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DETERMINATION OF CHLORINE IN COAL BY THE HIGH TEMPERATURE COMBUSTION METHOD

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BRIEF HISTORY

The ISO Recommendation R 352, *Determination of Chlorine in Coal by the High Temperature Combustion Method*, was drawn up by Technical Committee ISO/TC 27, *Solid Mineral Fuels*, the Secretariat of which is held by the British Standards Institution (B.S.I.).

Work on this question by the Technical Committee began in 1953 and led, in 1957, to the adoption of a Draft ISO Recommendation.

In May 1958, this Draft ISO Recommendation (No. 242) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies:

Austria	India	Portugal
Belgium	Israel	Republic of South Africa
Burma	Italy	Romania
Chile	Japan	Spain
Czechoslovakia	Mexico	United Kingdom
Denmark	Netherlands	U.S.S.R.
Germany	New Zealand	Yugoslavia
Greece	Poland	

One Member Body opposed the approval of the Draft: France.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in December 1963, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 352 December 1963

DETERMINATION OF CHLORINE IN COAL BY THE HIGH TEMPERATURE COMBUSTION METHOD

1. PRINCIPLE

Coal is burnt in a stream of oxygen, in a tube furnace at a temperature of 1250 or 1350 °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 mercuric oxycyanide to sodium hydroxide, which is determined volumetrically.

2. APPARATUS

All graduated apparatus should be of the best analytical quality obtainable and the balance used should be sensitive to 0.1 mg.

2.1 **Furnace,** capable of heating a tube of approximately 28 mm external diameter over a length of approximately 15 cm to a maximum temperature of 1250 or 1350 °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).

2.2 **Aluminous porcelain tube,** of approximately 28 mm external diameter, 3 mm wall thickness and 65 cm length, which is gas-tight at the working temperature. A straight tube is most convenient and is 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.

2.3 **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.

2.4 **Combustion boats,** of iron-free, unglazed porcelain, 62.5 mm long, 12.5 mm wide and 10 mm deep.

2.5 **Heat-resistant wire,** about 1.5 mm thick and having a bent end to remove the boats from the tube.

2.6 **Silica pusher,** with a disk end for pushing the boat into the hot zone. The pusher passes through a T-piece fitted into the bung at the inlet end of the tube and is held in a rubber sleeve (see note below) 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.

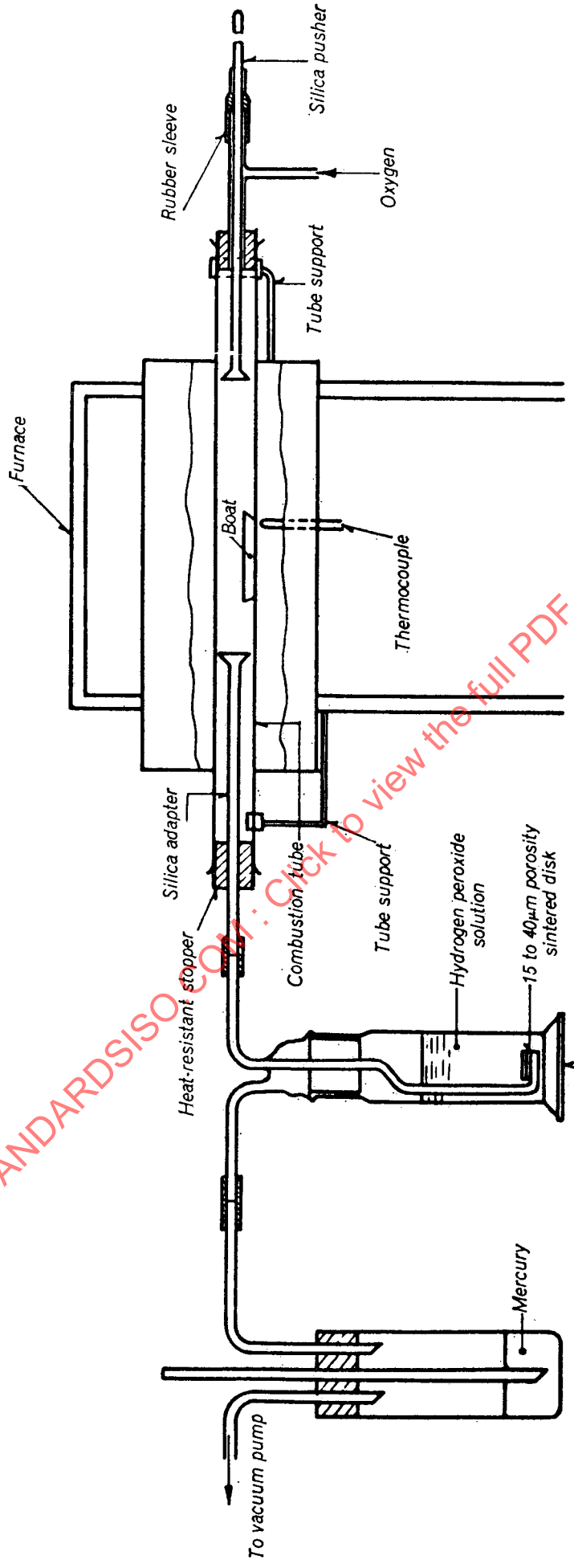

FIGURE. — **Suitable apparatus**

2.7 **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 is such that the disk is covered to a depth of at least 2.5 cm by the absorbing solution. The silica adapter, or the reaction tube fitted with a tubulure, is connected to the first absorber. This is connected in series with the second absorber.

Alternatively, one may use a single narrow absorber with a sintered glass disk of 15 to 40 μm maximum pore size, about 35 mm diameter and 15 cm deep, so that the bubbler is covered to a depth of at least 9 cm.

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

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

3. REAGENTS

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

3.1 *Kaolin*, or

3.2 *Ferric phosphate*, if the determination is to be carried out at 1250 °C; or

3.3 *Aluminium oxide* (alumina), finely divided, if the determination is to be carried out at 1350 °C.

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

3.5 *Mercuric oxycyanide solution*, saturated. Filter, neutralize with the sulphuric acid (3.7) and store in a dark-glass bottle; do not keep longer than 4 days.

3.6 *Sodium borate solution*, 0.050 N.

3.7 *Sulphuric acid*, 0.025 N.

3.8 *Mixed indicator solution*

Solution A. Dissolve 0.125 g of o-carboxybenzene-azo-dimethyl-aniline (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 bisdimethylamino-phenazothionium 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 one week.

4. PROCEDURE

Before commencing the determination, mix the air-dried sample of coal, ground to pass a sieve of 0.2 mm aperture, for at least 1 minute, preferably by mechanical means.

Raise the temperature of the furnace to 1250 °C or 1350 °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 ferric phosphate (3.2) if the determination is being carried out at 1250 °C, or with about 0.5 g of the aluminium oxide (3.3) if the determination is being carried out at 1350 °C (see Note 1 below). 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 bung. 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 22.5 cm from the centre of the hottest zone and secure the bung carrying the pusher and the oxygen inlet. 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 boat should be at the centre of the hottest zone (see Note 2 below). Allow the boat to remain in the hottest zone for a further 4 minutes. 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 to 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 mercuric oxycyanide solution (3.5) (a sufficient excess for coals containing up to 1.2 per cent 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 coal and the expulsion of coal 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 1350 °C for 30 minutes in a stream of oxygen, cooled and stored in a tightly closed container until required.
2. For certain coals, which liberate volatile matter at a high rate, the early stage of heating may give a carryover 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 about 240 mm from the centre of the hottest zone. At the end of the first minute move the boat forward about 40 mm, at the end of each of the next 8 minutes, move the boat forward about 20 mm, and at the end of the tenth minute, move the boat forward about 40 mm. Allow the boat to remain in the hottest zone for a further 4 minutes.

5. BLANK DETERMINATION

Carry out a blank determination under the same conditions, but omitting the coal.