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Solid biofuels — Determination of major elements — Al, Ca, Fe, Mg, P, K, Si, Na and Ti

Biocombustibles solides — Détermination des éléments majeurs — Al, Ca, Fe, Mg, P, K, Si, Na et Ti

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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

The committee responsible for this document is ISO/TC 238, *Solid biofuels*.

Introduction

The elements described as major elements of solid biofuels are in fact major elements of the fuel ashes more than of the fuels. The determination of these elements can be used to assess ash behaviour in a thermal conversion process or to assess utilization of ashes. Moreover, fuel contamination or process additives are indicated by high values of certain elements. Contamination of fuel with sand or soil is indicated by high values of several elements.

In this International Standard, wet chemical methods are described.

Solid biofuels — Determination of major elements — Al, Ca, Fe, Mg, P, K, Si, Na and Ti

1 Scope

This International Standard describes methods for the determination of major elements of solid biofuels respectively of their ashes, which are Al, Ca, Fe, Mg, P, K, Si, Na, Ti. The determination of other elements such as barium (Ba) and manganese (Mn) is also possible with the methods described in this International Standard.

This International Standard includes two parts: Part A describes the direct determination on the fuel, this method is also applicable for sulfur and minor elements, Part B gives a method of determination on a prepared 550 °C ash.

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 7980, *Water quality — Determination of calcium and magnesium — Atomic absorption spectrometric method*

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*

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

EN 14780[1)], *Solid Biofuels — Sample preparation*

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 18122[2)], *Solid biofuels — Determination of ash content*

ISO 18134-3[2)], *Solid biofuels — Determination of moisture content — Oven dry method — Part 3: Moisture in general analysis sample*

3 Terms and definitions

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

1) To be replaced by ISO 14780.

2) To be published.

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

3.2
certified reference material
CRM
reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which 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

Al	Aluminium
Ca	Calcium
Fe	Iron
Mg	Magnesium
P	Phosphorus
K	Potassium
Si	Silicon
Na	Sodium
Ti	Titanium

4.2 Abbreviated terms

CRM	Certified Reference Material
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
FES	Flame Emission Spectrometry
SRM	Standard Reference Material

NBS National Bureau of Standards

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

5 Principle

The sample is digested in a closed vessel by the help of reagents, temperature, and pressure. The digestion is either carried out directly on the fuel (part A) or on a 550 °C prepared ash (part B).

The detection of the elements can be done by ICP-OES, ICP-MS, FAAS, or FES.

6 Reagents

All reagents should be of analytical grade or better. If minor elements are also to be determined, the best qualities should be used.

6.1 Water, containing negligible amounts of major elements, i.e. amounts that do not contribute significantly to the determinations. Deionised water will normally fulfil this requirement.

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

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

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

CAUTION — Hydrofluoric acid might lead to health hazards.

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

6.6 Use of certified reference materials (CRM or SRM).

Use certified reference materials, issued by an internationally recognized authority, to check if the accuracy of the calibration meets the required performance characteristics. Examples of certified reference materials are: NBS 1570 spinach leaves, NBS1571 orchard leaves, NBS 1573 tomato leaves, and NBS 1575 pine needles.

When, due to matrix effects or concentration range limitations, no good recoveries for the certified reference materials can be obtained, calibration with at least two CRM or SRM materials can 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, resistance heated oven or heating block that can be used at a temperature of at least 220 °C with an accuracy of ±10 °C.

7.2 Microwave oven, intended for laboratory use and equipped with temperature control.

7.3 Sample digestion vessels, intended for the heating system used, normally made of a fluoro plastic.

7.4 Balance.

7.4.1 Part A, balance with a resolution of at least 1 mg.

7.4.2 Part B, balance with a resolution of at least 0,1 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[3)].

The moisture content of the test sample shall be determined as described in ISO 18134-3.

9 Procedure

9.1 Digestion

9.1.1 Part A: Direct determination on the fuel

The decomposition shall be carried out in closed vessels. It can be done in a heating oven, a heating block or in a microwave oven.

— Mix 500 mg of ground and homogenized sample, weighed to the nearest 1 mg, with 3,0 ml H_2O_2 (30 %), 8,0 ml HNO_3 (65 %), and 1,0 ml HF (40 %) in a closed digestion vessel. A reaction time of minimum 5 min shall be kept before closing the vessel. Closing the digestion vessel too early can result in a fast pressure build up, sometimes exceeding the maximum pressure limit of the vessel.

If the sample is expected to have an ash content above 10 %, 2,0 ml HF (40 %) should be used.

— The heating of the vessel shall not be too fast. Heat the sample according to the following heating programmes for digestion:

Resistance heating[4)]: Step 1: Ramp to 220 °C over 1 h

Step 2: Hold for 1 h at 220 °C

Microwave heating[5)]: Step 1: Ramp to 190 °C over 15 min

Step 2: Hold for 20 min at 190 °C

If the maximum pressure limit of the vessel is exceeded during the digestion and by that an opening of the relief valve has occurred, the digestion should be discarded due to possible loss of Si (in form of gaseous SiF_4).

NOTE 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 that the sample is held longer at this temperature and that comparable results can be obtained, e.g. by the use of equivalent biomass reference materials.

3) To be replaced by ISO 14780.

4) The stated temperature refers to heating device (e.g. oven).

5) The stated temperature refers to digest solution.

— After cooling to room temperature, HF is neutralised by adding 10 ml H3BO3 (4 %).

If 2,0 ml HF (40 %) was used for the digestion, 20 ml H_3BO_3 (4 %) should be used for the neutralization.

— Reheat the sample according to the following heating programmes for neutralization:

Resistance heating[4]: Step 1: Heat rapidly to 180 °C

Step 2: Hold for 15 min at 180 °C

Microwave heating[5]: Step 1: Heat rapidly to 150 °C

Step 2: Hold for 15 min at 150 °C

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

9.1.2 Part B: Determination on a prepared 550°C ash

— Heat the sample according to the procedure described in ISO 18122 to obtain ash. Make sure that the ashing procedure is performed exactly according to this procedure as deviations in ashing temperature, time, and air refreshing rate will influence the results. In deviation of ISO 18122, only crucibles made of platinum or graphite can be used for the preparation of the ash, but larger types of crucibles can be used. The use of the stated additives in ISO 18122 to ensure complete combustion is not allowed in the preparation. Also a continuous ashing by refilling of the sample on the previous ash in the crucible is not allowed.

To prepare a sufficient amount of ash for the digestion of larger amounts of sample, compared to the procedure given in ISO 18122, often will be necessary. The ash percentage on dry basis obtained for the prepared ash, thus, shall be calculated and compared to obtained results for the ash content on dry basis determined exactly according to ISO 18122. If the ash content for the prepared ash is also known, the results for major elements determined for the prepared ash can be calculated to fuel basis.

— Homogenize the prepared ash in an agate mortar and reignite the homogenized ash at 550 °C for 30 min.

NOTE 1 The weighing of the test portion of the ash for the digestion has to be carried out immediately after the preparation.

For the digestion of the ash similar working steps, as for the digestion of the fuel, are evident:

— Mix 50 mg of ground and homogenized ash, weighed to the nearest 0,1 mg, with 2,0 ml H_2O_2 (30 %), 3,0 ml HNO_3 (65 %), and 2,0 ml HF (40 %) in a closed decomposition vessel. A reaction time of minimum 5 min shall be kept before closing the vessel.

— Digest the sample following one of the heating programmes described in 9.1.1 for digestion.

If the maximum pressure limit of the vessel is exceeded during the digestion and by that an opening of the relief valve has occurred, the digestion should be discarded due to possible loss of Si (in form of gaseous SiF4).

— After cooling to room temperature, the HF is neutralized by adding 20 ml H_3BO_3 (4 %) and 10 ml deionised water.

NOTE 2 The water is necessary to keep K in solution for bio-ashes with high KCl content.

— Reheat the sample according to the heating programmes for neutralization described in 9.1.1.