SLOVENSKI STANDARD

SIST-TS CEN/TS 15289:2006

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Trdna biogoriva ï Dolo ļ evanje celotnega ģvepla in klora

Solid Biofuels - Determination of total content of sulphur and chlorine

Feste Biobrennstoffe - Bestimmung des Gesamtgehaltes an Schwefel und Chlor

Biocombustibles solides - Détermination de la teneur en chlore et en soufre

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Feste Biobrennstoffe - Bestimmung des Gesamtgehaltes an Schwefel und Chlor

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The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Foreword

This Technical Specification (CEN/TS 15289:2006) has been prepared by Technical Committee CEN/TC 335 “Solid biofuels”, the secretariat of which is held by SIS.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this CEN Technical Specification: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

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

Chlorine may be present in different organic and inorganic compounds and should exceed or equal the water soluble amount that can be determined by CEN/TS 15105:2005.

Oxygen combustion in a closed oxygen bomb is the preferred method to digest biomass samples. Decomposition in closed vessels is an appropriate alternative method. Other analytical techniques (e.g. high temperature combustion in a tube furnace, Wickbold or Schöninger combustion, Eschka method) may also be used. The determination of the resultant chlorine and sulphur 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 sulphur and chlorine contents of biofuels can be found in Annex C of CEN/TS 14961:2005.

1 Scope

This Technical Specification describes methods for the determination of the total sulphur and total chlorine content in solid biofuels. The method describes a procedure for the digestion and different analytical techniques for the quantification of the elements in the digestion solution.

The method is applicable for all biofuel samples containing more than 50 mg/kg of chlorine and/or sulphur.

2 Normative references

The following referenced documents are indispensable for the application 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.

CEN/TS 14588:2003, *Solid biofuels – Terminology, definitions and descriptions.*

CEN/TS 14774-3, *Solid Biofuels – Methods for the determination of moisture content – Oven dry method – Part 3: Moisture in general analysis sample.*

CEN/TS 14780, *Solid biofuels – Methods for sample preparation.*

CEN/TS 14918, *Solid biofuels – Method for the determination of calorific value.*

CEN/TS 15296, *Solid biofuels – Calculation of analyses to different bases.*

CEN/TS 15290, *Solid biofuels – Determination of major elements.*

EN ISO 10304-1, *Water quality – Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulphate ions, using liquid chromatography of ions – Part 1: Method for water with low contamination (ISO 10304-1:1992).*

EN ISO 11885, *Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (ISO 11885:1996).*

ISO 587, *Solid mineral fuels – Determination of chlorine using Eschka mixture*

ASTM D516-02, *Standard test method for sulphate ion in water.*

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

DIN 51727, *Testing of solid fuels – determination of chlorine content.*

3 Terms and definitions

For the purposes of this Technical Specification, the terms and definitions given in CEN/TS 14588:2003 apply.

4 Principle

4.1 General

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

4.2 Digestion of the biofuel and transfer of acidic gaseous components into solution

— Combustion in an oxygen bomb and absorption of the acidic gas components in an absorption solution (method A);

— Decomposition in closed vessels as described in CEN/TS 15290 (method B).

4.3 Determination of sulphate and chloride in the receiving solution

— Ion chromatography applying the principles of EN ISO 10304-1;

— ICP, applying the principles of EN ISO 11885 (determination as sulphur and chlorine);

— Other suitable analytical methods.

NOTE A large number of applicable methods for the quantification of sulphate and chloride exists but detection limits and precision vary significantly.

4.4 Automatic equipment

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

X-ray fluorescence may be used to determine sulphur and chlorine directly in the solid biofuel samples.

NOTE An equipment validated only with e.g. straw reference materials is not automatically suitable for the determination of sulphur and chlorine in e.g. 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 below listed reagents concern only 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 sulphur, i.e. amounts that do not contribute significantly to the determination.

5.2 Water

Deionised water will normally fulfil the requirements of 5.1.

5.3 Oxygen

Pure 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, acetobutyratcapsules, polyethelene bags.

6 Apparatus

6.1 General

— Analytical balance, with a resolution of at least 0,1 mg;

— General laboratory equipment as volumetric flasks and measuring cylinders.

6.2 Method A

6.2.1 Pellet press, capable of applying a force of 0,1 MN 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 sulphur and chlorine. The combustion bomb may be the same as used for the determination of the calorific value (see CEN/TS 14918).
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

Closed vessels for the decomposition, see CEN/TS 15290.

7 Preparation of the test sample

The test sample is the general analysis test sample with a nominal top size of 1 mm or less prepared in accordance with CEN/TS 14780.

NOTE For some instrumental methods and/or solid biofuels it may 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.

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 CEN/TS 14774-3, using another portion of the test sample.

8 Procedure

8.1 Digestion

8.1.1 Method A: Combustion in a closed bomb

Solid biofuel samples are usually tested 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 CEN/TS 14918.

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