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BSI Standards Publication

Solid biofuels — Determination of the water soluble chloride, sodium and potassium content

National foreword

This British Standard is the UK implementation of EN 15105:2011. It supersedes DD CEN/TS 15105:2005 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/17, Solid biofuels.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Solid biofuels - Determination of the water soluble chloride, sodium and potassium content

Biocombustibles solides - Méthodes de détermination de la teneur en chlorure, sodium et potassium solubles dans l'eau

Feste Biobrennstoffe - Bestimmung des wasserlöslichen Gehaltes an Chlorid, Natrium und Kalium

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Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (EN 15105:2011) has been prepared by Technical Committee CEN/TC 335 “Solid biofuels”, the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by August 2011, and conflicting national standards shall be withdrawn at the latest by August 2011.

This document supersedes CEN/TS 15105:2005.

In the pre-normative project BIONORM I&II a robustness test has been performed to find out if all critical parameters in the standard were addressed. Based on the results of that test it has been concluded that all critical parameters were covered. Only minor technical changes were necessary which have been implemented in the revised text. The revision also includes a change of deliverable from Technical Specification to European Standard and updated normative references.

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Introduction

The elements chlorine, sodium and potassium are present in solid biofuels. They can contribute significantly to utilisation problems such as corrosion, fouling and slagging in furnaces. Also they affect the gaseous emissions from the thermal processes.

The chlorine content in solid biofuels is mainly present as water soluble inorganic salts such as sodium and potassium chlorides or other ion-exchangeable forms. Determination of the water soluble chloride content is thus an alternative and simple method to achieve information of the level of chlorine in solid biofuels. The content of water soluble chloride shall however not be mistaken for the total content of chlorine in the fuels.

In solid biofuels sodium and potassium can be present as both minerals and salts. The salts of these elements are extractable with water and are readily volatile during thermal conversion. By determination of the water soluble content of sodium and potassium an estimate of the aggressive content of the elements in relation to potential slagging and fouling problems can be achieved. For some biofuels, such as straw, experience has shown that the water soluble content of sodium and potassium correspond to the total content of the elements. The content of water soluble sodium and potassium shall not be mistaken for the total content of the elements.

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1 Scope

This European Standard specifies a method for the determination of the water soluble chloride, sodium and potassium content in solid biofuels by extraction with water in a closed container and their following quantification by different analytical techniques.

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.

EN 14588:2010, *Solid biofuels — Terminology, definitions and descriptions*

EN 14774-3, *Solid biofuels — Determination of moisture content — Oven dry method — Part 3: Moisture in general analysis sample*

FprEN 14780, *Solid biofuels — Sample preparation*

EN 15296, *Solid biofuels — Conversion of analytical results from one basis to another*

EN 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 sulphate (ISO 10304-1:2007)*

EN ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007)*

ISO 9964-1, *Water quality — Determination of sodium and potassium — Part 1: Determination of sodium by atomic absorption spectrometry*

ISO 9964-2, *Water quality — Determination of sodium and potassium — Part 2: Determination of potassium by atomic absorption spectrometry*

ISO 9964-3, *Water quality — Determination of sodium and potassium — Part 3: Determination of sodium and potassium by flame emission spectrometry*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 14588:2010 and the following apply.

3.1
water soluble content of chloride, sodium and potassium
amount of the elements chloride, sodium and potassium which can be extracted with water using the extraction procedure specified in this European Standard

4 Principle

The fuel sample is heated with water in a closed container at 120 °C for 1 hour. The concentrations of chloride, sodium and potassium in the obtained water extract are determined by one of the following techniques:

— chloride: Ion-Chromatography (IC) or potentiometric titration with silver nitrate;

NOTE Be aware that when potentiometric titration with silver nitrate is used, any contents of water soluble bromide and iodide will be included in the determination.

— sodium and potassium: Flame Emission Spectroscopy (FES) or Flame Atomic Absorption Spectroscopy (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

5 Reagents

Water, containing negligible amounts of chloride, sodium and potassium i.e. amounts that do not contribute significant to the determinations. Deionised water will normally fulfil this requirement.

6 Apparatus

6.1 Heating oven or autoclave, capable of being maintained at a temperature of (120 ± 5) °C.

6.2 Vessel, made of fluoropolymer with a volume of about 100 ml and provided with a tight screw cap.

The vessel and the cap shall be capable of withstanding at least 125 °C at 232 kPa. If only the water soluble content of chloride is to be determined, an equivalent Pyrex glass vessel can be used.

6.3 Balance, with a resolution of at least 1 mg.

6.4 General laboratory equipment as volumetric flasks and measuring cylinders.

If sodium and potassium are to be determined, the use of glass equipments shall be avoided.

6.5 Membrane filtering apparatus, with membrane filters of mean pore size 0,45 μm.

7 Preparation of the test sample

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

If the results are to be calculated other than on an “as determined” basis, the moisture content of the test sample shall be determined concurrently by the method described in EN 14774-3, using another portion of the test sample.

8 Procedure

8.1 Extraction

a) Weigh, in an empty clean vessel (see 6.2), 1,0 g of the analysis sample to the nearest 1 mg.

b) Add 50,0 ml water, swirl the content and close the vessel tight.

c) Leave the closed vessel in a heating oven or an autoclave at 120 °C for 60 min.

d) Take the closed vessel out of the oven or the autoclave and let it cool to room temperature.

WARNING — Do not attempt to open the vessel before it is cool.

e) Transfer the content of the vessel to a 100 ml volumetric flask. Wash the inside of the vessel with small portions of water; add the washings to the volumetric flask and fill it to the 100 ml volume with water.

f) Filter a portion of the solution (see e)) through a membrane filter of pore size 0,45 μm, discarding the first portion of the filtrate. Alternatively the filtering can be carried out using a syringe equipped with a 0,45 μm pore size filter tip.

NOTE If only the water soluble content of chloride is to be determined, filtering may be omitted or a coarse folded filter paper may be used instead of the membrane filter.

8.2 Detection methods

8.2.1 General

Complete the determination by measuring the concentration of the elements in the prepared solution; for chloride by using one of the methods stated in 8.2.2 and for sodium and potassium by using one of the methods stated in 8.2.3.

8.2.2 Methods for the determination of chloride concentration

For the determination of the chloride concentration one of the following methods shall be used:

— Ion-chromatographic determination according to the principles of EN ISO 10304-1;

— Potentiometric titration with silver nitrate according to Std. Meth. 4500-Cl- D [7] or equivalent national standards e.g. [3], [4] or [6].

Other methods may be used, provided that it can be proved that the obtained results are comparable to results obtained by determinations using one of the above stated methods, within the performance characteristics of these methods.

8.2.3 Methods for the determination of sodium and potassium concentration

For the determination of the concentration of sodium and potassium one of the following methods shall be used:

— ICP-OES according to the principles of EN ISO 11885;

— FAAS according to the principles of ISO 9964-1 and ISO 9964-2;

— FES according to the principles of ISO 9964-3.

For the instrumental technique used, an initial control for eventual interferences shall be performed using a standard addition method and/or a dilution method.

Other methods may be used, provided that it can be proved that the obtained results are comparable to results obtained by determinations using one of the above stated methods, within the performance characteristics of these methods.

8.3 Blank test

Carry out a blank test, using the same procedure and methods as described in 8.1 and 8.2 but omitting the test portion. This assesses both the contents of the elements in the reagents and any contamination from equipments and in the laboratory atmosphere. This shall not be quantitatively significant.

The measured blank value has to be subtracted from the sample value.

NOTE 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.

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9 Calculation

The water soluble content of the element in the sample as analysed, w_X, expressed in mg/kg is given by the equation:

$$w_X = \frac{(c - c_0) \times V}{m}$$

where

c is the concentration of the element (chloride, sodium or potassium), in mg/l, in the extract solution (see 8.1 e));

c_0 is the concentration of the element (chloride, sodium or potassium), in mg/l, in the extract solution of the blank experiment (see 8.3);

V is the volume, in ml, of the extract solution;

m is the mass, in g, of the test portion used.

Report the results as the mean of duplicate determinations.

The results shall be calculated to a dry basis or to an as received basis according to EN 15296.

10 Performance characteristics

The achievable performance of the method is given in Annex A showing the results obtained by a European intercomparison 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 water soluble chloride, sodium and potassium and the olive residue samples with high amounts of water soluble chloride and potassium.

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 product (or sample) tested;

c) Reference to this European Standard (EN 15105);

d) Method for the determination

e) The 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 European 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 in 2008 in accordance with CEN/TS 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 is reported on dry basis.

The performance data according to ISO 5725-2 [1] are presented in Tables A.1, A.2 and A.3.

NOTE 1 See Table A.1 for definition of the symbols used in Tables A.1 to A.3.

NOTE 2 A guideline can be found in EN 15296 on how to use these validation parameters.

Table A.1 — Performance data for water soluble chloride

Sample	n	l	o	x	s_R	CV_R	s_r	CV_r
			%	mg/kg	mg/kg	%	mg/kg	%
wood chips	7	35	15	26	13	45	5	19
exhausted olive residues	7	35	0	2 100	150	7,4	49	2,4

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

Table A.2 — Performance data for water soluble sodium

Sample	n	l	0	x	s_R	CV_R	s_r	CV_r
			%	mg/kg	mg/kg	%	mg/kg	%
wood chips	There is not enough data available							
exhausted olive residues	8	40	0	99	16	16	8	8,4

Table A.3 — Performance data for water soluble potassium

Sample	n	l	0	x	s_R	CV_R	s_r	CV_r
			%	mg/kg	mg/kg	%	mg/kg	%
wood chips	6	29	4,4	634	20	3,1	9	1,4
exhausted olive residues	7	35	0	22 400	1 060	4,8	524	2,3

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