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Carbonaceous materials used in the production of aluminium — Calcined coke and calcined carbon products — Determination of total sulfur by the Eschka method

Produits carbonés utilisés pour la production de l'aluminium — Coke calciné et produits carbonés calcinés — Dosage du soufre total par la méthode Eschka

Reference number
ISO 5931:2000(E)

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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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 5931 was prepared by Technical Committee ISO/TC 47, *Chemistry*, Subcommittee SC 7, *Aluminium oxide, cryolite, aluminium fluoride, sodium fluoride, carbonaceous products for the aluminium industry*.

Annex A of this International Standard is for information only.

Introduction

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 this reference method (see clause 9).

Carbonaceous materials used in the production of aluminium — Calcined coke and calcined carbon products — Determination of total sulfur by the Eschka method

1 Scope

This International Standard specifies a reference method for determining the total sulfur content of calcined coke and calcined carbon products by the Eschka method, provided that they contain a minimum of 0,1 % by mass and preferably less than 4 % by mass of sulfur.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 4787:1984, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity*.

ISO 4788:1980, *Laboratory glassware — Graduated measuring cylinders*.

ISO 5069-2:1983, *Brown coals and lignites — Principles of sampling — Part 2: Sample preparation for determination of moisture content and for general analysis*.

ISO 6375:1980, *Carbonaceous materials for the production of aluminium — Coke for electrodes — Sampling*.

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. The sulfate is then extracted using a hydrochloric acid solution and the sulfur content, in the form of sulfate, is determined gravimetrically by precipitation of the sulfate 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, calicined magnesium oxide with one part by mass of anhydrous sodium (or potassium) carbonate. Pass the mixture entirely through a test sieve of 212 μm nominal size of openings.

4.2 Hydrochloric acid, concentrated, ρ approximately 1,18 g/ml, approximately 36 % by mass.

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 l.

4.4 **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 (see 5.8).

4.5 **Methyl red**, indicator solution.

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

4.6 **Ammonia**, concentrated solution, no less than 25 % by mass.

4.7 **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.

5 Apparatus

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

5.2 **Graduated glassware**, complying with the requirements for class A in ISO 4788 and in accordance with ISO 4787.

5.3 **Electrically heated muffle furnace**, capable of being maintained at (800 ± 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 approximately 25 ml capacity.

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**, with a maximum pore size of 7 µm, of glazed porcelain or sintered glass.

Before commencing the filtration, dry the Gooch crucible and pad for 1 h in the air oven (5.7) at (130 ± 10) °C and weigh it to the nearest 0,1 mg.

5.7 **Air oven**, capable of being maintained at (130 ± 10) °C.

5.8 **Filter paper** or **filter-paper pad**, doubly acid-washed, ashless, close-textured and/or medium-textured.

To prepare the filter-paper pad, shake doubly acid-washed filter-paper clippings (cut into pieces 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 sufficient paper pulp to form a pad 5 mm thick onto the cone and level it with a flat-ended glass rod. Allow the excess water to drain off by removing the finger from the stem and as drainage ceases, lightly tamp the pad around the edges with the glass rod. Finally wash with water to render the filter ready for use.

5.9 **Dessicator**.

6 Preparation of test sample

The test sample is the representative sample prepared in accordance with ISO 6375. Expose the test sample, distributed in a thin layer, to the laboratory atmosphere for the minimum time required for the moisture content to reach approximate 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 8), then, after weighing the test portion (see 7.1), determine the moisture content using another portion of the test sample.

7 Procedure

7.1 Test portion

Take two test portions of 1 g, each weighed to the nearest 0,1 mg. Carry out the procedure given in 7.2 to 7.6 on each test portion.

7.2 Loading the crucible

Weigh 4 g of the Eschka mixture (4.1). Divide this mixture into three portions, 0,5 g, 1,0 g and 2,5 g, and weigh each to the nearest 0,1 mg. For this purpose, it may be convenient to calibrate two glass tubes for the 0,5 g and 1,0 g portions.

Uniformly cover the bottom of the crucible with the 0,5 g portion of the Eschka mixture. In another suitable vessel, mix the test portion thoroughly with the 2,5 g portion of the Eschka mixture. Transfer this mixture to the 25 ml crucible. Level the contents by tapping the crucible gently on the laboratory benchtop and cover the contents uniformly with 1,0 g portion of the Eschka mixture.

NOTE The 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

Place the loaded crucible (or crucibles) on the cold insulating plate (5.5) and insert into the muffle furnace (5.3) maintained at 800 °C, and heat for at least 3 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 into supports of light porous firebrick upon removal from the muffle furnace.

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, stop the determination and repeat the test. Wash the crucible thoroughly with about 50 ml of hot water, then add the washings to the contents of the beaker.

7.5 Extraction

Place a watch-glass on the beaker and, tilting the watch-glass to leave an opening, carefully add enough hydrochloric acid (4.2) to dissolve the solid matter (17 ml will normally be required) while warming the contents of the beaker to enhance solution. Boil for 5 min to expel carbon dioxide. Filter (5.8) and collect the filtrate in a 400 ml conical beaker.

NOTE A medium-textured, doubly acid-washed filter-paper or a filter-paper pad can be used to speed filtration.

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 just enough hydrochloric acid (4.2) to 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 then reduce the heat slightly until the solution ceases to boil. Using a pipette, add, over a period of 20 s, 10 ml of the cold barium sulfate solution to the middle of the hot, stirred solution. Keep the solution just below the 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 (see 5.8) 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 5.8);

c) by suction through a pad of filtration mineral fibre in a Gooch crucible (5.6).

Wash the precipitate with hot water, using no more than 250 ml, until the last 20 ml of the washings give no 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) maintained at 800 °C, and heat for 15 min. Cool in a desiccator (5.9) and reweigh to the nearest 0,1 mg.

If technique c) is used, dry the Gooch crucible (5.6) and pad for 1 h in the air oven (5.7) at 130 °C, cool in a desiccator (5.9) and reweigh to the nearest 0,1 mg.

7.7 Blank

Carry out a blank determination using the same procedure specified in 7.2 to 7.6, but omitting the test portion . In 7.5, 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).

8 Expression of results

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

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

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 control;

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

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

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

The results of the determination described in this International Standard shall be reported on the “air-dried” basis. Calculation of the results to other bases is dealt with in ISO 1170 (see reference [1] of the Bibliography).

9 Precision

9.1 General

The precision data for this method were obtained in accordance with ISO 5725:1986[2].

9.2 Repeatability, r

Two successive results obtained by the same operator, working with the same apparatus under constant conditions and using the same test material, shall be considered acceptable if they do not differ by more than 0,05 % (absolute).

9.3 Reproducibillty, R

Two independent results obtained by different operators, working in different laboratories under comparable conditions and using the same test material, shall be considered acceptable if they do not differ by more than 0,1 % (absolute).

10 Test report

The test report shall include the following information:

a) a complete identification of the test sample;

b) a reference to this International Standard, i.e. ISO 5931:2000;

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

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 $m_{\mathrm{BaSO_4}}$ equivalent to 25 ml of potassium sulfate solution is given by the formula

$$m_{\mathrm{BaSO_4}} = \frac{M_{\mathrm{BaSO_4}}}{M_{\mathrm{K_2SO_4}}} \times \frac{25\rho_{\mathrm{K_2SO_4}}}{1\,000}$$

where

$\rho_{\mathrm{K_2SO_4}}$ is the concentration, expressed in grams per litre, of the potassium sulfate solution;

$M_{\mathrm{BaSO_4}}$ is the relative molecular mass of barium sulfate;

$M_{\mathrm{K_2SO_4}}$ is the relative molecular mass of potassium sulfate.

Thus, the sulfur content w_{S} of the sample, expressed as a percentage by mass, is given by the equation

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

where

M_{S} is the relative molecular mass of sulfur;

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 test portion determination;

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

Hence

$$w_{\mathrm{S}} = \frac{13{,}74\left(m_2 - m_3 + 0{,}033\,48\rho_{\mathrm{K_2SO_4}}\right)}{m_1}$$

Bibliography

[1] ISO 1170, *Coal and coke — Calculation of analyses to different bases*.

[2] ISO 5725:1986[1], *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests*.

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[1] Now withdrawn.

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