

International Standard



351

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Solid mineral fuels — Determination of total sulfur — High temperature combustion method

Combustibles minéraux solides — Dosage du soufre total — Méthode par combustion à haute température

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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.

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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 351 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*.

ISO 351 was first published in 1975. This second edition cancels and replaces the first edition of which it constitutes a minor revision (deletion of the temperature 1250 °C).

Solid mineral fuels — Determination of total sulfur — High temperature combustion method

1 Scope and field of application

This International Standard specifies a method of determining the total sulfur content of hard coal, brown coal, lignite and coke by the high temperature combustion method.

NOTE — An alternative method for the determination of total sulfur is given in ISO 334.

2 References

ISO 334, *Coal and coke — Determination of total sulphur — Eschka method.*

ISO 1170, *Coal and coke — Calculation of analysis to different bases.*

3 Principle

Burning of a sample of coal or coke in a stream of oxygen, in a tube furnace at a temperature of 1 350 °C. Absorption in hydrogen peroxide of the acid gases (oxides of sulfur and chlorine) formed and subsequent volumetric determination. A correction is made to take account of any chlorine liberated. A suitable additive prevents the retention of sulfur in the ash.

4 Reagents

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

4.1 Aluminium oxide (alumina) finely divided.

4.2 Hydrogen peroxide, solution, containing 30 ml of 30 % (*m/m*) H_2O_2 per litre neutralized with sodium tetraborate solution (4.4) using the mixed indicator solution (4.6).

4.3 Mercury(II) oxycyanide saturated solution at 20 °C (approximately 45 g/l).

WARNING — This compound and its solution are toxic and shall be handled with great care.

Saturate a suitable volume of distilled water with mercury(II) oxycyanide [$3\text{Hg}(\text{CN})_2 \cdot \text{HgO}$] by prolonged agitation; filter and neutralize the filtrate with the sulfuric acid (4.5), using bromothymol blue as an external indicator.

Store the solution in a dark glass bottle; do not keep longer than 4 days.

4.4 Sodium tetraborate decahydrate, standard volumetric solution, $c(1/2 \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) = 0,50 \text{ mol/l}$.

4.5 Sulfuric acid, standard volumetric solution, $c(1/2 \text{H}_2\text{SO}_4) = 0,025 \text{ mol/l}$.

4.6 Mixed indicator solution.

4.6.1 Solution A — Dissolve 0,125 g of 2-(4-dimethylamino-phenylazo)benzoic acid (methyl red) in 60 ml of ethanol or industrial spirit, and dilute to 100 ml with water.

4.6.2 Solution B — Dissolve 0,083 g of 3,7-bis(dimethyl-amino)phenothiazin-5-ylum chloride (methylene blue) in 100 ml of ethanol or industrial spirit. Store in a dark glass bottle.

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

4.7 Oxygen.

4.8 Soda asbestos (1,2 to 1,7 mm).

5 Apparatus

Usual laboratory apparatus (including graduated glassware in accordance with the relevant International Standards) and

5.1 Balance, accurate to 0,1 mg.

5.2 Furnace, capable of heating a tube of approximately 28 mm external diameter over a length of approximately 150 mm to a maximum temperature of 1 350 °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).

5.3 Combustion tube, of aluminous porcelain, of approximately 28 mm external diameter, 3 mm wall thickness and 650 mm length, which is gastight 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.

5.4 Oxygen cylinder, fitted with a needle valve to control the rate of flow of oxygen (4.7), and a flow meter to measure up to 300 ml/min. The oxygen should, as a precautionary measure, be passed through a U-tube packed with soda-asbestos (4.8).

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

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

5.7 Silica pusher, with a disc 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 the 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.

5.8 Two absorbers, of about 150 ml capacity, which may be large boiling tubes, wide-necked bottles or Drechsel bottles, each containing a sintered glass disc of 15 to 40 µm maximum pore size in the gas distribution tube. The diameter shall be such that the disc 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 disc 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.

6 Preparation of sample

The coal or coke used for the determination of total sulfur content is the analysis sample ground to pass a sieve of 212 µm

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.

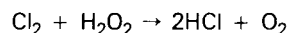
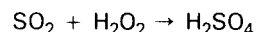
7 Procedure

Raise the temperature of the furnace (5.2) to 1 350 °C. Weigh to the nearest 0,1 mg about 0,5 g of the sample (clause 6), transfer to a combustion boat (5.5) and spread uniformly. Cover with about 0,5 g of the aluminium oxide (4.1). Measure 100 ml of the hydrogen peroxide solution (4.2) and either divide this amount between the two absorbers (5.8) or pour the whole into the single absorber.

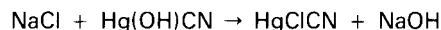
Adjust the water-pump so that a rapid stream of air is drawn through the absorber(s) and a constant stream of air through the pressure regulator. Insert the silica adapter into the combustion tube (5.3) and secure the stopper. Adjust the oxygen (4.7) flow to 300 ml/min.

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 (5.7) and the oxygen inlet. At the end of each of the next six 1 min 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 the note). Allow the boat to remain in the hottest zone for a further 4 min. Disconnect the absorber(s) and withdraw the boat on to a refractory sheet.

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 (4.6) and titrate with the sodium tetraborate solution (4.4). This gives the total acidity due to chlorine and oxides of sulfur according to the reactions



After titration the chloride ion is present as sodium chloride. Add 20 ml of the mercury(III) oxycyanide solution (4.3) (a sufficient excess for samples containing up to 1,2 % of chlorine) to convert the sodium chloride to sodium hydroxide



Titrate the liberated alkali with the sulfuric acid (4.5).

NOTE — 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, and for certain cokes of very low volatile matter (for example foundry cokes), the rate of pushing shall 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

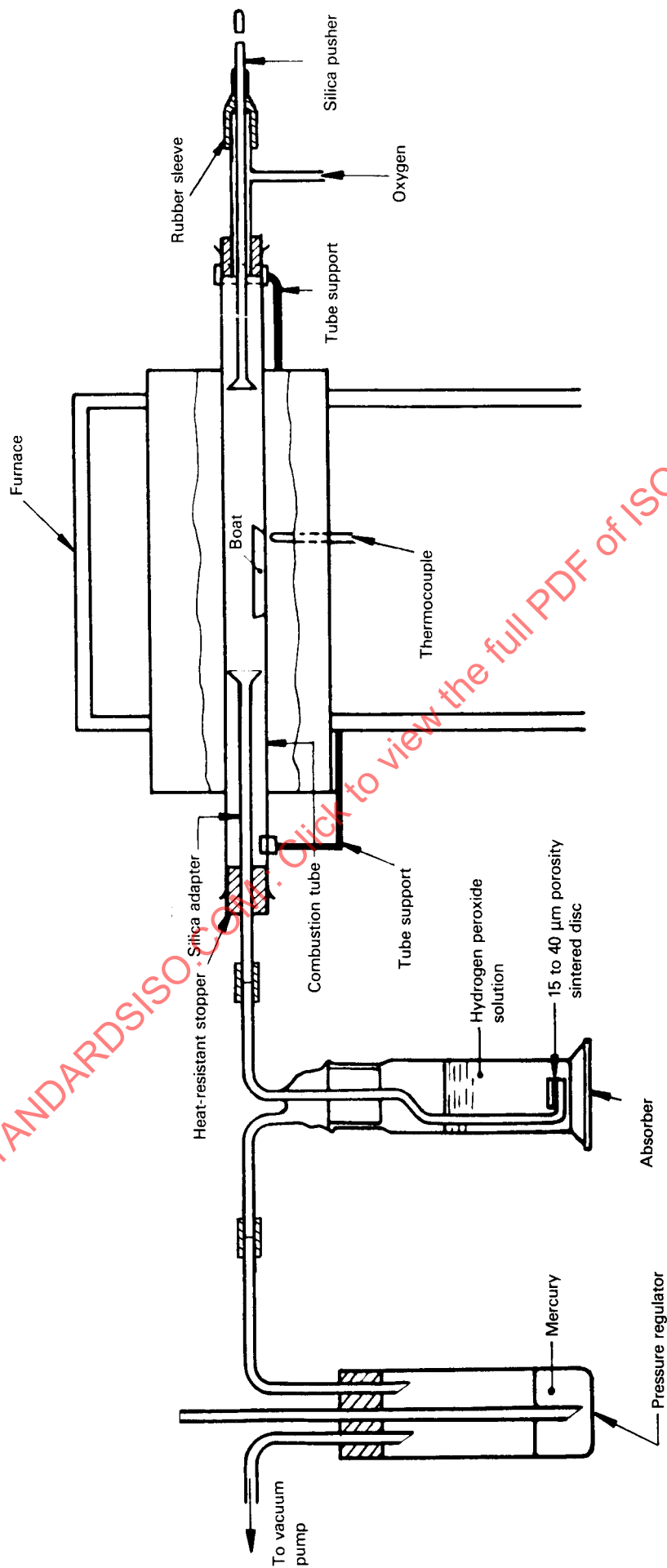


Figure — Arrangement of absorption train and furnace