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Solid biofuels — Determination of total content of sulfur and chlorine

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

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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).

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.