INTERNATIONAL STANDARD

ISO 16994

First edition
2015-04-01

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 16994:2015(E)

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

Published in Switzerland

Contents

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 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*.

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.

Oxygen combustion in a closed oxygen bomb 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 EN 14918[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 biofuels can be found in CEN/TS 14961:2005, Annex C.

---

1) To be replaced by ISO 18125.

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.

EN 14780[2], *Solid biofuels — Sample preparation*

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

ISO 16967:2015, *Solid biofuels — Determination of major elements*

EN 14918[3], *Solid biofuels — Determination of calorific value*

ISO 18134-3[4], *Solid biofuels — Determination of moisture content — Oven dry method — Part 3: Moisture in general analysis simple*

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)*

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

ISO 16967, *Solid biofuels — Determination of major elements*

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 replaced by ISO 14780.

[3] To be replaced by ISO 18125.

[4] 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 bomb 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 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, issued by an internationally recognized authority, 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 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

- Analytical balance, with a resolution of at least 0,1 mg;
- 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 bomb, suitable for the determination of sulfur and chlorine. The combustion bomb may be the same as used for the determination of the calorific value (see EN 14918[5]).

The bomb 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 calorimeter bombs can be used because the principle of construction, the materials used for construction, or the surfaces in the bombs may adsorb or react with the acidic gases formed during combustion or it may not be possible to clean the bomb 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 EN 14780[6].

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[7], using another portion of the test sample.

8 Procedure

8.1 Decomposition

8.1.1 Method A: Combustion in a closed bomb

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 bomb 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 EN 14918[5].
- 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.

---

[5] To be replaced by ISO 18125.

[6] To be replaced by ISO 14780.

[7] To be published.

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 bomb [also see EN 14918[8] 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 2 % (m/m) 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 have 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 bomb and tighten the cover securely. Before ignition, the bomb 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 may contribute significantly to the measured chlorine content. This can be avoided by using highly pure combustible sample holder without cotton threats.

NOTE 2 The bomb 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 bomb pressure slowly before opening the bomb.

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

— Thoroughly rinse the bomb, 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 bomb washings or can be analysed separately from the solution of the combustion bomb.

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 bomb 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 EN 14918[8] 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] To be replaced by ISO 18125.

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.

NOTE 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 % m/m, is given by Formula (1):

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

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 % m/m.

9.3 Total sulfur

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

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

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 molar mass of sulfur divided by the molar mass of sulfuric acid;

M_{ad} is the moisture content in the analysis test sample, in % m/m.

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;

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.