INTERNATIONAL STANDARD

ISO 16994

Second edition
2016-07-01

Solid biofuels — Determination of total content of sulfur and chlorine

Biocombustibles solides — Détermination de la teneur totale en soufre et en chlore

Reference number
ISO 16994:2016(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.

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).

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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 238, *Solid biofuels*.

This second edition cancels and replaces the first edition (ISO 16994:2015), of which it constitutes a minor revision.

Introduction

Sulfur and chlorine are present in solid biofuels in varying concentrations. During the combustion process, they are usually converted to sulfur-oxides and chlorides. The presence of these elements and their reaction products can contribute significantly to corrosion and to environmentally harmful emissions.

Chlorine can be present in different organic and inorganic compounds and is to exceed or equal the water soluble amount that can be determined by ISO 16995.

Combustion in an oxygen atmosphere in a closed combustion vessel is the preferred method to digest biomass samples for a determination of the total content of sulfur and chlorine. An advantage of the method is that the digestion can be carried out in connection with the determination of the calorific value according to ISO 18125[1)]. Decomposition in closed vessels is an appropriate alternative method. Other analytical techniques (e.g. high-temperature combustion in a tube furnace and Eschka method) may also be used. The determination of the resultant chlorine and sulfur compounds can be done by different techniques, e.g. ion chromatography, ICP, titrimetry.

Automatic equipment and alternative methods may be used when these methods are validated with biomass reference samples of an adequate type and also meet the requirements of Clause 10.

A list with typical sulfur and chlorine contents of solid biofuels can be found in ISO 17225-1:2014, Annex B.

1) To be published.

Solid biofuels — Determination of total content of sulfur and chlorine

1 Scope

This International Standard describes methods for the determination of the total sulfur and total chlorine content in solid biofuels. This International Standard specifies two methods for decomposition of the fuel and different analytical techniques for the quantification of the elements in the decomposition solutions. The use of automatic equipment is also included in this International Standard, provided that a validation is carried out as specified and that the performance characteristics are similar to those of the method described in this International Standard.

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 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*

ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO 14780[2)], *Solid biofuels — Sample preparation*

ISO 16559, *Solid biofuels — Terminology, definitions and descriptions*

ISO 16967:2015, *Solid biofuels — Determination of major elements — Al, Ca, Fe, Mg, P, K, Si, Na and Ti*

ISO 18125[2)], *Solid biofuels — Determination of calorific value*

ISO 18134-3, *Solid biofuels — Determination of moisture content — Oven dry method — Part 3: Moisture in general analysis sample*

CEN Guide 13:2008, *Validation of environmental test methods*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16559 and the following apply.

3.1
reference material
RM
material or substance one or more of whose property values are sufficiently homogeneous and well-established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials

2) To be published.

3.2
certified reference material
CRM
reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence

3.3
NIST standard reference material
SRM
CRM issued by NIST that also meets additional NIST-specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterisations and provides information regarding the appropriate use(s) of the material

4 Principle

4.1 General

The determination of total sulfur and total chlorine content is performed in two steps (4.2 and 4.3) or by using automatic equipment (see 4.4).

4.2 Decomposition of the biofuel

— Combustion in an oxygen atmosphere in a combustion vessel and absorption of the acidic gas components in an absorption solution (method A).

— Digestion in closed vessels as described in ISO 16967:2015, Part A (method B).

4.3 Determination of sulfate and chloride in the decomposition solution

— Ion chromatography, in accordance with the principles of ISO 10304-1.

— ICP, in accordance with the principles of ISO 11885 (determination as sulfur and chlorine).

4.4 Automatic equipment

Automatic equipment may be used when the method is validated with biomass reference samples of an adequate biomass type. If automatic equipment is used, sulfur and chlorine compounds may be detected as gaseous components (e.g. by infrared methods). Examples for automatic analysers include elemental analysers, AOX-analysers.

If automatic equipment or X-ray fluorescence are used, the method shall be validated for the respective main origin based biomass group (see ISO 17225-1:2014, Table 1: woody biomass, herbaceous biomass, or fruit biomass) according to CEN Guide 13:2008, Clause 3 validation of alternative methods with one of the following two approaches:

— full validation as applies to reference methods;

— relative validation in which a comparison is made to the reference method, e.g. by participation in inter-laboratory comparison tests.

NOTE Equipment validated only with, for example, straw reference materials, is not automatically suitable for the determination of sulfur and chlorine in, for example, wood samples, because of the usually significant lower concentrations of the elements in wood and/or the unknown influences of the different matrix.

5 Reagents

The reagents listed below relate to the digestion method specified in 8.1.1 (method A). Reagents for the digestion method B and the different detection methods according to 8.2 are specified in the corresponding standards.

5.1 General

All reagents shall be at least of analytical grade and suitable for their specific purpose. Particularly, they shall contain negligible amounts of chlorine and sulfur, i.e. amounts that do not contribute significantly to the determination.

5.2 Water, de-ionized water will normally fulfil the requirements of 5.1

5.3 Oxygen, pure oxygen with an assay of at least 99,5 % (V/V).

5.4 Combustion aid/enhancer, various substances may be used, e.g. benzoic acid, paraffin oil, acetobutyrate capsules, polyethylene bags.

5.5 Use of certified reference materials (CRM or SRM).

Use certified reference materials to check if the accuracy of the calibration meets the required performance characteristics. Examples of certified reference materials are SRM 1570 spinach leaves, SRM 1571 orchard leaves, SRM 1573 tomato leaves, and SRM 1575 pine needles.

When, due to matrix effects or concentration range limitations, no good recoveries for the certified reference materials can be obtained, calibration with at least two CRM or SRM materials, could solve these problems (for example, CRM 101 spruce needles and CRM 100 beech leaves). In that case, CRM or SRM materials other than used for the calibration shall be used for verification purposes.

NOTE A CRM or SRM is prepared and used for the following three main purposes:

a) to help develop accurate methods of analysis;

b) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit;

c) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

6 Apparatus

6.1 General

6.1.1 Analytical balance, with a resolution of at least 0,1 mg.

6.1.2 General laboratory equipment, such as volumetric flasks and measuring cylinders.

6.2 Method A

6.2.1 Pellet press, capable of applying a force of 0,1 Nm, equipped with a die to press a pellet with a diameter of about 13 mm.

6.2.2 Combustion vessel, suitable for the determination of sulfur and chlorine.

The combustion vessel may be the same as used for the determination of the calorific value (see ISO 18125).

The combustion vessel shall not leak during the test and shall permit a quantitative recovery of the liquid. Its inner surface may be made of stainless steel or any other material that will not be affected by the combustion process or products.

Note that not all combustion vessels of calorimeters can be used because the principle of construction, the materials used for construction, or the surfaces in the combustion vessels may adsorb or react with the acidic gases formed during combustion or it may not be possible to clean the combustion vessel completely.

6.3 Method B

Sample digestion vessels and an associated heating device (see ISO 16967).

7 Preparation of the test sample

The test sample is the general analysis test sample with a nominal top size of 1 mm prepared in accordance with ISO 14780.

NOTE It might be necessary to prepare a test sample with a lower nominal top size than 1 mm (e.g. 0,25 mm) in order to keep the stated precision and repeatability limits. If a nominal size below 1 mm is used, the correctness of results is to be controlled by a CRM prepared to the nominal size used for the sample.

As the results are to be calculated on dry basis, the moisture content of the test sample shall be determined concurrently by the method described in ISO 18134-3, using another portion of the test sample.

8 Procedure

8.1 Decomposition

8.1.1 Method A: Combustion in a closed combustion vessel

Solid biofuel samples are usually combusted in a pellet form due to the low density and their combustion behaviour.

— Take a sample of approximately 1 g (unless the combustion vessel is designed for other sample amounts).

— Press the sample with a suitable force to produce a compact unbreakable pellet that is weighed to 0,1 mg. If the calorific value is determined simultaneously, the sample amount may eventually be adjusted according to the specification in ISO 18125.

— Transfer the sample into a quartz glass or metal crucible.

The combustion may be carried out using a combustion aid (5.5).

a) Liquid combustion aid: After the mass of the sample pellet is determined, the auxiliary liquid material shall be added drop-wise on the pellet placed in the crucible (allowing the liquid to be adsorbed); the added amount has to be determined exactly by weighing.

b) Combustion bag or capsule: The sample may be filled in powdered form into a combustion bag or capsule with precisely known weight. The sample mass is calculated by weighing the sample in the combustion bag or capsule and subtracting the mass of the bag or capsule.

c) Solid combustion aid: After the mass of the sample is determined, add an appropriate amount of the aid (e.g. benzoic acid) and determine the added amount of the aid exactly by weighing. Mix the sample and the aid carefully and prepare a pellet of the whole mix as described above. Ensure that the weight of the pellet equals the weight of the sample and the weight of the aid.

— Add 1 ml water into the combustion vessel (also see ISO 18125 if the calorific value is determined simultaneously). Alternatively, the water can be omitted or more water (up to 5 ml) can be used. If the content of chlorine or sulfur exceeds a mass fraction of 2 %, alkaline solutions may be used to neutralize the acidic compounds produced. When ion chromatography is used for determination, the absorption solution may be the mobile phase, e.g. a carbonate/bicarbonate solution. In all cases, the calibration of the method and the blank tests has to be done with the same amount and the same kind of receiving solution.

— Place the crucible in position and arrange the firing wire. Assemble the combustion vessel and tighten the cover securely. Before ignition, the combustion vessel is filled with 30 bar oxygen.

NOTE 1 If the chlorine content of the sample is very low, the cotton thread usually used for ignition can contribute significantly to the measured chlorine content. This can be avoided by using highly pure combustible sample holder without cotton threats.

NOTE 2 The combustion vessel can be flushed with oxygen to reduce the nitrous oxide formation during the combustion process especially when the concentration of sulfur and chlorine is determined by ion chromatography (some peaks in the chromatogram might not be separated satisfactorily).

— After combustion, release the combustion vessel pressure slowly before opening it.

— Transfer the content of the combustion vessel to a volumetric flask (50 ml or 100 ml).

— Thoroughly rinse the combustion vessel, the cover, and the crucible, including the combustion residues in the crucible, with water and collect all the rinse water carefully. Transfer it into the volumetric flask and fill the flask to volume. While rinsing, take care that the ash that was formed after the combustion is collected in the flask as well.

If the sample contains high concentrations of sulfur and/or chlorine (>2 %), the combustion gas should be let through a gas washing bottle with a disk to ensure that all acidic gas components are dissolved. The solution from this gas washing bottle can be combined with the combustion vessel washings or can be analysed separately from the solution of the combustion vessel.

NOTE 3 If the sample contains high amounts of ash (>5 %), then chlorine and sulfur can be trapped in the combustion residues. In that case, the combustion residue can be analysed for the chlorine and sulfur content, e.g. with XRF or an ash fusion procedure. Alternatively, a low sample intake in combination with a combustion aid can be used.

NOTE 4 Special care is necessary when samples with low contents of chlorine and/or sulfur (e.g. virgin wood) are analysed after samples with high contents of these elements (e.g. herbaceous samples or waste samples). The most efficient way of cleaning the combustion vessel is multiple combustions of pure benzoic acid (see 8.1.3 blank test).

For some subsequent analytical methods, a chemical treatment of the solution is necessary before filling up to volume. Some analytical methods require a filtered solution.

The calorific value may be determined simultaneously. In this case, the requirements of ISO 18125 shall be observed. The content of other halogens (fluoride, bromide, and iodide) can be determined by a similar method (see EN 14582).

8.1.2 Method B: Digestion in a closed vessel

The method for the digestion in closed vessels is described in ISO 16967. For the determination of chlorine, an amount of 0,8 ml H_2O_2 per 100 mg of sample shall be used for the digestion. This larger amount compared to ISO 16967 is used to avoid losses of chlorine.

8.1.3 Blank test

Carry out a blank test, using the same procedures and methods as described in 8.1.1 (method A) or 8.1.2 (method B), respectively, using benzoic acid for method A. This assesses both the contents of the elements in the reagents and any contamination from equipment and the laboratory atmosphere. This contribution shall not be quantitatively significant.

The measured blank value has to be subtracted from the sample value. At high element level, the blank should be less than 10 % of the sample content. For low element level (a content below 500 mg/kg in the sample), it is adequate that the contents of the elements in the blank solution are 30 % or less of the contents of the elements in the sample solution.

8.2 Detection methods

8.2.1 Ion chromatography

Ion chromatography is the recommended method for the detection of sulfate and chloride. The determination should be according to the principles of ISO 10304-1.

NOTE The solution obtained from the digestion can be filtered using a syringe equipped with a 0,45 µm pore size filter tip to avoid damage of the ion chromatograph.

8.2.2 Other detection methods

The following methods are standardized at international levels and can be used provided that they have been validated and that the performance characteristics are similar to those of the method described in this International Standard.

Table 1 — Other methods for the detection of sulfate and chloride

Method	Cl	S	References (examples)
ICP	X	X	ISO 11885
Photometric (colourimetric)	X		DIN 51727
Turbidimetric		X	ASTM D516-07
Coulometric	X		DIN 38405-1 (method D1–3)
Potentiometric titration	X		DIN 38405-1 (method D1–2)

8.3 Calibration of the apparatus

When the analytical system is evaluated for the first time, establish a calibration function for the measurement in accordance with the manufacturers' instructions. Adjust the established calibration function during the analysis, if necessary. Check the performance of the instrument using the accepted standard procedures like replicate analysis, use of standard reference material (SRM) and/or CRM, control samples and create control charts. The calibration and quality control scheme shall be organized and maintained in such a way that the required uncertainty of measurement can be obtained. The results of the validation study of BioNorm2 (see Annex A) demonstrates what is achievable with commercial instruments that are used by experienced laboratories.

8.4 Analyses of the decomposition solutions

Analyse test portions of the digests in accordance with the manufacturer's instructions.

9 Expression of results

9.1 General

The results shall be reported as the mean of duplicate determinations. The results shall be calculated on dry basis according to 9.2 and 9.3. The results may be calculated to other bases, e.g. to as-received basis according to ISO 16993.

9.2 Total chlorine

The total content of chlorine in the sample on dry basis, $w_{\mathrm{Cl,d}}$, expressed in mass fraction (%) , is given by Formula (1):

$$w_{\mathrm{Cl,d}} = \frac{(c - c_0) \times V}{m} \times 100 \times \frac{100}{(100 - M_{\mathrm{ad}})} \tag{1}$$

where

- c is the concentration of chloride in the solution, in mg/l;
- c_0 is the concentration of chloride in the solution of the blank experiment, in mg/l;
- V is the volume of the solution, in l;
- m is the mass of the test portion used, in mg;
- M_{ad} is the moisture content in the analysis test sample, in mass fraction (%).

9.3 Total sulfur

The total content of sulfur in the sample on dry basis, $w_{\mathrm{S,d}}$, expressed in mass fraction (%), is given by Formula (2):

$$w_{\mathrm{S,d}} = \frac{(c - c_0) \times V}{m} \times 0{,}3338 \times 100 \times \frac{100}{(100 - M_{\mathrm{ad}})} \tag{2}$$

where

- c is the concentration of sulfate in the solution, in mg/l;
- c_0 is the concentration of sulfate in the solution of the blank experiment, in mg/l;
- V is the volume of the solution, in l;
- m is the mass of the test portion used, in mg;
- 0,3338 is the stoichiometric ratio of the relative molar masses of sulfur and sulfate;
- M_{ad} is the moisture content in the analysis test sample, in mass fraction (%).

10 Performance characteristics

The achievable performance of the method is given in Annex A showing the results obtained by a European comparison study carried out for a sample of wood chips and a sample of an exhausted olive residue. These two samples represent the extremity of the method. The wood chip sample represents samples with low contents of sulfur and chlorine and the olive residue samples, with high amounts of sulfur and chlorine.

11 Test report

The test report shall include at least the following information:

a) identification of the laboratory performing the test and the date of the test;

b) identification of sample tested;

c) a reference to this International Standard, i.e. ISO 16994:2016;

d) methods used for digestion and for determination;

e) results of the test including the basis in which they are expressed, as indicated in Clause 9;

f) any unusual features noted during the determination;

g) any operation not included in this International Standard, or regarded as optional.

Annex A
(informative)

Performance data

The round robin was carried out by laboratories in Austria, Belgium, Denmark, Finland, Germany, Ireland, Italy, The Netherlands, Spain, Sweden, and the United Kingdom. The variety of instruments and other analytical conditions were used in accordance with the quality parameters specified in the method.

The tests were carried out using two samples: wood chips and exhausted olive residues produced in the EU-project BioNorm according to ISO 14780. The sample "wood chips" was made of German coniferous wood chips; the chips were dried and milled to 1 mm by means of cutting mill. The sample "exhausted olive residues" was obtained from olive oil industry in Spain from a typical outdoor storage facility. In the original sample, stones and other natural impurities were present. These impurities and stones were removed manually and the sample was prepared from the residues in two steps using a coarse cutting mill equipped with a 10 mm sieve and a laboratory cutting mill equipped with WC cutting tools and a 1 mm sieve.

All data are reported on dry basis.

The performance data according to ISO 5725-2 are presented in Table A.1 and Table A.2.

NOTE 1 See Table A.1 for definition of the symbols used in Table A.1 and Table A.2.

NOTE 2 A guideline can be found in ISO 16993:2016, Annex C on how to use these validation parameters.

Table A.1 — Performance data for sulfur (S)

Sample	n	l	o %	x mass fraction %	s_R mass fraction %	CV_R %	s_r mass fraction %	CV_r %
wood chips	20	90	5,2	0,009	0,003	34	0,001	12
exhausted olive residues	23	111	1,8	0,12	0,021	17	0,007	5,4

Definition of symbols:

n	number of laboratories after outlier elimination;
l	number of outlier free individual analytical values;
o	percentage of outlying values from replicate determination;
x	overall mean;
s_R	reproducibility standard deviation;
CV_R	coefficient of the variation of the reproducibility;
s_r	repeatability standard deviation;
CV_r	coefficient of the variation of the repeatability.

Table A.2 — Performance data for chlorine (Cl)

Sample	n	l	o %	x mass fraction %	s_R mass fraction %	CV_R %	s_r mass fraction %	CV_r %
wood chips	17	75	7,4	0,006	0,003	52	0,001	13
exhausted olive residues	16	75	0	0,20	0,02	8,0	0,01	2,8

Table A.3 — List of techniques for the round robin

Chlorine (24 participating laboratories)		**Sulfur** (28 participating laboratories)	
Used method	**No. of laboratories**	**Used method**	**No. of laboratories**
Ion chromatography	16	Ion chromatography	13
Titration	2	S-Analyzer	12
ICP	2	ICP	3
Eschka	1	—	—
Photometry	1	—	—
Coulometry	1	—	—
Cl^-Analyzer	1	—	—

Bibliography

[1] ISO 351[3)], *Solid mineral fuels — Determination of total sulfur — High temperature combustion method*

[2] ISO 352[4)], *Solid mineral fuels — Determination of chlorine — High temperature combustion method*

[3] 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*

[4] ISO 16993:2016, *Solid biofuels — Conversion of analytical results from one basis to another*

[5] ISO 16995, *Solid biofuels — Determination of the water soluble chloride, sodium and potassium content*

[6] ISO/TS 16996, *Solid biofuels — Determination of elemental composition by X-ray fluorescence*

[7] ISO 17225-1:2014, *Solid biofuels — Fuel specifications and classes — Part 1: General requirements*

[8] ISO 21748, *Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation*

[9] ASTM D516-07, *Standard test method for sulphate ion in waste*

[10] ASTM D3177, *Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke*

[11] ASTM D4239-14, *Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion*

[12] DIN 38405-1, *German standard methods for the examination of water, waste water and sludge; anions (group D); determination of chloride ions (D1)*

[13] DIN 51724-1, *Testing of solid fuels — Determination of sulfur content — Part 1: Total sulfur*

[14] DIN 51727, *Testing of solid fuels — Determination of chlorine content*

[15] EN 14582, *Characterization of waste — Halogen and sulfur content — Oxygen combustion in closed systems and determination methods*

[16] NIST definitions: http://ts.nist.gov/MeasurementServices/ReferenceMaterials/DEFINITIONS.cfm

[17] NIST Technical note 1297:1994, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results

3) This is a withdrawn standard.

4) This is a withdrawn standard.

ICS 27.190; 75.160.10
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