INTERNATIONAL STANDARD

ISO 18806

First edition
2019-09

Solid mineral fuels — Determination of chlorine content

Combustibles minéraux solides — Dosage de la teneur en chlore

Reference number
ISO 18806:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
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, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This first edition cancels and replaces ISO/TS 18806:2014, which has been technically revised.

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.

Solid mineral fuels — Determination of chlorine content

1 Scope

This document specifies two methods (high temperature combustion and high pressure vessel combustion) for the determination of chlorine in solid mineral fuels. It is applicable to solid mineral fuels.

The chlorine in the absorption solution can be determined using different finishes, such as coulometric or potentiometric titration, spectrophotometry or ion chromatography.

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

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

3 Terms and definitions

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

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

4.1 Method A — High temperature combustion

The sample is combusted in an oxygen atmosphere at high temperature. The gaseous combustion products collected in a trap filled with water include dissolved chloride compounds.

4.2 Method B — High pressure vessel combustion

The sample is combusted in an oxygen atmosphere in a high pressure vessel containing an absorption solution. The combustion products collected in an absorption solution include dissolved chloride compounds.

5 Reagents

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), e.g. spectroscopic carbon, iron phosphate ($FePO_4$), tungsten or quartz.

5.1.3 Deionised water, with a specific conductivity not higher than 0,2 mS/m at 25 °C.

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 Check for a possible contribution of the cotton fuse to the chlorine content.

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 (5.1.3).

6 Apparatus

6.1 Method A

An example for the equipment for high-temperature combustion is given below. This equipment is suitable for manual determinations and is well established.

Automated systems with autosamplers can also be used if their main features comply with the manual apparatus specified below, i.e. mainly temperature of the oven, the use of fused silica glass tubes, and the absorption unit.

6.1.1 Fused silica combustion tube, absorber and headpiece (see Figure 1).

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).

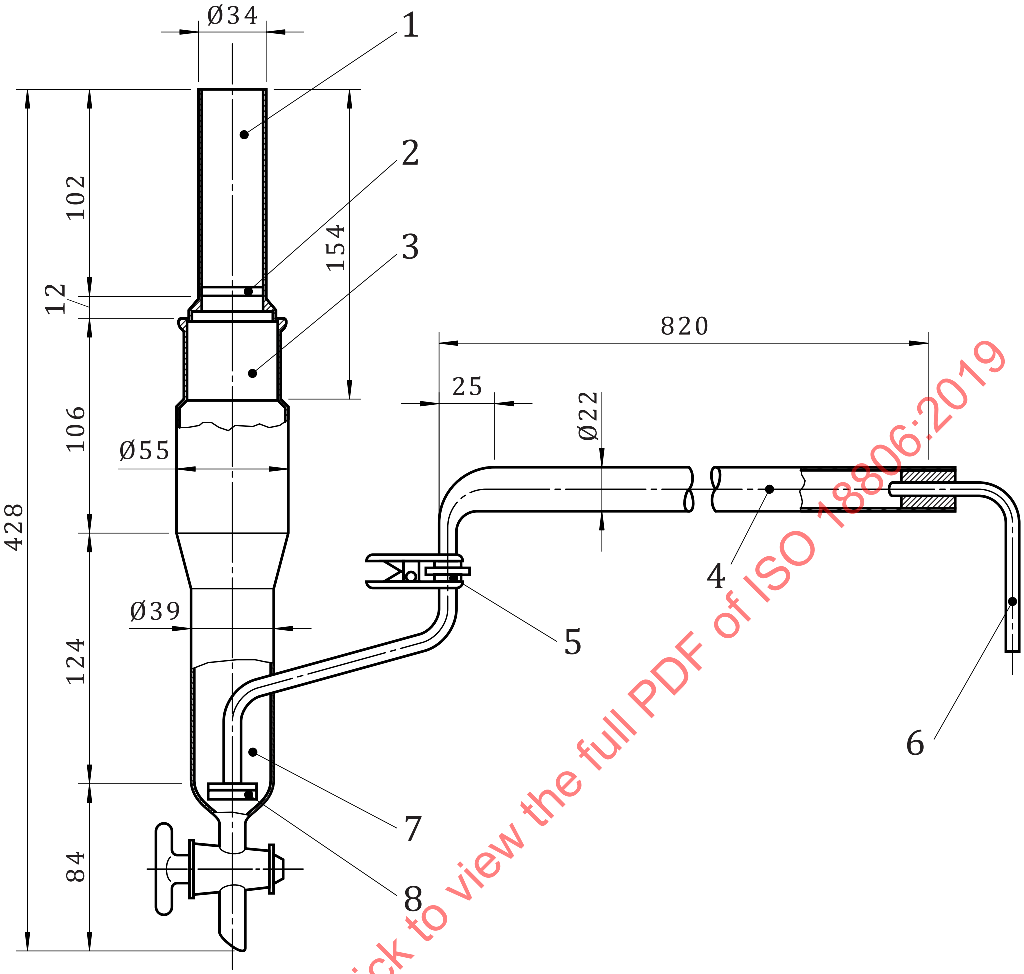
6.1.4 Magnet.

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

6.1.6 Flow meter.

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

Dimensions in millimetres

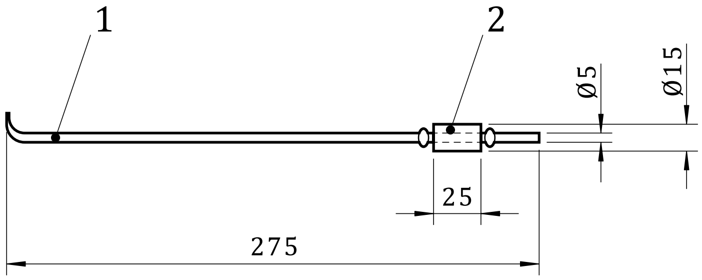


Key

1 headpiece
2 sintered glass disc (pore size of 90 µm to 150 µm)
3 V45/50 conical ground joint (see ISO 383)
4 combustion tube
5 VS 13 spherical joint (see ISO 641)
6 oxygen inlet
7 absorber
8 sintered glass disc (pore size of 90 µm to 150 µm)

Figure 1 — Example of an apparatus for Method A

Dimensions in millimetres



Key

1 silica pusher
2 iron inlay

Figure 2 — Example of a silica pusher

6.2 Method B

6.2.1 Digestion unit.

6.2.1.1 Digestion vessel, capable of withstanding safely the pressures developed during combustion and with an 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 vessel with oxygen and discharging afterwards.

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

6.2.1.4 Ignition circuit.

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.

6.2.3 Alternate digestion equipment.

The apparatus employed for determination of calorific value in accordance with ISO 1928 can be used simultaneously for chlorine determination provided it meets the specifications of 6.2.1. Attention is drawn to the fact that deionised water should be used as absorption solution.

7 Test sample

The sample 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 separate portion of the equilibrated test sample by the method described in ISO 687, ISO 5068-2 or ISO 11722, as appropriate.

8 Procedure

8.1 Blank value determination

Measure blank values using the same method A or B employed for the analysis sample. Perform a complete analysis without the analysis sample. Include combustion aid, if used. Measure blank values regularly, e.g. on a daily basis or when series of analyses are started.

8.2 Method A — High temperature combustion

8.2.1 General

The following subclauses specify the manual procedure.

When using automated systems, the temperature may be set lower than specified below. This is permitted only if the use of this lower temperature will give identical results compared to (1 250 ± 25) °C, which shall be verified using certified reference materials. If appropriate, moistening of the oxygen flow is allowed.

8.2.2 Preparation

Adjust the tube furnace to establish a temperature of (1 250 ± 25) °C in the combustion zone. To prevent any condensation of combustion products, 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.

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.

8.2.3 Combustion procedure

Depending on the chlorine content, weigh, to an accuracy of 0,1 mg, about 50 mg to 1 000 mg of the sample prepared in accordance with Clause 7 into a combustion boat. Push the boat into the combustion tube using the silica pusher (6.1.3) until the tube can be closed with the oxygen inlet (6.1.7).

Carefully place the front end of the pusher into the handle of the combustion boat. Otherwise problems with removing the boat after the test can 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.

Use the magnet (6.1.4) to initially move the pusher and the combustion boat containing the sample into the combustion zone so that only the front portion of the sample is ignited. Once the sample has reached red heat (approximately one minute after ignition), push the sample into the combustion zone to burn it completely. High temperature coke samples can be pushed into the combustion zone directly.

Combustion time depends on the mineral content of the sample. It can be about 20 min for coals having 10 % to 20 % mass fraction ash. After combustion has been terminated, transfer the absorption liquid from the headpiece and absorber into a 250 ml volumetric flask. Rinse the headpiece and absorber with deionised water and add the rinsings to the flask. Fill up to the mark with deionised water, V_D.

8.3 Method B — High pressure vessel combustion

8.3.1 Preparation

Regularly inspect vessel parts for wear and corrosion. Pay particular attention to the condition of the threads of the main closure. Observe the manufacturers' instructions and any local regulations regarding the safe handling and use of the vessel. Before starting a test, ensure that no gas leakage occurs.

NOTE Gas leakage can be checked easily by completely immersing the pressurized vessel in cold water.

8.3.2 Combustion procedure

Depending on the chlorine content, weigh, to an accuracy of 0,1 mg, about 50 mg to 1 000 mg of the sample prepared in accordance with Clause 7 into a crucible.

If appropriate, chlorine can be determined simultaneously with the calorific value in accordance with ISO 1928 (for details, see 6.2.3).

Mix samples that are not easily combustible (e.g. having more than 30 % mass fraction ash) with 0,1 g to 0,2 g of combustion aid (5.2.2) to achieve complete combustion. Transfer 5 ml to 10 ml of the absorption solution (5.2.4) into the vessel. Rotate the vessel to wet the inner surface.

When the chlorine determination is performed simultaneously with the calorific value determination in accordance with ISO 1928, the volume of the absorption solution may be reduced to 1 ml. Complete absorption of the chlorine present in the coal sample shall be verified using certified reference materials.

Place the crucible in its support and attach the fuse. Assemble the combustion vessel and charge it slowly with oxygen to a pressure of maximum (3,0 ± 0,2) MPa. Fire the fuse to initiate combustion. After combustion is complete, cool the vessel to ambient temperature. Release the pressure at a moderate rate and carefully dismantle the vessel.

Add about 40 ml of absorption solution (5.2.4) to the vessel. Close and shake or rotate the vessel in such a manner as to rinse all interior surfaces, the combustion crucible and the pressure release valve with the absorbing solution.

and/or

Rinse the interior surfaces of the vessel, the combustion crucible and the pressure release valve with the absorption solution (5.2.4).

Depending on the chlorine content, transfer all absorption solutions to a 50 ml or 100 ml volumetric flask. 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).

If ion chromatography is used for the chloride determination, an aliquot of the sample solution can be filtered through a 0,45 µm disposable filter to protect the chromatography column.

9 Determination of dissolved chloride

The chloride content in the digestion solution is determined using different methods, e.g. coulometric or potentiometric titration, spectrophotometry or ion chromatography. The use of an ion-selective electrode is not within the specifications of this document.

For details of the determination, refer to the respective standards.

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, for example, coming from the combustion aid or eluent), and any dilution steps in accordance with Formula (1):

$$w(\mathrm{Cl}_{\mathrm{ad}}) = \frac{(\beta_S - \beta_B) \times V_D}{m \times 10} \times \frac{V_M}{V_A} \quad (1)$$

where

$w(\mathrm{Cl}_{\mathrm{ad}})$ is the chlorine content of the sample as analysed (air-dried), given in % 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 milligrams;

10 conversion factor;

NOTE The conversion factor of 10 results from the conversion of 1 l to 1 000 ml (1 000) and mg/mg to % mass fraction (0,01).

V_M/V_A is the dilution factor. If no dilution has been made, this term will be equal to one ($V_M/V_A = 1$).

Report the chlorine % mass fraction in the air-dried sample, as average of duplicate determinations, for the range:

— of > 0,1 % rounded to 0,01 % mass fraction;

— of ≤ 0,1 % rounded to 0,001 % mass fraction.

The calculation of results to other bases shall be in accordance with ISO 1170.

11 Precision

11.1 Precision data origin

The precision data were calculated from the results of an interlaboratory study performed in 2016. For details, see Annex B.

11.2 Repeatability limit, *r*

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 representative portions taken from the same analysis sample, shall not differ by more than the value calculated from the formula in Table 1, second column.

11.3 Reproducibility limit, *R*

The means of the results of duplicate determinations, performed in each of two laboratories on representative portions taken from the same test sample, shall not differ by more than the value calculated from the formula in Table 1, third column.

Table 1 — Repeatability and reproducibility limits

Concentration range % mass fraction	**Repeatability limit** *r*	**Reproducibility limit** *R*
0,005 % to 0,35 % (50 mg/kg to 3 500 mg/kg)	$r = 0{,}001\ 9 + 0{,}042 \cdot w_{Cl}$	$R = 0{,}003 + 0{,}129 \cdot w_{Cl}$
NOTE Chlorine content, w_{Cl}, is given as % mass fraction.		

11.4 Quality control

For quality control procedures, follow Annex A.

12 Test report

The test report shall include the following:

a) the identification of the sample tested;

b) the method used by reference to this document, i.e. ISO 18806:2019;

c) the date of the determination;

d) 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 the 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 (a 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.

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

Annex B
(informative)

Results of the interlaboratory study (precision data)

B.1 Samples and participants

The precision data were calculated from the results of an interlaboratory study performed in 2016. Six samples were distributed (see Table B.1).

Table B.1 — Samples

Sample name	Type/origin	Expected chlorine range in % mass fraction (for information, also in mg/kg)
A	Canadian low volatile bituminous coal	0,005 (50)
B	Chinese brown coal	0,011 (110)
C	Colombian anthracite	0,035 (350)
D	Australian medium volatile hard coal	0,041 (410)
E	Polish medium volatile hard coal	0,11 (1 100)
G	US American High volatile C bituminous coal	0,35 (3 500)

Samples A and G were previously used for an interlaboratory study, sample D is a certified reference material. These samples were regarded as homogenous. Samples B, C and D were prepared in one laboratory and tested for homogeneity.

Samples were filled in plastic bottles and sent to the laboratories at the end of August 2016. Results in triplicate were submitted between 2016-09-26 and 2016-10-28.

Eighteen laboratories from Australia, Canada, China, Colombia, Denmark, Germany, Spain and USA took part in this interlaboratory study. The laboratories were free to choose either the high temperature or high pressure vessel combustion method. Two laboratories submitted results for both high temperature and high pressure vessel combustion, which gave 20 sets of results. Laboratories determined reported moisture (moisture in the general analysis test sample). Except for one laboratory, the moisture reported was almost the same in each sample.

B.2 Evaluation

All the data received were evaluated in accordance with ISO 5725-2. Data were taken as reported; no calculation to dry basis was made. Outliers were identified and removed. In a first step, high temperature and high pressure vessel combustion were evaluated separately, but no significant differences were observed. Therefore, a combined treatment of the data was performed.

No data from the use of an ion-selective electrode were included because of a significant bias to the average results, especially at higher concentrations. Therefore, the use of an ion-selective electrode for the chloride determination is not allowed.

The results are listed in Table B.2.