INTERNATIONAL STANDARD

ISO 334

Second edition
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Solid mineral fuels — Determination of total sulfur — Eschka method

Combustibles minéraux solides — Dosage du soufre total — Méthode Eschka

Reference number
ISO 334:1992(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 334 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Sub-Committee SC 5, *Methods of analysis*.

This second edition cancels and replaces the first edition (ISO 334:1975), of which it constitutes a technical revision.

Annex A of this International Standard is for information only.

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Introduction

An alternative reference method to that specified in this International Standard is given in ISO 351:1984, *Solid mineral fuels — Determination of total sulfur — High temperature combustion method*.

Instrumental methods for a more rapid determination of total sulfur are now available. If such a method is to be used, it is important to demonstrate that the method is free from bias, when compared to this reference method, and will give levels of repeatability and reproducibility which are the same as, or better than, those quoted for the reference method (see clause 9).

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Solid mineral fuels — Determination of total sulfur — Eschka method

1 Scope

This International Standard specifies a reference method for determining the total sulfur content of hard coal, brown coals and lignites, and coke by the Eschka method.

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 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 test portion is ignited in intimate contact with Eschka mixture in an oxidizing atmosphere, to remove combustible matter and to convert the sulfur to sulfate. This is then extracted with hydrochloric acid solution and determined gravimetrically by precipitation with barium chloride.

4 Reagents

WARNING — Care should be exercised when handling the 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 Eschka mixture.

Mix two parts by mass of light, calcined magnesium oxide with one part by mass of anhydrous sodium (or potassium) carbonate. The mixture shall entirely pass a test sieve of 212 µm nominal size of openings.

4.2 Hydrochloric acid, concentrated, ρ approximately 1,18 g/ml, approximately 36 % (m/m).

4.3 Potassium sulfate, solution.

Weigh, to the nearest 0,1 mg, about 2 g of potassium sulfate, previously dried at a temperature of 105 °C to 110 °C. Dissolve in water and dilute to 1 litre.

4.4 Barium chloride, approximately 85 g/l solution.

Dissolve 100 g of barium chloride dihydrate in water and dilute to 1 litre. Filter before use through a close-textured, doubly acid-washed filter-paper or filter-paper pad.

4.5 Methyl red, indicator solution.

Dissolve 1 g of 2-(4-dimethylaminophenylazo)benzoic acid, sodium salt (methyl red) in 1 litre of water.

4.6 Ammonia, concentrated solution, not less than 25 % (*m/m*).

4.7 Silver nitrate, 17 g/l solution.

Dissolve 17 g of silver nitrate in water and dilute to 1 litre. Store in a dark glass bottle.

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.

5.3 Electrically heated muffle furnace, capable of being maintained at a temperature of 800 °C ± 25 °C. The ventilation through the muffle furnace shall be such as to give about five air changes per minute.

5.4 Crucible, of platinum, silica or glazed porcelain, of capacity approximately 25 ml.

5.5 Flat plate, 6 mm thick, of silica (or other suitable refractory material), which fits easily into the muffle furnace (5.3).

5.6 Gooch crucible, of glazed porcelain or sintered glass.

5.7 Air oven, capable of being maintained at a temperature of 130 °C ± 10 °C.

6 Preparation of test sample

The test sample is the general analysis test sample prepared in accordance with ISO 1988, ISO 2309 or ISO 5069-2, as appropriate. Expose the sample, in a thin layer, for the minimum time required for the moisture content to reach approximate equilibrium with the laboratory atmosphere (this is particularly important for brown coals and lignites).

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 8), then, after weighing the test portion (see 7.1), 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.

7 Procedure

7.1 Test portion

7.1.1 For coal

Take a test portion of the mass given in table 1 (for the expected total sulfur content), weighing to the nearest 0,1 mg.

Table 1 — Test portion for coal

Expected total sulfur content % (*m/m*)	Mass of test portion g
< 5	1,0
5 to 10	0,5
> 10	0,25

7.1.2 For coke

Take a test portion of 1 g, weighing to the nearest 0,1 mg.

7.2 Charging the crucible

Cover the bottom of the crucible (5.4) uniformly with 0,5 g of the Eschka mixture (4.1), weighed to the nearest 0,1 mg. Mix the test portion intimately with 2,5 g of the Eschka mixture, weighed to the nearest 0,1 mg, in a suitable vessel. Transfer the mixture to the 25 ml crucible. Level the contents by tapping the crucible gently on the bench and cover the contents uniformly with 1,0 g of the Eschka mixture, weighed to the nearest 0,1 mg.

NOTE 1 The entire 4 g of the Eschka mixture should be weighed out and the 0,5 g and 1 g portions, required for the bottom and top layers, should be extracted from this. For this purpose, it is convenient to calibrate a small glass tube for each bath of Eschka mixture, to deliver 0,5 g and 1 g without weighing. The bottom layer of Eschka mixture below the test portion mixture reduces attack on the porcelain surface, so that the extraction of sulfate with hot water is complete even when the surface deteriorates.

7.3 Ignition

7.3.1 For coal

Place the charged crucible (and any others up to the limit of the muffle furnace capacity) in the cold muffle furnace (5.3) and raise the temperature to 800 °C ± 25 °C in about 1 h, maintaining this temperature for at least a further 1,5 h. Withdraw the crucible (or crucibles) and allow to cool.

NOTE 2 The cracking of porcelain crucibles can be prevented, if they are slowly cooled by insertion in supports of light porous firebrick on removal from the muffle furnace.

7.3.2 For coke

Place the charged crucible (or crucibles) on the cold insulating plate (5.5) and insert into the muffle furnace (5.3) at a temperature of 800 °C ± 25 °C, maintaining this temperature for at least a further 1,5 h. Withdraw the crucible (or crucibles) and allow to cool. (See note 2 to 7.3.1.)

7.4 Recovering the residue

Transfer the ignited mixture from the crucible to a 400 ml beaker containing 25 ml to 30 ml of water. If unburnt particles are present, the determination shall be stopped and the test repeated. Wash the crucible thoroughly with about 50 ml of hot water, and add the washings to the contents of the beaker.

7.5 Extraction

Place a watch-glass on the beaker and then, while tilting the watch-glass, carefully add enough hydrochloric acid (4.2) to dissolve the solid matter (17 ml will normally be required), warming the contents of the beaker to effect solution. Boil for 5 min to expel carbon dioxide and filter, collecting the filtrate in a 400 ml conical beaker.

NOTE 3 A medium-textured, doubly acid-washed filter-paper or a filter-paper pad is recommended for speed of filtration.

To prepare the filter-paper pad, shake doubly acid-washed filter-paper clippings, in pieces with areas of approximately 1 cm^2, with water in a bottle until the paper is thoroughly disintegrated. Place a porcelain filter cone of 25 mm in a 75 mm funnel, close the stem of the funnel with a finger and add water until the cone is immersed and the funnel stem is full. Shake, onto the cone, sufficient paper pulp to form a pad 5 mm thick, and level it with a flat-ended glass rod. Allow the excess water to drain away by removing the finger from the stem and as drainage ceases, lightly tamp the pad round the edges with the glass rod. A final wash with water renders the filter ready for use.

Wash the filter with five 20 ml portions of hot water.

Add 2 or 3 drops of the methyl red indicator solution (4.5) to the combined filtrate and washings, and then cautiously add the ammonia solution (4.6) until the colour of the indicator changes and a trace of precipitate is formed. Add enough hydrochloric acid (4.2) to just redissolve the precipitate and then add 1 ml in excess.

7.6 Precipitation of barium sulfate

After extraction, dilute the solution, if necessary, to approximately 200 ml and cover the beaker containing the solution with a watch-glass. Heat the covered beaker until the solution boils and then reduce the heating slightly until ebullition of the solution ceases. Then add 10 ml of the cold barium chloride solution (4.4) from a pipette with a delivery time of approximately 20 s, so that the barium chloride solution falls into the centre of the hot solution, while it is being agitated. Keep the solution just below boiling point for 30 min.

Filter the solution using one of the following techniques.

a) By gravity through an ashless, close-textured, doubly acid-washed filter-paper of diameter 100 mm to 125 mm. Carefully fold the filter-paper and fit it into a fluted, long-stemmed 60° funnel, so that the stem remains full of liquid during the filtration.

b) By gravity through a filter-paper pad prepared from ashless, doubly acid-washed filter-paper (see note 4 to 7.5).

c) By suction through a pad of filtration mineral fibre in a Gooch crucible (5.6). Before commencing the filtration, dry the Gooch crucible and pad for 1 h at a temperature of 130 °C ± 10 °C and weigh, to the nearest 0,1 mg.

Wash the precipitate with hot water, using not more than 250 ml, until the last 20 ml of the washings give not more than a faint opalescence with the silver nitrate solution (4.7).

If technique a) or b) is used, place the wet filter-paper or pad in the previously ignited and weighed crucible (5.4) on the cold flat plate (5.5).

If technique b) is used, after transferring the filter-paper pad to the crucible, wipe the funnel successively with two halves of an ashless filter-paper and place this paper in the crucible with the pad. Insert the crucible slowly into the muffle furnace (5.3), at a temperature of 800 °C ± 25 °C, and then heat for 15 min. Cool in a desiccator and reweigh, to the nearest 0,1 mg.

If technique c) is used, dry the Gooch crucible (5.6) and pad for 1 h at a temperature of 130 °C ± 10 °C, cool in a desiccator and reweigh, to the nearest 0,1 mg.

7.7 Blank test

Carry out a blank test using the same procedure as for the determination, but omitting the test portion (as described in 7.2 to 7.6). Using a one-mark pipette, add 25,0 ml of the potassium sulfate solution (4.3) to the filtrate before adding the methyl red indicator solution (4.5), as described in 7.5.

8 Expression of results

The sulfur content, w_S, of the sample, expressed as a percentage by mass, is given by the equation

$$w_S = \frac{13{,}74(m_2 - m_3 + 0{,}033\ 48\rho_{K_2SO_4})}{m_1}$$

where

m_1 is the mass, expressed in grams, of the test portion;

m_2 is the mass, expressed in grams, of barium sulfate found in the determination;

m_3 is the mass, expressed in grams, of barium sulfate found in the blank test;

$\rho_{K_2SO_4}$ is the mass concentration, expressed in grams per litre, of the potassium sulfate solution (4.3).

NOTE 4 The derivation of the factors used in the equation is given in annex A .

Report the result, as the mean of duplicate determinations, to the nearest 0,1 % (*m/m*).

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

9 Precision

9.1 Repeatability limit

The results of duplicate determinations, carried out at different times, in the same laboratory, by the same operator with the same apparatus on representative portions taken from the same test sample, should not differ by more than 0,05 % absolute.

9.2 Reproducibility critical difference

The means of the results of duplicate determinations, carried out in each of two laboratories on representative portions taken from the same sample after the last stage of sample preparation, should not differ by more than 0,1 % absolute, at a 95 % confidence level.

10 Test report

The test report shall include the following particulars:

a) the identification of the sample;

b) the method used by reference to this International Standard;

c) the date of the test;

d) the results and the form in which they are expressed;

e) any unusual features noted during the determination;

f) any operation not included in this International Standard, or regarded as optional.

Annex A

(informative)

Derivation of factors used in the calculation in clause 8

In this annex, relative atomic masses and relative molecular masses are represented by the chemical formulae in square brackets. The relative atomic masses given in table A.1 were used in the calculations.

Table A.1

Element	Symbol	Relative atomic mass
Barium	Ba	137,33
Oxygen	O	15,999
Potassium	K	39,098
Sulfur	S	32,06

The mass, expressed in grams, of barium sulfate equivalent to 25 ml of potassium sulfate solution is given by the formula

$$\frac{[BaSO_4]}{[K_2SO_4]} \times \frac{25\rho_{K_2SO_4}}{1\,000}$$

where $\rho_{K_2SO_4}$ is the mass concentration, expressed in grams per litre, of the potassium sulfate solution.

Thus, the sulfur content w_S of the sample, expressed as a percentage by mass, is given by the equation

$$w_S = \frac{100}{m_1}\left(\frac{[S]}{[BaSO_4]} \times m_2 - \frac{[S]}{[BaSO_4]} \times \left(m_3 - \frac{[BaSO_4]}{[K_2SO_4]} \times \frac{25\rho_{K_2SO_4}}{1\,000}\right)\right)$$

where

m_1 is the mass, expressed in grams, of the test portion;

m_2 is the mass, expressed in grams, of barium sulfate found in the determination;

m_3 is the mass, expressed in grams, of barium sulfate found in the blank test.

Hence

$$w_S = \frac{13{,}74(m_2 - m_3 + 0{,}033\,48\rho_{k_2SO_4})}{m_1}$$