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Coal and coke — Determination of chlorine using Eschka mixture

Charbon et coke — Dosage du chlore à l'aide du mélange Eschka

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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.

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).

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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 587:1997), of which it constitutes a minor revision. The changes compared to the previous edition are as follows:

- updating of referenced documents;
- 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.

Coal and coke — Determination of chlorine using Eschka mixture

1 Scope

This document specifies a method of determining the chlorine content of hard coal, brown coals and lignites, and coke using Eschka mixture.

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 known mass of sample is ignited in intimate contact with Eschka mixture in an oxidizing atmosphere to remove combustible matter and to convert the chlorine to alkaline chlorides. These are extracted with nitric acid or water and determined by either the Volhard or the Mohr method, or by potentiometric titration using an Ion Selective Electrode (ISE).

5 Reagents

WARNING — Care should be exercised when handling reagents, many of which are toxic and corrosive.

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

5.1 For all methods

5.1.1 Eschka mixture.

Mix two parts by mass of light, calcined magnesium oxide with one part of anhydrous sodium or potassium carbonate. The mixture shall entirely pass a test sieve of 0,212 mm nominal aperture.

5.1.2 **Nitric acid**, concentrated, chlorine-free, mass fraction approximately 70 %.

5.2 For the Volhard and ISE methods

5.2.1 **Silver nitrate**, standard volumetric solution, $c(\text{AgNO}_3) = 0,025 \text{ mol/l}$.

Heat crushed, crystalline silver nitrate at 125 °C for two to three hours. Dissolve 4,247 g in water and dilute to 1 l. Store in an amber glass bottle.

5.3 For the Volhard method only

5.3.1 **3,5,5-Trimethylhexan-1-ol**.

5.3.2 **n-Hexan-1-ol**.

5.3.3 **Potassium thiocyanate**, standard volumetric solution, $c(\text{KSCN}) \approx 0,025 \text{ mol/l}$.

Dissolve 2,4 g of potassium thiocyanate in water and dilute to 1 l. Titrate against the silver nitrate solution (5.2.1) and calculate the exact equivalence.

5.3.4 **Iron (III) alum (ammonium iron (III) sulfate) indicator**, saturated solution.

Saturate 100 ml of water with approximately 125 g of iron (III) alum $[(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$ and add sufficient nitric acid (5.1.2) to remove the brown colour.

5.4 For the Mohr method only

5.4.1 **Silver nitrate**, standard volumetric solution, $c(\text{AgNO}_3) = 0,050 \text{ mol/l}$.

Weigh 8,494 g of silver nitrate, dried as in (5.2.1), dissolve in water and dilute to 1 l. Store in an amber glass bottle.

5.4.2 **Potassium chromate**, indicator solution.

Dissolve 5 g of potassium chromate in 100 ml of water.

6 Apparatus

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

6.2 **Graduated glassware**, conforming to the requirements for Grade A in the International Standards prepared by ISO/TC 48.

6.3 **Electrically heated muffle furnace**, capable of being maintained at a temperature of 675 °C + 25 °C, with adequate ventilation.

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 Potentiometric titration assembly, equipped with a chloride ion selective electrode and double junction reference electrode.

7 Preparation of the 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.

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, 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 Combustion

Weigh, to the nearest 0,1 mg, a test portion of approximately 1 g, for samples with an expected chlorine content greater than 0,1 %, or 2 g for samples with a lower expected chlorine content.

Cover the bottom of the crucible (6.4) uniformly with 0,5 g of the Eschka mixture (5.1.1). Thoroughly mix the test portion with 2,5 g of the Eschka mixture in a suitable container. Transfer the mixture to the crucible, level the contents by gently tapping the crucible on the bench and cover uniformly with a further 1 g of the Eschka mixture.

NOTE 1 It is convenient to weigh out initially 4 g of the Eschka mixture and to extract the portions required for the bottom and top layers using a small glass tube, calibrated for each batch of Eschka mixture, to deliver 0,5 g and 1 g portions without weighing. The bottom layer of Eschka mixture reduces attack on silica and porcelain surfaces so that extraction of chlorine with hot water is complete even when the surface deteriorates.

For coals, place the charged crucible in the cold muffle furnace (6.3) and raise the temperature to $675\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ in about one hour. Maintain this temperature for a further two hours. Withdraw the crucible and allow to cool.

For coke, place the charged crucible on the cold flat plate (6.5) and insert into the muffle furnace at a temperature of $675\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$. Maintain this temperature for two hours. Withdraw the crucible and allow to cool.

NOTE 2 Cracking of the porcelain crucibles is prevented if they are cooled slowly by insertion into supports constructed from a light, porous refractory material after removal from the muffle furnace.

8.2 Completion

Complete the determination by either the Volhard (8.2.1), the Mohr (8.2.2) or the ISE method (8.2.3).

8.2.1 Volhard method

Transfer the incinerated mixture to a beaker, wash the crucible with about 125 ml of hot water and add the washings to the beaker. If unburnt particles are present, stop the test and repeat the determination,

extending the combustion time. Cautiously add 20 ml of the nitric acid (5.1.2) and cover the beaker with a clock glass, swirling or stirring the contents, if necessary, to help dissolution.

If necessary, filter the solution through a rapid-filtering, hardened, acid-washed filter paper, collecting the filtrate in a conical flask. Wash the paper with a small quantity of hot water (for example four lots of 5 ml to 10 ml), cool to room temperature and add 20 ml of the silver nitrate solution (5.2.1) to the flask and mix thoroughly. Immediately add 5 ml of the 3, 5, 5-trimethylhexan-1-ol (5.3.1) or *n*-hexan-1-ol (5.3.2), shake the solution for one minute to coagulate the precipitate, add eight to ten drops of the iron (III) alum indicator solution (5.3.4) and titrate with the potassium thiocyanate solution (5.3.3). The end-point is reached when the solution becomes faintly orange-pink in colour.

NOTE Filtration is usually unnecessary when using 1 g test portions of low-ash fuels, but is required when dealing with larger test portions or with high-ash fuels.

8.2.2 Mohr method

Transfer the incinerated mixture to a beaker, wash the crucible with hot water, collect the washings in the beaker and crush the residue in the beaker with a flat-ended glass rod. If unburnt particles are present, stop the determination and repeat the test extending the combustion time.

Heat the solution to boiling point and filter, using a filter paper pad or rapid filtering paper, collecting the filtrate in a conical flask. Wash the residue with five portions (5 ml each) of hot water, collecting the washings in the flask. Neutralize the solution with the nitric acid (5.1.2), using a pH paper. Add ten drops of the potassium chromate indicator (5.4.2) and titrate with the silver nitrate solution (5.4.1). The end-point is indicated by the first appearance of a brown coloration.

8.2.3 ISE method

Transfer the incinerated mixture to a beaker, wash the crucible with 50 ml to 70 ml of hot water and add the washings to the beaker. If unburnt particles are present, stop the determination and repeat the test extending the combustion time. Cautiously add 20 ml of the nitric acid (5.1.2) and cover the beaker with a clock glass, swirling or stirring the contents, if necessary, to help dissolution.

If necessary, filter the solution through a rapid-filtering, hardened, acid-washed filter paper, collecting the filtrate in a conical flask. Wash the paper with a small quantity of hot water (the total volume of the filtrate should not exceed 100 ml) and cool to room temperature.

NOTE Filtration is usually unnecessary when using 1 g test portions of low-ash fuels, but is required when dealing with larger test portions or with high-ash fuels.

Titrate with 0,025 M silver nitrate solution (5.2.1), using the potentiometric titration assembly (6.6).

8.3 Blank test

Carry out a blank test, using the same procedure as described in 8.1 and 8.2 but omitting the test portion. This assesses both the chlorine in the reagents and any contamination in the laboratory atmosphere. This shall not be quantitatively significant.

9 Expression of results

9.1 Volhard method

The chlorine mass fraction (w_{Cl}) of the sample, as analysed, expressed as a percentage, is given by the [Formula \(1\)](#)

$$w_{\text{Cl}} = \frac{3,545c_1(V_2 - V_1)}{m} \quad (1)$$

where

- c_1 is the amount-of-substance concentration, in moles per litre, of the potassium thiocyanate solution ([5.3.3](#));
- V_1 is the volume, in millilitres, of the potassium thiocyanate solution ([5.3.3](#)) used in the determination ([8.2.1](#));
- V_2 is the volume, in millilitres, of the potassium thiocyanate solution ([5.3.3](#)) used in the blank test ([8.3](#));
- M is the mass, in grams, of the test portion;
- 3,545 is the factor, in g·%·l/(mol·ml). Its derivation is provided in [Annex A](#).

9.2 Mohr titration

The chlorine mass fraction (w_{Cl}) of the sample, as analysed, expressed as a percentage by mass, is given by the [Formula \(2\)](#)

$$w_{\text{Cl}} = \frac{3,545c_2(V_3 - V_4)}{m} \quad (2)$$

where

- c_2 is the amount-of-substance concentration, in moles per litre, of the silver nitrate solution ([5.4.1](#));
- V_3 is the volume, in millilitres, of the silver nitrate solution ([5.4.1](#)) used in the determination ([8.2.2](#));
- V_4 is the volume, in millilitres, of the silver nitrate solution ([5.4.1](#)) used in the blank test ([8.3](#));
- m is the mass, in grams, of the test portion.

9.3 ISE method

The chlorine mass fraction (w_{Cl}) of the sample, as analysed, expressed as a percentage, is given by the [Formula \(3\)](#)

$$w_{\text{Cl}} = \frac{3,545c_3(V_5 - V_6)}{m} \quad (3)$$