INTERNATIONAL
STANDARD

ISO
625

Second edition
1996-02-15

Solid mineral fuels — Determination of carbon and hydrogen — Liebig method

Combustibles minéraux solides — Dosage du carbone et de l'hydrogène — Méthode de Liebig

Reference number
ISO 625:1996(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 625 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This second edition cancels and replaces the first edition (ISO 625:1975), which has been technically revised.

Annex A of this International Standard is for information only.

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Introduction

An alternative method to that specified in this International Standard is given in ISO 609:1996, *Solid mineral fuels — Determination of carbon and hydrogen — High temperature combustion method.*

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Solid mineral fuels — Determination of carbon and hydrogen — Liebig method

1 Scope

This International Standard specifies a method of determining the total carbon and the total hydrogen in hard coal, brown coal and lignite, and coke, by the Liebig method.

The results include the carbon in the carbonates and the hydrogen combined in the moisture and in the water of constitution of silicates. A determination of moisture is carried out at the same time, and an appropriate correction is applied to the hydrogen value obtained by combustion. A determination of carbon dioxide may also be made and the total carbon value corrected for the presence of mineral carbonates.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 331:1983, *Coal — Determination of moisture in the analysis sample — Direct gravimetric method.*

ISO 687:1974, *Coke — Determination of moisture in the analysis sample.*

ISO 925:1980, *Solid mineral fuels — Determination of carbon dioxide content — Gravimetric method.*

ISO 1015:1992, *Brown coals and lignites — Determination of moisture content — Direct volumetric method.*

ISO 1170:1977, *Coal and coke — Calculation of analyses to different bases.*

ISO 1988:1975, *Hard coal — Sampling.*

ISO 2309:1980, *Coke — Sampling.*

ISO 5068:1983, *Brown coals and lignites — Determination of moisture content — Indirect gravimetric method.*

ISO 5069-2:1983, *Brown coals and lignites — Principles of sampling — Part 2: Sample preparation for determination of moisture content and for general analysis.*

3 Principle

A known mass of coal or coke is burnt in a current of oxygen in a tube impervious to gases, the products of the incomplete combustion being further 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 gravimetrically. Oxides of sulfur are retained by lead chromate, chlorine by a silver gauze roll and oxides of nitrogen by granular manganese dioxide.

4 Reagents and materials

WARNING — Care should be exercised when handling reagents, many of which are toxic.

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Magnesium perchlorate, anhydrous, less than 1,2 mm in size and preferably within the size range 1,2 mm to 0,7 mm.

WARNING — Due regard must be taken of local regulations when disposing of exhausted magnesium perchlorate. Regeneration of magnesium perchlorate must not be attempted, owing to the risk of explosion.

4.2 Sodium hydroxide on an inert base, preferably of a coarse grading, for example 3,0 mm to 1,5 mm, but not finer than the grading 1,2 mm to 0,7 mm, and preferably of the self-indicating type.

4.3 Manganese dioxide, granular, 1,2 mm to 0,7 mm.

Manganese dioxide in the granular form and the size required can be prepared as follows.

Dissolve manganese sulfate in water and boil the solution. Make the solution alkaline with ammonium hydroxide and add solid ammonium persulfate, in small portions, to the boiling solution until precipitation is complete. Filter through a hardened fast-filter paper, wash with water by decantation, then with dilute sulfuric 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 1,2 mm to 0,7 mm size.

4.4 Copper gauze, of mesh approximately 1 mm and 10 mm wide.

4.5 Copper oxide, wire form, chopped to particles approximately 3 mm long with a diameter of approximately 0,2 mm.

4.6 Lead chromate, fused, size range 2,4 mm to 1,2 mm.

4.7 Pure silver gauze, of mesh approximately 1 mm, made of wire approximately 0,3 mm in diameter.

4.8 Oxygen, hydrogen-free, preferably prepared 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.

4.9 Glass wool.

5 Apparatus

5.1 Analytical balance, capable of weighing to the nearest 0,1 mg.

5.2 Purification train, for absorbing water vapour and carbon dioxide from the oxygen used for the combustion. Assemble the train using a series of U-tubes containing the following reagents in the order stated, in the direction of flow:

a) magnesium perchlorate (4.1) for absorbing water;

b) sodium hydroxide on an inert base (4.2) for absorbing carbon dioxide;

c) magnesium perchlorate for absorbing the water evolved in the reaction between carbon dioxide and sodium hydroxide.

The purification train shall be large enough to render frequent recharging unnecessary, even with continuous use.

5.3 Combustion assembly

5.3.1 Furnaces. The combustion tube is heated by three furnaces. For the 1,25 mm combustion tube described in clause 6, the following approximate lengths are appropriate:

a) furnace No. 1 (to heat the boat and its contents to 925 °C) — 250 mm;

b) furnace No. 2 (to keep the entire copper oxide section of the tube heated to 800 °C) — 500 mm;

c) furnace No. 3 (to cover the lead chromate and the roll of pure silver gauze and to heat the former to about 500 °C) — 200 mm.

5.3.2 Combustion tube, of fused silica or suitable hard glass. The diameter of the tube shall be 12 mm to 15 mm. A suitable length is 1,25 m.

5.3.3 Combustion boat, of platinum, porcelain or fused silica, approximately 70 mm long.

5.4 Absorption train, for absorbing the water and carbon dioxide evolved by the combustion of the sample. Assemble the train using the following reagents in the order stated, in the direction of flow.

a) magnesium perchlorate (4.1) for absorbing the water evolved during the combustion;

b) granular manganese dioxide (4.3) for absorbing oxides of nitrogen;

c) magnesium perchlorate for absorbing the water evolved from the manganese dioxide;

d) sodium hydroxide on an inert base (4.2) for absorbing carbon dioxide;

e) magnesium perchlorate for absorbing the water produced in the reaction between carbon dioxide and sodium hydroxide.

Midvale tubes (figure 1), which provide a large area of reaction, are used for all the reagents except manganese dioxide, which is contained in a guard tube (figure 2), providing a long contact time with minimum mass.

A typical absorption train, with details of the packing, is shown in figure 3. A is the absorber for water, B is a guard-tube absorber for oxides of nitrogen, and C absorbs any water evolved from the manganese dioxide. Carbon dioxide is absorbed in D, the magnesium perchlorate in the upper portion absorbing any water produced in the reaction between carbon dioxide and sodium hydroxide. A second carbon dioxide absorber, E, should be added as a precautionary measure.

Dimensions in millimetres

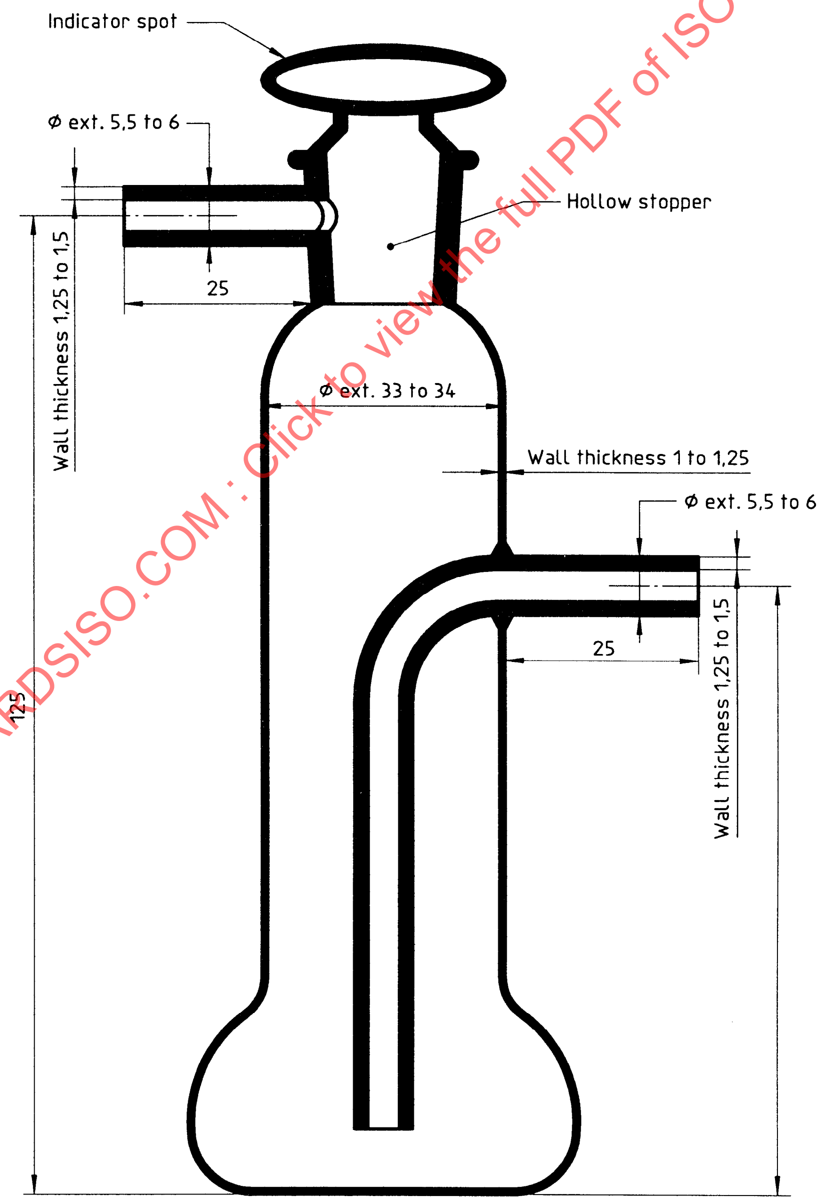


Figure 1 — Midvale tube

Dimensions in millimetres

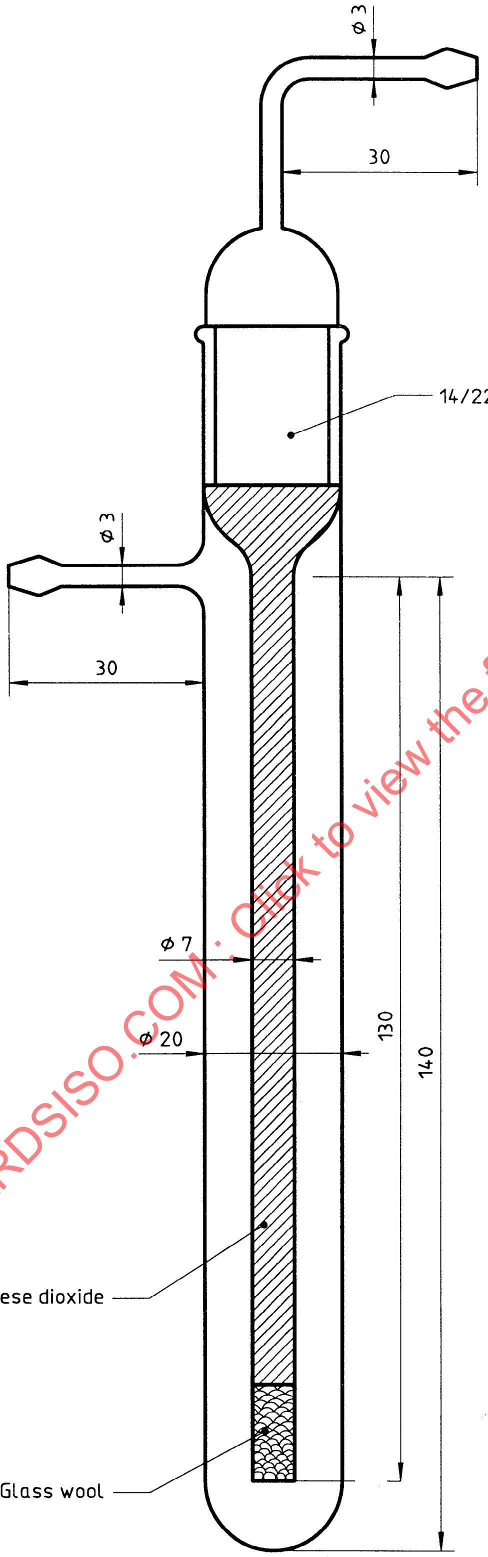
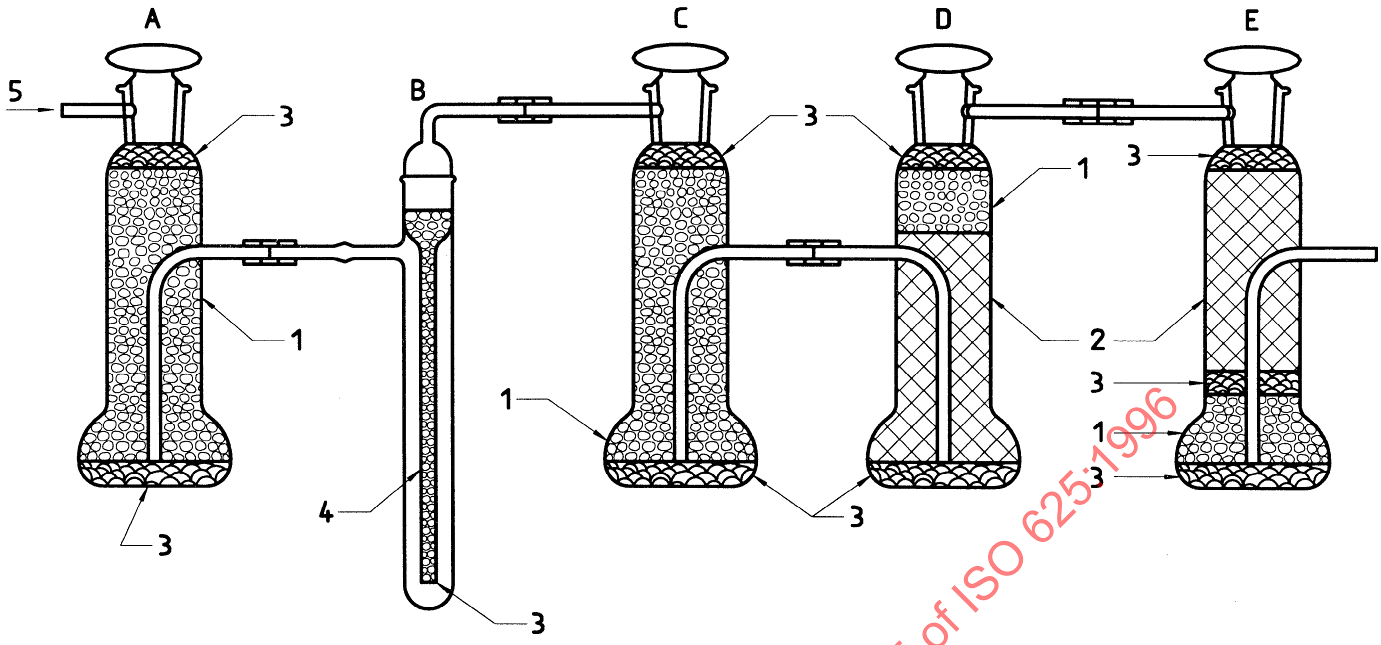


Figure 2 — Guard tube



Key

1 Magnesium perchlorate, 1,2 mm to 0,7 mm size

2 Sodium hydroxide (see 4.2), 1,2 mm to 0,7 mm size

3 Glass wool

4 Manganese dioxide

5 Inlet

NOTE — In this illustration the optional second carbon dioxide absorber, E, is shown.

Figure 3 — Absorption train

Stoppered U-tubes may be used, if preferred, in place of the Midvale tubes.

Place glass wool (4.9), previously dried at 105 °C for 1 h, above and below the absorbents to prevent the carry-over of dust by the flow of oxygen, and to prevent the cracking of the Midvale tube by the heat of reaction.

If water is condensed in the first absorber, some nitrogen dioxide 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, in the order of 0,05 % of hydrogen. This can only be avoided by heating the absorption tube to a temperature that is sufficiently high to prevent condensation of water.

NOTE 1 Oxides of nitrogen formed in the combustion would, in the absence of precautions, be absorbed by the sodium hydroxide and measured as carbon dioxide. The error in the carbon determination thus caused, in the order of 0,2 % of carbon, is substantially avoided by the use of a guard tube (see figure 2) in which the gases pass through an annular space to allow oxidation of nitrogen monoxide to nitrogen dioxide which is absorbed by the manganese dioxide.

5.5 Oxygen flow-rate controller, a reducing valve on the oxygen cylinder together with a small needle valve and flowmeter, capable of measuring a flow of up to 100 ml/min, immediately before the purification train, is generally adequate. It may be useful to attach a bubbler device at the exit end of the assembled apparatus to give a visual indication of the rate of flow.

5.6 Heat-resistant stopper (acrylonitrile or chloroprene) for connecting the absorption train to the combustion tube.

5.7 Copper gauze roll, for constraining the reagents in the appropriate sections of the combustion tube (5.3.2). Roll the copper gauze into rolls 10 mm long and of sufficient diameter to ensure a close fit in the combustion tube.

5.8 Copper gauze spiral, through which passes a stout copper wire provided with a loop to facilitate removal from the combustion tube (5.3.2).

5.9 Silver gauze roll, for absorbing chlorine. Roll the pure silver gauze (4.7) to form a plug, 100 mm long and of sufficient diameter to ensure a close sliding fit in the combustion tube (5.3.2). A stout, pure silver wire is passed through the centre of the roll to facilitate its removal from the tube.

5.10 Heat-resistant wire, approximately 2,5 mm thick and 500 mm long, with a bent end to place the boat in the correct position in the combustion tube and to transfer the used boat from the combustion tube onto a rigid refractory sheet.

6 Preparation of the apparatus

6.1 Preparation of the combustion tube

For a combustion tube 1,25 mm long and 12 mm to 15 mm in diameter, the following arrangement of the spacing is suitable:

— 10 mm space for a rubber stopper;

— 300 mm space to allow the furnace to be removed behind and away from the boat;

— 80 mm occupied by a copper gauze spiral (5.8) (see note 2);

— 70 mm space for the combustion boat (5.3.3);

— 50 mm space to prevent the front of the boat being heated too soon;

— 10 mm occupied by a plug roll of the copper gauze (5.7) (see note 2);

— 450 mm occupied by the copper oxide (4.5);

— 10 mm occupied by a plug roll of the copper gauze (see note 2);

— 100 mm occupied by the lead chromate (4.6);

— 10 mm occupied by a plug roll of the copper gauze;

— 100 mm occupied by a roll of the pure silver gauze (5.9);

— 50 mm space, with that section of tube wrapped on the outside with mineral fibre to prevent condensation of water inside;

— 10 mm space for a heat-resistant stopper (5.6).

The arrangement is shown in figure 4.

NOTE 2 The copper gauze spiral and rolls are oxidized during the preliminary heating in a current of oxygen.

6.2 Conditioning the combustion tube

Before starting a determination with a newly-packed combustion tube, heat the tube throughout its length, while passing a current of purified oxygen at a rate of 12 ml/min. Heating shall be continued for 3 h, with furnace No. 1 at a temperature of 925 °C, furnace No. 2 at a temperature of 800 °C and furnace No. 3, containing that 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 end of the tube shall be heated in such a manner that, without charring the rubber stopper, condensation of steam is avoided.

6.3 Conditioning the absorption train

Connect the absorption train to the apparatus and purge with purified oxygen for 20 min, with the furnaces at their working temperatures. Disconnect absorbers A and D (and E, if used) (see figure 3) from the absorption train, seal the side-arms and close the taps, and allow them to cool to room temperature in a draught-free enclosure. Wipe each absorber with a clean lint-free cloth, remove the seals from the side-arms and weigh each absorber with a minimum of handling. Reconnect the absorption train to the combustion tube and reopen the taps. Particular care shall be 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 connections 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 a period of 2 h, remove and weigh absorbers A and D (and E, if used) 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 a proper condition for use.

NOTE 3 Under certain conditions of humidity, wiping the absorbers with a cloth may induce a static charge, which, if significant, could affect the weighing. The use of static eliminators should therefore be considered.

Dimensions in millimetres

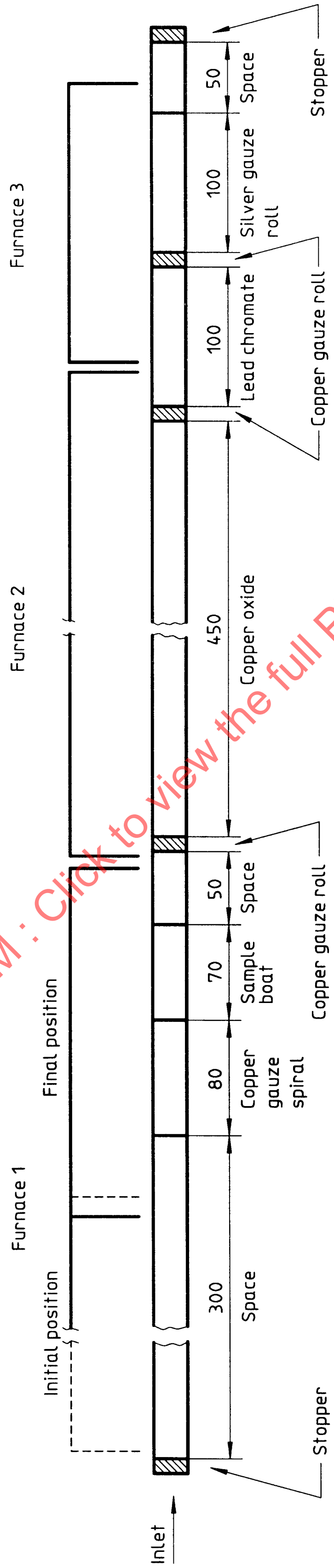


Figure 4 — Arrangement of the spacing in the combustion tube

7 Preparation of test sample

Prepare the test sample for general analysis in accordance with ISO 1988, ISO 2309 or ISO 5069-2, as appropriate. Ensure that the moisture content of the sample is in equilibrium with the laboratory atmosphere, exposing it, if necessary, in a thin layer for the minimum time to achieve equilibrium.

Before commencing the determination, thoroughly mix the test sample for at least 1 min, preferably by mechanical means.

After weighing the test portion (see clause 8), determine the moisture content using a further portion of the test sample by the method described in ISO 331, ISO 687, ISO 1015 or ISO 5068, as appropriate. A further portion should be set aside if the determination of carbon dioxide (ISO 925) is required.

8 Procedure

When starting the first determination of each day, raise the temperatures of the furnaces (5.3.1) to 925 °C, 800 °C and 500 °C respectively, while passing purified oxygen (4.8) through at a rate of 12 ml/min. Connect the absorption train (5.4) and purge for 20 min. Disconnect the train and weigh absorbers A, D and E, as described in 6.3. Switch off furnace No. 1 and allow it to cool.

Weigh accurately between 0,2 g and 0,3 g of the test sample, to the nearest 0,1 mg, and spread evenly over the bottom of a cool, previously ignited combustion boat (5.3.3). Connect the weighed absorption train to the combustion tube (5.3.2) as described in the previous paragraph. Place the combustion boat and the oxidized copper gauze spiral (5.8) in the combustion tube at the appropriate positions, insert the rubber stopper connecting the purification train and pass purified oxygen through the apparatus at a rate of 12 ml/min. Switch on furnace No. 1 and start the combustion by heating the copper gauze spiral. When the furnace is at 800 °C, gradually draw it forward to cover the combustion boat and its contents (see note 5), maintaining the passage of a steady stream of oxygen through the whole system while the sample is being burned. Continue until all visible carbon has disappeared (see note 4) and until the portion of the combustion tube containing the sample has been raised to 925 °C.

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 described in 6.3 and weigh them (see note 7).

Carefully inspect the ash in the boat for unburnt carbon; if present, this invalidates the determination, which shall then be repeated.

Particular care must be taken during the combustion of brown coals and lignites, since heating too rapidly could result in incomplete combustion.

NOTES

4 Two hours are usually sufficient to complete the combustion of coal samples and 1 h may be sufficient for most coke samples.

5 Midvale tubes, used particularly for the absorption of carbon dioxide, cool slowly and up to 60 min should be allowed before weighing. When not connected to the apparatus, the Midvale tubes should be protected from atmospheric contamination by closing the taps and fitting guard seals of plugged rubber tubing to the open limbs. It is usual to weigh the absorption tubes without guard seals, after wiping.

9 Blank test

Carry out a blank test using the same procedure as described in clause 8, but omitting the test portion.

If the increase in mass of Midvale tube during the blank test is consistently greater than 0,001 g, the contents shall be discarded and the tube repacked. Furthermore, if at any time the increase in mass of tube E exceeds 0,05 g, the contents of tube D should be discarded and the tube repacked.

10 Expression of results

10.1 Total carbon content

The total carbon content, w_C, of the sample as analysed, expressed as a percentage by mass, is given by the equation

$$w_C = 27{,}29 \times \frac{m_2 - m_3}{m_1}$$

where

m_1 is the mass, in grams, of the test portion;

m_2 is the increase in mass, in grams, of absorbers B and C, determined in the test;

m_3 is the increase in mass, in grams, of absorbers B and C, determined in the blank test (see clause 9).