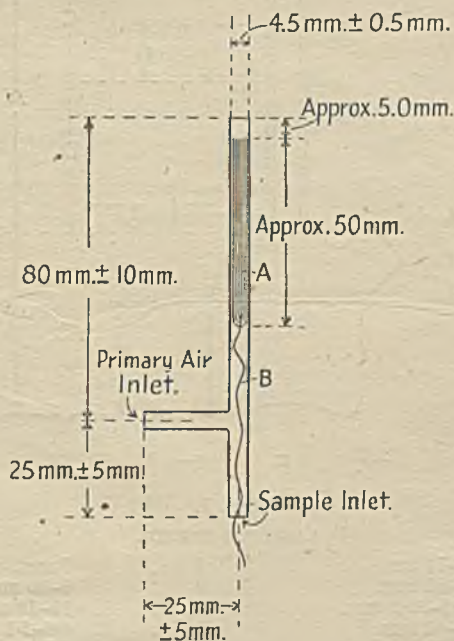


FIG. 2.  
BURNER FOR GASES.

(e) *Drechsel Bottle*, of 125–200 ml. capacity, coupled to the absorber as shown in Fig. 5.

(f) *Flowmeter*, to measure the air consumption of the apparatus. The design is optional, but the capillary type shown in Fig. 1, using light oil, is suitable. A capillary diameter of approximately 1 mm. and length 10 cm. is recommended. The calibration range should be 1–5 litres of air per minute with a scale which is marked at intervals of not less than 0.5 litre/minute, and which can be read accurately by interpolation to the nearest 0.1 litre/minute. Only a small error is introduced by measuring the gases after combustion instead of before, and it is convenient to instal the flowmeter at the



discharge end of the absorbing system (see Fig. 1). A bottle containing lump calcium chloride is inserted between the Drechsel bottle and flowmeter in order to remove excess moisture from the gases entering the flowmeter.

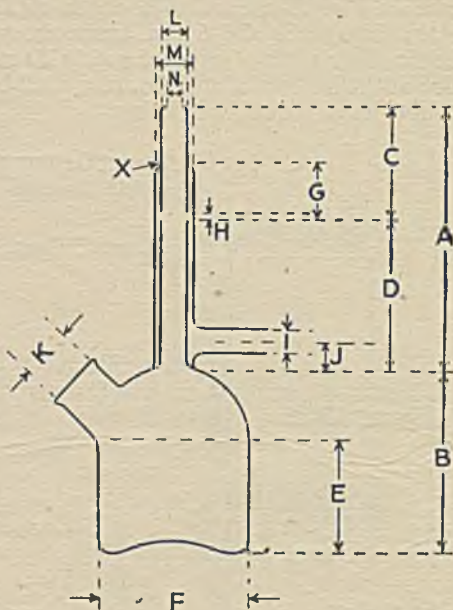


FIG. 3.

## LAMP FOR LIQUIDS.

A . . . . .	69-71 mm.	I . . . . .	7 mm. ext. diam.
B . . . . .	46-50 mm.	J . . . . .	6-10 mm.
C . . . . .	29.5-30.5 mm.	K . . . . .	10-18 mm.
D . . . . .	38-42 mm.	L . . . . .	4.9-5.1 mm. int. diam.
E . . . . .	28-32 mm.		6.7 mm. ext. diam.
F . . . . .	approx. 40 mm.	M . . . . .	10.5 mm. ext. diam.
G . . . . .	14-18 mm.	N . . . . .	3.9-4.1 mm. int. diam.
H . . . . .	1-2 mm.		

The central wick tube is rounded off to form the slight constriction at N after the edges have been "trued."

The two parts of the wick tube must be in line and there must be no constriction at the joint with the main body of the lamp.

There must be no bulge at the joint X.

(g) *Electric Blank*.—An electric heater which may be coked into a chimney, in place of a lamp burning sulphur-free material for the blank test, is shown in Fig. 6. The details of design are optional, but shall be such that when the current is adjusted to give a dissipation of approximately 110 watts, the elements will glow at a medium red heat.

The recommended form consists of two elements of  $\frac{5}{32}$ -inch diameter porcelain sleeves wrapped with asbestos paper and wound closely with No. 34 S.W.G. nichrome wire, suspended from a heat-resistant glass rod, by wires passing through the porcelain sleeves. Connections to the elements, which may be in series or in parallel, according to the voltage available, are brought in through heat-resistant glass tubes passing through a cork which fits the chimney. These tubes are plugged with asbestos and sealed with de Khotinski cement.

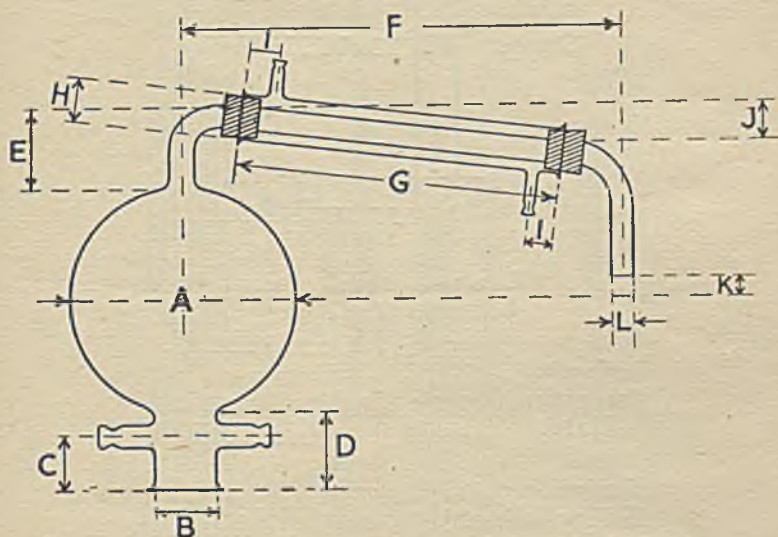


FIG. 4.  
CHIMNEY.

A . . . . .	105 mm.	G . . . . .	140–160 mm.
B . . . . .	30 mm. int. diam.	H . . . . .	19.5–20.5 mm.
C . . . . .	25 mm.	I . . . . .	18–22 mm.
D . . . . .	33–37 mm.	J . . . . .	15–25 mm.
E . . . . .	30–40 mm.	K . . . . .	5–15 mm.
F . . . . .	200–220 mm.	L . . . . .	9 mm. ext. diam.

(h) *Rubber Band*, of approximately  $1\frac{1}{8}$  inch diameter and  $1\frac{1}{2}$  inch length to seal the cork joint between the chimney and the lamp.

(i) *Cotton Wicking*.—Clean unused cotton wicking, weighing about 5–6 mg. per cm., of the type and quality usually sold as 13s/14 ends, scoured, and bleached.

(j) *Air Supply*.—A supply of air, free from serious contamination with sulphurous impurities and under a steady pressure of approximately 2 inches of mercury.

A higher degree of freedom from sulphurous impurities is required for Method C than for Methods A and B. For Method C the weight

of sulphur found in the blank test, due to the air, must be less than 0.2 mg. and preferably less than 0.1 mg. Some of the sulphur found in the blank test originates from the reagents and distilled

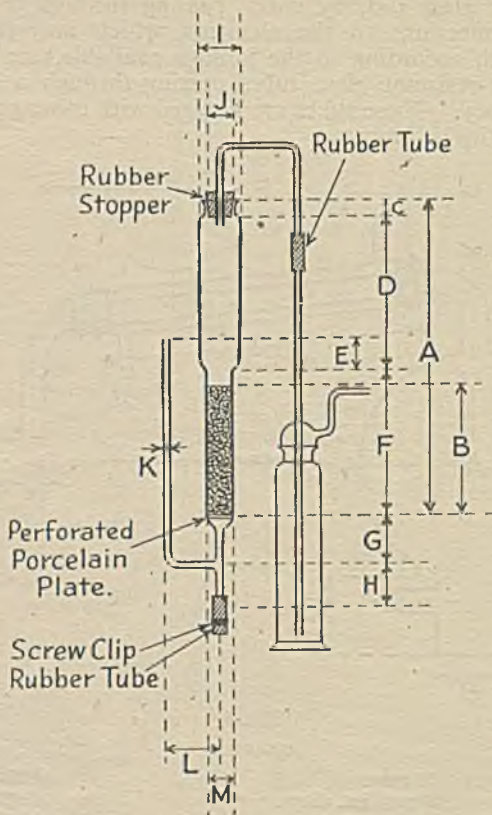


FIG. 5.

## ABSORBER SYSTEM.

A . . . . .	300 mm.	H . . . . .	25 mm.
B . . . . .	120 mm.	I . . . . .	35 mm.
C . . . . .	20 mm.	J . . . . .	25 mm.
D . . . . .	140 mm.	K . . . . .	9 mm.
E . . . . .	30 mm.	L . . . . .	30 mm.
F . . . . .	140 mm.	M . . . . .	25 mm.
G . . . . .	25 mm.		

water, and an allowance should be made for this when assessing the purity of the air supply. For Method A, the air supply must also be free from acid fumes or materials which will form strong acids in the apparatus, *e.g.*, carbon tetrachloride fumes.



If the air has been purified (Note 3) by scrubbing with aqueous reagents, steps must be taken to remove excessive humidity which might lead to difficulty in regulating the lamps, owing to the condensation of drops of water in the rubber tubing where it is constricted by

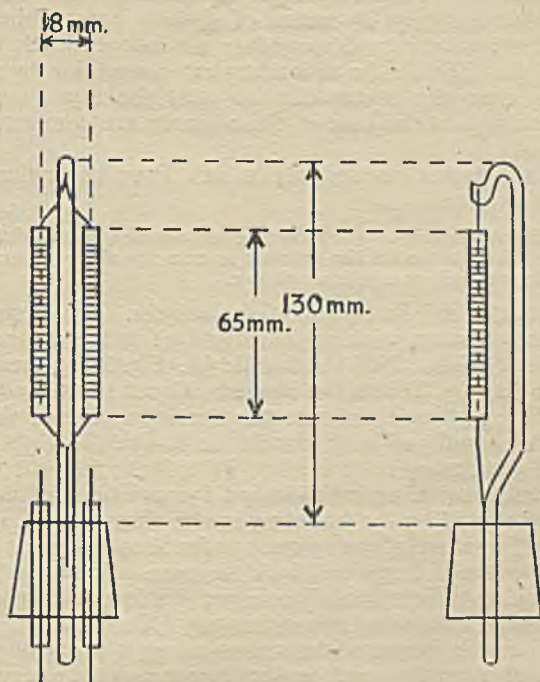


FIG. 6.  
ELECTRIC BLANK.

screw clips. This may be achieved by passing the air through a coil of tubing immersed in ice, followed by a small separating vessel.

NOTE 3.—The procedure to be adopted for air purification depends on the location of the laboratory. In residential districts, simple scrubbing in a continuous washer with constantly replaced tap-water provides an adequate degree of purification. In industrial districts, it may be necessary to use 1 per cent. aqueous caustic soda or stronger reagents. Treatment with concentrated sulphuric acid, followed by an alkali wash and passage over activated charcoal, has proved successful in difficult cases. Bottled oxygen blended with bottled nitrogen or carbon dioxide provides an atmosphere of low, though not negligible, sulphur content. If bottled gas is used, a low-pressure reservoir, such as two 15-litre aspirator bottles coupled to form a water displacement gas-holder, is usually required in addition to constant pressure discharge valves on the cylinders.

### PREPARATION AND ASSEMBLY OF APPARATUS

3. (a) *General.* Wash the chimney, absorber, Drechsel bottle, and connecting tube with distilled water. Assemble the apparatus as shown in Fig. 1, making the connections between the chimney, absorber, etc., with rubber tubing. Connect the air manifold to the lamps and chimneys by means of  $\frac{3}{16}$ -inch bore rubber tubing, and control the primary and secondary air independently by means of screw clips. Divide the secondary air connection by means of a tee-piece after the screw clip, so that the two diametrically opposite openings at the base of the chimney are connected to the tee-piece.

Connect the jacket on the outlet tube from the chimney to a supply of tap water.

NOTE 4.—*Safety Warning.* When burning gas samples, surround the chimney with a safety shield to protect the operator in case the chimney bursts through the accidental ignition of an explosive mixture.

(b) *Preparation of Burner for Gas Samples.* Tie a number of lengths of new cotton wicking (usually five) in the centre with an extra length of wick. Pull the bundle (A, Fig. 2) by means of the extra length (B, Fig. 2) into the burner. Comb the strands of wick parallel before pulling them into the burner, and trim the bundle square. The bundle of wick should be sufficiently tight to resist the flow of gas through the burner, in order to prevent the flame from fluctuating or being extinguished by variations of pressure in the chimney caused by the bubbling in the absorber. Connect the burner with the source of gas by means of rubber tubing.

(c) *Preparation of Lamp for Liquid Samples.* Prepare a bundle of wick by winding three turns of wick round a former consisting of a strip of wood or cardboard approximately 170 mm. long. Remove the wick from the former without unwinding it or cutting through the loops, and insert the resulting six lengths into the reservoir of the lamp through the filling tube. Pull the wick up into the wick tube by means of a hooked wire so that 30 or 40 mm. project from the top. Cut through the loops and comb the threads out parallel with any suitable instrument, e.g., forceps. Draw the wick back into the wick tube and trim off level with the top. Push any wick extruding from the filling tube into the reservoir. In some cases it may be necessary to use more or less than six lengths of wicking.

If isopentane or other very volatile material is to be burned, pull or tap the wick down to within 5–10 mm. of the division in the wick tube, and plug the wick tube above this level with a bundle of wick about 10 mm. long, and consisting of 10 or 12 lengths of wick similar to that in the burner for gas samples. Generally, it should not be pushed down so far as to touch the main wick.

### LIGHTING AND CONTROL OF THE BURNERS AND LAMPS

4. (a) Insert the burners or lamps for a batch of tests together with the lamp or electric heater being used for the blank test into the



chimneys and turn the secondary air on to give a volume of approximately 2 litres/minute per lamp. (Note 5.) Do not turn on the primary air. Remove each burner or lamp in turn from the chimney, light and replace it. If several are removed at the same time there may be an excessive drop in pressure in the air manifold.

(b) In the case of the burner, turn on the gas and ignite it. Turn on the primary air and, after making any necessary adjustments to the gas and primary air, re-insert the burner into the chimney while temporarily restricting the secondary air. Readjust the flame if necessary by regulating the gas and air supplies.

(c) In the case of the lamp, turn on the primary air and light the lamp, lowering the wick if necessary by tapping the lamp. Replace the lamp in the chimney while temporarily restricting the secondary air. Roll the rubber band down over the cork joint. Make any necessary further adjustment to the flame while the lamp is in the chimney by tapping the lamp to lower the wick and by regulating the primary and secondary air supplies.

(d) When all the burners or lamps have been lighted, adjust the total quantity of air supplied to each burner or lamp, including the blank, so that each receives the same amount as that requiring the greatest quantity.

(e) After a lamp has burned for a few minutes and the initial surplus liquid in the wick consumed, it may be necessary to raise the wick a little with forceps to restore the flame to its original size. The wick in the gas burner should not need adjustment provided that it has been correctly fitted.

(f) Liquefied gas samples should be drawn from below the liquid level in the sample container and allowed to evaporate in the connections leading to the burner. If there is no bottom connection, invert the sample container. A rubber bulb, such as a small football bladder, contained in a net bag, slightly compressed by a weight, may be connected into the sample line to the burner to ensure a steady pressure from such sample containers and also from gas samples which are being measured with a bellows-type meter.

(g) To prevent blow-back of gas sample into the air manifold the primary air connections to all gas burners must be made through a Drechsel bottle containing a little distilled water.

NOTE 5.—The total air requirement per lamp varies with the type of fuel and the rate of burning. It is usually 2.0–2.5 litres/minute. The quantity of primary air also varies with the type of fuel and is of the order 0.1–0.3 litres/minute, but is not measured separately. If the correct quantities of primary and secondary air are used and the wick properly trimmed, the flame will be steady and will burn without smoking. Poor trimming or excessive primary air will cause the flame to be irregular and pierced by a jet of primary air. This latter condition must be avoided as it results in incomplete combustion of the sample.

#### QUANTITY AND MEASUREMENT OF SAMPLE

5. (a) *Quantity.* The amount of sample required depends on the sulphur content, but normally use not less than the following amounts:

Product.	Quantity.
Gases and liquefied gases . . . . .	7 g.
Volatile liquids and kerosines . . . . .	10 ml.
Gas oils . . . . .	2 g.

In the case of materials with a sulphur content of 0.005 per cent. or less, which are being tested by Method C, the above quantities should be doubled.

(b) *Gases and Liquefied Gases.* Gases and liquefied gases may be measured by weighing the sample container before and after burning the gas, or by the use of a dry gas meter in the case of gas samples.

(c) *Volatile Liquids and Kerosines.* (Notes 6 and 7.) Volatile liquids and kerosines may be measured by volume. Alternatively, the sample may be weighed into the lamp, burned to dryness, and the last traces removed from the wick by burning 2 ml. of alcohol or sulphur-free petroleum product.

NOTE 6.—*Samples containing Tetraethyl Lead.* For Methods B and C, first free the sample from T.E.L. by vigorous agitation at room temperature with one-fifth of its volume of 38–40 per cent. wt./wt. hydrochloric acid for 1 hour. Separate the acid and wash the sample with distilled water till free from acid. Ascertain whether removal of T.E.L. is complete by testing a small portion of the acid-washed sample with bromine in carbon tetrachloride.

NOTE 7.—*Samples containing Gummy Material.* Deposition of gum on the wick can be prevented or reduced by diluting the sample with *sec.*-butyl alcohol and, after burning to dryness, burning 2 ml. of *sec.*-butyl alcohol to clear the wick. Burn the sulphur in any char formed from gummy samples by raising the wick at the end of the combustion, using sufficient primary air to burn the top portion of wick.

(d) *Gas Oils.* (Note 7.) Weigh the gas oil into the lamp, adding diluent first, to prevent flooding the wick with neat gas oil. Alternatively, pull the wick clear of the bottom of the lamp and tap it down after the gas oil and diluent are thoroughly mixed. Burn to dryness, and then burn 2 ml. of sulphur-free diluent to clear the wick. If the diluent is not sulphur-free, an allowance must be made for the sulphur. The volume of diluent required is usually between 1 and 5 times the volume of gas oil.

## METHOD A (VOLUMETRIC)

### APPARATUS

6. As in Section 2.

### REAGENTS

7. (a) *Hydrochloric Acid Solution*, containing 2.275 g. of HCl per litre. The strength of the solution is such that 1 ml. is equivalent to 1 mg. sulphur.

(b) *Sodium Carbonate Solution*, containing 3.306 g. of  $\text{Na}_2\text{CO}_3$  per litre. 10 ml. of this solution should exactly neutralize 10 ml. of the hydrochloric acid solution.



- (c) *Indicator*, B.D.H. 4.5, or other indicator of similar pH range.  
 (d) *Ethyl Alcohol*, absolute, of sulphur content less than 0.001 per cent.  
 (e) *Diluent*.—Alkylate, petroleum spirit, *isooctane* or other volatile petroleum product, of low and known sulphur content.  
 (f) *sec.-Butyl Alcohol*, of negligible sulphur content.  
 (g) *Distilled Water*, neutral to the indicator chosen.

#### PROCEDURE

8. (a) Prepare and assemble the apparatus as in Section 3, washing the chimney, absorber, Drechsel bottle, and connecting tube with neutral distilled water.

(b) Pipette 20 ml. of the sodium carbonate solution into the absorber and place approximately 30 ml. of neutral distilled water in the Drechsel bottle.

(c) In the case of liquid samples charge the lamps with the sample as in Section 5.

(d) Light the burners or lamps as in Section 4.

(e) When burning is complete, turn off the air supply and remove the burner or lamp from the chimney. Remove the water connections from the condenser, disconnect the chimney and condenser, and wash the inside with neutral distilled water, collecting the washings in a beaker. Drain the solution from the absorber into the beaker by loosening the screw clip on the drain tube at the bottom of the absorber. Remove the adhering solution from the absorber by washing down the inlet tube with a jet of neutral distilled water and then directing a larger quantity round the inside of the top of the absorber, while holding the rubber drain-tube between the fingers. When the washings cover the beads, blow gently through the inlet tube, and then collect the washings in the beaker by releasing the rubber drain tube. Repeat this operation twice. Then drain the contents of the Drechsel bottle into the beaker and wash the bottle and tube with neutral distilled water, collecting the washings in the beaker.

(f) Add 6 drops of indicator solution to the contents of the beaker and titrate with the hydrochloric acid. If the solution is acidic prior to titration, repeat the determination, burning less sample.

(g) In a similar way, wash out the apparatus used in the blank test and titrate.

#### CALCULATION AND REPORTING

9. (a) Calculate the sulphur content by means of the following formula:

$$\text{Sulphur, per cent. wt.} = \frac{B - A}{W \times 10}$$

where  $A$  = volume in ml. of HCl required for the sample,

$B$  = volume in ml. of HCl required for the blank, and

$W$  = weight in g. of sample burned.

(b) Report the result to the nearest 0.01, as the sulphur content of the sample, and indicate that the determination was made in accordance with Method A, e.g.:—

Sulphur content (I.P.—107/45 (T) Method A) = . . . per cent. wt.

#### PRECISION

10. Test results should not differ from the mean by more than the following amounts:

Product.	Sulphur, per cent. weight.	Repeatability (One operator and apparatus).	Reproducibility (Different operators and apparatus).
Gases, liquefied gases, volatile liquids and kerosines.	Up to 0.50 Above 0.50	0.01 per cent. 4 per cent. of mean	0.02 per cent. 8 per cent. of mean
Gas oils	Up to 1.50 Above 1.50	0.03 per cent. 4 per cent. of mean	0.06 per cent. 8 per cent. of mean

### METHOD B (GRAVIMETRIC)

#### APPARATUS

11. As in Section 2.

#### REAGENTS

12. (a) *Hydrochloric Acid Solution*, consisting of concentrated hydrochloric acid (approx. 36 per cent. wt./wt.) in an equal volume of distilled water.

(b) *Sodium Carbonate Solution*, containing 100 g. of anhydrous sodium carbonate per litre in distilled water.

(c) *Indicator*, B.D.H. 4.5 or other indicator of similar pH range.

(d) *Bromine Water*, consisting of a saturated solution of bromine in distilled water. The sulphate content of the bromine must not be greater than 0.005 per cent. by weight.

(e) *Ethyl Alcohol*, absolute, of sulphur content less than 0.0005 per cent. by weight.

(f) *Diluent*.—Alkylate, petroleum spirit, *isooctane* or other volatile petroleum product of low and known sulphur content.

(g) *sec.-Butyl Alcohol*, of negligible sulphur content.

#### PROCEDURE

13. (a) Prepare and assemble the apparatus as in Section 3.

(b) Pipette 20 ml. of the sodium carbonate solution into the absorber and place approximately 30 ml. of distilled water and 1 ml. of the sodium carbonate solution in the Drechsel bottle.



(c) In the case of liquid samples containing tetraethyl lead, remove the lead as in Note 6. Charge the lamps as in Section 5.

(d) Light the burners or lamps as in Section 4.

(e) Proceed as in Section 8 (e), except that the distilled water need not be neutral.

(f) Cover the beaker with a watch-glass and reduce the volume of solution to 200–300 ml. by boiling (Note 8). Filter the solution while hot through a 12.5 cm. Whatman No. 40 filter paper into a second beaker, and wash any solution remaining on the inside of the first beaker and on the stirring rod, if used, into the filter with hot distilled water. Wash the filter twice by directing a jet of distilled water round the edge of the paper. Add 10 ml. of bromine water to the contents of the second beaker, stir, and add 10 ml. of hydrochloric acid. Cover the beaker with a watch-glass and heat to boiling. When the bromine has been expelled, add a few drops of indicator. If necessary, render the solution acid by addition of hydrochloric acid and expel the additional bromine liberated. Again determine if the solution is acid, repeating the process if it is not.

When the solution is acid, add slowly to the boiling solution so that it does not cease boiling, 10 ml. of barium chloride solution from a pipette inserted under the watch-glass. If a high sulphur content is anticipated, add only 1–2 ml. of barium chloride to “seed” the solution, and add the balance of the barium chloride solution after the first precipitate is observed. This will give a precipitate which is easily separable by filtration. Boil the solution for at least 30 minutes after precipitation, and allow to cool undisturbed for at least 6 hours.

Heat or boil the solution again, and filter while hot through an ashless filter paper, e.g., 12.5 cm. Whatman No. 44, decanting the supernatant liquor before transferring the precipitate to the filter with a jet of hot distilled water. If possible, wash the precipitate twice by decantation before transferring to the filter. Loosen any precipitate adhering to the beaker by means of a rubber “policeman” and wash into the filter with distilled water. Wash the filter eight times by directing a jet of hot distilled water round the edge of the paper, allowing the filter to drain completely after each wash.

After the final wash, allow the filter paper containing the precipitate to drain and then transfer it to a porcelain or platinum crucible for ignition. Allow the ignited precipitate to cool and weigh to the nearest 0.0001 g.

(g) In a similar way, wash out the apparatus used in the blank test and determine the sulphur.

NOTE 8.—It is an advantage to have an anti-bump stirring rod in the beaker when the solution is being boiled. A suitable rod consists of a plain glass rod with about 1 cm. of glass tubing sealed to the lower end and annealed. When the solution cools the tubing fills with solution which must be shaken out before reheating the solution.

## CALCULATION AND REPORTING

14. (a) Calculate the sulphur content by means of the following formula:

$$\text{Sulphur, per cent. wt.} = \frac{(A - B) \times 13.73}{W}$$

where

$A$  = weight in g. of barium sulphate obtained from sample,  
 $B$  = weight in g. of barium sulphate obtained from blank, and  
 $W$  = weight in g. of sample burned.

(b) Report the result to the nearest 0.001 as the sulphur content of the sample and indicate that the determination was made in accordance with Method B, e.g. :—

Sulphur content (I.P.—107/45 (T) Method B) = . . . per cent. wt.

## PRECISION

15. Test results should not differ from the mean by more than the following amounts:

Product.	Sulphur, per cent.	Repeatability (One operator and apparatus).	Reproducibility (Different operators and apparatus).
Gases, liquefied gases, volatile liquids and kerosines	0.001–0.100 Above 0.100	0.001 per cent. 1 per cent. of mean	0.002 per cent. 2 per cent. of mean
Gas oils	0.001–0.300 Above 0.300	0.003 per cent. 1 per cent. of mean	0.006 per cent. 2 per cent. of mean

## METHOD C (TURBIDIMETRIC)

## APPARATUS

16. (a) As in Section 2.

(b) *Turbidimeter*, of any convenient type.

(c) *Standard Dipper*, for measuring a standard quantity of approximately 0.3 g. of the barium chloride crystals.

(d) *Nessler Jars*, having a graduation corresponding to the standard volume (Note 9).

## REAGENTS

17. (a) 0.99–1.01*N* *Hydrochloric Acid*.

(b) 0.25*N* *Sodium Carbonate Solution*, containing 13.25 g. of anhydrous sodium carbonate made up to 1 litre with distilled water.

(c) *Bromine in Sodium Hydroxide Solution*, containing 10 g. of bromine and 10 g. of sodium hydroxide made up to 1 litre with distilled water. The sulphate content of the bromine must not be greater than 0.005 per cent. by weight.



(d) *Aqueous Sodium Hydroxide Solution*, containing 20 g. of sodium hydroxide in 100 ml.

(e) *Phenolphthalein Indicator*, containing 0.2 g. of phenolphthalein in 60 ml. of 90 per cent. ethyl alcohol and made up to 100 ml. with distilled water.

(f) *Alcohol-Glycerol Solution*, containing 33–34 per cent. by vol. of glycerol of A.R. quality, in ethyl alcohol. The alcohol need not be anhydrous, but must be free from impurities, including traces of hydrocarbon, which cause a precipitate when the solution is mixed with the test solution.

(g) *Barium Chloride Crystals*,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , passing a 20-mesh B.S. sieve and retained on a 30-mesh B.S. sieve.

(h) *Acid Sodium Chloride Solution*, consisting of a 1.0*N*-aqueous solution of sodium chloride containing 200 ml. of 1.0*N*-hydrochloric acid per litre.

(i) *Standard Sodium Sulphate Solution*, containing  $4.4375 \pm 0.001$  g. of sodium sulphate made up to 1 litre with distilled water. This solution is used in preparing solutions containing 0.02 mg. per ml. of sulphur for standardizing the turbidimeter.

(j) *Distilled Water*, free from sulphate.

(k) *Ethyl Alcohol*, absolute, containing less than 0.00005 per cent. wt. of sulphur.

(l) *Diluent*.—Alkylate, petroleum spirit, *isooctane* or other volatile petroleum product, of low and known sulphur content.

#### PROCEDURE

18. (a) *Calibration of Turbidimeter*. (i) Dilute a mixture of 15 ml. of the standard acid sodium chloride solution and an appropriate volume of the standard sodium sulphate solution with distilled water to the standard quantity (Note 9) required for the turbidimeter.

(ii) Add the standard volume of alcohol-glycerol solution, mix with the “policeman,” and, after allowing the air bubbles to clear, determine the initial turbidity. Add 0.3 g. of barium chloride crystals, using the standard dipper, and mix with the “policeman” until the crystals are dissolved. After the lapse of a standard time (Note 9) remove any air bubbles adhering to the sides of the cell and measure the final turbidity.

(iii) Vary the volume of sodium sulphate solution used to enable the entire working range of the instrument to be covered.

(iv) Make a blank determination on the reagents used for calibration and make the necessary allowance when drawing the calibration curve. Select the scale so that the curve covers the range 0.0 to 1.0 mg. and the sulphur content can be read to the nearest 0.001 mg.

NOTE 9.—The standard conditions vary with the make of turbidimeter. In the case of one instrument which is known to be satisfactory for this work the standard volume chosen for the test solution prior to the addition of the alcohol-glycerol is 100 ml. The volume of alcohol-glycerol used is 20 ml. and the standard time for precipitation is 10 minutes. An instrument should be chosen

such that the scale subdivisions correspond to approximately 0.01 mg. sulphur, and so that 0.001 mg. sulphur can be obtained by interpolation.

(b) Prepare and assemble the apparatus as in Section 3.

(c) Pipette 20 ml. of the sodium carbonate solution into the absorber, retaining the last few drops in the pipette. Add these to the Drechsel bottle, to which also add approximately 30 ml. of distilled water.

(d) In the case of liquid samples containing tetraethyl lead, remove the lead as in Note 6. Charge the lamps as in Section 5.

(e) Light the burners or lamps as in Section 4.

(f) Proceed as in Section 8 (e), except that the distilled water need not be neutral.

(g) Pipette 10 ml. of the 1 per cent. bromine in sodium hydroxide solution and follow by 15 ml. of the 1.0*N* hydrochloric acid (this may be added from a burette) into the beaker containing the test solution. Cover the beaker with a watch-glass and boil to expel bromine and to reduce the solution to less than the standard volume (Note 9).

(h) Allow the solution to cool, add a few drops of phenolphthalein and render alkaline by addition of the 20 per cent. sodium hydroxide solution. Neutralize with, and add 3 ml. excess of, 1.0*N* hydrochloric acid.

(i) Filter the solution cold through a 12.5-cm. No. 44 Whatman filter paper into a Nessler jar. Wash any solution remaining on the beaker and rod into the filter with distilled water. After the filter has drained, wash with distilled water into the Nessler jar, and make the volume up to a standard quantity (Note 9). Mix the contents of the Nessler jar with the stirring rod and transfer to the turbidimeter cell.

(k) Add the standard quantity (Note 9) of alcohol-glycerol solution by means of a pipette and mix with the "policeman." Allow the air bubbles to clear and measure the initial turbidity. Add 0.3 g. of barium chloride crystals, using the standard dipper, and mix with the "policeman" until the crystals are dissolved. After the lapse of a standard time (Note 9) measure the final turbidity.

#### CALCULATION AND REPORTING

19. (a) Deduce the weight of sulphur precipitated as barium sulphate from the difference in turbidity before and after precipitation by reference to the calibration curve. If the determination was made on an aliquot portion of the test solution, multiply the weight of sulphur found in the aliquot by the appropriate factor.

(b) Calculate the sulphur content by means of the following formula:

$$\text{Sulphur, per cent. wt.} = \frac{A - B}{W \times 10}$$

where  $A$  = weight of sulphur in mg. obtained from the sample,  
 $B$  = weight of sulphur in mg. obtained from the blank, and  
 $W$  = weight in g. of sample burned.



(c) Report the result to the nearest 0.0001 as the sulphur content of the sample, and indicate that the determination was made in accordance with Method C, *e.g.* :—

Sulphur content (I.P.—107/45 (T) Method C) = . . . per cent. wt.

#### PRECISION

20. Test results should not differ from the mean by more than the following amounts:

Product.	Sulphur, per cent.	Repeatability (One operator and apparatus).	Reproducibility (Different operators and apparatus).
Gases, liquefied gases, volatile liquids and kerosines	0.0001–0.0050 Above 0.0050	0.0002 per cent. 4 per cent. of mean	0.0004 per cent. 8 per cent. of mean
Gas oils	0.0001–0.0150 Above 0.0150	0.0006 per cent. 4 per cent. of mean	0.0012 per cent. 8 per cent. of mean

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