INTERNATIONAL STANDARD

ISO 334

Fourth edition
2020-08

Coal and coke — Determination of total sulfur — Eschka method

Charbon et coke — Dosage du soufre total — Méthode Eschka

Reference number
ISO 334:2020(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 27, *Coal and coke*, Subcommittee SC 5, *Methods of analysis*.

This fourth edition cancels and replaces the third edition (ISO 334:2013), of which it constitutes a minor revision. The changes compared to the previous edition are as follows:

- updating of referenced documents;
- amending of Introduction;
- adding of the provision of terms and definitions.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The objective of this document is to provide a reference method for determining the total sulfur content in coal and coke with Eschka 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 10).

Coal and coke — Determination of total sulfur — Eschka method

1 Scope

This document 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 687, *Solid mineral fuels — Coke — Determination of moisture in the general analysis test sample*

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

ISO 5068-2, *Brown coals and lignites — Determination of moisture content — Part 2: Indirect gravimetric method for moisture in the analysis sample*

ISO 11722, *Solid mineral fuels — Hard coal — Determination of moisture in the general analysis test sample by drying in nitrogen*

ISO 13909-4, *Hard coal and coke — Mechanical sampling — Part 4: Coal — Preparation of test samples*

ISO 18283, *Hard coal and coke — Manual sampling*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

A test portion is ignited in intimate contact with the Eschka mixture in an oxidizing atmosphere at 800 °C 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.

5 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.

5.1 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.

5.2 Hydrochloric acid.

Concentrated ρ approximately 1,18 g/ml, mass fraction approximately 36 %.

5.3 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 l.

5.4 Barium chloride, approximately 85 g/l solution.

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

5.5 Methyl red indicator solution.

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

5.6 Ammonia, concentrated solution, mass fraction not less than 25 %.

5.7 Silver nitrate, 17 g/l solution.

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

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.

6.3 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.

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

6.5 Flat plate, 6 mm thick, of silica (or other suitable refractory material) which fits easily into the muffle furnace (6.3).

6.6 Gooch crucible, of glazed porcelain or sintered glass.

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

7 Preparation of test sample

The sample shall be the general analysis test sample, prepared to a nominal top size of 212 µm by the preparation procedures specified in ISO 13909-4 or ISO 18283.

The sample should be brought in moisture equilibrium with the laboratory atmosphere by exposure in a thin layer on a tray. Exposure time shall be kept to a minimum (this is particularly important for brown coals and lignites).

The sample shall be thoroughly mixed for at least 1 min immediately before analysis, preferably by mechanical means.

If the results are to be calculated other than on an "air-dried" basis (see Clause 9), then, after weighing the test portion (see 8.1), determine the moisture content using a further portion of the test sample by the method specified in ISO 687, ISO 5068-2 or ISO 11722.

8 Procedure

8.1 Test portion

8.1.1 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 %	Mass of test portion g
<5	1,0
5 to 10	0,5
>10	0,25

8.1.2 For coke

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

8.2 Charging the crucible

Cover the bottom of the crucible (6.4) uniformly with 0,5 g of the Eschka mixture (5.1), 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.

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 the Eschka mixture to deliver 0,5 g and 1 g without weighing. The bottom layer of the 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.

8.3 Ignition

8.3.1 For coal

Place the charged crucible (and any others up to the limit of the muffle furnace capacity) in the cold muffle furnace (6.3) 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 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.

8.3.2 For coke

Place the charged crucible (or crucibles) on the cold insulating flat plate (6.5) and insert into the muffle furnace (6.3) 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 in 8.3.1.

8.4 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.

8.5 Extraction

Place a watch glass on the beaker and then, while tilting the watch glass, carefully add enough hydrochloric acid (5.2) 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 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 around 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 two or three drops of the methyl red indicator solution (5.5) to the combined filtrate and washings, and then cautiously add the ammonia solution (5.6) until the colour of the indicator changes and a trace of precipitate is formed. Add enough hydrochloric acid (5.2) to just redissolve the precipitate and then add 1 ml in excess.

8.6 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 (5.4) 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 in 8.5).

c) By suction through a pad of filtration mineral fibre in a Gooch crucible (6.6). 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 (5.7).

If technique a) or b) is used, place the wet filter paper or pad in the previously ignited and weighed crucible (6.4) on the cold flat plate (6.5).

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 (6.3), 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 (6.6) 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.

8.7 Blank testing

Carry out a blank test using the same procedure as for the determination, but omitting the test portion (as described in 8.2, 8.3, 8.4, 8.5, and 8.6). Using a one-mark pipette, add 25,0 ml of the potassium sulfate solution (5.3) to the filtrate before adding the methyl red indicator solution (5.5), as described in 8.5.

9 Expression of results

Sulfur mass fraction, w_S, expressed as a percentage by mass, is given by Formula (1)

$$w_S = \frac{13{,}74\left(m_2 - m_3 + 0{,}033\,48\,\rho_{K_2SO_4}\right)}{m_1} \tag{1}$$

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;
13,74	is the factor, expressed in %;
0,03348	is the factor, expressed in l;
$\rho_{K_2SO_4}$	is the mass concentration, expressed in grams per litre, of the potassium sulfate solution (5.3).

NOTE The derivation of the factors used in Formula (1) is given in Annex A.

Report the result, as the mean of duplicate determinations, to the nearest 0,1 %.