INTERNATIONAL STANDARD 352

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Hard coal and coke — Determination of chlorine — High temperature combustion method

Houille et coke — Dosage du chlore — Méthode par combustion à haute température

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 27 has reviewed ISO Recommendation R 352 and found it technically suitable for transformation. International Standard ISO 352 therefore replaces ISO Recommendation R 352-1963 to which it is technically identical.

ISO Recommendation R 352 was approved by the Member Bodies of the following countries :

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Yugoslavia

The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

France

The Member Body of the following country disapproved the transformation of ISO/R 352 into an International Standard :

Czechoslovakia

Printed in Switzerland

INTERNATIONAL STANDARD

ISO 352-1975 (E)

Hard coal and coke – Determination of chlorine – High temperature combustion method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method of determining the chlorine content of hard coal and of coke by the high temperature combustion method. An alternative method for the determination of chlorine is given in ISO 587.1)

2 PRINCIPLE

The sample of coal or coke is burnt in a stream of oxygen, in a tube furnace at a temperature of 1 250 or 1 350 °C, and the acid gases (chlorine and oxides of sulphur) formed are absorbed in hydrogen peroxide. The acid solution is neutralized with sodium borate and the sodium chloride formed is converted by reaction with mercury(II) oxycyanide to sodium hydroxide, which is determined volumetrically.

3 REAGENTS

All reagents shall be of analytical reagent quality and distilled water shall be used throughout.

3.1 Kaolin, or

3.2 Iron(III) phosphate, if the determination is to be carried out at 1 250 °C; or

3.3 Aluminium oxide (alumina), finely divided, if the determination is to be carried out at 1 350 °C.

3.4 Hydrogen peroxide solution, 1 % (by volume), neutralized with the sodium borate solution (3.6).

3.5 Mercury(II) oxycyanide saturated solution.

Saturate a suitable volume of distilled water with mercury(II) oxycyanide ($3Hg(CN)_2.HgO$)2) by prolonged agitation; filter and neutralize the filtrate with the sulphuric acid (3.7), using bromothymol blue as an external indicator. Store the solution in a dark glass bottle; do not keep longer than 4 days.

3.6 Sodium borate, 0,050 N solution.

3.7 Sulphuric acid, 0,025 N.

3.8 Mixed indicator solution

Solution A – Dissolve 0,125 g of 4′-dimethylaminoazobenzene-2-carboxylic acid (methyl red) in 60 ml of ethanol or industrial spirit and dilute to 100 ml with water.

Solution B – Dissolve 0,083 g of 3,7-bisdimethylaminophenazothionium chloride (methylene blue) in 100 ml of ethanol or industrial spirit. Store in a dark glass bottle.

Mix equal volumes of solution A and solution B. Discard the mixed solution after 1 week.

4 APPARATUS

All graduated apparatus shall be of the best analytical quality obtainable and the balance used shall be sensitive to 0,1 mg.

4.1 Furnace, capable of heating a tube of approximately 28 mm external diameter over a length of approximately 150 mm to a maximum temperature of 1 250 or 1 350 °C. The furnace may, conveniently, be heated electrically, using either silicon carbide resistance rods (controlled by a variable transformer) or a resistance wire (controlled by a variable resistance).

4.2 Aluminous porcelain tube, of approximately 28 mm external diameter, 3 mm wall thickness and 650 mm length, which is gas-tight at the working temperature. A straight tube is most convenient and may be used in conjunction with an adapter of fused silica having a bell-shaped end, which gives a narrow clearance with the inner wall of the heated tube, and a heat-resistant stopper (acrylonitrile or chloroprene is suitable). Alternatively, the tube may have, at the exit, a beak end, with a tubulure to enable condensation products to be washed out after a test; or a straight tube of aluminous porcelain may be used in conjunction with a borosilicate glass adapter, having a cap-shaped end which fits on the outer wall of the tube.

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1) ISO 587, *Coal and coke – Determination of chlorine using Eschka mixture.*

2) WARNING : This compound and its solution are toxic and must be handled with great care.

4.3 Oxygen cylinder, fitted with a needle valve to control the rate of flow of oxygen, and a flow meter to measure up to 500 ml/min. The oxygen should, as a precautionary measure, be passed through a U-tube packed with soda-asbestos.

4.4 Combustion boats, of iron-free, unglazed porcelain, 62,5 mm long, 12,5 mm wide and 10 mm deep.

4.5 Heat-resistant wire, about 1,5 mm thick and having a bent end to remove the boats from the tube.

4.6 Silica pusher, with a disk end for pushing the boat into the hot zone. The pusher passes through a T-piece fitted into the stopper at the inlet end of the tube and is held in a rubber sleeve (see note) which fits over the free arm of the T-piece. The sleeve prevents the escape of oxygen (which enters at the stem of the T) although permitting movement of the pusher.

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

4.7 Two absorbers, of about 150 ml capacity, which may be large boiling tubes, wide-necked bottles or Drechsel bottles, each containing a sintered glass disk of 15 to 40 μm maximum pore size in the gas distribution tube. The diameter shall be such that the disk is covered to a depth of at least 25 mm by the absorbing solution. Connect the silica adapter, or the reaction tube fitted with a tubulure, to the first absorber. Connect this in series with the second absorber.

Alternatively, use a single narrow absorber with a sintered glass disk of 15 to 40 μm maximum pore size, about 35 mm diameter and 150 mm deep, so that the bubbler is covered to a depth of at least 90 mm.

To avoid leakage at the rubber sleeve of the inlet end due to the resistance of the sintered glass bubbler, connect the second absorber to a water-pump through a pressure regulator containing mercury with an open-ended tube dipping into it.

A convenient assembly of the apparatus is illustrated in the figure.

5 PREPARATION OF SAMPLE

The coal or coke used for the determination of chlorine content is the analysis sample ground to pass a sieve of 0,2 mm aperture. If necessary expose the sample in a thin layer for the minimum time required for the moisture content to reach approximate equilibrium with the laboratory atmosphere.

Before commencing the determination, mix the air-dried sample for at least 1 min, preferably by mechanical means.

6 PROCEDURE

Raise the temperature of the furnace to 1 250 °C or 1 350 °C, as the case may be. Weigh, to the nearest 0,1 mg, about 0,5 g of the sample, transfer to a combustion boat and spread uniformly.

Cover with about 0,5 g of the kaolin (3.1) or about 0,15 g of the iron(III) phosphate (3.2) if the determination is being carried out at 1 250 °C, or with about 0,5 g of the aluminium oxide (3.3) if the determination is being carried out at 1 350 °C (see note 1). Measure 100 ml of the hydrogen peroxide solution (3.4) and either divide this amount between the two absorbers or pour the whole into the single absorber.

Adjust the water-pump so that a rapid stream of air is drawn through the absorber(s) and a constant stream of air through the pressure regulator. Insert the silica adapter into the combustion tube and secure the stopper. Adjust the oxygen flow to 300 ml/min.

Insert the charged boat from the inlet end of the combustion tube so that its centre is 240 mm from the centre of the hottest zone and secure the stopper carrying the pusher and the oxygen inlet. At the end of each of the next six one-minute periods, push the boat forward about 40 mm, withdrawing the silica pusher each time to prevent distortion. After the last push, the boat should be at the centre of the hottest zone (see note 2). Allow the boat to remain in the hottest zone for a further 4 min. Disconnect the absorber(s) and withdraw the boat onto a sheet of asbestos.

Wash the adapter, collecting the washings in the single absorber or in the first of the two absorbers; transfer the contents of the absorber(s) into a 250 ml conical filtration beaker, and then wash out the absorber(s) and collect the washings in the same filtration beaker. Add 2 or 3 drops of the mixed indicator solution (3.8) and titrate with the sodium borate solution (3.6). This gives the total acidity due to chlorine and oxides of sulphur according to the following reactions :

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$

After titration the chloride ion is present as sodium chloride. Add 20 ml of the mercury(II) oxycyanide solution (3.5) (a sufficient excess for samples containing up to 1,2 % of chlorine) to convert the sodium chloride to sodium hydroxide :

$$NaCl + Hg(OH)CN \rightarrow HgClCN + NaOH$$

Titrate the liberated alkali with the sulphuric acid (3.7).

NOTES

1 The use of a covering material such as fine aluminium oxide provides a safeguard against rapid decomposition of the sample and its expulsion from the boat, with a resultant deposition of carbon in the tube. If the aluminium oxide to be used has a high chlorine content, it should be heated at 1 350 °C for 30 min in a stream of oxygen, cooled and stored in a tightly closed container until required.

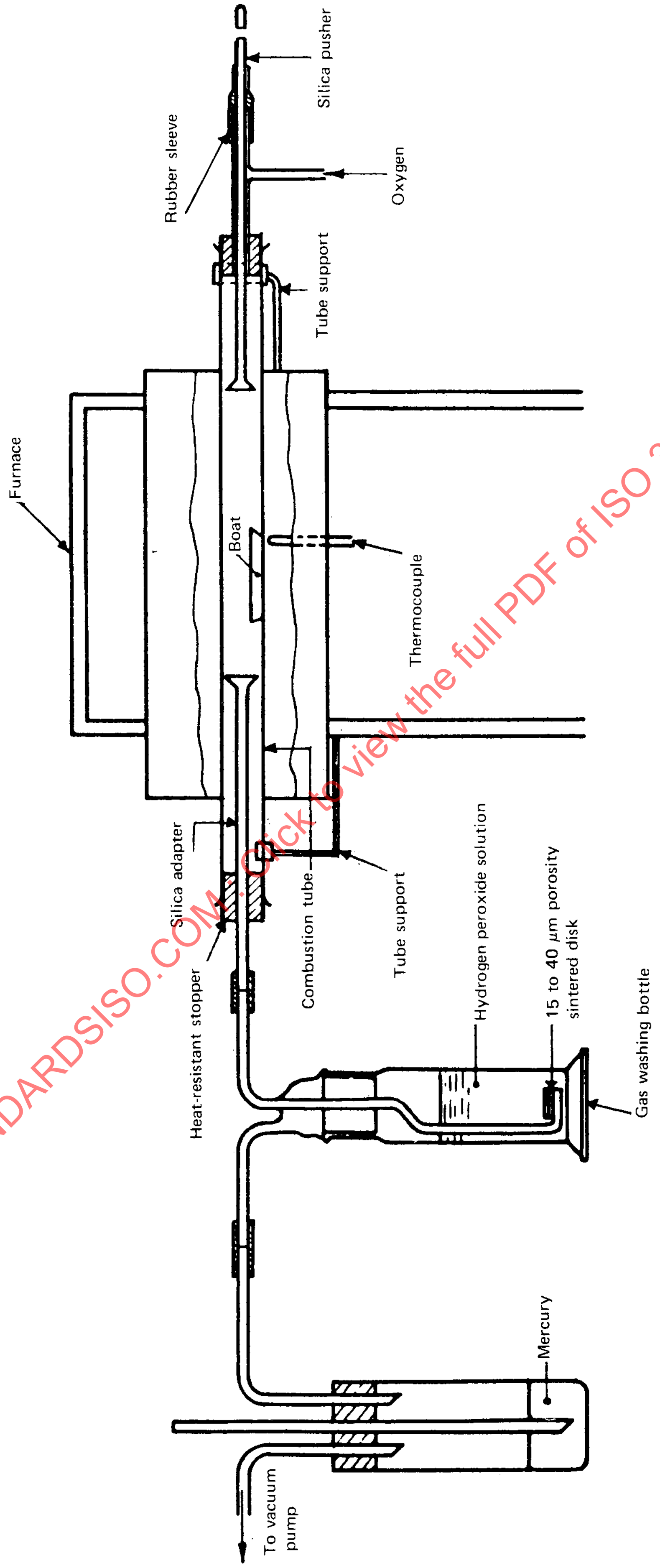

FIGURE — **Suitable apparatus**