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Trdna alternativna goriva - Metode za določevanje žvepla (S), klora (Cl), fluora (F) in broma (Br)

Solid recovered fuels - Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content

Feste Sekundärbrennstoffe - Verfahren zur Bestimmung des Gehaltes an Schwefel (S), Chlor (Cl), Fluor (F) und Brom (Br)

Combustibles solides de récupération - Méthodes pour la détermination de la teneur en soufre (S), en chlore (Cl), en fluor (F), et en brome (Br)

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Solid recovered fuels - Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content

Combustibles solides de récupération - Méthodes pour la détermination de la teneur en soufre (S), en chlore (Cl), en fluor (F), et en brome (Br)

Feste Sekundärbrennstoffe - Verfahren zur Bestimmung des Gehaltes an Schwefel (S), Chlor (Cl), Fluor (F) und Brom (Br)

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Foreword

This document (EN 15408:2011) has been prepared by Technical Committee CEN/TC 343 “Solid recovered fuels”, the secretariat of which is held by SFS.

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of an identical text or by endorsement, at the latest by September 2011, and conflicting national standards shall be withdrawn at the latest by September 2011.

This document supersedes CEN/TS 15408:2006.

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Introduction

Determination of total sulphur, chlorine, fluorine and bromine content of solid recovered fuels (SRF) is necessary for environmental and technical reasons both in the production and combustion stage.

During the combustion process they are usually converted to sulphates and halides. These reaction products contribute significantly to corrosion and environmentally harmful emissions.

This method consists of an oxygen combustion procedure followed by trapping of sulphur, chloride, fluoride and bromide in an absorbing solution and subsequent determination by different techniques.

Alternatively, direct automatic techniques can be used for S and Cl determination. Other methods could also be used provided that it is demonstrated that they give the same results.

1 Scope

This European Standard specifies the determination of S, Cl, F and Br in solid recovered fuels of various origin and composition after combustion in oxygen atmosphere. This method is applicable for concentrations over 0,025 g/kg, depending on the element and on the determination technique. In the case of fluorine this method is applicable for concentration over 0,015 g/kg.

Insoluble halides and sulphate present in the original sample or produced during the combustion step are not completely determined by these methods.

This European Standard provides recommendations concerning standardised methods for determination of halides and sulphate in the solution obtained after combustion.

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 15357:2011, *Solid recovered fuels — Terminology, definitions and descriptions*

EN 15413[1)], *Solid recovered fuels — Methods for the preparation of the test sample from the laboratory sample*

EN 15414-3, *Solid recovered fuels — Determination of moisture content using the oven dry method — Part 3: Moisture in general analysis sample*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

EN ISO 10304-1:2009, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (ISO 10304-1:2007)*

EN ISO 17294-2, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of 62 elements (ISO 17294-2:2003)*

ISO 9297, *Water quality — Determination of chloride — Silver nitrate titration with chromate indicator (Mohr's method)*

ISO 10359-1, *Water quality — Determination of fluoride — Part 1: Electrochemical probe method for potable and lightly polluted water*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 15357:2011 and the following apply.

3.1
halogen content
sum of halogens contained as organic and inorganic compounds in the solid recovered fuels, which can be converted to halides (fluoride, chloride, bromide, iodide) by combustion and then absorbed or dissolved in aqueous solution

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[1)] To be published.

NOTE The above definition is valid for this empirical European Standard only and do not comply with scientific definitions of halogen content.

3.2
oxygen combustion
combustion of material in oxygen atmosphere

4 Safety remarks

The safety in handling of potentially hazardous materials is dealt with relevant national and European regulations, which every laboratory should refer to.

In addition the following information is given:

— only experienced personnel can use the oxygen combustion apparatus, following the operating instructions described in the manufacturer manual;

— precautions shall be taken by the operator for reactive gas (oxygen) at high temperature and high pressure.

5 Principle

The determination of S, Cl, F and Br is carried out in two steps or by using automatic equipment:

— the sample is oxidized by combustion in a bomb containing oxygen under pressure. Halogenated and sulphur compounds are converted respectively to fluoride, chloride, bromide and sulphate which are absorbed and/or dissolved in an absorption solution (water or KOH 0,2 mol/l solution);

— analysis of Cl, F and S and Br by ion chromatography or other suitable technique, are reported in the reference documents listed in Clause 2: for Cl, F, S and Br in EN ISO 10304-1, for F only in ISO 10359-1. Br is preferably determined by “Inductively Coupled Plasma Mass Spectrometry” (ICP-MS) according to EN ISO 17294-2 since several oxidation states of Br occur after oxygen combustion.

6 Apparatus

Apart ordinary laboratory apparatus, the following devices are required:

6.1 Oxygen combustor

Equipped with a combustion bomb made of stainless steel or any other material that will not be affected by the combustion process or products (the materials used may adsorb or react with acid gases formed during combustion or it may be not possible to clean the bomb completely between combustions). The bomb is equipped with oxygen inlet and safety valve and electrical contacts for spark generation. Many commercially available systems can be used. The combustion bomb may be the same as used for the determination of the calorific value.

Carefully check the characteristics of the combustion bomb, in order to be sure that it is suitable for the processing of materials with significant chlorine content (chlorine resistant combustion bombs are commercially available).

The combustion apparatus is equipped with automatic ignition system and oxygen gas supply.

6.2 Balances

— Analytical balance resolution ± 0,1 mg;

— balance accuracy ± 0,1 g.

6.3 Ion chromatograph

An ion chromatograph with suitable anion separator column, pre-column, background suppressor and conductivity cell.

6.4 Apparatus for titrimetry

Any suitable apparatus can be used, with colorimetric or potentiometric final point determination.

6.5 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Any suitable apparatus with normal resolution and pneumatic sample introduction system.

6.6 Automatic analyzer

Commercial instruments for S and Cl determination.

7 Reagents

All reagents shall be at least of analytical grade and suitable for their specific purposes. Particularly, they shall be free of sulphur and halogens.

7.1 Water of grade 1 as specified by EN ISO 3696.

7.2 Oxygen

Should be free of combustion material, minimum 99,99 % purity.

7.3 Nitrogen

Should be chromatographic grade for the ion chromatograph.

7.4 Eluent for ion chromatography

Carbonate/hydrogen carbonate mixed solution is suitable as eluent for ion chromatographic separation. Other eluents can be used, following the working instruction with the particular column used.

7.5 Absorbing solution

Water is appropriate for most application. If the content of chlorine is > 1 % or if bromine shall be determined, alkaline KOH 0,2 mol/l solution is more efficient for trapping the gases. As a preliminary check, XRF analysis can be used to check for the presence of Br or high chlorine content.

7.6 Stock standard solutions

1 000 mg/l chlorine, fluorine, bromine and sulphate commercially available standard solutions are used to prepared working and calibration solution by properly dilution.

7.7 Certified reference material (CRMs)

The trapping yield can be checked using a material with characteristic similar to SRF, e.g. a solid waste certified reference material.

7.8 Control mixtures

To create an appropriate control mixture, choose the control substances in combination so that all elements that shall be determined in the samples are represented. The amount of halogen and sulphur contents shall be in the same range of the element contents of the samples and approximately in the middle of the working range of the determination techniques. The mixture of the control substances needs to be homogenized using a pebble mill.

EXAMPLE An example of a mixture of control substances for the determination of fluorine, chlorine, bromine and sulphur is:

0,50 g 4-fluoro-benzoic acid; 2,0 g 4-chloro-benzoic acid; 0,25 g 4-bromo-benzoic acid; 0,25 g 4-iodo-benzoicacid; 2,0 g sulphanilic acid and 55,0 g cellulose are mixed. The mixture is homogenized, e.g. in a pebble mill. This mixture contains 1,13 g/kg fluorine; 7,547 g/kg chlorine; 1,656 g/kg bromine; 2,132 g/kg iodine and 6,17 g/kg sulphur.

8 Interferences and sources of error

The container in which the sample is delivered and stored can be a source of errors. Its material shall be chosen according to the elements to be determined. Grinding or milling samples includes a risk of contamination of the sample by the environment.

NOTE In fuels with high contents of sulphur bound to iron, the method can show different result.

9 Procedure

9.1 Sample conservation and pre-treatment

The laboratory samples shall be stored according to guidelines defined in Annex A.

9.2 Sample preparation

The test portion shall be prepared from the laboratory sample according to EN 15413.

In addition, for the purposes of this method, the target size should be 1 mm or below.

The amount of test portion is usually 1 g. For some instruments it may be necessary to weigh a lower amount: in this case a nominal size less than 1 mm is required in order to ensure the homogeneity of the test portion, according to EN 15413.

Whereas the determination is carried out on dry basis, the moisture content shall be determined according to EN 15414-3.

NOTE In some cases, when the sample is not homogeneous as regards chlorine-containing particles, finer particle size (e.g. 0,5 mm) would make better repeatability of analysis (see Annex C).

9.3 Bomb combustion

Set up the instrument following the manufacturer instructions.

Weigh about 1 g of test material. The test portion, weighed to 0,1 mg, can be:

— pressed to produce an unbreakable pellet;

— placed and weighed directly in a capsule (with 20 % water or without water);

— placed and weighed directly in a small PE bag (with 20 % water or without water);

— mixed with a combustion enhancer, like benzoic acid or any other not containing significant amounts of elements of interest.

The amount of sample used has to be reduced accordingly when a combustion aid (benzoic acid, PE-bag, capsule) is used because the combustion aid introduces an additional significant heating value. It is in many systems important not to exceed the max temperature rise in the bomb for safety reasons and for getting best results; the temperature rise is to be kept in a small band adjusting the amount of sample and combustion aid. This is expecially important when heating value is subsequently determined.

Add 10 ml of 0,2 mol/l KOH solution; fill the bomb with oxygen and set up the system following the operator instructions. If the chlorine content is < 1 % or bromine is not to be determined, water can be used instead of KOH solution.

Start the combustion. After combustion, equilibrate at room temperature for at least 10 min. After opening the bomb, check the completeness of combustion, by analysing residues. If unburned fractions are present the sample shall be discharged. Quantitatively recover the absorbing solution in a 100 ml tared bottle and fill up to the final volume with water.

Determine chloride, fluoride, sulphate and bromide by using the proper method, EN ISO 10304-1, ISO 9297, ISO 10359-1 or EN ISO 17294-2.

NOTE Robustness study (see Annex C), showed that the method is not applicable in its current form to some samples (e.g. containing tyre pieces) because the prepared pellet tend to break during combustion.

9.4 Calibration

Prepare a series of calibration solutions by dilution of the stock concentrated solution. These solutions are stable for at least 1 month if stored refrigerated.

9.5 Analysis of calibrations samples

Measure the calibration samples according to the instrument user's manual.

Calculate the regression curve.

9.6 Analysis of samples

Measure the samples according to the instrument user's manual.

The samples shall be analysed with the same analytical conditions as for the calibration samples.

10 Calculation and evaluation

10.1 General

Results are referred to the dry material. Calculation shall take into consideration any eventual intermediate dilution of the solution.