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Methods for

Analysis and testing of coal and coke —

Part 7: Ultimate analysis of coke

UDC [662.66 + 662.74]:543.84

Cooperating organizations

The Solid Fuel Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

Association of Consulting Engineers
British Carbonization Research Association*
British Cast Iron Research Association
British Ironfounders' Association
British Mechanical Engineering Confederation
Central Electricity Generating Board*
Chamber of Coal Traders
Coke Oven Managers' Association*
Combustion Engineering Association*
Council of Ironfoundry Associations
Department of Energy
Domestic Solid Fuel Appliances Approval Scheme
Greater London Council
Health and Safety Executive
Heating and Ventilating Contractors' Association
Institute of British Foundrymen*
Institute of Fuel
Institution of Heating and Ventilating Engineers
Low Temperature Coal Distillers' Association of Great Britain Ltd.
National Coal Board*
Society of British Gas Industries
Solid Fuel Advisory Service
Water-tube Boilermakers' Association
Women's Solid Fuel Council

The organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

British Coal Exporters' Federation
British Gas Corporation
British Steel Corporation
Cement Makers' Federation
Chemical Industries Association
Electricity Supply Industry in England and Wales
Institute of Trading Standards Administration
London Coal Exporters' Association
Scientific Instruments Manufacturers' Association of Great Britain
Society of Chemical Industry
Solid Smokeless Fuels Federation
Independent experts

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Contents

Foreword

BS 1016 comprises a series of Parts dealing with methods for the analysis and testing of coal and coke. It is gradually being restructured and Parts in the new series have been allocated numbers from 100 onwards. The current Parts are as follows, with new Part numbers (which will be given to revisions when they are published) in parentheses where appropriate.

— *Part 1: Total moisture of coal (Part 101);*

— *Part 2: Total moisture of coke (Part 102);*

— *Part 6: Ultimate analysis of coal (Part 106);*

— *Part 7: Ultimate analysis of coke (Part 106);*

— *Part 8: Chlorine in coal and coke (Part 106);*

— *Part 9: Phosphorus in coal and coke (Part 106);*

— *Part 10: Arsenic in coal and coke (Part 106);*

— *Part 11: Forms of sulphur in coal (Part 106);*

— *Part 14: Analysis of coal ash and coke ash (Part 114);*

— *Part 15: Fusibility of coal ash and coke ash (Part 113);*

— *Part 16: Methods for reporting results (Part 100);*

— *Part 17: Size analysis of coal (Part 109);*

— *Part 18: Size analysis of coke (Part 110);*

— *Part 20: Determination of Hardgrove grindability index of hard coal (Part 112);*

— *Part 21: Determination of moisture-holding capacity of hard coal (Part 103);*

— *Part 104: Proximate analysis;*

— *Part 105: Determination of gross calorific value;*

— *Part 107: Caking and swelling properties of coal;*

— *Part 108: Tests special to coke;*

— *Part 111: Determination of abrasion index of coal.*

The methods given in BS 1016 are specified for the analysis of coal or of coke or, in some instances, for the analysis of both coal and coke. Experience has shown that, in general, the methods may also be used for the analysis of manufactured smokeless fuels (other than coke) made by a conventional process. However, as no systematic survey has been made of their applicability to all such fuels, it is not possible to state whether the ultimate analysis methods for coal (see Part 6) or those for coke will be more appropriate for a particular fuel; usually the former are likely to be satisfactory for fuels prepared at temperatures below 800 °C.

The revision of Part 7 has been undertaken in order to complete the introduction of metric units and to adopt a uniform presentation. No technical changes have been made to the methods retained from the previous edition of this Part, but the Liebig method has been deleted as it is now little used for the determination of carbon and hydrogen in coke.

The high temperature method for the determination of carbon and hydrogen is technically equivalent to ISO 609. Similarly, the method for nitrogen and the method for sulphur correspond technically with those specified in ISO 333 and ISO 351, respectively.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 10, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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1 Scope

This Part of BS 1016 describes methods of determining carbon, hydrogen, nitrogen and sulphur in the analysis sample of coke.

2 References

The titles of the publications referred to in this standard are listed on the inside back cover.

3 Definitions

For the purposes of this Part of BS 1016 the following definitions apply.

3.1
coke

the solid residue of the distillation of coal at high temperature (above 800 °C)

3.2
ultimate analysis

the analysis of coke expressed in terms of its carbon, hydrogen, nitrogen, sulphur and oxygen contents

3.3
moisture in the analysis sample

the part of the total moisture retained in the analysis sample of coke

3.4
ash

the inorganic matter remaining after the coke has been incinerated to constant mass under standardized conditions

3.5
repeatability

the maximum acceptable difference between duplicate determinations carried out at different times in the same laboratory on the same analysis sample by the same operator using the same apparatus

3.6
reproducibility

the maximum acceptable difference between the mean of duplicate determinations carried out in one laboratory and the mean of duplicate determinations carried out in any other laboratory on representative samples taken from the same gross sample after the last stage of the reduction process

4 Introduction

The determination of the total amounts of carbon, hydrogen, nitrogen and sulphur, regardless of their origin, is described, the results being normally reported on the dry basis. The sum of the percentages, expressed on the dry basis, of carbon, hydrogen (after deducting the hydrogen present as moisture in the sample), nitrogen, sulphur and ash may be deducted from 100 to give an estimate of the oxygen content[1]. The value so obtained for oxygen may be inaccurate because it includes the cumulative errors of all the determinations made, and it should therefore be reported as "oxygen (plus errors)".

5 Sample

The coke used for the ultimate analysis shall be the analysis sample having a top size not greater than 0.2 mm (ground to pass a 212 μm test sieve complying with the requirements of BS 410), taken and prepared according to BS 1017-2.

The sample shall be thoroughly mixed, preferably by mechanical means, immediately before the determination.

6 Carbon and hydrogen

6.1 Principle. A known mass of coke is burned at a temperature of 1 350 °C in a rapid current of oxygen, so that all the carbon is converted to carbon dioxide and all the hydrogen to water. Chlorine and oxides of sulphur are retained in the apparatus by silver gauze. The water formed is absorbed by magnesium perchlorate and the carbon dioxide by sodium hydroxide on an inert base. A determination of moisture is carried out at the same time and the value for hydrogen is corrected for that present as moisture in the sample.

6.2 Special reagents. All reagents, unless otherwise specified, shall be of analytical reagent quality. Distilled or deionized water complying with the requirements of BS 3978 shall be used throughout.

6.2.1 *Magnesium perchlorate*[2], 1.2 mm to 0.7 mm.

6.2.2 *Sodium hydroxide on an inert base,* preferably of coarse grading, for example 3.0 mm to 1.5 mm, but not finer than 1.2 mm to 0.7 mm, and preferably of the self-indicating type.

WARNING. Reagents containing asbestos as the base material should not be used.

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[1] A method for the direct determination of oxygen in coke has been published; see B P Kirk and H C Wilkinson, *Talanta,* 1970, 17,475.

[2] This is the quality of reagent referred to as "magnesium perchlorate (dried)", sometimes known as "Anhydrone".

6.2.3 *Aluminium oxide,* finely divided, approximately 0.1 mm.

6.2.4 *Sodium borate solution,* 0.05 N.

6.2.5 *Hydrogen peroxide solution* containing 3 parts of 100 volume H_2O_2 and 97 parts of water, neutralized with the sodium borate solution (see **6.2.4**) to the screened indicator (see **6.2.6**).

6.2.6 *Screened indicator.* Proceed as follows.

A) Dissolve 0.125 g of methyl red in 100 ml of ethanol (95 % *v*/*v*).

B) Dissolve 0.083 g of methylene blue in 100 ml of ethanol (95 % *v*/*v*); store in a dark glass bottle.

Mix equal volumes of A) and B) immediately before use.

6.2.7 *Pure silver gauze,* one mesh per millimetre, 0.3 mm diameter wire.

6.2.8 *Oxygen,* hydrogen-free.

6.3 Special apparatus. The following special apparatus is required.

6.3.1 *Purification trains.* Two purification trains, one for removing water and carbon dioxide from the oxygen used for the combustion and the other for similarly purifying the air (see note) used for sweeping out the absorption train before and after a determination. The trains shall be assembled using the following reagents in the order stated.

a) Magnesium perchlorate (see **6.2.1**) for removing water.

b) Sodium hydroxide on an inert base (see **6.2.2**) for removing carbon dioxide.

c) Magnesium perchlorate (see **6.2.1**) for removing water produced in the reaction between carbon dioxide and sodium hydroxide.

The trains should be large enough to avoid the necessity for frequent recharging.

NOTE The air used should not be taken from a compressed air system, as this is liable to contain organic matter, but should be drawn through the trains from the atmosphere by means of a pump or aspirator.

6.3.2 *Heating unit.* An electrically heated furnace designed to carry a tube of 28.5 mm outside diameter and to heat it over a length of about 125 mm to give a temperature of 1 350 °C at the centre of the hot zone and a temperature-distribution curve similar to that shown in Figure 1.

NOTE Furnaces of the type normally used for the determination of carbon or sulphur in steel are not suitable, because of the absence of the auxiliary section to maintain the silver gauze roll at the correct temperature.

6.3.3 *Combustion tube.* A tube, 22 mm internal diameter and 28.5 mm outside diameter by 0.65 m long, made of refractory aluminous porcelain that is not permeable to gases at 1 400 °C[3].

6.3.4 *Combustion boat.* A combustion boat of iron-free unglazed porcelain, 70 mm long by 12.5 mm wide by 10 mm deep, that does not blister, discolour or change in weight on heating at 1 350 °C in oxygen for 3 h.

6.3.5 *Silica pusher.* A sealed tube or rod of silica, 6 mm diameter by approximately 450 mm long, flattened at one end to form a disc of 12 mm diameter for pushing the boat into the furnace. The pusher passes loosely through a glass or metal T-piece, one end of which fits into the rubber stopper that closes the inlet end of the combustion tube, the other being sealed with a rubber sleeve through which the pusher slides (see, for example, Figure 4). Oxygen is admitted through the limb of the T-piece. The pusher is marked in millimetres from the disc end for convenience in measuring how far the boat is pushed into the combustion tube.

6.3.6 *Nickel-chromium wire.* A length of stiff nickel-chromium wire with a hooked end, to extract the boat from the furnace on to a piece of refractory tile.

6.3.7 *Absorption train.* A typical absorption train, giving details of the packing for absorbing the water and carbon dioxide produced by combustion of the coke, is shown in Figure 2.

Midvale tubes, which provide a large area for reaction, shall be used to prevent excessive pressure in the apparatus and so minimize the danger of leakage through the rubber sleeve carrying the silica pusher.

Assemble the train using the following reagents in the order stated.

a) Magnesium perchlorate (see **6.2.1**) to absorb water.

b) Sodium hydroxide on an inert base (see **6.2.2**) to absorb carbon dioxide.

c) Magnesium perchlorate (see **6.2.1**) to absorb water produced in the reaction between carbon dioxide and sodium hydroxide.

Place glass wool above and below the absorbent to prevent carry-over of dust by the rapid flow of oxygen and also to reduce the possibility of the heat of the reaction cracking the tube containing the sodium hydroxide on an inert base.

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[3] Suitable material is marketed under the trade names *Pythagoras, Thermal 525 Ware* or *Triangle H.*

6.3.8 *Flowmeters.* Two flowmeters, one capable of measuring rates of flow of oxygen of up to 300 ml/min and the other capable of measuring rates of flow of air up to 250 ml/min.

6.3.9 *Pressure gauge.* A manometer to measure the back pressure on the system, normally 5 mbar[4] to 7 mbar.

6.3.10 *Heat-resistant stopper.* A heat-resistant stopper (acrylonitrile or chloroprene rubber) for attaching the absorption train to the combustion tube.

6.3.11 *Silver gauze roll.* A silver gauze roll (see **6.2.7**), through which passes a stout silver wire for ease of removal, 75 mm long and of sufficient diameter to ensure a close sliding fit in the combustion tube.

NOTE The silver gauze roll can absorb sulphur equivalent to 7 % of the sample; for higher sulphur contents, the mass of the coke sample should be proportionally reduced. The roll should be cleaned periodically by immersion in boiling distilled water for 5 min, then in concentrated ammonia solution ($d = 0.88$) for 2 min and finally in boiling distilled water for 5 min, after which it should be dried. The total sulphur content of samples examined between two cleanings of the roll should not exceed 0.035 g. The roll tends to shrink with continual use and it is important to check its diameter to ensure the close sliding fit in the combustion tube.

6.4 Preparation of apparatus. Insert the combustion tube into the furnace so that it projects 75 mm at the exit end. Wrap this projecting portion with mineral fibre[5] to prevent condensation of water in the tube. Insert the rubber stopper carrying the silica pusher at the inlet end of the combustion tube and connect the oxygen supply to the limb of the T-piece. Insert the silver gauze roll into the exit end of the combustion tube to a distance of about 75 mm. With the furnace at its working temperature of 1 350 °C, connect, by means of the heat-resistant stopper, a bubbler containing the hydrogen peroxide solution to the exit end of the combustion tube. Burn about 0.5 g of the sample by the procedure described in **6.5**. Determine the amount of oxides of sulphur passing the roll by titration of the hydrogen peroxide with the sodium borate solution, using the screened indicator. Repeat the combustion of 0.5 g portions of the sample, moving the silver gauze roll in 5 mm steps, until a position is found where the titre of the sodium borate solution is not more than 0.2 ml. This indicates the retention of at least 99 % of the oxides of sulphur by the silver gauze roll. Use this location in all determinations. When the combustion tube is not in use protect it from atmospheric contamination by fitting stoppers.

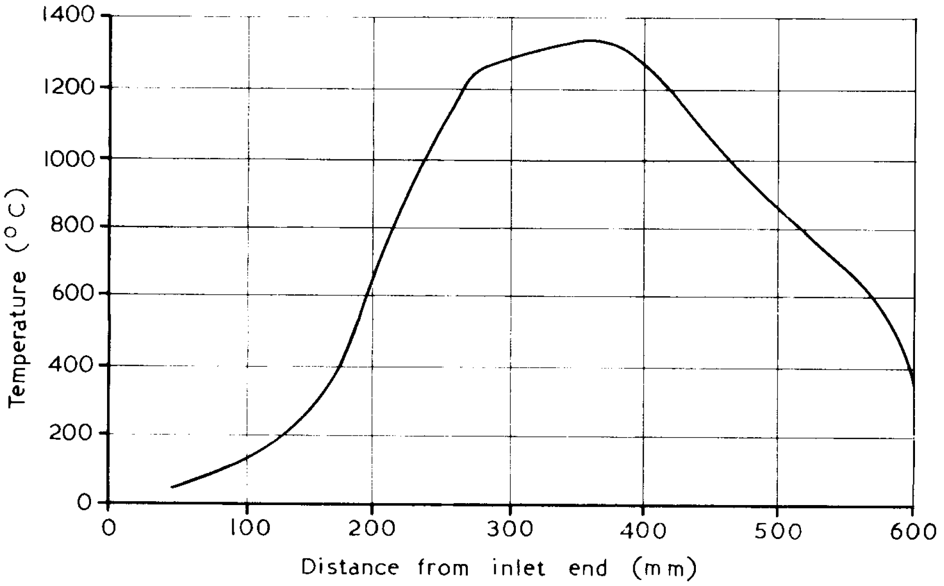

Figure 1 — Temperature distribution curve for the carbon and hydrogen furnace

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[4] 1 mbar = 10^2 N/m^2 = 0.1 kPa.

[5] WARNING. Material containing asbestos should not be used for this purpose.

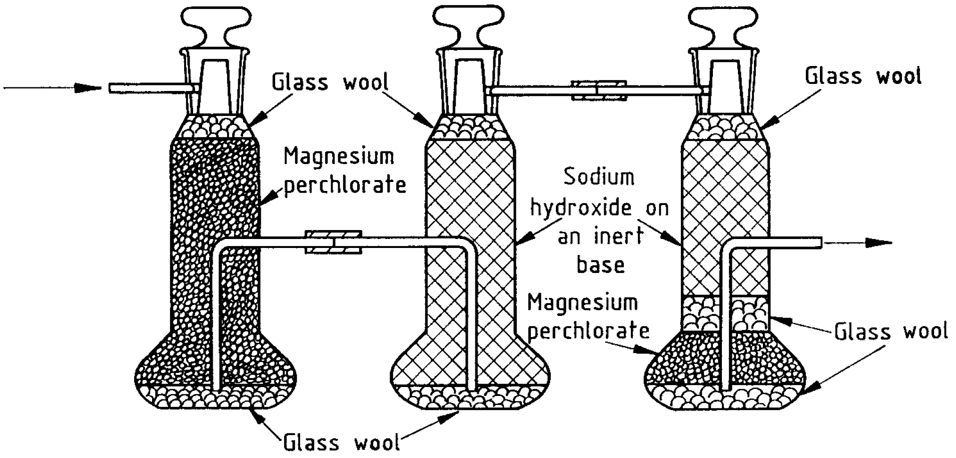

Figure 2 — Absorption train for carbon and hydrogen determination

6.5 Procedure

6.5.1 *Determination of the blank of the apparatus.* Raise the temperature of the furnace to 1 350 °C and pass the oxygen through the combustion tube at a rate of 300 ml/min. Connect an assembled absorption train to the apparatus by means of a heat-resistant stopper and purge for 10 min. Ensure that the inlet of the water-absorption tube is flush with the inner end of the heat-resistant stopper in the combustion tube and that the joints between the absorption tubes are made glass to glass, using the rubber tubing merely as a seal. Disconnect the absorption train from the combustion tube and connect to the air purification train. Draw purified air through the train at a rate of 200 ml/min to 250 ml/min for 10 min. Disconnect the absorption train (see note 1), wipe each absorber with a clean, dry cloth free from loose fibres, allow to cool to the balance room temperature (usually about 15 min to 20 min) in an enclosure free from dust, e.g. a cabinet resembling a balance case, and weigh. Reassemble the absorption train and reconnect it to the combustion tube. Pass purified oxygen through the apparatus at 300 ml/min for 10 min, disconnect the absorption train, displace the oxygen in it by purified air, cool and weigh each unit, observing the same precautions as for the initial weighings. If the total change in mass of the absorption tubes is less than 0.5 mg the apparatus is in a proper condition for use (see note 2).

NOTE 1 Protection of the absorption train from atmospheric contamination when not in use is necessary. Apparatus having ground-in stoppers can be protected by closing the stoppers but tubes open to the atmosphere should have guard stoppers of plugged rubber tubing. It is usual to weigh absorption tubes without the guard stoppers.

NOTE 2 The blank should be redetermined regularly and also when some part of the apparatus is replaced.

6.5.2 *Determination of carbon and hydrogen in the sample.* Raise the temperature of the furnace to 1 350 °C, check that the silver gauze roll is in its correct position, connect an absorption train to the combustion tube and pass the oxygen at a rate of 300 ml/min for 10 min. Disconnect the absorption train, purge with purified air, wipe, cool and weigh as described in the blank determination (see note 1).

Weigh about 0.5 g of the sample to the nearest 0.1 mg and spread evenly over the bottom of a clean, dry boat. (Determine the moisture in the coke simultaneously by the method described in BS 1016-104.2. Add about 0.5 g of the aluminium oxide, so as to cover completely the sample in the boat. (The total moisture in the aluminium oxide shall be determined by heating 2 g to 1 350 °C in the apparatus and absorbing the water in magnesium perchlorate.)

Reconnect the weighed absorption train, disconnect the rubber stopper and insert the charged boat into the combustion tube to a position such that its centre is 240 mm from the centre of the hottest zone. With the silica pusher fully withdrawn, replace the rubber stopper and continue to pass the oxygen at 300 ml/min. At the end of each of the next 6 one-minute intervals (see note 2), push the boat forward 40 mm, withdrawing the silica pusher each time, if necessary, to prevent its distortion. Allow the boat to remain in the hottest zone for a further 4 min. Alternatively continuous mechanical pushing of the boat may be used provided the heating schedule specified is maintained. Disconnect the absorption train, purge with purified air, wipe and cool as before but for 1 h and weigh as in the blank determination.

NOTE 1 The conditioning of the absorption train need not be made before every determination if the apparatus is in regular use, provided that the technique of wiping before weighing is followed.

NOTE 2 For unreactive cokes, e.g. a foundry coke of less than 0.5 % volatile matter or a coke with a critical air blast (CAB, see BS 1016-108.6) greater than 2.1 litres/min, the rate of pushing should reduce according to the following procedure: insert the charged boat so that its centre is 240 mm from the centre of the hottest zone; at the end of the first minute move the boat forward 40 mm; at the end of the next minute move the boat forward 20 mm and repeat this at one-minute intervals seven more times. After a further one-minute interval (i.e. after 10 min) move the boat forward 40 mm and allow the boat to remain in the hottest zone for a further 4 min.

6.6 Calculation of results

$$C_{ad} = \frac{27.29 m_3}{m_1}$$

and

$$H_{ad} = \left(\frac{11.19 m_2}{m_1} \times 0.1119 M_{ad}\right)$$

where

m_1	is the mass of the sample taken (in g)
m_2	is the increase in mass of the water-absorption tube, less the mass of the moisture in the aluminium oxide used (in g)
m_3	is the total increase in mass of the absorption tubes containing sodium hydroxide on an inert base (in g)
C_{ad}	is the percentage of total carbon in the analysis sample
H_{ad}	is the percentage of total hydrogen in the analysis sample
M_{ad}	is the percentage of moisture in the analysis sample (see BS 1016-104.2).

7 Nitrogen

7.1 Principle. A small amount of the sample is finely ground and a known mass of this material is heated with concentrated sulphuric acid in the presence of a catalyst to destroy the organic material and to convert the nitrogen to ammonium sulphate. Ammonia is released by steam distillation from an alkaline solution, absorbed in boric acid solution and titrated directly with 0.01 N sulphuric acid.

7.2 Special reagents. All reagents, unless otherwise specified, shall be of analytical reagent quality. Distilled or deionized water complying with the requirements of BS 3978 shall be used throughout.

NOTE Error may arise from the presence of ammonia in the water. The ammonia may be removed either by the use of a suitable ion exchange resin or by protracted boiling.

7.2.1 *Sulphuric acid,* $d = 1.84$, nitrogen-free.

7.2.2 *Sulphuric acid,* 0.01 N.

7.2.3 *Mixed catalyst,* containing by mass

87 parts of potassium sulphate,

13 parts of mercuric sulphate.

The mixture shall be thoroughly ground in a mortar before use.

7.2.4 *Boric acid solution, saturated.* Dissolve 60 g of boric acid in 1 litre of hot water. Allow to stand for 3 days, decant and use the clear solution.

7.2.5 *Alkaline sodium sulphide solution.* 400 g of sodium hydroxide plus 40 g of sodium sulphide ($Na_2S.9H_2O$) per litre.

7.2.6 *Screened indicator.* Proceed as follows.

A) Dissolve 0.125 g of methyl red in 100 ml of ethanol (95 % *v*/*v*).

B) Dissolve 0.083 g of methylene blue in 100 ml of ethanol (95 % *v*/*v*); store in a dark glass bottle.

Mix equal volumes of A) and B) immediately before use.

7.2.7 *Sucrose.*

7.3 Special apparatus. The following special apparatus is required.

7.3.1 *Digestion flask.* A Kjeldahl flask of borosilicate glass, preferably pistol shaped, of 50 ml capacity.

7.3.2 *Stopper.* A light, loosely fitting, blown glass stopper for closing the mouth of the flask.

7.3.3 *Heating unit.* The flask may be heated by gas, using a microburner, or by electricity[6].

7.3.4 *Distillation apparatus.* A suitable distillation apparatus of borosilicate glass, fitted with a splash head to arrest the passage of any entrained sodium hydroxide solution, an upright condenser and a 100 ml conical flask, is shown in Figure 3 (see also BS 1428-B2).

7.3.5 *Burette.* A 25 ml class A burette complying with the requirements of BS 846.

7.4 Procedure. Grind a small portion of the analysis sample of coke to pass a sieve of 63 µm aperture, complying with the requirements of BS 410. Weigh 0.10 g of the ground sample to the nearest 0.1 mg, transfer completely to the digestion flask, add 2 g of the catalyst (see **7.2.3**) and shake to mix. Add 4 ml of the sulphuric acid (see **7.2.1**) and mix again.

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[6] A unit using 100 W electric heating mantles to heat a number of flasks simultaneously is obtainable commercially.

Place the flask either on the electrical heating unit, with the heat input adjusted, or over the microburner flame, so that the solution boils steadily. Continue boiling until the solution becomes clear (see note 1).

During the digestion, steam out the distillation apparatus for 30 min (see note 2), close the connection between the steam generator and the distillation flask and blow out any waste from the previous distillation. Pour 20 ml of the alkaline sodium sulphide solution into the distillation flask through the funnel (see Figure 3) and rinse with water. Measure 2 ml of the boric acid solution into the receiver and add four drops of the mixed indicator solution, adjusting the height of the receiver so that the end of the condenser tube dips below the surface of the liquid.

Allow the acid digest to cool for 5 min and dilute by adding 10 ml of water, at first in drops with shaking, until the reaction is less violent. Pour the diluted digest through the funnel into the distillation flask; rinse the digestion flask into the funnel with water, then rinse the tap funnel with water. The total volume of liquid in the distillation flask should not exceed half the capacity of the flask, or frothing and priming may occur.

Pass steam into the distillation apparatus and distil for 5 min from the time the steam enters the condenser, at a rate of about 4 ml of distillate per minute. To ensure complete absorption of the ammonia, the contents of the receiver should remain cold. Lower the receiver so that the condenser end is about 25 mm above the surface of the liquid and continue distillation for 1 min longer. Rinse the end of the condenser tube with water.

Titrate the ammonia present in the distillate with the sulphuric acid (see **7.2.2**) until the grass-green colour changes to steel-grey, a further drop then giving the purple (acid) colour.

NOTE 1 Normally, this should take 1½ h or less. However, an unreactive coke (see note 2 to **6.5.2**) may take over 10 h before the solution becomes clear. No loss of nitrogen will occur even with this long digestion period and clearing of the solution shall always be used as a guide to the end of the digestion period.

NOTE 2 There is no need to steam out for 30 min between individual distillations carried out in a series of determinations.

7.5 Determination of the blank. Carry out a blank determination at the same time and under the same conditions as the actual determination but using 0.1 g of the sucrose instead of the coke.

NOTE If the splash head removes all entrained sodium hydroxide, the results of the blank determination should not exceed 0.1 ml of 0.01N sulphuric acid. Steam removes alkali compounds from some glasses and, if higher blank results are found, the apparatus should be replaced.

7.6 Calculation of result

$$N = \frac{(V_1 - V_2) \times 0.014}{m}$$

where

m is the mass of sample taken (in g)

V_1 is the volume of 0.01 N acid used in the sample determination (in ml)

V_2 is the volume of 0.01 N acid used in the blank determination (in ml)

N is the percentage of nitrogen in the analysis sample.

8 Total sulphur

8.1 Introduction. An alternative method for the determination of total sulphur, the Eschka method, is described in BS 1016-106.4.1. The high temperature method is particularly suitable where a large number of determinations has to be made or results are required rapidly.

8.2 *Text deleted*

8.3 High temperature method

8.3.1 *Principle.* A known mass of the sample is burnt in a stream of oxygen at a temperature of 1 350 °C. The oxides of sulphur formed, together with any chlorine present, are absorbed in neutral hydrogen peroxide and determined volumetrically. A correction is made to take account of the chlorine. Aluminium oxide is added to prevent the retention of sulphur in the ash.

As the procedure is identical with that given in BS 1016-8, a determination of chlorine content of the coke can be made simultaneously with that of its sulphur content.

8.3.2 *Special reagents.* All reagents, unless otherwise specified, shall be of analytical reagent quality. Distilled or deionized water complying with the requirements of BS 3978 shall be used throughout.

8.3.2.1 *Sodium borate solution,* 0.05 N.

8.3.2.2 *Sulphuric acid,* 0.025 N.

8.3.2.3 *Hydrogen peroxide solution* containing 3 parts of 100 volume H_2O_2 and 97 parts of water, neutralized with the sodium borate solution (see **8.3.2.1**) to the screened indicator (see **8.3.2.4**).

8.3.2.4 *Screened indicator.* Proceed as follows.

A) Dissolve 0.125 g of methyl red in 100 ml of ethanol (95 % *v*/*v*).

B) Dissolve 0.083 g of methylene blue in 100 ml of ethanol (95 % *v*/*v*); store in a dark glass bottle.

Mix equal volumes of A) and B) immediately before use.

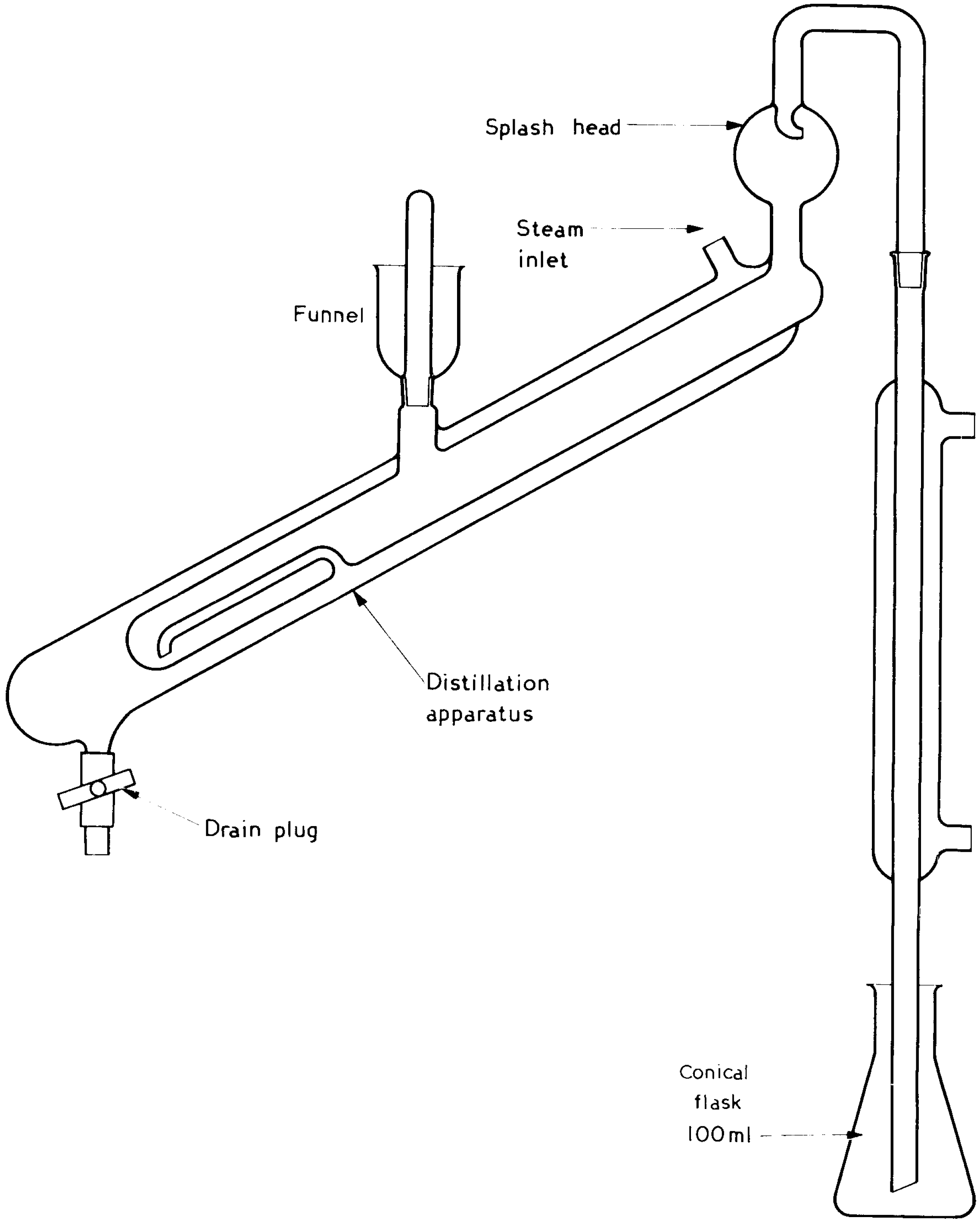

Figure 3 — Nitrogen distillation apparatus

8.3.2.5 *Mercury II oxycyanide solution.* Saturate about 100 ml of water with mercury II oxycyanide ($3H_g(CN)_2.H_gO$) by prolonged agitation; filter and neutralize the filtrate with the 0.025 N sulphuric acid, using the screened indicator. Store the solution in a dark bottle; do not keep longer than 4 days.

WARNING. This compound and its solution are toxic and should be handled with great care.

8.3.2.6 *Aluminium oxide.* Finely divided, approximately 0.1 mm.

8.3.2.7 *Oxygen.*

8.3.2.8 *Sodium hydroxide on an inert base,* preferably of coarse grading, for example 1.7 mm to 1.2 mm, and preferably of the self-indicating type.

WARNING. Reagents containing asbestos as the base material should not be used.

8.3.3 *Special apparatus.* A suitable assembly of the special apparatus required is shown in Figure 4. It consists of the following items.

8.3.3.1 *Heating unit,* as specified in **6.3.2**.

8.3.3.2 *Combustion tube,* as specified in **6.3.3**.

8.3.3.3 *Combustion boat,* as specified in **6.3.4**.

8.3.3.4 *Silica pusher,* as specified in **6.3.5**.

8.3.3.5 *Nickel-chromium wire,* as specified in **6.3.6**.

8.3.3.6 *Flowmeter (300 ml/min),* as specified in **6.3.8**.

8.3.3.7 *Pressure gauge,* as specified in **6.3.9**.

8.3.3.8 *Heat-resistant stopper,* as specified in **6.3**.

8.3.3.9 *Silica adaptor.* A translucent silica tube, 10 mm outside diameter by approximately 250 mm long, terminating at one end in a funnel of 20 mm outside diameter.

8.3.3.10 *Purification train.* A tower containing sodium hydroxide on an inert base (see **8.3.2.8**) for removing any oxides of sulphur from the oxygen supply.

8.3.3.11 *Absorption vessel.* A gas washing tube or bottle with a sintered disc of porosity grade P 40 complying with the requirements of BS 1752, of such a size that a 90 mm seal of liquid is obtained with 100 ml of liquid in the vessel.

8.3.3.12 *Pressure regulator.* A bottle containing mercury, fitted with inlet and outlet tubes and a third tube capable of being moved up or down to regulate the suction on the system.

8.3.3.13 *Vacuum pump.*

8.3.4 *Preparation of apparatus.* Insert the combustion tube into the furnace so that it projects 100 mm at the exit end. Insert at this end the heat-resistant stopper carrying the silica adaptor and adjust the latter so that the open end of the funnel is in the position where, in the carbon and hydrogen determination, the hotter end of the silver gauze roll is located (see **6.4**). Insert the rubber stopper carrying the silica pusher at the inlet end of the combustion tube and connect the oxygen supply through the purification train to the limb of the T-piece.

8.3.5 *Procedure.* Raise the temperature of the furnace to 1 350 °C and pass purified oxygen through the combustion tube. Weigh about 0.5 g of the sample to the nearest 0.1 mg, spread uniformly in the boat and cover with 0.5 g of the aluminium oxide. Measure 100 ml of the hydrogen peroxide solution into the absorption vessel and assemble the apparatus. Adjust the rate of flow by means of the vacuum pump and the depth of seal in the mercury regulator to maintain a slight suction in the combustion tube with oxygen entering at 300 ml/min.

Remove the rubber stopper carrying the silica pusher and insert the charged boat into the combustion tube to a position such that its centre is 240 mm from the centre of the hottest zone. With the silica pusher fully withdrawn, replace the rubber stopper and continue to pass purified oxygen at 300 ml/min. At the end of each of the next 6 one-minute periods, push the boat forward 40 mm (see note 2 to **6.5.2**), withdrawing the silica pusher each time, if necessary, to prevent its distortion. Allow the boat to remain in the hottest zone for a further 4 min. Alternatively, continuous mechanical pushing of the boat may be used provided that the heating schedule specified is maintained. Disconnect the absorption vessel and remove the silica adaptor. Withdraw the boat on to a refractory tile.

Wash the silica adaptor with water, collecting the washings in a 250 ml flask. Transfer the contents of the absorption vessel to the flask, washing the vessel with water and collecting the washings in the same flask. The total bulk of liquid should not exceed 150 ml.

Add two or three drops of the screened indicator and titrate with the 0.05 N sodium borate solution to the neutral steel-grey colour. Add 20 ml of the mercuric oxycyanide solution (sufficient excess for cokes containing up to 1.2 % chlorine) and titrate with the sulphuric acid to the neutral steel-grey colour.

8.3.6 *Determination of the blank.* Carry out a blank determination under the same conditions as the actual determination but omitting the sample.

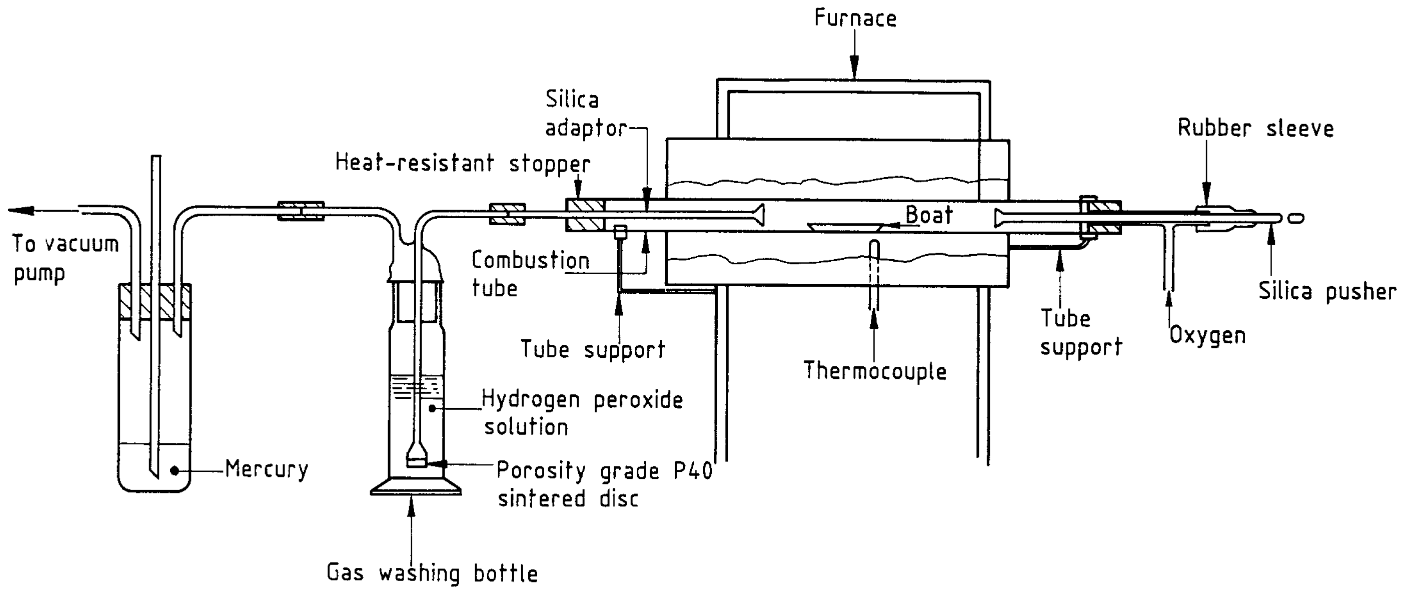

Figure 4 — Absorption train and furnace for sulphur (high temperature method)

8.3.7 *Calculation of result*

$$S = \frac{0.0802}{m}[V_1 - V_2 - 0.5(V_3 - V_4)]$$

where

m is the mass of the sample taken (in g)

V_1 is the volume of 0.05 N sodium borate used in the determination (in ml)

V_2 is the volume of 0.05 N sodium borate used in the blank determination (in ml)

V_3 is the volume of 0.025 N sulphuric acid used in the determination (in ml)

V_4 is the volume of 0.025 N sulphuric acid used in the blank determination (in ml)

S is the percentage of total sulphur in the analysis sample.

9 Reporting of results

The results (preferably the means of duplicate determinations carried out at different times) for carbon, nitrogen and sulphur shall each be reported on the dry basis to the nearest 0.1 %. The result for hydrogen shall be reported to the nearest 0.01 %.

Where the oxygen has not been determined directly, the difference from 100 of the sum of the percentages of carbon, hydrogen, nitrogen, sulphur, moisture and ash shall be reported as "oxygen (plus errors)".

For the calculation of results to bases other than "as analysed", see BS 1016-16.

10 Precision of the determinations

When the methods described in this Part of BS 1016 are operated satisfactorily the numerical values for repeatability and reproducibility (see clause **3**) should not exceed those given below; otherwise reference should be made to **6.4** in BS 1016-16:1981.

	Repeatability	**Reproducibility**
	% absolute	% absolute
Carbon	0.20	0.30
Hydrogen	0.10	0.15
Nitrogen	0.05	0.10
Total sulphur	0.05	0.10

Publications referred to

BS 410, *Specification for test sieves.*

BS 846, *Specification for burettes.*

BS 1016, *Methods for analysis and testing of coal and coke.*

BS 1016-8, *Chlorine in coal and coke.*

BS 1016-16, *Methods for reporting results.*

BS 1016-104, *Proximate analysis.*

BS 1016-104.2, *Determination of moisture content of the general analysis sample of coke.*

BS 1016-104.4, *Determination of ash.*

BS 1016-106, *Ultimate analysis of coal and coke.*

BS 1016-106.4, *Determination of total sulfur content.*

BS 1016-106.4.1, *Eschka method.*

BS 1016-108, *Tests special to coke.*

BS 1016-108.6, *Determination of critical air blast.*

BS 1017, *Methods for sampling of coal and coke.*

BS 1017-2, *Sampling of coke.*

BS 1428, *Microchemical apparatus.*

BS 1428-B2, *Specification for ammonia distillation apparatus (Markham).*

BS 1752, *Specification for laboratory sintered or fritted filters including porosity grading.*

BS 3978, *Specification for water for laboratory use.*

ISO 333, *Coal — Determination of nitrogen — Semi-micro Kjeldahl method*7).

ISO 351, *Solid mineral fuels — Determination of total sulfur — High temperature combustion method*7).

ISO 609, *Coal and coke — Determination of carbon and hydrogen — High temperature combustion method*7).

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7) Referred to in the foreword only.

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