IS 1350-4-1 (1974): Methods of Test for Coal and Coke, Part IV: Ultimate Analysis - Section I : Determination of Carbon and Hydrogen [PCD 7: Solid Mineral Fuels]

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(Superseding IS : 1351 – 1959)
(Reaffirmed 2000)

Indian Standard

METHODS OF TEST FOR COAL AND COKE

PART IV ULTIMATE ANALYSIS

Section I Determination of Carbon and Hydrogen

(First Revision)

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Indian Standard

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Section I Determination of Carbon and Hydrogen

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AMENDMENT NO. 1 OCTOBER 2011
TO
IS 1350 (PART 4/SECTION 1) : 1974 METHODS OF TEST FOR COAL AND COKE

PART 4 ULTIMATE ANALYSIS

Section 1 Determination of Carbon and Hydrogen

(First Revision)

(*Page* 3*, clause* **0.3**) — Substitute the following for the existing clause:

‘In this standard, two methods of determination of carbon and hydrogen have been prescribed. The one given in **5.1** is a modification of the Fentons Method developed at the Central Institute for Mining and Fuel Research (CIMFR), Dhanbad. The CIMFR Method, as it is called, is considerably quicker than the Liebig Method and is popular in the country. The High-Temperature Method given in **5.3** is based on the following publication issued by the International Organization for Standardization:

> ISO/R 609-1967 Determination of carbon and hydrogen in coal and coke by the high-temperature combustion method’.

(*Page* 12*, clause* **5.2**) — Delete.

(PCD 7)

Reprography Unit, BIS, New Delhi, India

Indian Standard

METHODS OF TEST FOR COAL AND COKE

PART IV ULTIMATE ANALYSIS

Section I Determination of Carbon and Hydrogen

(First Revision)

0. FOREWORD

0.1 This Indian Standard (Part IV/Sec 1) (First Revision) was adopted by the Indian Standards Institution on 18 January 1974, after the draft finalized by the Solid Mineral Fuels Sectional Committee had been approved by the Chemical Division Council.

0.2 Part of the contents of this standard was first published as IS : 1351-1959 'Methods of test for coal and coke — ultimate analysis'. In the light of the experience gained in the country and the ISO recommendations published on this subject, the Committee responsible for the preparations of this standard, decided to revise it and issue it as Part IV of IS : 1350*. This section (Section 1) covers the determination of carbon and hydrogen contents. Section 2 covers determination of nitrogen; sulphur having been covered in Part III of this standard. With the publication of the revised standard as Part IV of IS : 1350, IS : 1351-1959 shall stand withdrawn.

0.3 In this standard three methods of determination of carbon and hydrogen have been prescribed. The one given in **5.1** is a modification of the Fentons method developed at the Central Fuel Research Institute (CSIR), Dhanbad. The CFRI method, as it is called, is considerably quicker than the Liebig method given in **5.2** and is popular in the country. The high-temperature combustion method given in **5.3** and the Liebig method are based on the following publications issued by the International Organization for Standardization:

ISO/R 609-1967 Determination of carbon and hydrogen in coal and coke by the high-temperature combustion method

ISO/R 625-1967 Determination of carbon and hydrogen in coal and coke by the Liebig method

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*Methods of test for coal and coke.

0.4 In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

1. SCOPE

1.1 This standard (Part IV/Sec 1) prescribes the methods of determination of carbon and hydrogen contents in coal.

NOTE — These methods are applicable equally to coke, brown coals and lignites.

2. TERMINOLOGY

2.1 For the purpose of this standard the term ' ultimate analysis ' shall mean the analysis of coal expressed in terms of its carbon, hydrogen, nitrogen sulphur and oxygen contents.

3. QUALITY OF REAGENTS

3.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1960†) shall be employed in tests.

NOTE — ' Pure chemicals ' shall mean chemicals that do not contain impurities which affect the results of analysis.

4. SAMPLE

4.1 For the purpose of ultimate analysis, coal sample shall be prepared in accordance with **10** of IS : 436 (Part I)-1964‡ and coke sample, in accordance with **2.4** of IS : 436 (Part II)-1965§.

5. DETERMINATION OF CARBON AND HYDROGEN

5.0 General — The CFRI method given in **5.1** shall be used as a routine method and the Liebig method or the high-temperature combustion method shall be used as referee method in case of a dispute.

5.0.1 The results obtained include the carbon in the carbonates and the hydrogen combined in the moisture and in the water of hydration of silicates. A determination of carbon dioxide may be carried out in accordance with **4** of IS : 1352-1959|| and the total carbon value corrected for the presence of mineral carbonates. Similarly, determination of moisture is carried out at the same time in accordance with **6** of IS : 1350 (Part I)-1969¶ and appropriate correction is applied to the hydrogen value obtained by combustion.

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*Rules for rounding off numerical values (*revised*).

†Specification for water, distilled quality (*revised*).

‡Methods for sampling of coal and coke: Part I Sampling of coal (*revised*).

§Methods for sampling of coal and coke: Part II Sampling of coke (*revised*).

||Methods of test for coal and coke — special impurities.

¶Methods of test for coal and coke: Part I Proximate analysis (*first revision*).

5.1 The Central Fuel Research Institute (CFRI) Method

5.1.0 *Principle* — The sample is burnt in a current of oxygen. All the hydrogen is converted into water and all the carbon to carbon dioxide. The products are absorbed by suitable reagents and determined gravimetrically. Oxides of sulphur are retained by lead chromate, chlorine by silver gauze and oxides of nitrogen by red lead.

5.1.1 *Apparatus* — An assembly of the apparatus is shown in Fig. 1. Details are given below.

5.1.1.1 *Metering and purification train* — for regulating the flow of oxygen and absorbing water vapour and carbon dioxide present in oxygen. Assemble the train in the order stated:

a) *Calibrated U-tube type flowmeter* — for measuring gas flow which is about 200 to 250 ml per minute;

b) *Bubbler containing concentrated sulphuric acid* (*see* IS : 266-1961*) — for absorbing water;

c) *Bubbler* — empty. For retaining any acid which may come from (b) above;

d) *U-tube containing soda-asbestos* — for absorbing carbon dioxide; and

e) *U-tube containing anhydrous magnesium perchlorate* (*anhydrone*) — for absorbing the water evolved in the reaction between carbon dioxide and soda-asbestos.

NOTE — The purification train should be large enough to render frequent charging unnecessary even with continuous use.

5.1.1.2 *T-Piece inlet* — made of fused silica or hard glass.

5.1.1.3 *Pusher rod* — made of fused silica with a disc-end 12 mm in diameter for pushing the boat into the furnace.

5.1.1.4 *Combustion device* — consisting of the following and arranged as shown in Fig. 2:

a) *Furnaces* — The combustion device is heated by two furnaces, the lengths of which are given below for a combustion tube 80 cm in length. These are constructed by winding nichrome wire of diameter 0·38 mm on silica tube of internal diameter 25 mm and wall thickness 1 mm.

   1) *Furnace No.* 1 — 35 cm in length, to heat the boat and its contents and the platinum gauze (*see* Fig. 2) to a temperature of 800 to 900°C.

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*Specification for sulphuric acid (*revised*).

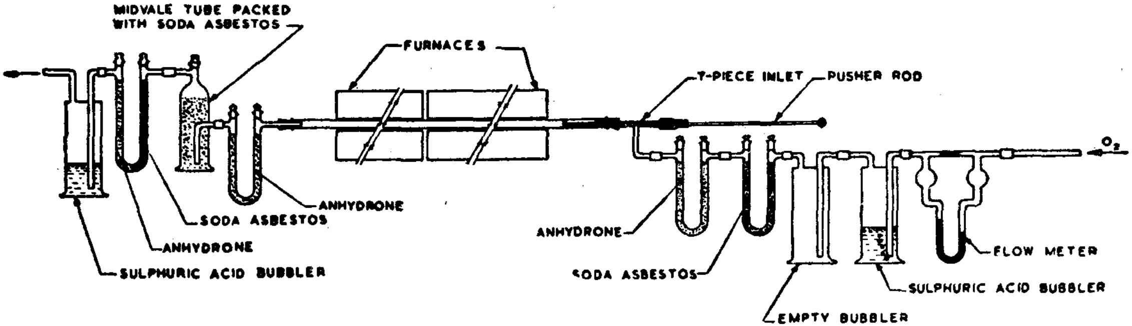

FIG. 1 ASSEMBLY OF APPARATUS — CFRI METHOD

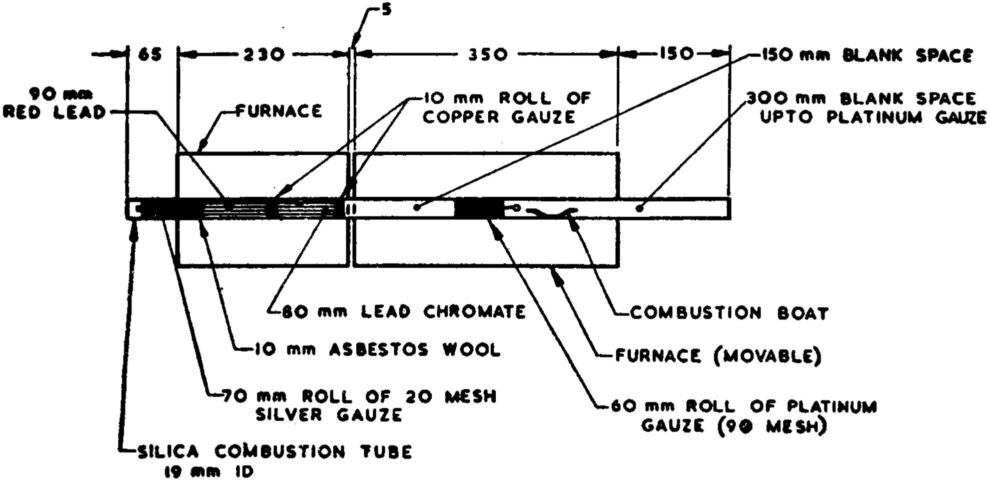

FIG. 2 DETAILS OF FURNACES AND COMBUSTION TUBE

2) *Furnace No.* 2 — 23 cm in length, to heat the copper gauze, lead chromate, red lead and silver gauze (*see* Fig. 2) to a temperature of 550°C up to a length of 9 cm and providing a temperature gradient from 550 to 250°C along the remaining 14 cm such that in the last 9 cm of length temperature is in the range of 350 to 250°C.

NOTE — If the supply voltage is 230 V, 50 cps, the control of temperature is conveniently effected by one kilowatt energy regulator.

b) *Combustion tube* — made of fused silica. For a combustion tube 80 cm long and 19 mm in internal diameter, the following arrangement of packing (*see* Fig. 2) beginning at the end connected to the purification train is suitable.

Arrangement of Packing	*Length*, cm
Space for stopper	1
Blank space	30
Plug of platinum gauze	6
Blank space	15
Roll of copper gauze	1
Packing of fused granular lead chromate	8
Roll of copper gauze	1
Packing of red lead	9
Packing of ignited asbestos wool	1
Roll of silver gauze	7
Space for stopper	1
Total	80

c) *Combustion boat* — made of unglazed porcelain or fused silica, approximately 8 cm long.

5.1.1.5 *Absorption train* — for absorbing the water and carbon dioxide evolved by the combustion of the sample. A typical absorption train with details of the packing is shown in Fig. 1. Assemble the train using the following reagents in the order stated:

a) *Anhydrous magnesium perchlorate* (*anhydrone*) — in a U-tube for absorbing the water evolved during combustion;

b) *Soda-asbestos* — in a Midvale tube for absorbing carbon dioxide;

c) *Soda-asbestos and anhydrous magnesium perchlorate* (*anhydrone*) — packed separately in the two arms of a U-tube, to absorb carbon dioxide and the water produced in the reaction between carbon dioxide and soda-asbestos; and

d) *Concentrated sulphuric acid* — contained in a bubbler to indicate the flow of oxygen and to prevent any back flow of air to the absorbents.

5.1.1.6 *Balance* — sensitive to 0·1 mg.

5.1.2 *Reagents*

5.1.2.1 *Concentrated sulphuric acid* — of relative density 1·84 (*see* IS : 266-1961*).

5.1.2.2 *Soda-asbestos* — size range 0·7 to 1·2 mm, preferably of self-indicating type.

5.1.2.3 *Anhydrous magnesium perchlorate* (*anhydrone*) — free from dust and within the size range 0·4 to 2·4 mm, preferably within the size range 0·7 to 1·2 mm.

> CAUTION — Regeneration of magnesium perchlorate should not be attempted owing to the risk of explosion. When exhausted, the magnesium perchlorate should be washed down the sink with a current of water.

5.1.2.4 *Platinum gauze* — made of platinum or platinum-rhodium alloy, 180 micron.

5.1.2.5 *Copper gauze* — 425 micron.

5.1.2.6 *Pure silver gauze* — approximately 710 micron.

5.1.2.7 *Oxygen* — hydrogen-free. Oxygen shall be prepared preferably from liquid air, and not by electrolysis. Electrolytically prepared oxygen shall be passed over red-hot copper oxide before use to remove any trace of hydrogen.

5.1.2.8 *Lead chromate* — fused, size range 0·7 to 1·2 mm.

5.1.2.9 *Red lead* — prepared by making a paste of lead oxide with water, flattening it out on a clock-glass, drying at 110°C, cutting it into small cubical pieces and then heating at 400°C till fully covered with red lead.

5.1.3 *Setting up the Apparatus and Blank Determination*

5.1.3.0 *General* — In setting up the assembly, use glass-to-glass joints and, as far as possible, a minimum of rubber connections to avoid leakage of gas. Grease used for lubricating should have low vapour pressure.

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*Specification for sulphuric acid (*revised*).

5.1.3.1 Before starting a determination with a newly packed combustion tube, heat the tube throughout its length as stated in **5.1.1.4**(a), while passing a current of oxygen at a rate of about 200 ml per minute, for a few minutes.

5.1.3.2 *Blank determinations* — For a blank determination connect the absorption train to the apparatus and purge it with oxygen for 20 minutes at the rate of 200 ml per minute with the furnaces at their working temperatures. Disconnect the absorbers from the train, stopper the side arms and close the taps and allow them to cool to the balance room temperature. Wipe each absorber with a clean cloth, remove the stoppers from the side arms and weigh. Re-connect the absorption train to the combustion tube and re open the taps, particular care being taken to ensure that the inlet of the water-absorption U-tube of the absorption train is flush with the inner end of the rubber stopper in the combustion tube and that all joints between the component parts of the absorption train are made by bringing the ends of tubes close together using the rubber tubing merely as a seal. After the absorption train has remained attached to the apparatus for 15 minutes, stop the oxygen flow, remove and weigh the absorbers as before, observing the same precautions as in the initial weighing. The difference in the mass of the anhydrone tube gives the blank value for moisture for 15 minutes (at 200 ml per minute flow of oxygen); and the difference in the masses of the Midvale tube and the guard tube added together gives the blank value for carbon dioxide.

5.1.4 *Procedure* — When starting the first determination on each day, raise the temperatures of the furnaces as given in **5.1.1.4**(a) while passing oxygen at the rate of 200 ml per minute. Connect the absorption train and purge for 20 minutes. Stop the oxygen flow, disconnect the train and weigh absorbers as described in **5.1.3.2**. Before commencing the determination, mix thoroughly for at least one minute preferably by mechanical means the air-dried sample of coal, ground to pass 212-micron IS Sieve. Re-expose a small portion of the sample to the air for a few hours and again mix before weighing out the quantity required for the determination.

IMPORTANT — A determination of moisture shall be made immediately on the remainder of this small sample.

5.1.4.1 Weigh accurately 0·2 to 0·25 g of the sample and spread it evenly over the bottom of a previously ignited boat. Cover it with folded platinum gauze. Connect the weighed absorption train to the combustion tube as described above and transfer the boat quickly to the combustion tube. Turn on the oxygen supply slowly. After 30 to 40 seconds increase the flow to 200 ml per minute and push the boat forward slowly by the pusher rod so that the other end of the boat just enters the high temperature furnace. The sample catches fire. After 2 to 3 minutes of combustion, push the boat further ahead by stages so that in 6 to 7 minutes, the rear end of the boat just enters the furnace. In about 30 seconds, the boat is pushed into the central and the hottest part. Though the combustion should be complete by this time, allow another 7 minutes to ensure decomposition of carbonates and removal of the products of combustion to the absorbers. Turn off the oxygen supply, detach the absorbers from the train, allow to cool to the balance room temperature and weigh as stated in **5.1.3.2**.

NOTE — On cooling, the pressure of oxygen inside the absorbers falls below atmospheric pressure. To equalize this, connect the train to the oxygen supply to fill the absorbers with oxygen. Alternatively, open the absorbers to air momentarily. This introduces to measurable error.

5.1.4.2 Carefully inspect the ash in the boat for unburnt carbon; if it is present, it shall invalidate the determination which shall then be repeated.

5.1.5 *Calculation* — Calculate the percentage of carbon and hydrogen by mass, as follows:

a) $C = 27{\cdot}29 \dfrac{m_2}{m_1}$, and

$C_1 = C - 0{\cdot}273\, CO_2$

b) $H = 11{\cdot}19 \dfrac{m_3}{m_1}$, and

$H_1 = H - 0{\cdot}111\,9\, M - (0{\cdot}1\, A \times 0{\cdot}111\,9)$

where

m_1 = mass in g of the sample taken for the test;

m_2 = increase in mass in g of the soda-asbestos tube;

m_3 = increase in mass in g of the magnesium perchlorate tube;

M = moisture in the sample as analysed, expressed as a percentage;

CO_2 = carbon dioxide in the sample (*see* **5.0.1**), expressed as a percentage;

C = total carbon in the sample as analysed, expressed as a percentage;

C_1 = total carbon less that present as carbon dioxide, expressed as a percentage;

H = total hydrogen in the sample as analysed, expressed as a percentage;

H_1 = total hydrogen less that present as moisture, expressed as a percentage; and

A = percentage of ash in coal sample as fired.

NOTE — The factor 0·1 A is the correction for the water of hydration associated with mineral matter in coal. This, however, varies from coal to coal; the average proportion being 10 percent of ash in the case of Indian coal. For precise estimation it is necessary to determine water of hydration, particularly in the case of high ash coals.

5.2 The Liebig Method

5.2.0 *Principle* — The sample is burnt in a current of oxygen, the products of the incomplete combustion being burnt over copper oxide; all the hydrogen is converted to water and all the carbon to carbon dioxide. These products are absorbed by suitable reagents and determined gravimatrically. Oxides of sulphur are retained by lead chromate, chlorine by silver gauze and oxides of nitrogen (*see* Note) by granular manganese dioxide. If water is condensed in the first absorber, some nitrogen peroxide may dissolve in it and be considered as water. Because of the conversion factor from water to hydrogen, the error in the hydrogen determination thus caused is small, of the order of 0·05 percent of hydrogen. This can be avoided only by heating the absorption tube to a sufficient temperature to prevent condensation of water.

NOTE — Oxides of nitrogen formed in the combustion would, in the absence of precautions, be absorbed by soda-asbestos and considered as carbon dioxide. The error in the carbon determination thus caused (of the order of 0·2 percent of carbon) is substantially avoided by the use of a guard tube (*see* Fig. 3) in which the gases pass through an annular-space to allow oxidation of nitric oxide to nitrogen peroxide, which is absorbed by the manganese dioxide.

5.2.1 *Apparatus*

5.2.1.1 *Purification train* — for absorbing water vapour and carbon dioxide present in the oxygen. Assemble the train using the following reagents in the order stated:

a) *Anhydrous magnesium perchlorate* (*anhydrone*) — for absorbing water,

b) *Soda-asbestos* — for absorbing carbon dioxide, and

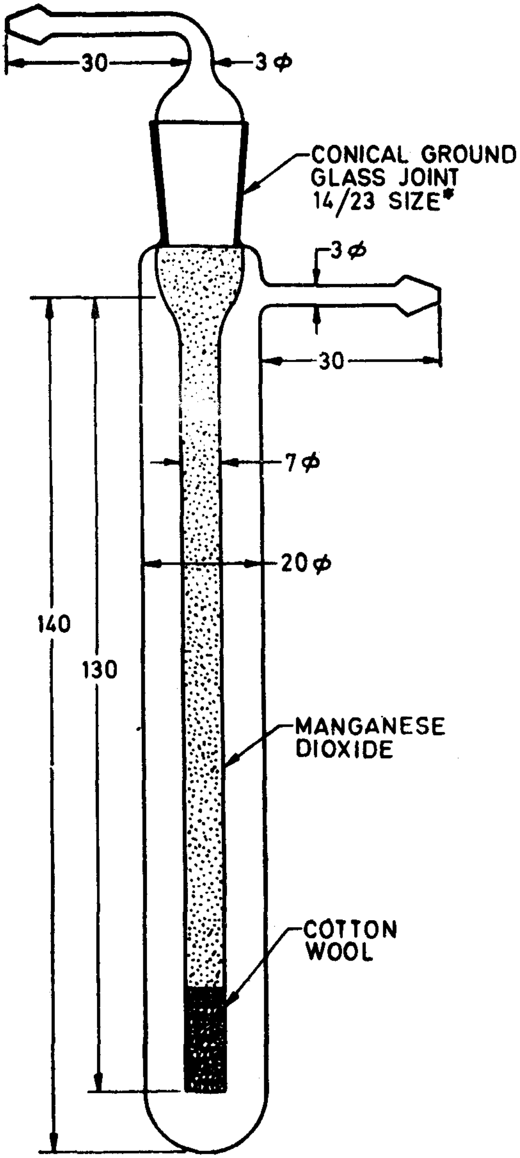
c) *Anhydrous magnesium perchlorate* (*anhydrone*) — for absorbing the water evolved in the reaction between carbon dioxide and soda-asbestos.

NOTE — The purification train should be large enough to render frequent recharging unnecessary even with continuous use.

5.2.1.2 *Combustion device* — consisting of the following:

a) *Furnaces* — The combustion tube is heated by three furnaces, the lengths of which are given below for a combustion tube 127 cm in length:

   1) *Furnace No.* 1 — to heat the boat and its contents to 925°C. The furnace covers a length of 24 cm.



*See IS : 5165-1969 Specification for interchangeable conical ground-glass joints

All dimensions in millimetres.

FIG. 3 GUARD TUBE

2) *Furnace No.* 2 — to heat the copper oxide section of tube throughout to 800°C. The furnace covers a length of 47 cm.
3) *Furnace No.* 3 — to cover the lead chromate and the roll of pure silver gauze, and to heat the former to about 500°C. The furnace covers a length of 21·5 cm.

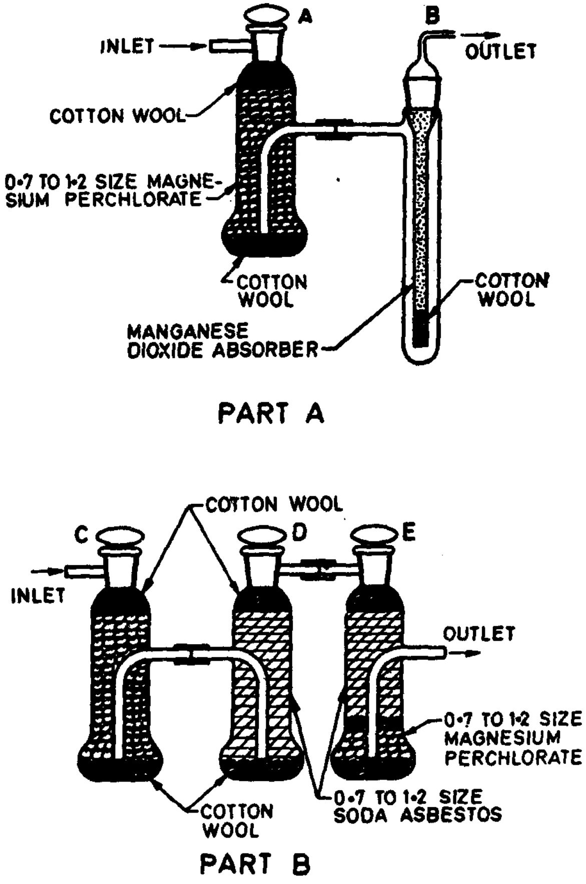
b) *Combustion tube* — of fused silica. For a combustion tube 127-cm long and 12 to 15 mm in diameter, the following arrangement of packing, beginning at the end connected to the purification train is suitable:

Arrangement of Packing	*Length,* cm
Space for a rubber stopper	1
Space to allow the furnace to be removed behind and away from the boat	30
Spiral of copper gauze through which passes a stout copper wire provided with a loop for convenience in withdrawal	8
Space for the boat	7
Space to prevent the boat being heated too soon	5
Roll of copper gauze	1
Packing of copper oxide	47
Roll of copper gauze	1
Packing of lead chromate	10
Roll of copper gauze	1
Roll of pure silver gauze	10
Blank space	5
Space for a rubber stopper	1
Total	127

NOTE — The copper gauze spiral and rolls are oxidized during preliminary heating in a current of oxygen.

c) *A combustion boat* — made of platinum, porcelain or fused silica, approximately 7 cm long.

5.2.1.3 *Absorption train* — for absorbing the water and carbon dioxide evolved by the combustion of the sample. A typical absorption train, with details of the packing is shown in Fig. 4. Assemble the train by joining



All dimensions in millimetres.

FIG. 4 ABSORPTION TRAIN FOR LIEBIG METHOD

Parts A and B as given in Fig. 4 using the following reagents in the order stated:

a) *Anhydrous magnesium perchlorate* (*anhydrone*) — for absorbing the water evolved during the combustion (*see A* in Fig. 4),

b) *Granular manganese dioxide* — for absorbing oxides of nitrogen (*see B* in Fig. 4),

c) *Anhydrous magnesium perchlorate* (*anhydrone*) — for absorbing the water evolved from the manganese dioxide (*see C* in Fig. 4).

d) *Soda-asbestos* — for absorbing carbon dioxide (*D* and *E* in Fig. 4), and

e) *Anhydrous magnesium perchlorated (anhydrone)* — for absorbing the water produced in the reaction between carbon dioxide and soda-asbestos (*see E* in Fig. 4).

NOTE 1 — Cotton wool is placed above and below the absorbents to prevent carry over of dust by the rapid flow of oxygen and the cracking of soda asbestos tube by the heat of reaction. In Fig. 4, *A* is the absorber for water, *B* for oxides of nitrogen, and *C* for water evolved from the manganese dioxide. *D* and *E* are absorbers for carbon dioxide *E* serving as a control to indicate when the packing in *D* is in need of replacement. Any water produced in the reaction between soda-asbestos and carbon dioxide is absorbed in *E*.

NOTE 2 — Stoppered U-tubes may be used, if preferred, in place of the Midvale tubes (*see* Fig. 5). Midvale tubes which provide a large area of reaction, are used to reduce the back pressure in the apparatus and to avoid the danger of leakage through the rubber sleeve carrying the pusher.

NOTE 3 — It is permissible to use sulphuric acid (relative density 1·84) in place of the solid reagents in the water absorbing units, in which case a separate bubbler is unnecessary, but particular care is required to ensure that the acid is not carried or drawn into any other part of the train during a determination.

5.2.1.4 *Control for oxygen flow rate* — A reducing valve on the oxygen cylinder together with a small needle valve immediately before the purification train is generally adequate. A bubbler device may usefully be attached at the exit end of the assembled apparatus to give a visual indication of the rate of flow.

5.2.1.5 *Balance* — sensitive to 0·1 mg.

5.2.2 *Reagents*

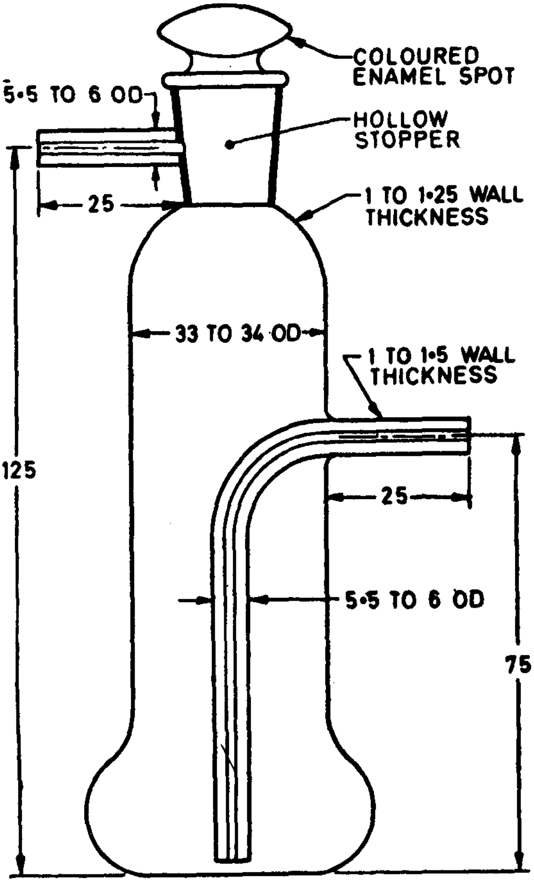
5.2.2.1 *Anhydrous magnesium perchlorate* (*anhydrone*) — same as in **5.1.2.3**.

5.2.2.2 *Manganese dioxide, granular* — Dissolve manganese sulphate in water and boil the solution. Make it alkaline with dilute ammonia and add solid ammonium persulphate, in small portions, to the boiling solution until precipitation is complete. Filter through a fast hardened paper, wash with water by decantation, then with dilute sulphuric acid and finally with water until acid-free. Transfer the moist precipitate to a mortar and place in an oven until most of the water has evaporated, but the powder is still damp. Press the mass into a cake with a pestle, using firm pressure. Complete the drying, break up the cake cautiously and sieve to separate the 0·7 to 1·2-mm size.

5.2.2.3 *Soda-asbestos* — same as **5.1.2.2**.

5.2.2.4 *Copper gauze* — same as in **5.1.2.5**.

5.2.2.5 *Copper oxide* — wire form.



All dimensions in millimetres.

FIG. 5 MIDVALE TUBE

5.2.2.6 *Lead chromate* — same as in **5.1.2.8**.

5.2.2.7 *Pure silver gauze* — approximately 10 meshes per centimetre, made of wire 0·3 mm in diameter.

5.2.3 *Setting up the Apparatus and Blank Determination.*

5.2.3.0 *General* — In setting up the assembly use glass-to-glass joints and as far as possible, a minimum of rubber connections to avoid leakage of gas. Grease used for lubricating should have low vapour pressure.

5.2.3.1 Before starting a determination with a newly-packed combustion tube, heat the tube throughout its length, while passing a current of oxygen at a rate of about 12 ml per minute. Heating should be continued for 3 hours, with furnace No. 1 at a temperature of 925°C, furnace No. 2 at a temperature of 800°C and furnace No. 3 containing the portion of the tube packed with lead chromate and pure silver gauze, at a temperature of about 500°C. The empty space adjacent to the exit and of the tube should be heated in such manner that, without charring the rubber stopper, condensation of steam is avoided.

5.2.3.2 *Blank determination* — For a blank determination, connect the absorption train to the apparatus and purge with oxygen for 20 minutes, with the furnaces at their working temperatures. Disconnect absorbers *A, D* and *E* from the absorption train, stopper the side arms and close the taps, and allow them to cool to the balance room temperature. Wipe each absorber with a clean cloth, remove the stoppers from the side arms and weigh each absorber. Re-connect the absorption train to the combustion tube and reopen the taps, particular care being taken to ensure that the inlet of the water-absorption tube of the absorption train is flush with the inner end of the rubber stopper in the combustion tube and that all joints between the component parts of the absorption train are made by bringing the ends of tubes close together, using the rubber tubing merely as a seal. After the absorption train has remained attached to the apparatus for 2 hours, stop the oxygen flow, remove and weigh absorbers *A, D* and *E* as before, observing the same precautions as in the initial weighing. If each of these absorbers is within 0·000 5 g of its previous mass, the apparatus is considered to be in proper condition for use.

NOTE — Absorbers *A, D* and *E* should be weighed full of oxygen before and after a determination, purging with air being unnecessary; absorbers *B* and *C* are not weighed.

5.2.4 *Procedure* — When starting the first determination on each day, raise the temperature of the furnaces to 925°C, 800°C and 500°C, respectively, while passing oxygen at the rate of 12 ml per minute. Connect the absorption train and purge for 20 minutes. Stop the oxygen flow; disconnect the train and weigh absorbers *A, D* and *E* as described in **5.2.3.2**. Switch off furnace No. 1 and allow it to cool. This may be done during the weighing of the absorption apparatus and of the sample to be burnt. Before commencing the determination, mix thoroughly for at least one minute, preferably by mechanical means, the air-dried sample of coal ground to pass 212-micron IS Sieve. Re-expose a small portion of the sample to the air for a few hours and again mix before weighing out the quantity required for the determination.

IMPORTANT — A determination of moisture shall be made immediately on the remainder of this small sample.

5.2.4.1 Weigh accurately 0·2 to 0·3 g of the sample and spread evenly over the bottom of a previously ignited boat. Connect the weighed absorption train to the combustion tube as described above. Place the boat and the oxidized copper roll in the combustion tube, insert the rubber stopper connecting the purification train and pass oxygen through the apparatus at a rate of about 12 ml per minute. Switch on furnace No. 1 and start the combustion by heating the copper roll; when this is at 800°C, gradually draw the furnace forward to cover the boat and its contents, keeping a steady stream of oxygen through the whole system while the sample is being burned. Continue heating until all visible carbon has disappeared and until the portion of the combustion tube containing the sample has been raised to 925°C.

5.2.4.2 After combustion is complete, switch off furnace No. 1, allow the exit end of the combustion tube to cool, and disconnect the absorption train. Wipe absorbers *A*, *D* and *E*, allow them to cool as before, and weigh.

Note — Two hours are usually sufficient to complete the combustion of coal samples and one hour may be sufficient for most coke samples.

5.2.4.3 Carefully inspect the ash in the boat for unburnt carbon; if it is present, it shall invalidate the determination, which shall then be repeated.

5.2.5 *Calculation* — Calculate the percentage of carbon and hydrogen as given in **5.1.5**.

5.3 High-Temperature Combustion Method

5.3.0 *Principle* — The sample is burnt in a rapid current of oxygen at a high temperature in an impervious tube; all the hydrogen is converted to water and all the carbon to carbon dioxide. These products are absorbed by suitable reagents and determined gravimetrically. Oxides of sulphur and chlorine are retained by a silver gauze roll at the outlet end of the tube.

5.3.1 *Apparatus*

5.3.1.1 *Purification trains* — Two, one for absorbing water vapour and carbon dioxide from the oxygen used for the combustion and the other for similarly treating the air used for sweeping out the absorption train before and after a determination. Assemble each train as prescribed in **5.2.1.1**.

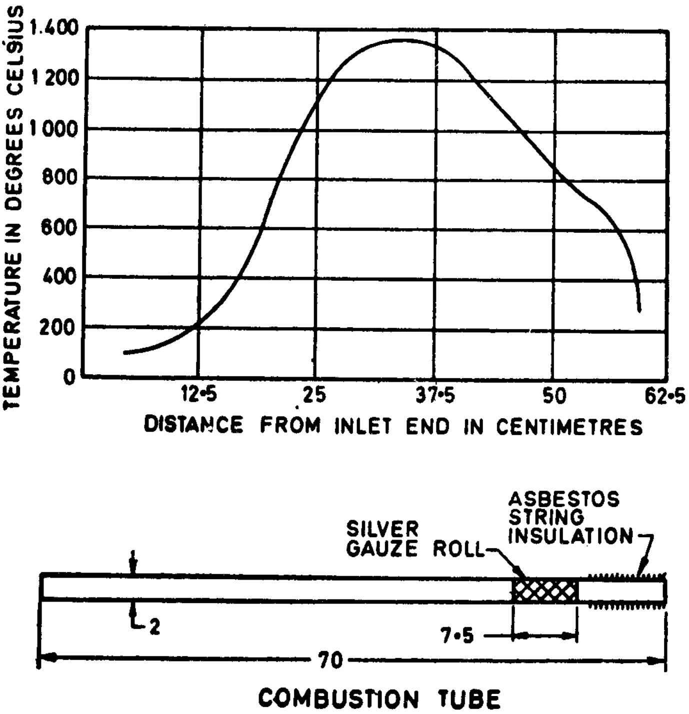
5.3.1.2 *Combustion device* — consisting of the following:

a) *A furnace* — capable of carrying a tube approximately 25 mm outside diameter and heating it over a length of approximately 12·5 cm to over 1 250°C and up to a maximum of 1 350°C. Suitable furnaces are as follows:

   1) molybdenum or tungsten wire wound,

2) platinium or platinum-rhodium wire wound, and
3) heated by silicon carbide rods.

A temperature-distribution curve for a typical furnace is shown in Fig. 6.



All dimensions in millimetres.

FIG. 6 TYPICAL TEMPERATURE-DISTRIBUTION CURVE FOR FURNACE

NOTE — Furnace 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.

b) *A combustion tube* — approximately 20 mm internal diameter and approximately 70 cm long, made of refractory aluminous porcelain which is not permeable to gases at 1 400°C.

c) *A combustion boat* — of iron-free unglazed porcelain approximately 6 cm long and 12·5 mm wide and 10 mm deep, capable of withstanding a temperature of 1 350°C.

Note — Boats should not blister, discolour or change in mass on heating in oxygen at 1 350°C for 3 hours. A suitable boat may last for about 10 to 20 determinations and should then be discarded because of the accumulation of fused ash. For high ash coals, it may be convenient to line the boat with alumina before adding the sample, in order to prevent fusion of the ash to the boat.

5.3.1.3 *An absorption train* — for absorbing the water and carbon dioxide evolved by the combustion of the sample. A typical absorption train, with details of packing is shown in Part B of Fig. 4. Midvale tubes (*see* Fig. 5), which provide a large area of reaction, are used to reduce the back pressure in the apparatus and to avoid the danger of leakage through the rubber sleeve carrying the pusher. Assemble the train (*see* Part B of Fig. 4) using the following reagents in the order stated:

a) *Anhydrous magnesium perchlorate* (*anhydrone*) — for absorbing the water evolved during the combustion (*see C* in Fig. 4),

b) *Soda-asbestos* — for absorbing carbon dioxide (*see D* and *E* in Fig. 4), and

c) *Anhydrous magnesium perchlorate* (*anhydrone*) — for absorbing the water evolved in the reaction between carbon dioxide and soda-asbestos (*see E* in Fig. 4).

Note — Cotton wool is placed above the absorbents to prevent carryover of dust by the rapid flow of oxygen and the cracking of the soda-asbestos tube by the heat of reaction. *C* is the absorber for water; *D* and *E* are the absorbers for carbon dioxide, *E* serving as a control to indicate when the packing in *D* is in need of replacement. Any water produced in *D* by the reaction between soda-asbestos and carbon dioxide is absorbed in *E*.

5.3.1.4 *Flow meters* — two; one capable of measuring rates of flow up to 300 ml per minute and the other to 250 ml per minute.

5.3.1.5 A U-gauze to measure the resistance of the system.

Note — The normal back pressure on the system is 50 to 79 mm H_2O.

5.3.1.6 *A heat-resisting stopper* — made of acrylonitrile or chloroprene for connecting the absorption train to the combustion tube.

5.3.1.7 *A silica pusher* — With a disc end 12 mm in diameter for pushing the boat into the furnace. It is about 45 cm long, made from 6 mm diameter silica rod flattened at one end, or from a 6 mm diameter silica tube sealed and flattened similarly. The pusher passes loosely through a glass T-piece, one end of which fits into the rubber stopper which closes the inlet end of the combustion tube, the other being sealed with a rubber sleeve through which the pusher slides. Oxygen is admitted through the limb of the T-piece. The pusher is marked from the disc-end for convenience in ascertaining the position of the boat in the combustion tube during pushing.

Note — This sleeve should be changed periodically to avoid loss by leakage.

5.3.1.8 *Balance* — sensitive to 0·1 mg.

5.3.2 *Reagents*

5.3.2.1 *Anhydrous magnesium perchlorate* (*anhydrone*) — same as in 5.1.2.3.

5.3.2.2 *Soda-asbestos* — same as in 5.1.2.2.

5 3.2.3 *Alumina* — finely divided, approximately 0·1 mm in size.

5.3.2.4 *Sodium borate solution* — 0·05 N approximately.

5.3.2.5 *Hydrogen peroxide* — 1 percent (*v*/*v*) neutral solution.

5.3.2.6 *Pure silver gauze* — same as in 5.1.2.6.

5.3.2.7 *Oxygen* — same as in 5.1.2.7.

5.3.3 *Preparation of the Apparatus*

5 3.3.1 *Preparation of combustion tube* — Insert the combustion tube into the furnace so that it projects 7·5 cm at the exit end. Wrap this projecting portion with asbestos string 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 purified oxygen supply to the limb of the glass T-piece.

5.3.3.2 *Preparation and location of silver gauze* — The roll of silver gauze through which passes a stout silver wire provided with a loop for convenience of withdrawal, should be 7·5 cm long and of sufficient diameter to ensure a close sliding fit in the combustion tube. Insert the silver gauze roll into the exit end of the combustion tube to a distance of about 7·5 cm. With the furnace at its working temperature of 1 350°C, connect a bubbler containing solution of the hydrogen peroxide to the exit end of the combustion tube by means of a heat-resisting stopper. Burn 0·5 g of coal containing 1 to 2 percent of sulphur by the procedure described below. Determine the amount of oxides of sulphur passing the silver gauze roll by titration of the hydrogen peroxide against the sodium borate solution. Move the silver gauze roll in 5-mm stages and repeat the test until a position is found where the volume of the sodium borate solution corresponding to the end point is not more than 0·2 ml, which will represent at least 99 percent retention of the oxides of sulphur by the silver gauze roll. Note its exact location.

NOTE — The silver gauze roll can absorb sulphur equivalent to 7 percent of the sample, for higher sulphur contents, the mass of the coal sample should be proportionately reduced. The roll should be periodically cleaned by boiling in water (to remove silver sulphate), in concentrated ammonia solution (to remove silver chloride) and finally in water, after which it should be dried. The total sulphur content of the samples examined between two cleanings of the roll should not exceed 0·035 g.

5.3.4 *Procedure* — Raise the furnace to its working temperature of 1 350°C and confirm that the silver gauze roll is in its correct position. Admit oxygen to the apparatus about 30 minutes before the temperature reaches 1 350°C and adjust the rate of flow to 300 ml/min. Before commencing the determination, mix thoroughly for at least 1 minute, preferably by mechanical means, the air-dried sample of coal, ground to pass 212-micron IS Sieve. A small portion of the sample should be re-exposed to air for a few hours and again mixed before weighing the quantity required for the determination.

> IMPORTANT — A determination of moisture shall be made immediately on the remainder of this small sample.

5.3.4.1 Spread about 0·5 g of the sample evenly over the bottom of a dried boat and weigh accurately. Cover with about 0·5 g of alumina (with care 0·5 g of alumina can be made to blanket completely the sample in the boat). Connect a previously weighed absorption train and insert the charged boat into the combustion tube to a position such that its centre is 22·5 cm from the centre of the hottest zone. With the silica pusher fully withdrawn, replace the rubber stopper and continue to pass oxygen at a rate of 300 ml/min. At the end of each of the next six one-minute periods push the boat forward about 3·75 cm, withdrawing the silica pusher each time to prevent distortion; after the last push the centre of the boat should be at the centre of the hottest zone.

NOTE 1 — Certain coals which liberate volatile matter at a high rate in the early stages of heating may give a carry over of carbon particles. For such coals, the rate of pushing should be reduced according to the following procedure:

> Insert the charged boat so that its centre is 22·5 cm from the centre of the hottest zone. At the end of the first minute, move the boat forward 38 mm. At the end of each of the next 8 minutes move the boat forward by 19 mm, and at the end of tenth minute move the boat forward by 38 mm. Allow the boat to remain in the hottest zone for a further 4 minutes.

NOTE 2 — For unreactive cokes, that is, those with less than 0·5 percent of volatile matter, the rate of pushing should also be reduced as described above.

5.3.4.2 Allow the boat to remain in the hottest zone for a further 4 minutes. Disconnect the absorption train, connect it to the purification train and purge it for 10 minutes with purified air at the rate of 200 to 250 ml/min. Disconnect the absorbers *C*, *D* and *E*, close the taps and stopper the central side arms and allow to cool.

NOTE — Midvale tubes used for the absorption of carbon dioxide cool slowly and 60 minutes should be allowed before weighing.

5.3.4.3 Wipe and remove the guard stoppers and weigh the absorbers.

NOTE — When not connected to the apparatus, the Midvale tubes should be protected from atmospheric contamination by closing the taps and fitting guard stoppers of plugged rubber tubing to the open limbs. It is usual to weigh the absorption tubes without guard stoppers, after wiping.

5.3.4.4 A bent nickel-chromium wire may be used to withdraw the heated boat, which is conveniently pulled on to a thick sheet of asbestos.

NOTE — The total moisture in the alumina is determined by heating 1 g to 1 350°C in the apparatus and absorbing the water in magnesium perchlorate. Drying of alumina at 108°C is unsuitable, since the water in the alumina is not liberated below 1 000°C. Only one or two determinations of moisture need be carried out on each bottle of alumina.

5.3.5 *Calculation* — Calculate the percentage of carbon and hydrogen by mass, as follows:

a) $C = 27{\cdot}29 \dfrac{m_2}{m_1}$, and

$C_1 = C - 0{\cdot}273\ CO_2$.

b) $H = 11{\cdot}19 \dfrac{m_3}{m_1}$, and

$H_1 = H - 0{\cdot}111\,9\,M - (0{\cdot}1\,A \times 0{\cdot}111\,9)$

where

m_1 = mass in g of the sample taken for the test,

m_2 = increase in mass in g of absorbers D and E,

m_3 = increase in mass in g of absorber C, less the moisture in the alumina used,

M = moisture in the sample as analysed, expressed as a percentage,

CO_2 = carbon dioxide in sample (*see* **5.0.1**) expressed as a percentage,

C = total carbon in the sample is analysed, expressed as a percentage,

C_1 = total carbon less that present as a carbon dioxide, expressed as a percentage,

H = total hydrogen in the sample as analysed expressed as a percentage,

H_1 = total hydrogen less that present as moisture, expressed as a percentage,

A = percentage of ash in coal sample as burnt (*see also* **5.1.5**).

6. EXPRESSION OF RESULTS AND PRECISION OF DETERMINATION

6.1 Expression of Results — The results, preferably the mean of duplicate determinations, shall be reported to the nearest 0·1 percent for the carbon determination and to the nearest 0·01 percent for the hydrogen determination.

6.2 Precision of Determination

6.2.1 *Repeatability* — The maximum acceptable difference between the results of duplicate determinations carried out at different times in the same laboratory by the same operator with the same apparatus on representative portions taken from the same analysis sample shall not differ by more than as follows:

For carbon ± 0·25 percent absolute, and

For hydrogen ± 0·12 percent absolute.

6.2.2 *Reproducibility* — The maximum acceptable difference between the mean of the results of duplicate determinations carried out in one laboratory and the mean of the results of duplicate determinations carried out in any other laboratory on representative portions from the same analysis sample shall not differ by more than as follows:

For carbon ± 0·6 percent absolute, and

For hydrogen ± 0·25 percent absolute.