SLOVENSKI STANDARD
SIST ISO 587:1998

01-februar-1998

Trdna fosilna goriva - Doloļ evanje klora z uporabo Eschkajeve zmesi

Solid mineral fuels -- Determination of chlorine using Eschka mixture

Combustibles minéraux solides -- Dosage du chlore à l'aide du mélange Eschka

Ta slovenski standard je istoveten z: **ISO 587:1997**

ICS:

75.160.10	Trda goriva	Solid fuels

SIST ISO 587:1998 **en**

INTERNATIONAL
STANDARD

ISO
587

Third edition
1997-05-15

Solid mineral fuels — Determination of chlorine using Eschka mixture

Combustibles minéraux solides — Dosage du chlore au moyen du mélange Eschka

Reference number
ISO 587:1997(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 587 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 587:1981), which has been technically revised.

Annex A of this International Standard is for information only.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

Solid mineral fuels — Determination of chlorine using Eschka mixture

1 Scope

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

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.*

ISO 9411-1:1994, *Solid mineral fuels — Mechanical sampling from moving streams — Part 1: Coal.*

ISO 9411-2:1993, *Solid mineral fuels — Mechanical sampling from moving streams — Part 2: Coke.*

3 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).

4 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.

4.1 For all methods

4.1.1 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.

4.1.2 Nitric acid, concentrated, chlorine-free, approximately 70 % (*m*/*m*).

4.2 For the Volhard and ISE methods

4.2.1 Silver nitrate, standard volumetric solution, $c(AgNO_3) = 0{,}025$ 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.

4.3 For the Volhard method only

4.3.1 3, 5, 5-trimethylhexan-1-ol.

4.3.2 *n*-Hexan-1-ol.

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

Dissolve 2,4 g of potassium thiocyanate in water and dilute to 1 l. Titrate against the silver nitrate solution (4.2.1) and calculate the exact equivalence.

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

Saturate 100 ml of water with approximately 125 g or iron(III) alum $[(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O]$ and add sufficient nitric acid (4.1.2) to remove the brown colour.

4.4 For the Mohr method only

4.4.1 Silver nitrate, standard volumetric solution, $c(AgNO_3) = 0{,}050$ mol/l.

Weigh 8,494 g of silver nitrate, dried as in (4.2.1), dissolve in water and dilute to 1 l. Store in an amber glass bottle.

4.4.2 Potassium chromate, indicator solution.

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

5 Apparatus

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

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

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

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

6 Preparation of the test sample

The test sample is the general analysis test sample prepared in accordance with ISO 1988, ISO 2309, ISO 5069-2, ISO 9411-1 or ISO 9411-2 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 equilibrated test sample for at least one minute, 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 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 % (m/m), or 2 g for samples with a lower expected chlorine content.

Cover the bottom of the crucible (5.4) uniformly with 0,5 g of the Eschka mixture (4.1.1). 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 (5.3) and raise the temperature to 675 °C ± 25 °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 (5.5) and insert into the muffle furnace at a temperature of 675 °C ± 25 °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.

7.2 Completion

Complete the determination by either the Volhard (7.2.1), the Mohr (7.2.2) or the ISE method (7.2.3).

7.2.1 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 (4.1.2) 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.1) 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 (4.2.1) to the flask and mix thoroughly. Immediately add 5 ml of the 3, 5, 5-trimethylhexan-1-ol (4.3.1) or *n*-hexan-1-ol (4.3.2), shake the solution for one minute to coagulate the precipitate, add eight to ten drops of the iron(III) alum indicator solution (4.3.4) and titrate with the potassium thiocyanate solution (4.3.3). The end-point is reached when the solution becomes faintly orange-pink in colour.

7.2.2 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 (4.1.2), using a pH paper. Add ten drops of the potassium chromate indicator (4.4.2) and titrate with the silver nitrate solution (4.4.1). The end-point is indicated by the first appearance of a brown coloration.

7.2.3 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 (4.1.2) 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.1) 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.

Titrate with 0,025 M silver nitrate solution (4.2.1), using the potentiometric titration assembly (5.6).

7.3 Blank test

Carry out a blank test, using the same procedure as described in 7.1 and 7.2 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.

---

1) 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 Expression of results

8.1 Volhard method

The chlorine content (W_{Cl}) of the sample, as analyzed, expressed as a percentage by mass, is given by the formula

$$W_{Cl} = \frac{3{,}545\, c_1 (V_2 - V_1)}{m}$$

where

c_1 is the concentration, in moles per litre, of the potassium thiocyanate solution (4.3.3);

V_1 is the volume, in millilitres, of the potassium thiocyanate solution (4.3.3) used in the determination (7.2.1);

V_2 is the volume, in millilitres, of the potassium thiocyanate solution (4.3.3) used in the blank test (7.3);

m is the mass, in grams, of the test portion.

8.2 Mohr titration

The chlorine content (W_{Cl}) of the sample, as analyzed, expressed as a percentage by mass, is given by the formula

$$W_{Cl} = \frac{3{,}545\, c_2 (V_3 - V_4)}{m}$$

where

c_2 is the concentration, in moles per litre, of the silver nitrate solution (4.4.1);

V_3 is the volume, in millilitres, of the silver nitrate solution (4.4.1) used in the determination (7.2.2);

V_4 is the volume, in millilitres, of the silver nitrate solution (4.4.1) used in the blank test (7.3);

m is the mass, in grams, of the test portion.

8.3 ISE method

The chlorine content (W_{Cl}) of the sample, as analyzed, expressed as a percentage by mass, is given by the formula

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

where

c_3 is the concentration, in moles per litre, of the silver nitrate solution (4.2.1);

V_5 is the volume, in millilitres, of the silver nitrate solution (4.2.1) used in the determination (7.2.3);

V_6 is the volume, in millilitres, of the silver nitrate solution (4.2.1) used in the blank test (7.3);

m is the mass, in grams, of the test portion.

8.4 All methods

Report the results as the mean of duplicate determinations, to the nearest 0,01 %.

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