INTERNATIONAL STANDARD

ISO 16968

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Solid biofuels — Determination of minor elements

Biocombustibles solides — Détermination des éléments mineurs

Reference number
ISO 16968:2015(E)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

ISO 16968 was prepared by the European Committee for Standardization (CEN) in collaboration with Technical Committee ISO/TC 238, *Solid biofuels*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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 ISO 17225-1. In this International Standard, 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).

Solid biofuels — Determination of minor elements

1 Scope

This International Standard is intended for the 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 other elements such as Selenium, Tin, and Thallium is also possible with the method described in this International Standard.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 16559, *Solid biofuels — Terminology, definitions and descriptions*

ISO 16993, *Solid biofuels — Conversion of analytical results from one basis to another*

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

ISO 17378-2:2014, *Water quality — Determination of arsenic and antimony — Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

ISO 18134-3[1], *Solid biofuels — Determination of moisture content — Oven dry method — Part 3: Moisture in general analysis simple*

EN 14780, *Solid Biofuels — Sample preparation*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16559 and the following apply.

3.1
reference material
RM
one or more material or substance of which property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, assessment of a measurement method, or assignment of values to materials

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[1] To be published.

3.2

certified reference material

CRM

reference material, accompanied by a certificate, one or more of which property values are certified by a procedure that establishes traceability to an accurate realisation of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence

3.3

NIST standard reference material

SRM

CRM issued by NIST that also meets additional NIST-specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterisations and provides information regarding the appropriate use(s) of the material

4 Symbols and abbreviated terms

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 Abbreviated terms

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

ICP-MS	Inductively coupled plasma mass spectrometry
NBS	National Bureau of Standards
NIST	National Institute of Standards and Technology[a]

[a] Known between 1901 and 1988 as the National Bureau of Standards (NBS), is a measurement standards laboratory, also known as National Metrological Institute (NMI), which is a non-regulatory agency of the United States Department of Commerce.

5 Principle

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

6 Reagents

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

6.1 Water, containing negligible amount of the minor elements, i.e. amount that do not contribute significantly to the determinations.

NOTE 1 Deionised water or doubly distilled water normally fulfils this requirement.

NOTE 2 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.

6.2 Hydrofluoric acid (HF), 40 % (w/w), ρ = 1,13 g/ml.

CAUTION — Hydrofluoric acid may lead to health hazards.

6.3 Hydrogen peroxide (H_2O_2), 30 % (w/w), ρ = 1,11 g/ml.

6.4 Nitric acid (HNO_3), ≥ 65 % (w/w), ρ = 1,41 g/ml.

6.5 Boric acid (H_3BO_3), 4 % (w/w).

6.6 Certified Reference Materials (CRM or SRM), issued by an internationally recognized authority, to check if the accuracy of the calibration meets the required performance characteristics.

EXAMPLE NBS 1570 spinach leaves, NBS1571 orchard leaves, NBS 1573 tomato leaves, and NBS 1575 pine needles.

When no good recoveries for the certified reference materials can be obtained, due to matrix effects or concentration range limitations, calibration with at least two CRM or SRM materials may solve these problems. In that case, CRM or SRM materials other than used for the calibration shall be used for verification purposes.

NOTE A CRM or SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

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 fluoroplastic.

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 EN 14780. For the milling of the sample, special attention shall be taken to 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 shall be determined as described in ISO 18134-3.

9 Procedure

9.1 Digestion

- In the digestion vessel, weigh 400 mg to 500 mg homogenized sample, to the nearest 1 mg.
- Add 2,5 ml hydrogen peroxide (30 %) and wait 1 min to 5 min.
- Add 5 ml nitric acid (65 %).
- Add 0,4 ml hydrofluoric acid (40 %) and close the sample digestion 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 shall 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.

  In some cases, it is possible to use boric acid to complex the hydrofluoric acid, especially when using GF-AAS or ICP-OES. This shall be validated for the actual instrument. Care shall be taken to use boric acid with the necessary purity.
- Heat the sample according to the following heating programmes for digestion:

  Resistance heating[2]: Step 1: Over 1 h heat to 220 °C, rate 3,33 °C/min

  Step 2: Hold for 1 h at 220 °C

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[2] The stated temperature refers to heating device (e.g. oven).

NOTE 2 Some available digestion bomb systems use fluoropolymer vessels, which cannot withstand temperatures above 170 °C. In such cases, this lower temperature can be used provided it can be shown that comparable results are obtained as when 220 °C is used, e.g. by the use of equivalent biomass reference materials.

Microwave heating[3]: Step 1: Over 15 min heat to 190 °C

Step 2: Hold for 20 min at 190 °C

— After cooling, transfer the digest to a volumetric flask. Rinse the digestion vessel carefully with high purity water and transfer the rinse solution to the volumetric flask. Add high purity water to the digest to an appropriate volume, depending on the detection method to be used.

9.2 Detection methods

— As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn can be detected by ICP-MS, ICP-OES, or GF-AAS provided that the detection limits of the used method are sufficient for the fuel specifications to be verified.

— As and Se can be determined using HG-AAS according to the principles described in ISO 17378-2.

— Hg can be determined using CV-AAS according to the principles described in EN 12338.

— ICP-OES can be used according to the principles described in ISO 11885.

— ICP-MS can be used according to the principles described in ISO 17294-2.

— Other instrumental methods may be used after validation with biomass reference material of a suitable type and provided that the performance characteristics are similar to those described in this International Standard.

9.3 Calibration of the apparatus

When the analytical system is evaluated for the first time, establish a calibration function for the measurement in accordance with the manufacturers' instructions. Adjust the established calibration function during the analysis if necessary. Check the performance of the instrument using the accepted standard procedures like replicate analysis, use of SRM and or CRM, control samples and control charts. The calibration and quality control scheme shall be organized and maintained in such a way that the required uncertainty of measurement can be obtained. The results of the validation study of BioNorm2 (Annex A) demonstrates what is achievable with commercial instruments that are used by experienced laboratories.

9.4 Analysis of the digests

Analyse the digests in accordance with the manufacturer's instructions.

9.5 Blank test

Carry out a blank test, using the same procedure and methods as described in 9.1 to 9.4, but omitting the test portion. This assesses both the contents of the elements in the reagents and any contamination from equipment and in the laboratory atmosphere. The obtained blank value should be subtracted from the value in the sample. This contribution shall not be quantitatively significant, if it is more than 30 % of the result, the blank value should be reported and the use of higher quality reagents should be considered.

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[3] The stated temperature refers to digest solution.

10 Calculations

The content of an element in the sample on dry basis, w_i, expressed in mg/kg, is calculated from the mean of duplicate determinations using Formula (1):

$$w_{\mathrm{i}} = \frac{(c_{\mathrm{i}} - c_{\mathrm{i},0}) \times V}{m} \times \frac{100}{(100 - M_{\mathrm{ad}})} \qquad (1)$$

where:

w_i is the concentration of the element in the sample, on a dry basis, in mg/kg;

c_i is the concentration of the element, in the diluted sample digest, in mg/l;

$c_{i,0}$ is the concentration of the element, in the solution of the blank experiment, in mg/l;

V is the volume of the diluted sample digest solution, in ml;

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

M_{ad} is the moisture content in the analysis test sample in % m/m;

The results may be calculated to other bases, e.g. as received basis according to ISO 16993.

11 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 most of the elements and the olive residue samples with high amount of most of the elements.

12 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 ISO 16968;

d) applied digestion procedure and selected test method for the determination;

e) results of the test including the basis in which they are expressed, as indicated in Clause 10;

f) any unusual features noted during the determination;

g) any operation not included in this International 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 according to EN 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 are reported on dry basis.

The performance data according to ISO 5725-2 are presented in Table A.1 to Table A.13. A list of techniques for the round robin is shown in Table A.14.

NOTE 1 See Table A.1 for definition of the symbols used in Table A.1 to Table A.13.

NOTE 2 A guideline can be found in ISO 16993:2015, Annex C on how to use these validation parameters.

Table A.1 — Performance data for Arsenic (As)

Sample	n	l	o %	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
wood chips	6	27	10	0,036	0,023	64	0,012	34
exhausted olive residues	8	38	7,3	0,60	0,057	9,5	0,036	6,0
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 Cadmium (Cd)

Sample	N	l	o %	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
wood chips	13	63	3,1	0,32	0,021	6,4	0,009	2,9
exhausted olive residues	8	40	0	0,025	0,0057	23	0,0050	20

Table A.3 — Performance data for Cobalt (Co)

Sample	N	l	o %	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
wood chips	9	43	4,4	0,34	0,033	9,7	0,010	2,9
exhausted olive residues	11	54	1,8	1,04	0,128	12	0,056	5,4

Table A.4 — Performance data for Chromium (Cr)

Sample	N	l	o %	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
wood chips	9	43	4,4	0,37	0,12	31	0,077	21
exhausted olive residues	15	72	4	14,3	3,4	24	1,08	7,6

Table A.5 — Performance data for Copper (Cu)

Sample	n	l	o %	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
wood chips	12	57	6,6	1,29	0,16	12	0,091	7,0
exhausted olive residues	15	75	0	25	2,2	8,6	0,85	3,4

Table A.6 — Performance data for Mercury (Hg)

Sample	N	l	o %	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
wood chips	6	27	3,6	0,0072	0,0016	23	0,0010	13
exhausted olive residues	10	44	2,2	0,012	0,0048	40	0,0026	22

Table A.7 — Performance data for Manganese (Mn)

Sample	N	l	o %	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
wood chips	14	69	1,4	261	18	6,78	3,78	1,4
exhausted olive residues	15	73	2,7	40,2	2,5	6,30	1,46	3,6