BRITISH STANDARD

BS 1016-6:
1977

Incorporating
Amendment Nos. 1
and 2

CONFIRMED
September 1997

Methods for

Analysis and testing of coal and coke —

Part 6: Ultimate analysis of coal

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

This British Standard, having been prepared under the direction of the Solid Fuel Standards Committee, was published under the authority of the Executive Board on 29 April 1977

First published March 1942
First revision December 1958
Second revision April 1969
Third revision April 1977

The following BSI references relate to the work on this standard:
Committee references SFC/45 and SFC/45/8
Draft for comment 73/42187DC

ISBN 0 580 09173 2

Amendments issued since publication

Amd. No.	Date of issue	Comments
6982	May 1992	
7689	May 1993	Indicated by a sideline in the margin

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 or those for coke (see Part 7) 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 6 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 coal.

The high temperature method for the determination of carbon and hydrogen is technically equivalent to ISO 609. Similarly, the method for nitrogen, the method for sulphur and the gravimetric method for carbon dioxide correspond technically with those specified in ISO 333, ISO 351 and ISO 925 respectively. There is no ISO titrimetric method for the determination of carbon dioxide.

In the foreword to the last revision of Part 6 it was stated that it might shortly be possible to specify a satisfactory procedure for the direct determination of oxygen in coal. Since then, ISO 1994 has been published on the basis of international collaborative work in which a number of UK laboratories took part. It has been decided that it is unnecessary to issue a British Standard on this subject but that, where a direct oxygen determination is needed, a reference should be made to ISO 1994. The definition of ultimate analysis of a coal consequently includes oxygen as one of its chemical constituents, this being identical with the ISO definition.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 14, 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, sulphur and carbon dioxide in the analysis sample of coal. In order to quote the ultimate analysis of coal a value for oxygen is required; this may be determined by the method specified in ISO 1994 or estimated as a difference figure and reported as “oxygen plus errors”.

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
ultimate analysis

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

3.2
moisture in the analysis sample

the moisture in the analysis sample of coal after it has attained approximate equilibrium with the laboratory atmosphere to which it has been exposed

3.3
ash

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

3.4
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

3.5
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 carbon includes that present in the mineral carbonates and the hydrogen includes that present both in the moisture and in the water of constitution of the argillaceous constituents of the mineral matter.

All the nitrogen is assumed to be present in the coal substance. Sulphur is normally present in three forms: as iron pyrites (FeS_2), as inorganic sulphates associated with the mineral matter, and as organic sulphur compounds in the coal substance.

Oxygen in the coal substance may be determined by one of the procedures given in ISO 1994. Alternatively, an estimate of the percentage of oxygen can be obtained on the air-dried basis by subtracting the sum of the determined percentages of moisture, ash, carbon, hydrogen, nitrogen and sulphur from 100. 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)”. A more satisfactory value for oxygen is obtained when the ultimate analysis is expressed on the dry, mineral matter free basis (see Part 16 of this standard).

The value for oxygen (d.m.m.f.) so calculated, can be checked by comparing the determined calorific value of the coal (corrected to the d.m.m.f. basis) with the calorific value calculated from the formula:

$$Q - 80.3\ C + 339\ H - 36.6\ O + 0.172\ O^2$$

where

C represents the determined value of carbon

H represents the determined value of hydrogen

O represents the value of oxygen calculated from the following formula:

$$O = 100 - (C + H + N) \text{ d.m.m.f. basis}$$

If the calculated and determined values of the calorific value agree within 125 J/g, then it can be considered that the determined values of C, H and N and therefore the calculated value of the oxygen content lie within the range of experimental error.

5 Sample

The coal 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 1017-1.

The sample received in the laboratory shall be brought into approximate equilibrium with the laboratory atmosphere by exposing it in a thin layer on a tray. The exposure time shall be kept to the minimum necessary for this purpose, particularly with coals liable to oxidation. The sample shall be thoroughly mixed, preferably by mechanical means, immediately before the determination. Duplicate determinations shall not be made at the same time in the same apparatus.

6 Carbon and hydrogen

6.1 Principle. A known mass of coal 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 insert 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*[1], 1.2 mm to 0.7 mm.

6.2.2 *Sodium hydroxide on an insert 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.

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

6.2.4 *Sodium borate solution,* 0.05N.

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 mm 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 insert 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[2].

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.

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

[2] Suitable material is marketed under the trade names *Pythagoras, Thermal 525 Ware* or *Triangle 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 coal, 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 insert 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.

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 of up to 250 ml/min.

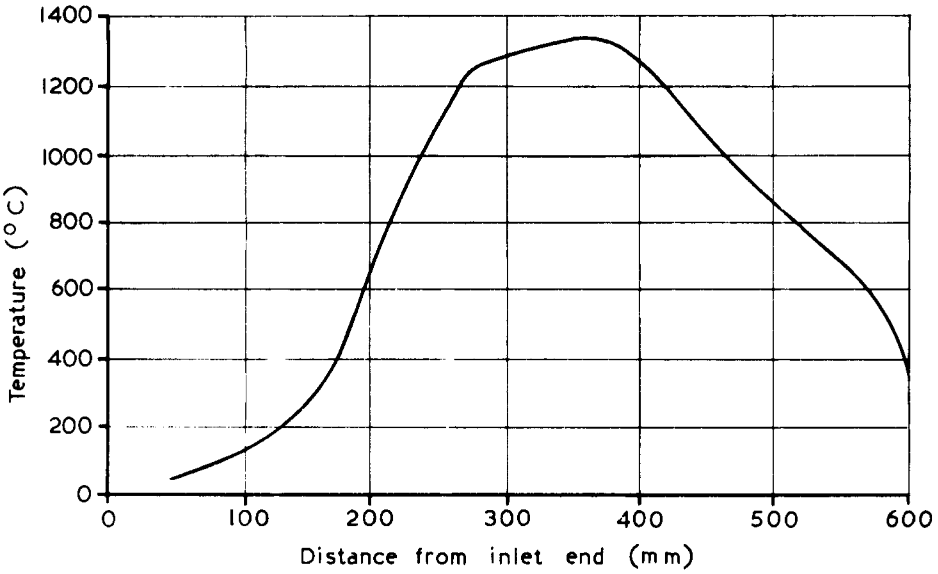

Figure 1 — Temperature distribution curve for the carbon and hydrogen furnace

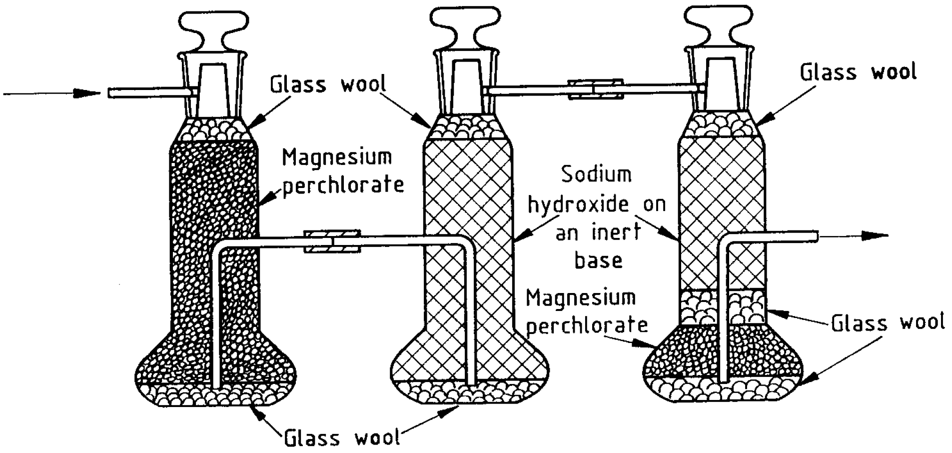

Figure 2 — Absorption train for carbon and hydrogen determination

6.3.9 *Pressure gauge.* A manometer to measure the back pressure on the system, normally 5 mbar[3] 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 coal 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[4] 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.

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[3] 1 mbar = 10^2 N/m^2 = 0.1 kPa.

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

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, then 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 coal simultaneously by the method described in BS 1016-104.1.) 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, with-drawing 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 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 It is known that certain exceptional coals may give erratic results with the pushing procedure specified, particularly coals that tend to liberate volatile matter at a high rate in the early stages of heating. If there is visual evidence of the carry-over of carbon particles, or if the sulphur content is over 2 %, the rate of pushing the coal should be reduced 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 mm) 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

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

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 insert 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 1016-104.1)

7 Nitrogen

7.1 Principle. A known mass of the sample 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 0.01N 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,* 0.01N.

7.2.3 *Mixed catalyst,* containing by mass

A) 32 parts of potassium sulphate,
1 part of selenium powder,
5 parts of mercuric sulphate;

or

B) 90 parts of potassium sulphate,
2 parts of selenium powder,
5 parts of vanadium pentoxide.

In either case, 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* for use with catalyst A) in **7.2.3**, 400 g of sodium hydroxide plus 40 g of sodium sulphide ($Na_2S.9H_2O$) per litre.

7.2.6 *Sodium hydroxide solution* for use with catalyst B) in **7.2.3**, 400 g of sodium hydroxide per litre.

7.2.7 *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.

7.2.8 *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[5].

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. Weigh 0.10 g of the sample to the nearest 0.1 mg, transfer completely to the digestion flask, add 2 g of either catalyst (see **7.2.3**) and shake to mix. Add 4 ml of the sulphuric acid (see **7.2.1**) and mix again.

Place the flask either on the electrical heating unit, with the heat input adjusted, or over the microburner flame, so that the solution becomes clear in 7 min to 10 min. After the solution becomes clear, continue boiling to give a total digestion time of 25 min to 30 min, in order to complete the conversion of the nitrogenous compounds into ammonium sulphate (see note 1).

During the digestion, steam out the distillation apparatus for 30 min (see note 2), close the connect on 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.

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

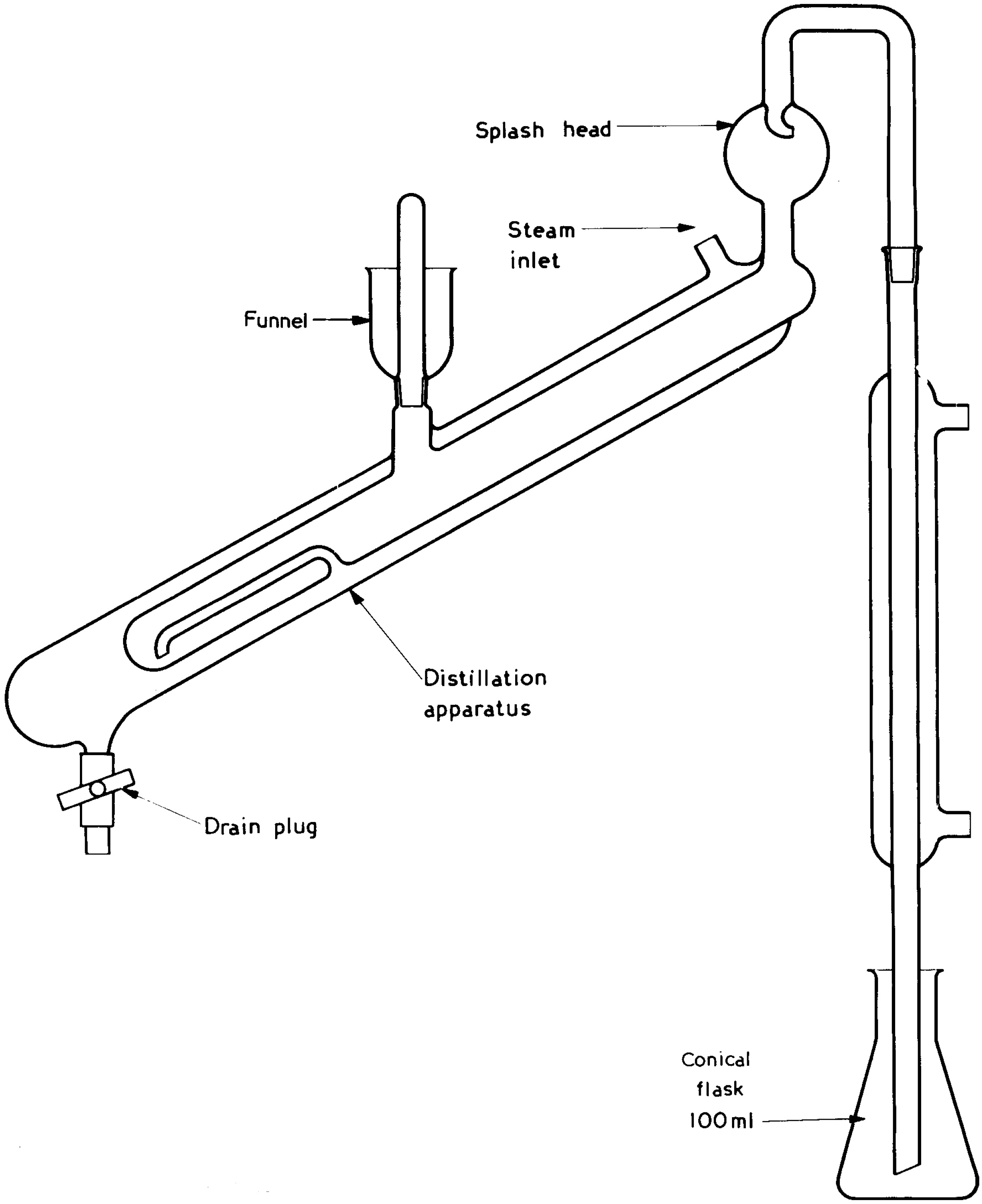

Figure 3 — Nitrogen distillation apparatus

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 The total digestion time should be carefully followed for the conditions specified.

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 coal.

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 0.01N acid used in the sample determination (in ml)

V_2 is the volume of 0.01N 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 sulfur, 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 burned 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 specified in BS 1016-8, a determination of chlorine content of the coal 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,* 0.05N.

8.3.2.2 *Sulphuric acid,* 0.025N.

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.

8.3.2.5 *Mercury II oxycyanide solution.* Saturate about 100 ml water with mercury II oxycyanide ($3Hg(CN)_2.HgO$) by prolonged agitation; filter and neutralize the filtrate with the 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 insert 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 **6.3.10**.

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 sodium borate solution to the neutral steel-grey colour. Add 20 ml of the mercuric oxycyanide solution (sufficient excess for coals 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.

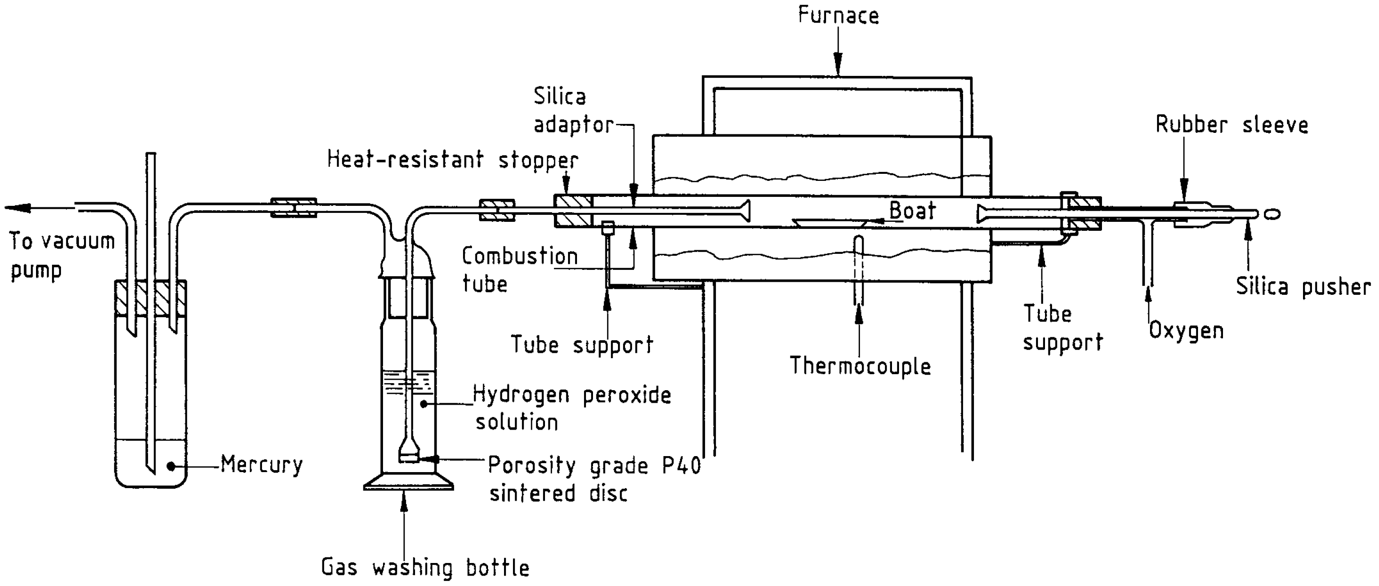

Figure 4 — Absorption train and furnace for sulphur (high temperature method)

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 sample taken (in g)
V_1	is the volume of 0.05N sodium borate used in the determination (in ml)
V_2	is the volume of 0.05N sodium borate used in the blank determination (in ml)
V_3	is the volume of 0.025N sulphuric acid used in the determination (in ml)
V_4	is the volume of 0.025N sulphuric acid used in the blank determination (in ml)
S	is the percentage of total sulphur in the analysis sample.

9 Carbon dioxide

9.1 Introduction. The carbon dioxide content of the mineral carbonates of a coal is required when the volatile matter (see BS 1016-104.3) or the carbon is to be calculated to other bases (see BS 1016-16).

A titrimetric and a gravimetric method are described. Either may be used for the determination of carbonates in all coals.

9.2 Titrimetric method

9.2.1 *Principle.* A known mass of the sample is treated with hydrochloric acid and the carbon dioxide evolved from the decomposition of the carbonates is absorbed in benzylamine solution. The benzylamine salt formed is titrated with a solution of potassium methoxide in toluene/methanol mixture using thymol blue as indicator.

9.2.2 *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.

9.2.2.1 *Hydrochloric acid,* 3N.

9.2.2.2 *Absorption mixture.* Mix 3 volumes of ethanol (95 % *v*/*v*) with 1 volume of benzylamine and 3 volumes of dioxan.

9.2.2.3 *Thymol blue indicator,* 0.2 % *v*/*v* in dioxan.

9.2.2.4 *Potassium methoxide solution.* Approximately 0.1N, in toluene/methanol mixture.

9.2.2.5 *Sodium carbonate solution.* Dissolve 1.2044 g of anhydrous sodium carbonate (previously dried at 260 °C for 30 min) in distilled water free from carbon dioxide and dilute to 500 ml in a volumetric flask complying with the requirements of BS 1792. This solution is equivalent to 1 mg of CO_2 per millilitre. The solution should not be stored for more than 2 months and should be kept in a stoppered hard glass bottle.

9.2.3 *Special apparatus.* A suitable closed circuit apparatus is shown in Figure 5 (see note). It consists of the following items.

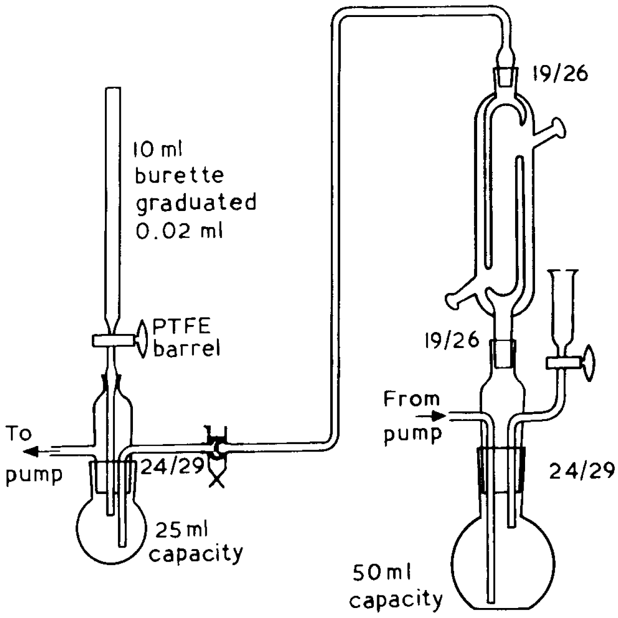

Figure 5 — Apparatus for carbon dioxide (titrimetric method)

9.2.3.1 *Reaction flask assembly.* A 50 ml flat bottom flask fitted with a tap funnel, a double surface condenser of 100 mm effective length and an air inlet tube reaching to the bottom of the flask.

9.2.3.2 *Absorption flask assembly.* A 25 ml round bottom flask fitted with a 10 ml burette. The burette is conveniently of the automatic type and the tap is preferably of PTFE. The air inlet tube should reach nearly to the bottom of the flask.

9.2.3.3 *Pump*[6]

NOTE An open circuit method may also be used provided that a more efficient absorption vessel than that described in **9.2.3.2** is available, e.g. that specified in ISO 1994.

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[6] The DYMK 1 pump, manufactured by Charles Austen Pumps Ltd., High Road, Byfleet Surrey, has been found suitable. A needle valve should be fitted in series to regulate the air flow.

9.2.4 *Procedure.* Weigh about 0.5 g of the sample to the nearest 0.1 mg, transfer to the reaction flask and add 5 ml of water free from carbon dioxide (see note 1). Close the flask with a glass stopper and shake vigorously. Remove the stopper and wash any coal adhering to it back into the flask. Place 7 ml of the absorption mixture in the absorption flask and add three drops of the indicator solution. With the tap funnel open, fit the reaction flask to the condenser assembly. Connect the inlet of the pump to the absorption flask and the outlet to the reaction flask. Switch on the pump, connect the ball joint and finally close the tap funnel (see note 2). Adjust the air circulation to about 35 ml/min and circulate for 5 min to absorb the carbon dioxide present in the air. Titrate the contents of the absorption flask with the potassium methoxide solution to the blue end point and, when this remains stable, place 2 ml of the hydrochloric acid in the tap funnel and admit the acid to the reaction flask, taking care not to admit air to the system. Wash the funnel three times into the flask with a little water free from carbon dioxide and leave the funnel half full of water to act as a seal. Bring the contents of the reaction flask to boiling point by heating with a microburner. During this operation carbon dioxide is evolved and the absorption mixture changes from blue through green to yellow. After 5 min titrate the contents of the absorption flask with the potassium methoxide solution to the blue end point (see note 3). Continue to boil and circulate air for a further 5 min, adjusting the end point at intervals. Absorption should be complete in about 10 min after heating has begun (see note 4).

NOTE 1 The water may be freed from carbon dioxide by boiling gently for 15 min.

NOTE 2 It is necessary to follow **9.2.4** precisely to avoid "suckback" in the apparatus. The sequence of operations given should be reversed when shutting down the apparatus.

NOTE 3 If the potassium methoxide fails to flow from the burette, remove the heat source and allow the flask to cool for 30 s.

NOTE 4 Further determinations may be made without changing the absorption mixture until 5 ml of the potassium methoxide solution have been added.

9.2.5 *Standardization of the potassium methoxide solution.* Pipette 10 ml of the sodium carbonate solution into the reaction flask and carry out the procedure given above, but omitting the coal sample. Calculate the equivalent in milligrammes of carbon dioxide *F* for each millilitre of the potassium methoxide solution:

$$F = \frac{10}{\text{volume of potassium methoxide (in ml)}}$$

Repeat the procedure twice, using fresh portions of sodium carbonate solution. Use the mean of the three determinations for calculation of the carbon dioxide content of coal samples.

9.2.6 ***Calculation of result***

$$CO_2 = \frac{FV}{10m}$$

where

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

V is the volume of the potassium methoxide in the determination (in ml)

F is the equivalent of 1 ml of the potassium methoxide solution (in mg of carbon dioxide)

CO_2 is the percentage of carbon dioxide in the analysis sample.

9.3 Gravimetric method

9.3.1 *Principle.* A known mass of the sample is treated with hydrochloric acid and the carbon dioxide evolved from the decomposition of the carbonates is absorbed and weighed.

9.3.2 *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.

9.3.2.1 *Sulphuric acid, d* = 1.84.

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

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

9.3.2.3 *Magnesium perchlorate*[7], 1.2 mm to 0.7 mm

9.3.2.4 *Hydrochloric acid,* 3N

9.3.2.5 *Copper phosphate,* granular, 1.2 mm to 0.7 mm

9.3.3 *Special apparatus.* Any system comprising a purification train, a reaction flask assembly and an absorption train may be used. A suitable apparatus is shown in Figure 6 and consists of the following items.

9.3.3.1 *Purification train.* A bubbler containing sulphuric acid (see **9.3.2.1**) and a U-tube containing sodium hydroxide on an inert base (see **9.3.2.2**).

9.3.3.2 *Reaction flask assembly.* A 300 ml flat bottomed flask fitted with a tap funnel, a double-surface condenser and a bulbed tube.

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

9.3.3.3 *Absorption train.* Three U-tubes packed as follows:

a) magnesium perchlorate (see **9.3.2.3**) to dry the gas;

b) granular copper phosphate (see **9.3.2.5**) to absorb hydrogen sulphide, followed by a guard of magnesium perchlorate;

c) sodium hydroxide on an inert base (see **9.3.2.2**) to absorb carbon dioxide, followed by a guard of magnesium perchlorate (see **9.3.2.3**) to absorb water produced in the reaction between carbon dioxide and sodium hydroxide.

9.3.4 *Procedure.* Weigh about 5 g of the sample to the nearest 0.01 g, transfer to the reaction flask and add 100 ml of water free from carbon dioxide (see note 1 to **9.2.4**). Close the flask by a rubber stopper and shake vigorously to wet the coal. Remove the stopper and wash any coal adhering to it back into the flask. Assemble the apparatus as shown in Figure 6 and draw air through it at a rate of about 50 ml/min for 10 min. Stop the circulation of air, remove the absorption tube and close the taps, also close the open end of the tube connected to it. Wipe the absorption tube with a clean dry cloth free from loose fibres, allow to cool to the balance room temperature in an enclosure free from dust, e.g. a cabinet resembling a balance case, and weigh after 15 min. Reconnect the absorption tube into the apparatus and circulate air as before. Place 25 ml of the hydrochloric acid (see **9.3.2.4**) in the tap funnel. Vent the system to air and admit the acid to the reaction flask. Close the vent and circulate air at about 50 ml/min through the system. Raise the temperature of the liquid in the reaction flask slowly so that it boils after about 15 min (see note). Continue boiling for a further 30 min, the rate of boiling being adjusted so that the condenser is not overloaded. Stop the circulation of air remove the absorption tube, condition and weigh as before.

NOTE The addition of a few drops of ethanol (95 % *v*/*v*) to the mixture in the reaction flask eliminates any tendency to frothing.

9.3.5 ***Calculation of result***

$$CO_2 = \frac{100 m_2}{m_1}$$

where

m_1 is the mass of the sample taken (in g)

m_2 is the increase in mass of the absorption tube (in g)

CO_2 is the percentage of carbon dioxide in the analysis sample.

10 Reporting of results

The results (preferably the means of duplicate determinations carried out at different times) for carbon, nitrogen, sulphur and carbon dioxide shall each be reported 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 by one of the procedures given in ISO 1994, 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.

11 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
Oxygen (direct determination)	0.3	0.5
Carbon (carbonates) as carbon dioxide	0.05	0.10

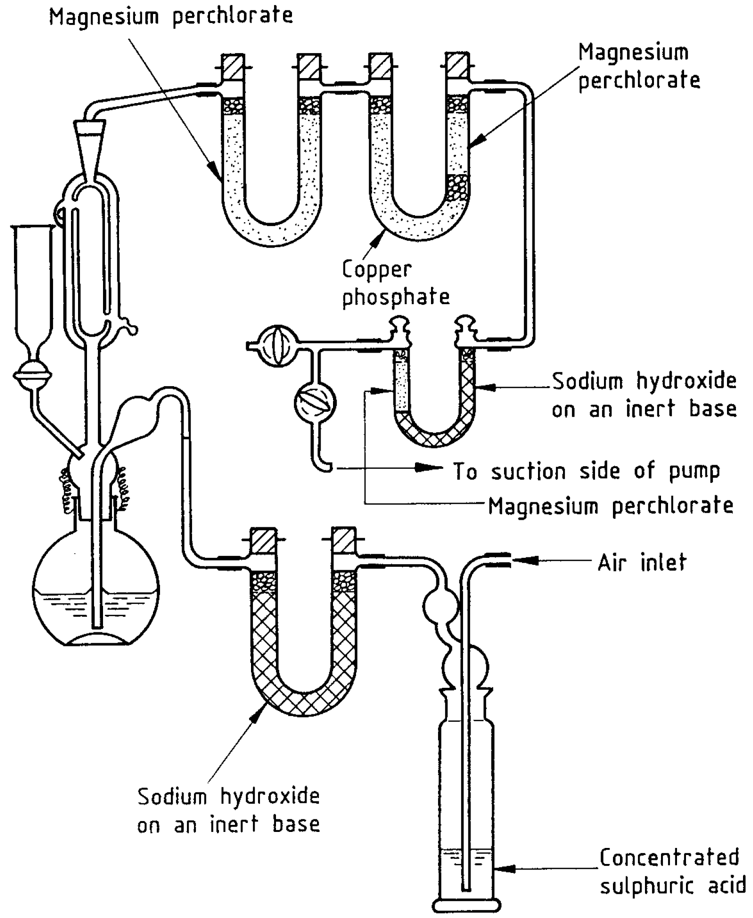

Figure 6 — Apparatus for carbon dioxide (gravimetric method)

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 1016-104.1, *Determination of moisture content of the general analysis sample of coal.*
BS 1016-104.3, *Determination of volatile matter content.*
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 1017, *Methods for sampling of coal and coke.*
BS 1017-1, *Methods for sampling coal.*
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 1792, *Specification for one-mark volumetric flasks.*
BS 3978, *Specification for water for laboratory use.*
ISO 333, *Coal — Determination of nitrogen — Semi-micro Kjeldahl method*8).

ISO 351, *Solid mineral fuels — Determination of total sulfur — High temperature combustion method*8).
ISO 609, *Coal and coke — Determination of carbon and hydrogen — High temperature combustion method*8).
ISO 925, *Solid mineral fuels — Determination of carbon dioxide content — Gravimetric method*8).
ISO 1994, *Hard coal — Determination of oxygen content.*

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8) Referred to in the foreword only.

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