SLOVENSKI STANDARD
SIST-TS CEN/TS 15297:2006

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Trdna biogoriva ï Doloļ evanje manjġih elementov

Solid Biofuels - Determination of minor elements

Feste Biobrennstoffe - Bestimmung von Spurenelementen

Biocombustibles solides - Détermination des éléments mineurs

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Solid Biofuels - Determination of minor elements

Biocombustibles solides - Détermination des éléments mineurs

Feste Biobrennstoffe - Bestimmung von Spurenelementen

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Foreword

This Technical Specification (CEN/TS 15297:2006) 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

The minor elements present in solid biofuels can in some cases be of environmental concern, e.g. it has been shown that certain energy crops will concentrate cadmium and in polluted areas other toxic elements may be found at elevated concentrations in the biofuels. This can be a problem if for example the ash from the combustion is to be put back in the forest as a fertilizer. Trace elements in biofuels are often present at very low concentrations requiring great care to avoid contamination in the sample preparation and decomposition steps. The typical concentrations of minor elements in solid biofuels can be found in CEN/TS 14961. In this technical specification wet chemical methods are described. Alternative methods such as X-ray fluorescence (XRF) or direct mercury analysers may be used when validated with suitable materials (biomass reference materials)

1 Scope

This Technical Specification is intended for determination of the minor elements Arsenic, Cadmium, Cobalt, Chromium, Copper, Mercury, Manganese, Molybdenum, Nickel, Lead, Antimony, Vanadium and Zinc in all solid biofuels. Further it describes methods for sample decomposition and suggests suitable instrumental methods for the determination of the elements of interest in the digests. The determination of Selenium, Tin and Thallium is also possible with the method described in this Technical Specification.

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 12338, *Water quality – Determination of mercury – Enrichment methods by amalgamation*

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

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

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

EN ISO 11969, *Water quality – Determination of arsenic – Atomic absorption spectrometric method (hydride technique) (ISO 11969:1996)*

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)*

3 Terms and definitions

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

4 Symbols and abbreviations

4.1 Symbols

As Arsenic

Cd Cadmium

Co Cobalt

Cr Chromium

Cu Copper

Hg Mercury

Mn Manganese

Mo Molybdenum

Ni Nickel

Pb Lead

Sb Antimony

V Vanadium

Zn Zinc

4.2 Abbreviations

CV-AAS	Cold vapour atomic absorption spectroscopy
GF-AAS	Graphite furnace atomic absorption spectroscopy
HG-AAS	Hydride generation atomic absorption spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry

5 Principle

The analysis sample is digested in a closed vessel made from a fluoro polymer using nitric acid, hydrogen peroxide and in some cases hydrofluoric acid in a microwave oven or a resistance oven or heating block. The digest is then diluted and the elements determined with suitable instruments.

6 Reagents

6.1 General

All reagents shall be of analytical grade or better. If the blank level is unacceptably high i.e. more then 30 % of the determined value, the use of ultra pure reagents should be investigated.

6.2 Water

Water containing negligible amounts of the minor elements i.e. amounts that do not contribute significantly to the determinations. Deionised water or doubly distilled water will normally fulfil this requirement.

NOTE The water used for analytical trace metal work is normally produced using a system for production of ultra pure water for laboratory use conductivity = 0,056 µS/cm.

6.3 Hydrofluoric acid (HF)

40 % (w/w), ρ = 1,13 g/ml

CAUTION — Hydrofluoric acid may lead to health hazards.

6.4 Hydrogen peroxide (H_2O_2)

30 % (w/w), ρ = 1,11 g/ml

6.5 Nitric acid (HNO_3)

65 % (w/w), ρ = 1,40 g/ml

7 Apparatus

7.1 Heating oven or heating block suitable for the decomposition system in use

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.

7.2 Microwave oven

Intended for laboratory use and preferably equipped with temperature control.

7.3 Sample digestion vessels

Intended for the heating system used, normally made of a fluoro plastic.

7.4 Balance

With a resolution of at least 1 mg.

7.5 Plastic volumetric flasks

8 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. For the milling of the sample special attention must be taken for the risk of contamination from the inner materials of the mill. These materials shall be chosen depending on the elements to be determined. If for example chromium and nickel have to be determined with a high accuracy at low levels stainless steel materials should be avoided for the parts of the mill having contact with the sample, using for example tungsten carbide or titanium instead. Due to the higher abrasion rate the use of high-speed mills should in general be avoided. The results are to be calculated on a dry basis. Therefore the moisture content of the test sample should be determined as described in CEN/TS 14774-3.

9 Digestion

9.1 Weigh, in the decomposition vessel, 400 mg – 500 mg homogenised sample, weighed to the nearest 1 mg.

9.2 Add 2,5 ml hydrogen peroxide (30 %) and wait 1 min – 5 min.

9.3 Add 5 ml nitric acid (65 %).

9.4 Add 0,4 ml hydrofluoric acid (40 %) and close the sample decomposition vessel. The hydrofluoric acid may be omitted provided that it can be shown that equivalent results can be obtained for the actual type of solid biofuel. When hydrofluoric acid is used the instrument used for the analysis must be equipped with components resistant to this.

NOTE 1 For this relatively low concentration of hydrofluoric acid the only modification normally necessary when using ICP-OES or ICP-MS instruments is to use a nebulizer resistant to hydrofluoric acid. The instrument manufacturer can give information regarding the use of hydrofluoric acid.

NOTE 2 It is in some cases possible to use boric acid to complex the hydrofluoric acid, especially when using GFAAS or ICP-OES. This must be validated for the actual instrument. Furthermore, the impurities in the boric acid may create a blank problem.

9.5 Digest the sample using one of the following procedures.