INTERNATIONAL
STANDARD

ISO
351

Third edition
1996-02-15

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

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

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996

Reference number
ISO 351:1996(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 351 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This third edition cancels and replaces the second edition (ISO 351:1984), which has been technically revised.

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996

© ISO 1996
All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Introduction

An alternative method to that specified in this International Standard is given in ISO 334:1992, *Solid mineral fuels — Determination of total sulfur — Eschka method*.

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996

This page intentionally left blank

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996

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

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996

1 Scope

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

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 587:1981, *Solid mineral fuels — Determination of chlorine using Eschka mixture.*

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

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 a sample of coal or coke is burnt in a stream of oxygen, in a tube furnace at a temperature of 1 350 °C. The acid gases formed (chlorine and oxides of sulfur) are absorbed in hydrogen peroxide and subsequently determined titrimetrically. A correction is made to take account of any chlorine liberated and a suitable combustion additive prevents the retention of sulfur in the ash.

4 Reactions

4.1 $SO_2 + H_2O_2 \rightarrow H_2SO_4$

4.2 $Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$

4.3 $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$

4.4 $Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$

4.5 $NaCl + Hg(OH)CN \rightarrow NaOH + HgClCN$

4.6 $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

5 Reagents

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.

5.1 Aluminium oxide (alumina), finely divided.

5.2 Hydrogen peroxide, approximately 3 % (*m/m*) neutral solution.

Dilute 100 ml of 30 % (*m/m*) hydrogen peroxide solution to 1 litre with water and neutralize with the sodium tetraborate solution (5.4) using the mixed indicator (5.6).

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

Saturate a suitable volume of water with mercury(II) oxycyanide by prolonged agitation; filter and neutralize the filtrate with the sulfuric acid (5.5), using bromothymol blue as an external indicator. Store in a dark glass bottle; do not keep for more than 4 d.

5.4 Sodium tetraborate, standard volumetric solution, $c(\mathrm{Na_2B_4O_7}) = 0{,}025$ mol/l.

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

5.5 Sulfuric acid, standard volumetric solution, $c(\mathrm{H_2SO_4}) = 0{,}012\,5$ mol/l.

5.6 Mixed indicator solution.

5.6.1 Solution A

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

5.6.2 Solution B

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

5.6.3 Mixed solution

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

5.7 Oxygen, laboratory grade, of purity at least 99,6 % (*m/m*).

5.8 Sodium hydroxide on an inert base, preferably of a coarse grading, for example 1,2 mm to 1,7 mm, and preferably of the self-indicating type.

6 Apparatus

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

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

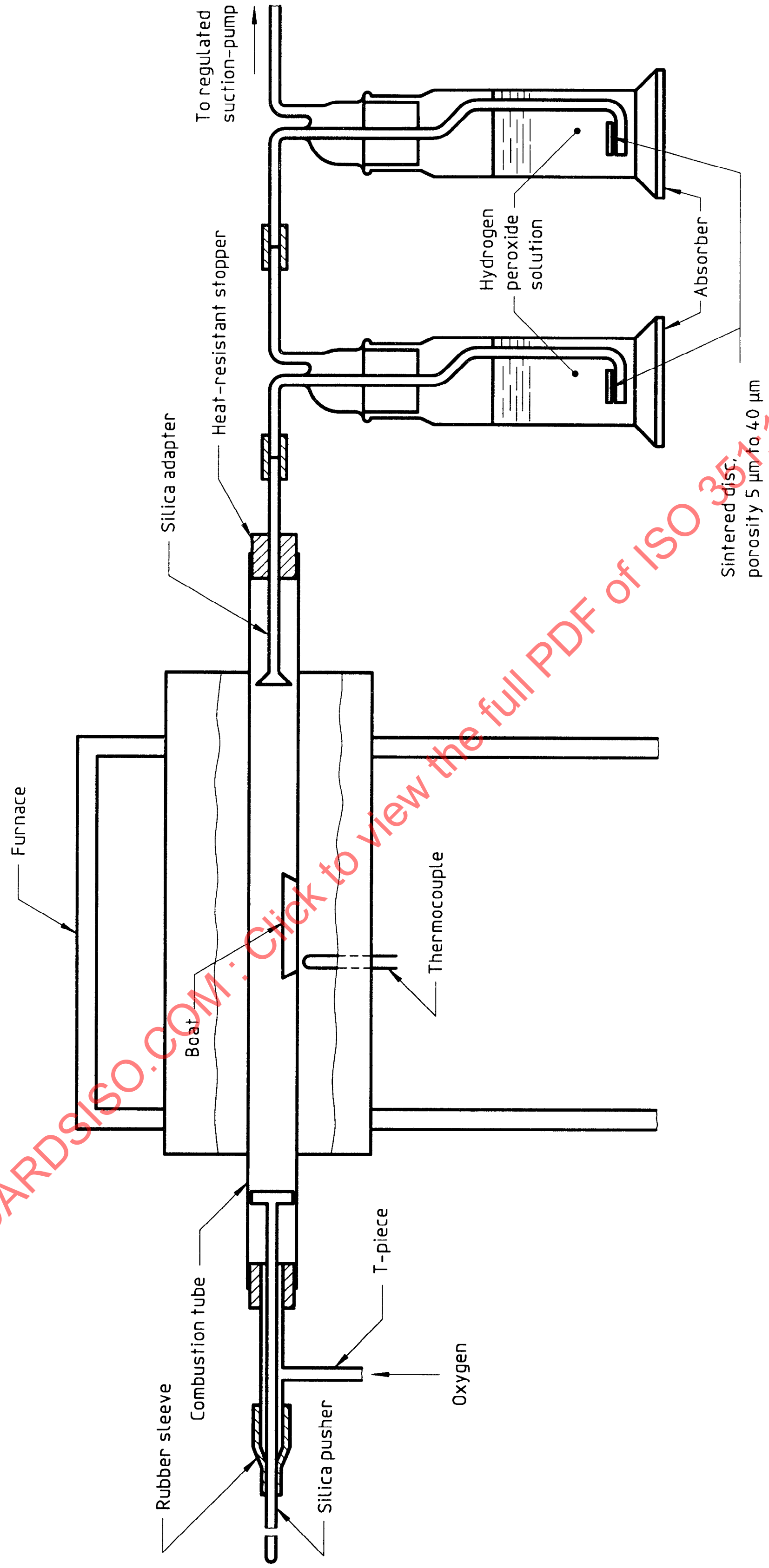
6.3 Furnace, capable of heating a tube, of approximately 28 mm external diameter over a length of 125 mm to 150 mm, to a temperature of 1 350 °C.

The furnace may be heated electrically, using either silicon carbide resistance rods (controlled by a variable transformer) or a resistance wire (controlled by a variable resistance).

6.4 Combustion tube, of approximately 28 mm external diameter, 3 mm wall thickness and 650 mm length, made of aluminous porcelain which is impervious to gases up to the working temperature (see figure 1).

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 from the inner wall of the heated tube, and a heat-resistant stopper (acrylonitrile or chloroprene is suitable). Alternatively, the tube may have, a beak end, at the exit, 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 onto the outer wall of the tube. In this case it will be necessary to lag the end of the combustion tube with a suitable heat-resistant mineral fibre to prevent condensation in the tube.

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996



STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996

Figure 1 — Arrangement of furnace and absorption train

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996

6.5 Oxygen cylinder, fitted with a needle valve to control the rate of flow of oxygen (5.7), and a flowmeter to measure up to 300 ml/min. The oxygen should, as a precautionary measure, be passed through a U-tube packed with sodium hydroxide on an inert base (5.8).

6.6 Combustion boat, of iron-free, unglazed porcelain, of minimum dimensions 45 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.

6.7 Heat-resistant wire, approximately 2 mm thick and 450 mm long, with a bent end to transfer the used boat from the combustion tube onto a rigid refractory sheet.

6.8 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 rubber stopper which closes the inlet end of the combustion tube, the other being sealed by a rubber sleeve (see note 1) 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 1 The rubber sleeve should be changed periodically to avoid leakage.

6.9 Two absorbers, of capacity about 150 ml, which may be large boiling tubes, wide-necked bottles or Dreschel bottles, each 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 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 about 35 mm in diameter and 150 mm deep, so that the bubbler disc (0,015 mm to 0,040 mm maximum pore size) 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 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 is illustrated in figure 1.

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.

If the results are to be calculated other than on an "air-dried" basis (see clause 10), 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 chlorine by the Eschka method (ISO 587) is required.

8 Procedure

Raise the temperature of the furnace (6.3) to 1 350 °C. Weigh, to the nearest 0,1 mg, about 0,5 g of the test sample (clause 7) and transfer to a combustion boat (6.6), taking care to spread uniformly. Cover evenly with about 0,5 g of the aluminium oxide (5.1). Measure 100 ml of the hydrogen peroxide solution (5.2) and either divide this amount between the two absorbers (6.9) or pour it all into the single absorber.

Adjust the suction-pump and pressure regulator (see 6.9) so that a rapid stream of air is drawn at constant pressure through the absorber(s). Insert the silica adapter into the combustion tube (6.4) and secure the stopper. Adjust the oxygen (5.7) 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 (6.8) and the oxygen inlet. 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, pulling back the 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, using the bent heat-resistant wire (6.7), withdraw the used combustion boat onto a thick sheet of suitable refractory material.

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, wash out the absorber(s) and collect the washings in the same filtration beaker. Add 2 or 3 drops of the mixed indicator solution (5.6) and titrate with the sodium tetraborate solution (5.4) to a neutral steel-grey colour. Note the titration volume. This procedure gives the total acidity due to oxides of sulfur and chlorine (see the equations in 4.1 to 4.4). Determine the correction for chlorine as described in either 8.1 or 8.2.

For certain coals which liberate volatile matter at a fast rate, the early stages of heating may give a carry-over of unburnt carbon particles. For such coals, and for certain cokes of very low volatile matter (for example foundry cokes), 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. After 1 min, move the boat forward 20 mm. At the end of each of the next eleven 1 min periods, move the boat forward about 20 mm. Allow the boat to remain in the hottest zone for a further 4 min.

8.1 Chlorine correction — Mercury(II) oxycyanide method

After titration with the sodium tetraborate solution (5.4), the chloride ion is present as sodium chloride. Add 20 ml of the mercury(II) oxycyanide solution (5.3) to convert the sodium chloride to sodium hydroxide (see note 2). Titrate the liberated alkali with the sulfuric acid (5.5) (see the equations in 4.5 and 4.6). Note the titration volume.

NOTE 2 For 0,5 g test portions of samples containing up to 1,2 % chlorine, 20 ml of mercury(II) oxycyanide solution is sufficient excess.

8.2 Chlorine correction — Eschka method

Determine the chlorine content of the test sample, using a further test portion, according to the procedure described in ISO 587.

9 Blank test

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

10 Expression of results

The total sulfur content, w_S, of the sample as analysed, expressed as a percentage by mass, is given by the equation in either 10.1 or 10.2, as appropriate.

Report the result, as the mean of duplicate determinations, to the nearest 0,01 % (*m/m*).

The results of the determination described in this International Standard are reported on the "air-dried" basis. Calculation of results to other bases is dealt with in ISO 1170.

10.1 Calculation using the mercury(II) oxycyanide method for chlorine correction

$$w_S = \frac{3{,}206[c_1(V_1 - V_2) - c_2(V_3 - V_4)]}{m}$$

where

m	is the mass, in grams, of the test portion;
V_1	is the volume, in millilitres, of the sodium tetraborate solution used in the determination;
V_2	is the volume, in millilitres, of the sodium tetraborate solution used in the blank test;
V_3	is the volume, in millilitres, of the sulfuric acid solution used in the determination;
V_4	is the volume, in millilitres, of the sulfuric acid solution used in the blank test;
c_1	is the concentration, expressed in moles per litre, of the sodium tetraborate solution;
c_2	is the concentration, expressed in moles per litre, of the sulfuric acid solution;
0,032 06	is the mass, in grams of sulfur, equivalent to 1 ml of 1 molar sodium tetraborate solution.

STANDARDSISO.COM : Click to view the full PDF of ISO 351:1996