SIST

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Trdna alternativna goriva - Metode za določevanje elementov v sledovih (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V in Zn)

Solid recovered fuels - Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn)

Feste Sekundärbrennstoffe - Verfahren zur Bestimmung des Gehaltes an Spurelementen (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn)

Combustibles solides de récupération - Méthodes de détermination de la teneur en éléments à l'état de traces (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V et Zn)

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Solid recovered fuels - Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn)

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Foreword

This document (EN 15411:2011) 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of an identical text or by endorsement, at the latest by March 2012, and conflicting national standards shall be withdrawn at the latest by March 2012.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes CEN/TS 15411:2006.

This document differs from CEN/TS 15411:2006 only editorially.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, 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 the United Kingdom.

Introduction

Accurate determination of trace element content in solid recovered fuels is important for environmental and technical reasons both in the production and combustion stage. After digestion of the solid recovered fuels using different methods, a number of analytical techniques can be used for the quantification of the trace element content. They include Inductively Coupled Plasma with optical or mass detection, graphite furnace Atomic Absorption Spectrometry and, when available, dedicated specific method (e.g. for mercury).

1 Scope

This European Standard specifies three methods of digestion for solid recovered fuels:

a) microwave assisted digestion with hydrofluoric, nitric and hydrochloric acid mixture;

b) hot water bath digestion of with hydrofluoric, nitric and hydrochloric acid mixture, after ashing of the SRFs sample;

c) oven digestion with nitric, perchloric and hydrofluoric acid mixture.

Instrumental determination of As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Sb, Se, Tl, V, Zn is performed by Inductively Coupled Plasma with optical or mass detection or graphite furnace Atomic Absorption Spectrometry. Hg can be analysed only after the microwave assisted procedure or, alternatively, by a direct analysis method (Hg direct – AMA).

The effectiveness of the digestion can be verified by qualitative X-ray fluorescence (XRF) analysis on the remaining residue. If necessary, an alternative digestion method (among those proposed) is used.

Method a) is recommended for general use, but the amount of the test portion can be very low in case of high concentration of organic matter.

Method b) is recommended for Solid Recovered Fuel (SRF) with high organic matter concentration that can be difficult to digest with the other methods. This method is not suitable for mercury.

Method c) is recommended for Solid Recovered Fuel (SRF) samples for which the other methods leave a significant insoluble residue.

Alternative digestion methods can be applied if their performance is proved to be comparable with those of the methods mentioned in a) to c) (see Annex C).

2 Normative references

The following referenced documents are indispensable for the application of this European Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13656, *Characterization of waste — Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture for subsequent determination of elements*

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

EN 15403, *Solid recovered fuels — Determination of ash content*

EN 15413, *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)*

3 Terms and definitions

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

3.1
digestion
mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacted with a reagent mixture

3.2
microwave unit
whole microwave digestion system (oven and associated equipment)

4 Safety remarks

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

In addition the following information is given:

— Only experienced personnel can use the microwave apparatus, following the operating instructions described in the manufacturer manual;

— Most of the reagents used within this European Standard are strongly corrosive and toxic. Safety precautions are absolutely necessary due to strong corrosive reagents, high temperature and high pressure;

— All procedures have to be performed in a hood or in closed force-ventilated equipment. By the use of strong oxidising reagents the formation of explosive organic intermediates is possible, especially when dealing with samples with a high organic content. Do not open pressurised vessels before they have cooled down. Avoid contact with the chemicals and the gaseous reaction products.

5 Principle

The test portion is digested using one of the proposed methods with a suitable acid mixture. The digested sample is then analysed by the most appropriate spectrometric technique, such as atomic absorption or emission spectroscopy.

6 Apparatus

6.1 Microwave unit

Intended for laboratory use and preferably equipped with temperature control.

6.2 Resistance heating oven

A resistance heated oven or heating block that can be used at a temperature of at least 220 °C and an accuracy of ± 10 °C.

6.3 Digestion vessels

The vessels used in the microwave unit shall be equipped with a pressure relieve valve or another technical equipment which avoids the bursting of the vessels at suddenly occurring excess pressure. The material of the vessels has to be inert to the acids used for digestion. The digestion vessel shall withstand the pressure of at least 8 bar. If the amount of organic carbon exceeds 100 mg, it has to be ensured that the digestion vessel is capable of withstanding higher pressures.

6.4 Inductively coupled plasma

Normal commercial instrumentation with optical or mass spectrometric detector (ICP-OES, ICP-MS).

6.5 Atomic absorption spectrophotometer

Normal commercial instrumentation, equipped with graphite furnace or hydride generation systems or cold vapour (GF-AAS, HG-AAS, CV-AAS).

6.6 X-ray fluorescence spectrometer

Energy or wavelength dispersion system suitable for qualitative analysis of the elements listed in this European Standard (with the exception of beryllium).

6.7 Balances

Analytical balance resolution ± 0,1 mg.

6.8 General equipment

General laboratory equipment, including volumetric graduated flasks and pipettes of adequate size.

Filter equipment of adequate chemical resistance and purity or centrifuge.

The use of glassware shall be excluded when free hydrofluoric acid is present.

The glassware used in the digestion procedure should be carefully pre-cleaned with for example 10 % nitric acid solution.

7 Reagents

All reagents shall be at least of analytical grade and suitable for their specific purposes. Other specific reagents are listed and described in the reference methods for digestion or instrumental determination listed in Clause 2.

NOTE Acids used in the preparation of standards and for sample processing are of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 % (v/v) is recommended for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulphuric acids are used.

7.1 Water of grade 1 as specified by EN ISO 3696:1995.

7.2 Nitric acid (HNO_3), 65 % (w/w), ρ 1,40 g/ml.

7.3 Hydrofluoric acid (HF), 40 % (w/w), ρ 1,14 g/ml.

7.4 Perchloric acid ($HClO_4$), 70 % (w/w), ρ 1,62 g/ml.

7.5 Hydrochloric acid (HCl), 65 % (w/w), ρ 1,40 g/ml.

8 Procedure

8.1 Sample conservation and pre-treatment

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

It is advisable to contact the people performing the sampling in order to agree a procedure for the laboratory sample preparation and storage before delivering to the laboratory. In particular, any treatment procedure which can increase the temperature of the material above 40 °C should be avoided, in order to avoid significant loss of mercury or other volatile compounds.

Furthermore, any possible source of contamination during the laboratory sample preparation (e.g. grinding with metallic apparatus) shall be avoided or reduced as much as possible.

The laboratory sample should be stored and delivered in sealed high-density plastic containers.

8.2 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.

Depending on the used digestion method, the amount of test portion ranges between 0,2 g and 0,5 g.

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

9 Digestion procedure

9.1 Method A

Weigh between 0,2 g to 0,5 g of the sample, to the nearest 0,1 mg, prepared according to Clause 8 and transfer it into the vessel. If necessary, the sample may be moistened with a minimum amount of water. Proceed according to the general principle of EN 13656.

After cooling, the solutions are transferred to volumetric flasks of suitable volume (e.g. 50 ml). Any residue shall be separated by filtration or centrifugation and the composition is controlled by XRF or any other suitable technique: if a significant amount of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary. The control on the residue can be avoided if its composition is known from previous analysis of the same kind of materials or on the basis of experience.

9.2 Method B (informative)

Weigh 0,2 g of ashed sample according to EN 15403 in a low pressure teflon bomb with relief valve and proceed according to the general principle of method reported in EN 13656. 4 ml aqua regia and 1 ml concentrated HF are added. After closing, the bombs are placed in a water bath at 90 °C for 3 h.

After cooling, the solutions are transferred to volumetric flasks of suitable volume (e.g. 50 ml). Any residue shall be separated by filtration or centrifugation and the composition is controlled by XRF or any other suitable technique: if a significant amount of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary. The control on the residue can be avoided if its composition is known from previous analysis of the same kind of materials or on the basis of experience.

9.3 Method C (informative)

Weight 0,5 g of sample in a teflon bomb. Add 10 ml of an acid mixture prepared by mixing 950 ml of nitric acid and 50 ml of perchloric acid. After closing the bombs are placed in an oven at 190 °C for at least 10 h (including heating up time). After cooling, the solutions are transferred to 50 ml plastic bottles and the bombs are washed with 5 ml of 0,1 M nitric acid solution and 0,5 ml of concentrated hydrofluoric acid. The solutions are taken to volume with 0,1 M nitric acid. In the case of incomplete digestion, the residue should be separated by filtration or centrifugation and then dissolved with nitric/perchloric/hydrofluoric acid mixture (5/0,5/4,5) in ultrasonic bath at 50 °C.

After cooling, the solutions are transferred to volumetric flasks of suitable volume (e.g. 50 ml). Any residue shall be separated by filtration or centrifugation and the composition is controlled by XRF or any other suitable technique: if a significant amount of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary. The control on the residue can be avoided if its composition is known from previous analysis of the same kind of materials or on the basis of experience.

10 Analysis of the digestion solutions

10.1 Preparation of the solution for analysis

If the digested sample contains particles which might clog the nebulizers of the measurement apparatus or which might interfere with the injection of the sample into the instrument, the sample solution may be centrifuged, allowed to settle or be filtered. In the case of filtration, dilute the content of the vessel before filtering, rinse and then fill to the mark of the volumetric flask. The method used has to be reported in the test report.

Solution containing hydrofluoric acid shall be processed with HF resistant apparatus.

10.2 Analytical step

Different techniques can be used for the analysis of the digested solutions.

NOTE Examples of such techniques are ICP MS according to the general principle of the method reported in EN ISO 17294-2, GF-AAS and CV-AAS/HG-AAS (Cold Vapour and Hydride Generation Atomic Absorption) according to the principle of the method reported in ASTM E885-88 or direct mercury analysis according to the method reported in EPA Method 7473.

Instruments shall be set up and calibrated following the manufacturers' instructions and the used reference methods.

11 Expression of results

The results are expressed in milligram per kilogram on a dry basis.

For procedure B on SRF ash, the following equation shall be used to express the results on dry original matter:

$$C_d = C_{ash} \times \frac{A_{ash}}{100}$$

where

C_d is concentration on dry basis in the original sample;

C_{ash} is concentration in the ash;

A_{ash} is ash content (%).

12 Quality control

To detect possible contaminations from vessels and/or reagents, blank tests shall be carried out by the same sample preparation procedure, using the same quantities of reagents.