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Solid mineral fuels — Determination of Chlorine content

Combustibles minéraux solides — Dosage de la teneur en chlore

Reference number
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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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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 on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of Analysis*.

TECHNICAL SPECIFICATION **ISO/TS 18806:2014(E)**

Solid mineral fuels — Determination of Chlorine content

1 Scope

This Technical Specification specifies two methods (high temperature combustion and bomb combustion) for the determination of chlorine in solid mineral fuels. It is applicable to hard coals, brown coals, coke, and tailings.

The chlorine in the digestion solution can be determined using different methods, e.g. an ion-selective electrode, coulometric or potentiometric titration, spectrophotometry, or ion chromatography. In this Technical Specification, the ion chromatographic separation with conductivity detection is described.

The method is applicable to determine the chlorine content higher than 0,005 per cent mass fraction.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 1213-2, *Solid mineral fuels — Vocabulary — Part 2: Terms relating to sampling, testing and analysis*

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

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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

EN ISO 10304-1, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1213-2 apply.

4 Principle

4.1 Method A — High temperature combustion in oxygen

The sample is combusted at high temperature in an oxygen atmosphere. The gaseous combustion products including the formed chloride are collected in a trap filled with water, in which they are dissolved.

4.2 Method B — Bomb combustion

The sample is combusted in a high pressure bomb in an oxygen atmosphere. The formed chloride is collected in an absorption solution inside the bomb.

5 Reagent

5.1 Method A

5.1.1 Oxygen, pure, with an assay of at least 99,5 % volume fraction.

5.1.2 Combustion aid (optional), spectroscopic carbon or iron phosphate ($FePO_4$).

5.2 Method B

5.2.1 Oxygen, pure, with an assay of at least 99,5 % volume fraction.

5.2.2 Combustion aid (optional), paraffin, benzoic acid, polyethylene combustion bags, acetobutyrate capsules, or other suitable materials.

5.2.3 Fuse, ignition wire (e.g. platinum) and cotton fuse (optional).

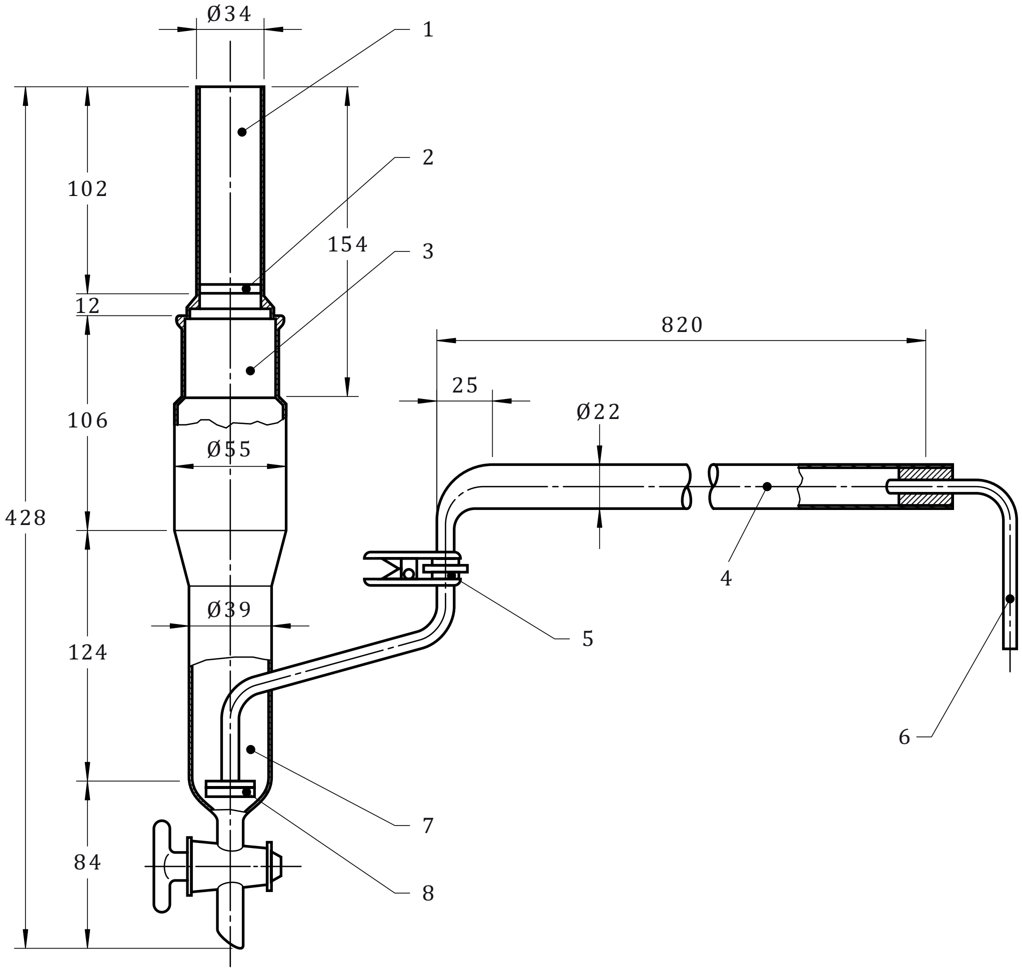
Note A possible contribution of the cotton fuse to the chlorine content should be considered.

5.2.4 Absorption solution, either eluent used for ion chromatographic determination, or alkaline solution (e.g. 0,2 mol/l KOH or 0,1 mol/l NaOH), or deionised water.

6 Apparatus

6.1 Method A

6.1.1 Fused silica combustion tube, absorber, and headpiece, the sintered glass discs in the absorber and the headpiece shall have a pore size of 90 µm to 150 µm (see Figure 1).



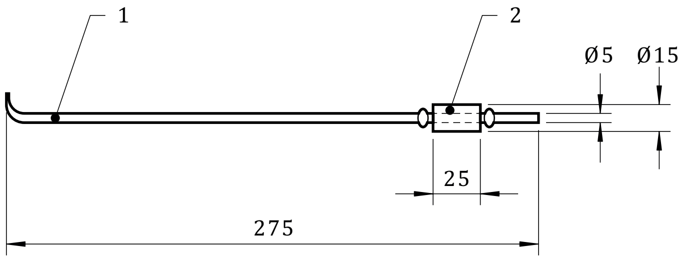
Key

1 headpiece
2 sintered glass disc
3 V45/50 conical ground joint (ISO 383)
4 combustion tube
5 VS 13 spherical joint (ISO 641)
6 oxygen inlet
7 absorber
8 sintered glass disc

Figure 1 — Apparatus for Method A

6.1.2 Porcelain combustion boat, with handle, e.g. 70 mm long, 10 mm wide, and 7 mm deep.

6.1.3 Silica pusher, with iron inlay (see Figure 2).



Key

1 silica pusher

2 iron inlay

Figure 2 — Silica pusher

6.1.4 Magnet.

6.1.5 Electrical tube furnace, about 300 mm long, capable of being heated to at least 1 300 °C and maintained at (1 250 ± 25) °C.

6.1.6 Flow meter.

6.1.7 Oxygen inlet, consisting of a pierced silicon stopper with a glass tube.

6.2 Method B

6.2.1 Digestion unit

6.2.1.1 Digestion bomb, with inner surface that is resistant to corrosion by acidic gases formed or emitted during combustion.

6.2.1.2 Pressure regulator, to control the filling of the bomb with oxygen and discharging afterwards.

6.2.1.3 Pressure gauge, with relieve valve operating at 3,5 MPa.

6.2.1.4 Ignition circuit.

If appropriate, the equipment for determination of calorific value according to ISO 1928 can be used simultaneously for chlorine determination. Attention is drawn to the fact that deionised water should be used as absorption solution and that 10 ml instead of 1 ml (as in ISO 1928) are used.

6.2.2 Crucible, of silica, nickel-chromium, platinum, or similar non-reactive material that is resistant to corrosion by acidic gases formed or emitted during combustion.

7 Preparation of sample

The coal or coke used for the determination of the chlorine content is the general analysis test sample ground to pass a sieve of 212 µm aperture. Expose the sample in a thin layer for the minimum time required for the moisture content to reach approximate equilibrium with the laboratory atmosphere. Before commencing the determination, mix the air-dried sample.

After weighing the test portion (see 8.2.2 or 8.3.2), determine the moisture content using a further portion of the test sample by the method described in ISO 687, ISO 5068-2, or ISO 11722, as appropriate.

8 Procedure

8.1 Blank Value Determination

Blank values shall be measured by performing a complete analysis (method A or method B, whatever used for analysis of samples) without sample but including combustion aid, if used. Blank values should be measured on a daily basis or when series of analyses are started.

8.2 Method A

8.2.1 Preparation

Adjust the tube furnace to ensure a temperature of (1 250 ± 25) °C in the combustion zone. Place the combustion tube in the furnace so that its projecting vertical section with the spherical ground joint is as near as possible to the hottest zone to prevent any condensation of combustion products.

Adjust the oxygen flow to (1 ± 0,1) l/min.

Mix samples having more than 30 % mass fraction ash with 0,1 g to 0,2 g of combustion aid to achieve uniform combustion.

8.2.2 Combustion procedure

Weigh, to an accuracy of 0,1 mg, about 50 mg to 1 000 mg (depending on the chlorine concentration) of the sample prepared according to Clause 7 into a combustion boat. Push the boat into the combustion tube using the silica pusher until the tube can be closed with the oxygen inlet.

NOTE Carefully place the front end of the pusher into the handle of the combustion boat. Otherwise problems to remove the boat after test might occur.

Fill the absorber with 150 ml deionised water. After starting the oxygen flow, mount the headpiece on the absorber and fill it with 20 ml deionised water.

To prevent deflagration, initially use the magnet to move the pusher together with the combustion boat containing the sample into the combustion zone so far only, that the front section of the sample is ignited only. After the sample has reached red heat (approximately one minute after ignition), push it into the combustion zone to burn it completely. High temperature coke samples can be pushed into the combustion zone directly.

Combustion time is depending on the ash of the sample. It is about 20 mins for coals having 10 % to 20 % mass fraction ash. After combustion has been terminated, transfer the absorption liquid from headpiece and absorber into a 250 ml volumetric flask. Rinse headpiece and absorber with deionised water and add to the flask. Fill up to the mark with deionised water (V_D).

8.3 Method B — Bomb Combustion

8.3.1 Preparation

Bomb parts shall be inspected regularly for wear and corrosion; particular attention shall be paid to the condition of the threads of the main closure. Manufacturers' instructions and any local regulations regarding the safe handling and use of the bomb shall be observed. Before starting a test ensure that no gas leakage occurs.

NOTE Gas leakage can be checked easily by complete immersing the pressurized bomb in cold water.

8.3.2 Combustion procedure

Weigh, to an accuracy of 0,1 mg, about 50 mg to 1 000 mg (depending on the chlorine concentration) of the sample prepared according to Clause 7 into a crucible.

Note If appropriate, chlorine can be determined simultaneously with calorific value according to ISO 1928 (for details see 6.2.1).

If not easily combusting samples are to be analysed, weigh into e.g. acetobutyrate capsules or use a combustion aid, e.g. benzoic acid.

Fill 10 ml of the absorption solution (5.2.4) into the bomb and wet the inner surface of the bomb, e.g. by carefully rotating it. Select an absorption solution that is capable to absorb the acidic combustion products completely.

Place the crucible in its support and fix it. Attach the ignition wire and assemble the bomb. Charge the bomb slowly with oxygen to a pressure of maximum (3,0 ± 0,2) MPa. Initiate the combustion by firing the fuse. After the combustion is completed let the bomb cool down to ambient temperature. Release the pressure at a moderate rate and dismantle the bomb carefully.

Transfer the chlorine absorbed solution into a volumetric flask by either

- Addition of, e.g. 40 ml absorption solution (5.2.4) to the bomb, closing and shaking the bomb in such a manner as to rinse all interior surfaces of the bomb, the combustion crucible, and the pressure release valve with absorbing solution; and/or
- Rinsing all interior surfaces of the bomb, the combustion crucible, and the pressure release valve with absorbing solution (5.2.4).

Transfer all solutions into a volumetric flask (e.g. 100 ml or 50 ml, depending on the chlorine content) and fill up to the mark (V_D) with absorption solution (5.2.4).

If appropriate, take an aliquot (V_A), transfer it to another volumetric flask and fill up to the mark (V_M). with absorption solution (5.2.4).

NOTE Before injecting the sample into the ion chromatograph, an aliquot of the sample solution can be filtered through an, e.g. 0,45 µm disposable filter in order to protect the column.

9 Determination of dissolved chloride

9.1 General

The chloride content in the digestion solution can be determined using different methods, e.g. an ion-selective electrode, coulometric or potentiometric titration, spectrophotometry, or ion chromatography.

In this Technical Specification, the ion chromatographic separation with conductivity detection is described in detail.

9.2 Determination by ion chromatography

9.2.1 General

The ion chromatographic separation with conductivity detection is performed according to EN ISO 10304-1.

As the chromatograms, especially retention times depend on concentrations and matrix, a calibration on the basis of matrix-adjusted reference materials is recommended.

9.2.2 Apparatus

— **Ion Chromatograph**, preferably with conductivity detection.

9.2.3 Reagent

— **Eluent**, suitable for the ion chromatographic equipment used.

10 Calculation and expression of results

Calculate the chlorine content in the solid mineral fuel from the chloride concentration in the digestion solution, the sample mass, blank values (if any, e.g. coming from combustion aid or eluent), and any dilution steps according to Formula (1):

$$w(Cl_{\mathrm{ad}}) = \frac{(\beta_{\mathrm{S}} - \beta_{\mathrm{B}}) \times V_{\mathrm{D}}}{m \times 10\ 000} \times \frac{V_{\mathrm{M}}}{V_{\mathrm{A}}} \qquad (1)$$

where

$w(Cl_{\mathrm{ad}})$ is the chlorine content of the sample as analysed (air dried), given in per cent mass fraction;

β_{S} is the mass concentration of chlorine in V_{M}, in milligrams per litre;

β_{B} is the mass concentration of chlorine in the blank determination, in milligrams per litre;

V_{D} is the volume of the digestion solution, in millilitres (e.g. Method A 250 ml; Method B 50 ml or 100 ml);

NOTE: V_{D} is the volume used for chloride determination if no dilution is necessary.

V_{M} is the volume of the (diluted) solution used for chloride determination, in millilitres;

V_{A} is the volume of the aliquot taken from the digestion solution, in millilitres;

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

$V_{\mathrm{M}}/V_{\mathrm{A}}$ is the dilution factor. If no dilution has been made, this term will be equal to one ($V_{\mathrm{M}}/V_{\mathrm{A}} = 1$).

Report the chlorine content in the air-dried sample, as average of duplicate determinations, for per cent mass fractions

- of >0,1 % rounded to 0,01 % mass fraction, and
- of ≤0,1 % rounded to 0,001 % mass fraction.

For the calculation of results to other bases, refer to ISO 1170.

11 Test report

The test report shall include the following particulars:

a) reference to this International Technical Specification (i.e. ISO/TS 18806);

b) the identification of the sample tested;

c) the results of the determination.

Annex A
(normative)

Quality control

A.1 Blank values

Determine the blank values for each series of analyses if a combustion aid (e.g. benzoic acid) is used. For this purpose combust the combustion aid (e.g. benzoic acid) only.

If combustion aid is used regularly, the use of a blank value control chart is recommended.

A.2 Reproducibility

When starting a series of analyses a control sample (reference material with same matrix as the samples) shall be analysed for a function check of combustion and chromatographic equipment. If appropriate, pure organic substances (e.g. 5-chloro-2-hydroxy-benzoic acid) can be used.

NOTE The use of a control chart for these results is recommended.

Annex B

(Informative)Results of the German Interlaboratory comparison 2009 for DIN 51727:2011 “Solid fuels-Determination of the chlorine content”

In 2009, a national interlaboratory comparison was conducted in Germany by the national committee FABERG Working Group 12.2 ‘Testing of solid fuels’.

The results are listed in Table B.1 for high temperature combustion and Table B.2 for bomb combustion.

Table B.1 — ILC results for method A (high temperature combustion)

German ILC FABERG WG ‘Testing of solid fuels’ Chlorine (high temperature combustion)								
Sample	**Russian hard coal**	**Brown coal (central German)**	**Brown coal (east German)**	**Imported hard coal 2**	**HT coke**	**Brown coal (Rhine basin)**	**German hard coal**	**Imported hard coal 1**
Number of laboratories	5	5	5	5	5	5	5	5
Number of laboratories (outliers removed)	4	5	5	5	5	5	5	5
Outliers	1	0	0	0	0	0	0	0
Average Chlorine (% mass fraction)	0,010	0,013	0,014	0,016	0,021	0,026	0,156	0,349
Repeatability standard deviation	0,000 5	0,003 3	0,001 5	0,001 3	0,000 6	0,001 9	0,002 8	0,010 6
Reproducibilty standard deviation	0,007 7	0,004 6	0,005 1	0,005 5	0,004 0	0,003 0	0,005 5	0,013 8
Relative repeatability standard deviation	5,4	25,5	10,7	8,1	3,0	7,1	1,8	3,0
Relative reproducibilty standard deviation	78	36	36	33	19	11	3,5	3,9

Table B.2 — ILC results for method B (bomb combustion)

German ILC FABERG WG 'Testing of solid fuels' Chlorine (bomb combustion)								
Sample	**Russian hard coal**	**Brown coal (central German)**	**Brown coal (east German)**	**Imported hard coal 2**	**HT coke**	**Brown coal (Rhine basin)**	**German hard coal**	**Imported hard coal 1**
Number of laboratories	7	6	6	6	7	6	7	7
Number of laboratories (outliers removed)	7	6	6	6	7	6	7	6
Outliers	0	0	0	0	0	0	0	1
Average Chlorine (% mass fraction)	0,018	0,019	0,020	0,023	0,024	0,030	0,157	0,357
Repeatability standard deviation	0,002 2	0,002 0	0,001 5	0,002 6	0,001 2	0,003 4	0,004 6	0,009 7
Reproducibilty standard deviation	0,010 3	0,009 2	0,007 8	0,016 3	0,004 4	0,008 7	0,013 3	0,025 2
Relative repeatability standard deviation	12,2	10,5	7,4	11,2	5,1	11,4	2,9	2,7
Relative reproducibilty standard deviation	58,0	49,1	39,0	71,6	18,0	29,2	8,5	7,1

In the German standard DIN 51727 the following precision data are given:

- **Precision (according ISO 5725-2)**;
- **Repeatability limit**.

The results of duplicate determinations, carried out in the same laboratory by the same operator with the same apparatus within a short interval of time on the same analysis sample, shall not differ by more than 0,02 % mass fraction (absolute).

- **Reproducibility limit**

The means of the results of duplicate determinations carried out in each of two laboratories, on representative portions taken from the same sample at the last stage of sample preparation, shall not differ by more than 0,03 % mass fraction (absolute).

Bibliography

[1] ISO 383, *Laboratory glassware — Interchangeable conical ground joints*

[2] ISO 641, *Laboratory glassware — Interchangeable spherical ground joints*

[3] ISO 1928, *Solid mineral fuels — Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value*

[4] DIN 51727:2011*Solid fuels — Determination of the chlorine content*

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