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Second edition
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Solid mineral fuels — Determination of carbon and hydrogen — High temperature combustion method

*Combustibles minéraux solides — Dosage du carbone et de
l'hydrogène — Méthode par combustion à haute température*



Reference number
ISO 609:1996(E)

Foreword

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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 609 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 609:1975), 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 625:1996, *Solid mineral fuels — Determination of carbon and hydrogen — Liebig method*.

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Solid mineral fuels — Determination of carbon and hydrogen — High temperature combustion 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 a high temperature combustion 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 stream of oxygen, at a temperature of 1 350 °C, in a tube impervious to gases. All the hydrogen is converted to water and all the carbon to carbon dioxide. These products are absorbed by suitable reagents and determined gravimetrically. The chlorine and oxides of sulfur which are formed are retained by a silver gauze roll at the outlet end of the tube.

4 Reagents and materials

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

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 Aluminium oxide (alumina), finely divided, approximately 0,1 mm in size.

4.4 Sodium tetraborate, standard volumetric solution, $c(\text{Na}_2\text{B}_4\text{O}_7) = 0,025 \text{ mol/l}$.

Dissolve 9,534 2 g of sodium tetraborate decahydrate in water and dilute to 1 litre. Mix thoroughly.

4.5 Hydrogen peroxide, approximately 30 % (m/m).

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

4.7 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.

4.8 Mixed indicator solution

4.8.1 Solution A

Dissolve 0,125 g of 2-(4-dimethylaminophenyl)-azo)benzoic acid, sodium salt (methyl red) in 100 ml of water.

4.8.2 Solution B

Dissolve 0,083 g of 3,7-bis(dimethylamino)phenothiazine-5-ylum chloride (methylene blue) in 100 ml of water. Store in a dark bottle.

4.8.3 Mixed solution

Mix equal volumes of solution A and solution B. Store in a dark bottle. Discard the mixed solution after 1 week.

4.9 Air, compressed.

4.10 Glass wool.

5 Apparatus

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

5.2 Graduated glassware, conforming to the requirements for class A in the International Standards prepared by ISO/TC 48, *Laboratory glassware and related apparatus*.

5.3 Two purification trains, 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 using a series of U-tubes or Midvale tubes containing the following reagents in the order stated, in the direction of flow:

- magnesium perchlorate (4.1) for absorbing water;
- sodium hydroxide on an inert base (4.2) for absorbing dioxide;
- magnesium perchlorate for absorbing the water evolved in the reaction between carbon dioxide and sodium hydroxide.

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

NOTE 1 Midvale tubes that have been freshly packed with absorbent and used in the purification train are thereby conditioned for subsequent use in the absorption train.

5.4 Combustion assembly

5.4.1 Heating unit, an electrically heated furnace or furnaces, designed to carry a combustion tube (5.4.2) and heat it to 1 350 °C over a distance of 125 mm in the hot zone, and yield a temperature-distribution profile similar to that shown in figure 1. The heating unit normally requires an auxiliary furnace to ensure that the silver gauze roll (5.9) is maintained at the correct temperature (approximately 600 °C to 800 °C). Suitable furnaces are, for example:

- molybdenum or tungsten wire wound;
- platinum or platinum-rhodium wire wound;
- heated by silicon carbide rods.

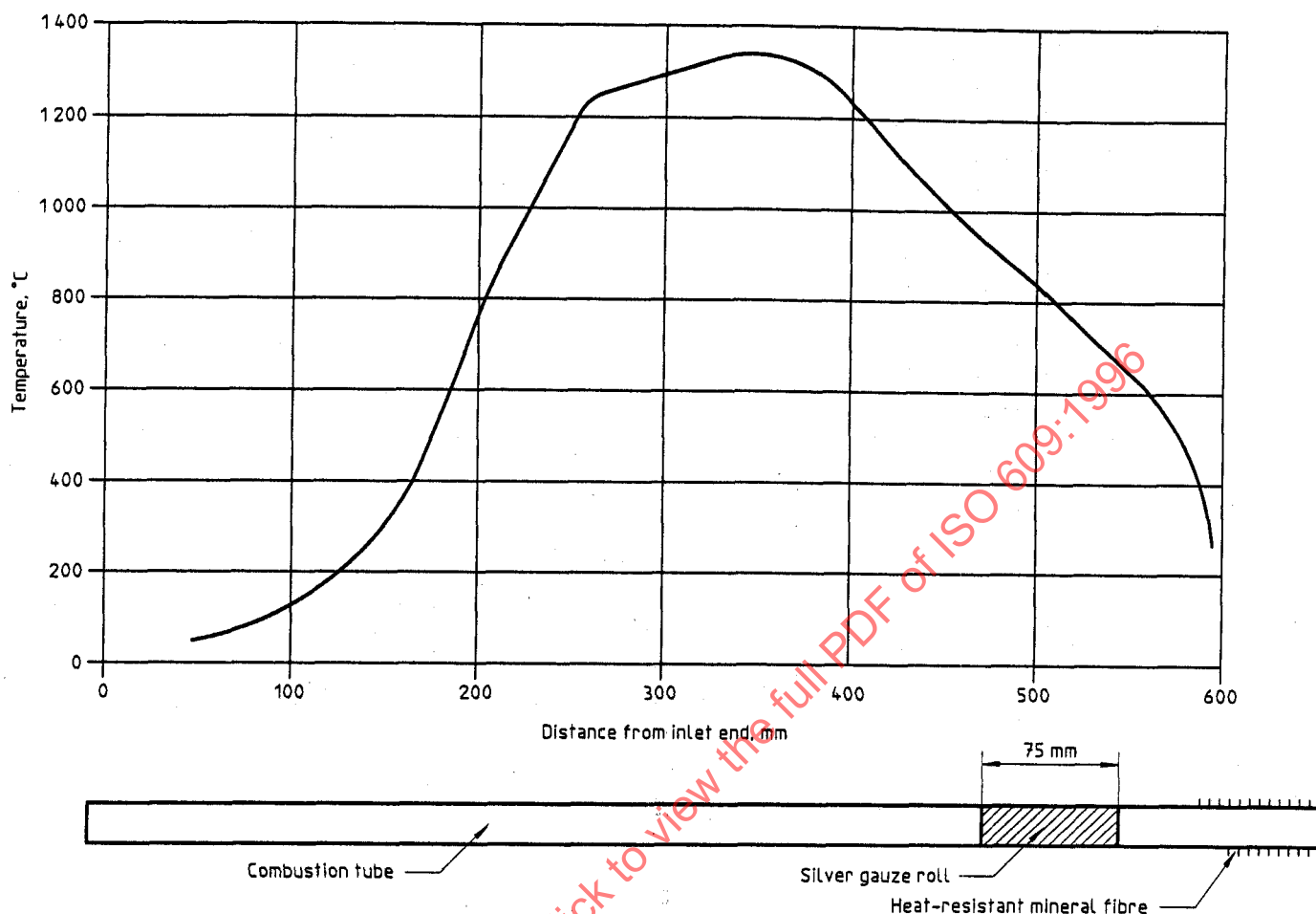


Figure 1 — Typical temperature-distribution curve for furnace

NOTES

2 Type c) has the lowest initial cost and has proved satisfactory in use.

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

5.4.2 Combustion tube, of approximately 28 mm external diameter, 3 mm wall thickness and 650 mm length, made of refractory aluminous porcelain which is impervious to gases up to a temperature of 1 400 °C. The end of the combustion tube shall be lagged with a suitable heat-resistant mineral fibre to prevent condensation in the tube.

5.4.3 Combustion boat, of iron-free, unglazed porcelain, approximately 60 mm long, 12,5 mm wide and 10 mm deep, for hard coal and coke samples and approximately 75 mm long, 15 mm wide and 10 mm

deep for brown coal and lignite, capable of withstanding a temperature of 1 350 °C.

NOTE 4. Combustion boats should not blister, discolour or change in mass on heating in oxygen at 1 350 °C for 3 h. A suitable boat lasts for about 10 to 20 determinations and should then be discarded because of the accumulation of fused ash. For coals with a high ash content, 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.

5.5 Absorption train, for absorbing the water and carbon dioxide evolved by the combustion of the sample. Midvale tubes (figure 2), which provide a large area of reaction, are used in order to reduce the back-pressure in the apparatus, and so obviate the danger of leakage through the rubber sleeve carrying the pusher. 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;

Dimensions in millimetres

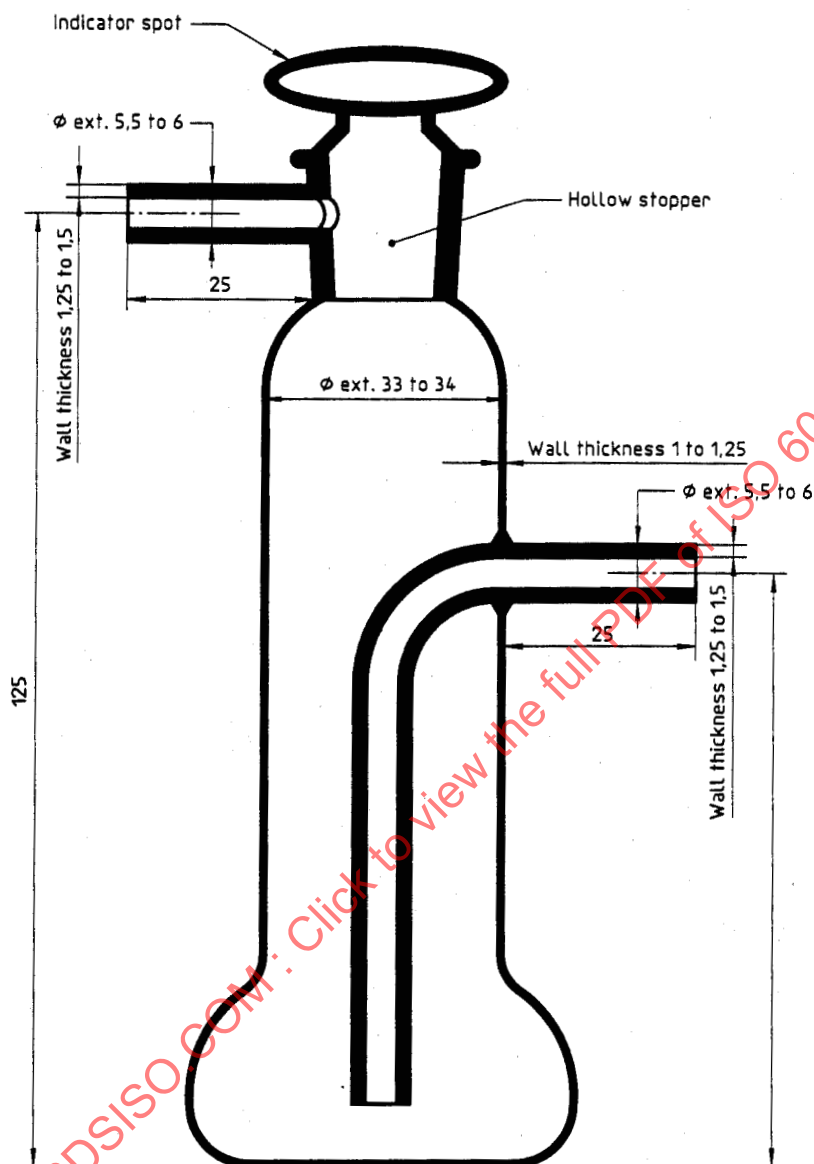


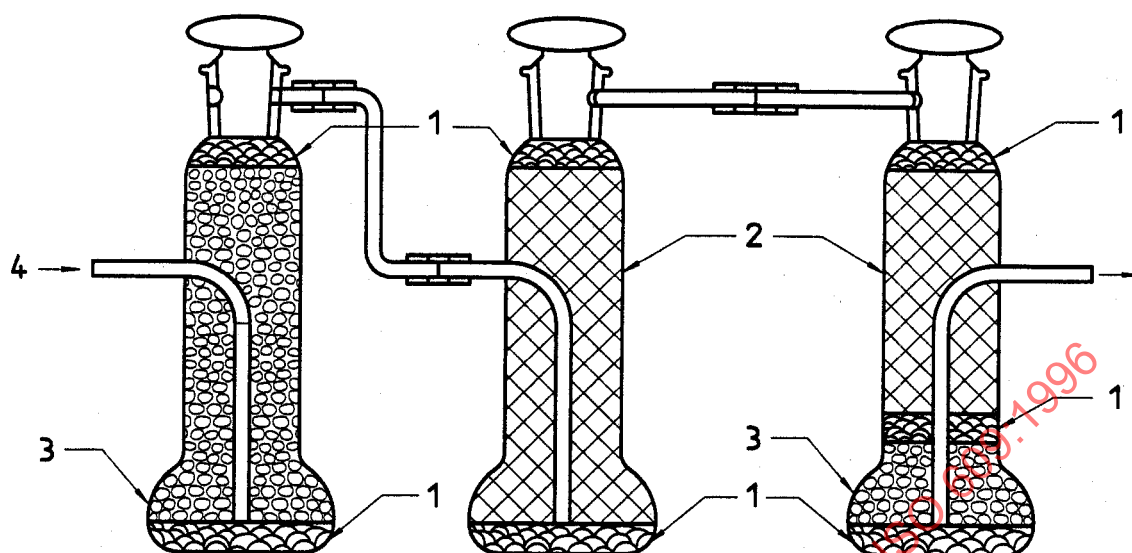
Figure 2 — Midvale tube

- 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.

Place glass wool (4.10), 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. A typical absorption train with details of the packing is shown in figure 3. A is the absorber for

water; B and C are the absorbers for carbon dioxide, C serving as a control to indicate when the packing in B is in need of replacement. Any water released in B by the reaction between sodium hydroxide and carbon dioxide is absorbed in C.

The inlet of the water-absorption tube shall be inserted through the heat-resistant stopper so that it is flush with the inner end of the stopper. All connections between the tubes shall be made of glass-to-glass, using the rubber connecting sleeves merely as seals.



Key

- | | |
|------------------------------|--|
| 1 Glass wool | 3 Magnesium perchlorate, 1,2 mm to 0,7 mm size |
| 2 Sodium hydroxide (see 4.2) | 4 Inlet |

Figure 3 — Absorption train

5.6 Two flowmeters, both capable of measuring rates of flow up to 300 ml/min of air.

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

5.8 Silica or steel pusher, made from rod or sealed tube, approximately 6 mm in diameter and 450 mm long, with a disc end, 12 mm in diameter, for pushing the boat into the hot zone of the combustion tube. The pusher passes loosely through a glass or metal T-piece, one end of which fits into the stopper which closes the inlet end of the combustion tube, the other being sealed by a rubber sleeve (see note 6), through which the pusher slides. The sleeve prevents the escape of oxygen which enters at the stem of the T-piece. The pusher is usually marked from the disc end, for convenience in ascertaining the position of the boat in the combustion tube during pushing.

NOTE 5 The rubber sleeve should be changed periodically to avoid leakage.

5.9 Silver gauze roll, for absorbing chlorine and oxides of sulfur. Roll the pure silver gauze (4.6) to form a plug, 75 mm long and of sufficient diameter to ensure a close sliding fit in the combustion tube (5.4.2). A stout, pure silver wire is passed through the centre of the roll to facilitate its removal from the tube.

5.10 Bubbler, for use when determining the correct location for the silver gauze roll (see 6.2). It may be a large boiling tube, wide-necked bottle, or Dreschel bottle, containing a sintered glass disc of 0,015 mm to 0,040 mm maximum pore size in the gas distribution tube. The diameter of the absorber shall be such that the disc is covered to a depth of at least 90 mm by the absorbing solution; a vessel 35 mm in diameter and 150 mm deep is suitable. A silica adapter, or the combustion tube fitted with a tubulure, is connected to the bubbler.

To avoid leakage at the rubber sleeve of the inlet end due to the resistance of the sintered glass bubbler, the bubbler is connected to a suction-pump through a pressure regulator adjusted to maintain slight suction at the inlet end of the combustion tube.

A convenient assembly of the apparatus for this purpose is illustrated in figure 4.

5.11 Heat-resistant wire, approximately 2,5 mm thick and 450 mm long, with a bent end 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

Insert the combustion tube (5.4.2) into the furnace (see 5.4.1) so that it projects 75 mm at the exit end. Wrap this projecting portion with mineral fibre to prevent condensation of water in the tube. Insert the rubber stopper carrying the silica or steel pusher (5.8) at the inlet end of the combustion tube and connect the purified oxygen supply (see 4.7 and 5.3) to the limb of the glass or steel T-piece.

NOTE 6 The distance the combustion tube projects from the furnace may be reduced to about 40 mm if an auxiliary furnace is fitted.

6.2 Location of the silver gauze roll

Insert the silver gauze roll (5.9) into the exit end of the combustion tube (5.4.2) to a distance of about 75 mm. With the main furnace at its working temperature of 1 350 °C and the auxiliary furnace (if fitted) at the temperature required to give a temperature-distribution curve as shown in figure 1, connect the bubbler (5.10) containing a 3 % (m/m) solution of the hydrogen peroxide (4.5) to the exit end of the combustion tube using a heat-resistant stopper (5.7), and switch on the suction-pump (see figure 4).

Burn 0,5 g of a coal containing 1 % (m/m) to 2 % (m/m) of sulfur using the procedure described in 8.2 (but excluding the absorption train). Wash the silica adapter (see 5.10) and the contents of the bubbler into a 250 ml conical filtration beaker, add 2 to 3 drops of the mixed indicator solution (4.8) and measure the amount of chlorine and oxides of sulfur passing through the silver gauze roll by titration of the hydrogen peroxide with the sodium tetraborate solution (4.4) to a neutral steel-grey colour.

Move the silver gauze roll forward in 5 mm stages and repeat the test until a position is found where the volume of the sodium tetraborate solution corresponding to the end point is not more than 0,2 ml, which will represent at least 99 % retention of the

oxides of sulfur by the silver gauze roll. Use this exact location in all subsequent determinations.

Disconnect the bubbler, pressure regulator (see 5.10) and suction-pump. Using the bent heat-resistant wire (5.11), withdraw the used combustion boat onto a thick sheet of suitable refractory material.

The roll tends to shrink with continual use and it is important to check its diameter to ensure a close sliding fit in the combustion tube.

When the combustion tube is not in use, protect the silver gauze roll from atmospheric contamination by sealing both ends of the tube.

NOTE 7 The silver gauze roll can absorb sulfur equivalent to 7 % (m/m) of the sample; for higher sulfur contents, the mass of the test portion should be proportionally reduced. The roll should be periodically cleaned by boiling in water (to remove silver sulfate), in concentrated ammonia solution (to remove silver chloride) and finally in water, after which it should be dried. The total sulfur content of samples examined between two cleanings of the roll should not exceed 0,035 g.

6.3 Conditioning the absorption train

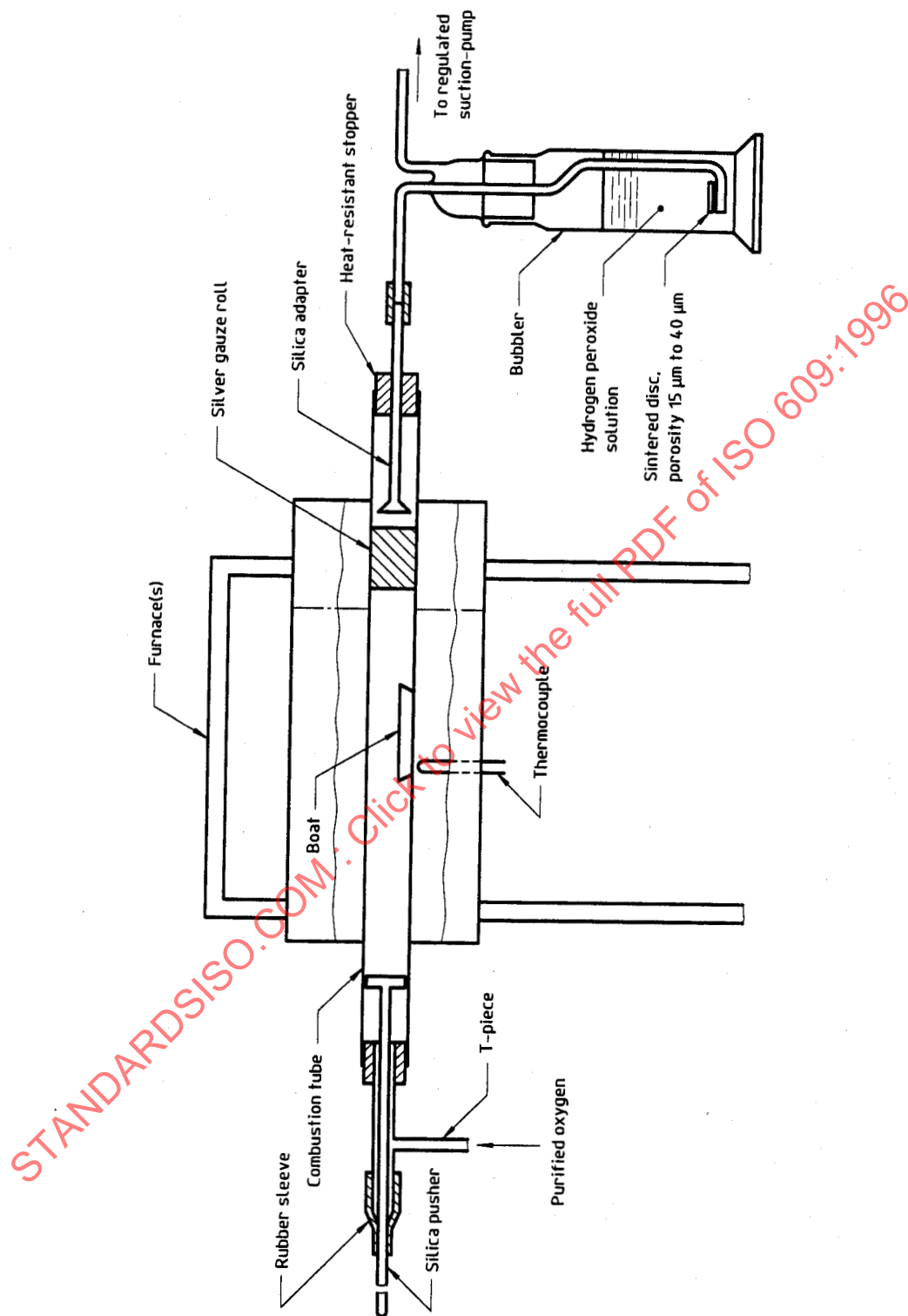
At the start of each working day, the Midvale tubes should be conditioned by purging them with purified air for 10 min whilst connected to the apparatus. After purging, the Midvale tubes should be sealed, cooled for about 20 min in a draught-free enclosure, wiped carefully with a lint-free cloth and weighed with the minimum of handling. Repeat this procedure until the change in mass of each tube is less than 1 mg.

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 required 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.



NOTE — During the test sample determination procedure, the bubbler is replaced by the absorption train and the suction-pump is disconnected.

Figure 4 — Arrangement of apparatus for the location of the silver gauze roll

8 Procedure

8.1 Initial operations

Raise the temperatures of the furnace or furnaces (see 5.4.1) so that the requirements of the temperature-distribution curve shown in figure 1 are met and confirm that the silver gauze roll (5.9) are in its correct position. Admit the purified oxygen (see 4.7 and 5.3) to the apparatus about 30 min before the temperature reaches 1 350 °C and adjust the rate of flow to 300 ml/min.

8.2 Combustion of the test portion

Weigh, to the nearest 0,1 mg, about 0,5 g of the test sample and spread evenly over the bottom of a clean, dry combustion boat (5.4.3). Completely cover the sample in the combustion boat with about 0,5 g of the aluminium oxide (4.3) (with care, 0,5 g of aluminium oxide can be made to completely blanket the sample in the boat). Connect a previously conditioned and weighed absorption train (5.5) and insert the charged boat into the combustion tube (5.4.2) from the inlet end so that its centre is 240 mm from the centre of the hottest zone. With the silica or steel pusher fully withdrawn, replace the rubber stopper and continue to pass the purified oxygen through at a rate of 300 ml/min. After 1 min, move the boat forward 40 mm. At the end of each of the next five 1 min periods, push the boat forward about 40 mm, withdrawing the silica or steel pusher (5.8) each time to prevent distortion; after the last push, the centre of the boat should be at the centre of the hottest zone (see 8.3). Allow the boat to remain in the hottest zone for a further 4 min.

8.3 Completion

Disconnect the absorption train (5.5) connect it to the air purification train (see 5.3) and purge it for 10 min with purified air at a rate of 200 ml/min to 250 ml/min. Disconnect the absorbers A, B and C, close the taps, seal the central side-arms and allow to cool in a draught-free enclosure (see note 8).

Wipe the Midvale tubes (see 5.5) carefully with a lint-free cloth, remove the guard seals and weigh the absorbers (see note 8) with a minimum of handling (see note 9).

Using the bent heat-resistant wire (5.11), withdraw the used combustion boat onto a thick sheet of suitable refractory material.

NOTE 8 For certain coals which liberate volatile matter at a high rate, the early stages of heating may give a carry-

over of unburnt 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 240 mm from the centre of the hottest zone. After 1 min, move the boat forward 20 mm. At the end of each of the next eleven 1 min intervals, move the boat forward by 20 mm. Allow the boat to remain in the hottest zone for a further 4 min.

For unreactive cokes, for example those with less than 0,5 % of volatile matter, the rate of pushing should also be reduced as described above.

NOTES

9 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. If at any time the increase in mass of tube C exceeds 0,05 g, the contents of tube B should be discarded and the tube repacked.

10 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.

9 Blank test

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

If the increase in mass of a Midvale tube during the blank test is consistently greater than 0,001 g, the contents shall 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;