SLOVENSKI STANDARD
oSIST prEN ISO 3884:2024

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Trdna alternativna goriva - Metode za določevanje glavnih elementov (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) (ISO/DIS 3884:2024)

Solid recovered fuels – Methods for the determination of the content of elements (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) (ISO/DIS 3884:2024)

Feste Sekundärbrennstoffe - Verfahren zur Bestimmung des Gehaltes an Elementen (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) (ISO/DIS 3884:2024)

Combustibles solides de récupération - Méthodes pour la détermination de la teneur en éléments (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) (ISO/DIS 3884:2024)

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Solid recovered fuels — Methods for the determination of the content of elements (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, Zn)

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Contents

Page

Foreword v
Introduction vi
1 Scope 1
2 Normative references 2
3 Terms and definitions 2
4 Symbols and abbreviations 2
5 Safety remarks 4
6 Principle 5
7 Reagents 5
8 Apparatus 5
9 Interferences and sources of errors 7
9.1 General information 7
9.2 Closed vessel system for microwave digestion 7
10 Preparation of the test sample 7
11 Procedure 8
11.1 General 8
11.2 Blank test 8
11.3 Method A (general method for SRF and major elements in ashed SRF) - Microwave assisted digestion with hydrochloric, nitric and hydrofluoric acid mixture (6 ml HCl; 2 ml HNO_3; 2 ml HF) 8
11.4 Method AT (method for SRF and major elements in ashed SRF) - Microwave assisted digestion with hydrochloric, nitric and tetrafluoroboric acid mixture (6 ml HCl; 2 ml HNO_3; 4 ml HBF_4) 10
11.5 Method B (e.g. plastic based SRF and others if method A cannot be applied) - Microwave assisted digestion with hydrochloric, nitric and hydrofluoric acid mixture (0,5 ml HCl; 6 ml HNO_3; 1 ml HF) 11
11.6 Method BT (e.g. plastic based SRF and others) - Microwave assisted digestion with hydrochloric, nitric and tetrafluoroboric acid mixture (0,5 ml HCl; 6 ml HNO_3; 2 ml HBF_4) 11
11.7 Method C (e.g. wood based SRFs) - Microwave assisted digestion with nitric acid, hydrogen peroxide and hydrofluoric acid mixture (2,5 ml H_2O_2; 5 ml HNO_3; 0,4 ml HF) 12
11.8 Method CT (e.g. wood based SRFs) - Microwave assisted digestion with nitric acid, hydrogen peroxide and tetrafluoroboric acid mixture (2,5 ml H_2O_2; 5 ml HNO_3; 0,8 ml HBF_4) 13
11.9 Method D (major elements in SRF ash) – digestion of ashed SRF with fluxing agent lithium metaborate (fused bead) 13
12 Analysis 14
12.1 Preparation of the solution for analysis 14
12.2 Analytical step 14
12.3 XRF analysis on ashed samples – sample preparation (major elements only) 14
13 Calculations 15
14 Quality control 15
15 Performance characteristics 15
16 Test report 15
Annex A (informative) **Calibration of the power adjustment** 17
Annex B (informative) **Validation and performance data (SRF22ERI)** 18

Annex C (informative) **Performance data (QUOVADIS)** **63**
Annex D (informative) **Results of ruggedness testing (QUOVADIS)** **76**
Bibliography **80**

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).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 300, *Solid recovered materials, including solid recovered fuels*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 343, *Solid recovered fuels*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Accurate determination of the element content in solid recovered fuels is important for environmental and technical reasons both in the production and combustion stage. Some of the elements determined by the application of one of the methods in this document are included in ISO 21640:2021[1] while other elements can have environmental implications both for emissions and for the bottom and fly ashes disposal or recovery. Furthermore, the determination of elements such as Al, Ca, Fe, Mg, P, K, Si, Na and Ti can be helpful to predict the melting behaviour and slagging of the ash.

The methods described in this document are providing multi-element digestions for a wide range of solid recovered fuels. The elements that are extractable and determined by these procedures can in many instances be described as 'total element contents', although this will be matrix dependent. After digestion a number of analytical techniques can be used for the accurate determination of major and minor element contents, e.g. Inductively Coupled Plasma with optical or mass detection (ICP-OES, ICP-MS), graphite furnace Atomic Absorption Spectrometry (GF-AAS) and specific direct methods (e.g. for Mercury, Sulphur).

Alternatively, X-ray fluorescence can be used as a fast method for a qualitative overview of ash forming elements and impurities of solid recovered fuels. After suitable calibration X-ray fluorescence is very useful for determining major elements or even minor elements (except Mercury and Beryllium) in solid recovered fuels according to ISO 22940:2021. For calibration of X-ray fluorescence, it is important to use several solid recovered fuel reference materials or solid recovered fuel samples that were carefully characterized after total digestion and measurement by ICP-OES, ICP-MS, GF-AAS or by other techniques such as elemental analysis using combustion technology on sulphur (see ISO 21663:2020[2]).

After ashing of solid recovered fuels X-ray fluorescence allows the simultaneous determination of major elements (Al, Ca, Fe, Mg, P, K, Si, Na, Ti) in the ashes after matrix-based calibration. Procedures are described in ISO 22940:2021 and EN 15309:2007.

Solid recovered fuels — Methods for the determination of the content of elements (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, Zn)

1 Scope

This document specifies methods for the determination of major and minor element concentrations in solid recovered fuels after digestion by the use of different acid mixtures and by addition of a fluxing agent for SRF ash.

a) Method A: Microwave assisted digestion with hydrochloric, nitric and hydrofluoric acid mixture (6 ml HCl; 2 ml HNO_3; 2 ml HF) followed by boric acid complexation;

b) Method AT: Microwave assisted digestion with hydrochloric, nitric and tetrafluoroboric acid mixture (6 ml HCl; 2 ml HNO_3; 4 ml HBF_4);

c) Method B: Microwave assisted digestion with hydrochloric, nitric and hydrofluoric acid mixture (0,5 ml HCl; 6 ml HNO_3; 1 ml HF) followed by boric acid complexation;

d) Method BT: Microwave assisted digestion with hydrochloric, nitric and tetrafluoroboric acid mixture (0,5 ml HCl; 6 ml HNO_3; 2 ml HBF_4);

e) Method C: Microwave assisted digestion with nitric acid, hydrogen peroxide and hydrofluoric acid mixture (2,5 ml H_2O_2; 5 ml HNO_3; 0,4 ml HF) and optional boric acid complexation;

f) Method CT: Microwave assisted digestion with nitric acid, hydrogen peroxide and tetrafluoroboric acid mixture (2,5 ml H_2O_2; 5 ml HNO_3; 0,8 ml HBF_4);

g) Method D: Digestion of the ashed SRF sample with fluxing agent lithiummetaborate in an oven at 1 050 °C.

This document is applicable for the following major and minor/trace elements:

Major elements: Aluminium (Al), Calcium (Ca), Iron (Fe), Potassium (K), Magnesium (Mg), Sodium (Na), Phosphorus (P), Sulphur (S), Silicon (Si) and Titanium (Ti).

Minor/trace elements: Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Mercury (Hg), Molybdenum (Mo), Manganese (Mn), Nickel (Ni), Lead (Pb), Antimony (Sb), Selenium (Se), Tin (Sn), Thallium (Tl), Vanadium (V) and Zink (Zn).

Method A is recommended for general use for SRF and ashed SRFs, but the amount of the test portion can be very low in case of high concentration of organic matter. Method AT can be used if an alternative to HF is necessary.

Method B with a higher volume of nitric acid is recommended for SRFs with high organic matter (e.g. suitable for high plastic content) that can be difficult to digest with less nitric acid or as a substitute for method A if appropriate equipment is not available. Method BT can be used if an alternative to HF is necessary.

Method C with combination of nitric acid and hydrogen peroxide and addition of hydrofluoric acid is recommended for wood based SRFs (e.g. demolition wood) or when there is a need for comparability to solid biofuel standards. Method CT can be used if an alternative to HF is necessary.

Method D is specifically applicable for determination of major elements in ashed SRF samples.

XRF can be used for the analysis of major elements (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti) after ashing (815 °C) of the samples and several major and minor/trace elements in SRF can be analysed by XRF after suitable calibration provided that the concentration levels are above instrumental detection limits of the XRF instrumentation and after proper preliminary testing and validation.

Digestion methods with HF and subsequent boric acid complexation or application of method D are recommended for determination of Si and Ti (better digestion efficiency).

Alternative digestion methods can be applied, if their performance is proved to be comparable with those of the methods described in this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 21637, *Solid recovered fuels — Terminology, definitions and descriptions*

ISO 21660-3, *Solid recovered fuels — Determination of moisture content using the oven dry method — Part 3: Moisture in general analysis sample*

ISO 22940:2021, *Solid recovered fuels — Determination of elemental composition by X-ray fluorescence*

EN 15309:2007, *Characterization of waste and soil — Determination of elemental composition by X-ray fluorescence*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21637 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

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 Symbols and abbreviations

A_{db}	ash content at 815 °C on a dry basis (A_DB)
Al	Aluminium (AL)
Al_{ash}	Aluminium in ashed SRF (ALASH)
Ca	Calcium (CA)
Ca_{ash}	Calcium in ashed SRF (CAASH)
Fe	Iron (FE)

Fe_{ash}	Iron in ashed SRF (FEASH)
K	Potassium (K)
K_{ash}	Potassium in ashed SRF (KASH)
Mg	Magnesium (MG)
Mg_{ash}	Magnesium in ashed SRF (MGASH)
Na	Sodium (NA)
Na_{ash}	Sodium in ashed SRF (NAASH)
P	Phosphorus (P)
P_{ash}	Phosphorus in ashed SRF (PASH)
S	Sulphur (Sulfur) (S)
S_{ash}	Sulfur in ashed SRF (SASH)
Si	Silicon (SI)
Si_{ash}	Silicon in ashed SRF (SIASH)
Ti	Titanium (TI)
Ti_{ash}	Titanium in ashed SRF (TIASH)
As	Arsenic (AS)
Ba	Barium (BA)
Be	Beryllium (BE)
Cd	Cadmium (CD)
Co	Cobalt (CO)
Cr	Chromium (CR)
Cu	Copper (CU)
Hg	Mercury (HG)
Mo	Molybdenum (MO)
Mn	Manganese (MN)
Ni	Nickel (NI)
Pb	Lead (PB)
Sb	Antimony (SB)
Se	Selenium (SE)
Sn	Tin (SN)
Tl	Thallium (TL)

V	Vanadium (V)
Zn	Zink (ZN)
GF-AAS	Graphite Furnace-Atomic Absorption Spectrometry
HG-AAS	Hydride Generation-Atomic Absorption Spectrometry
CV-AAS	Cold Vapour-Atomic Absorption Spectrometry
ICP-OES	Inductively coupled plasma-Optical Emission Spectrometry
ICP-MS	Inductively coupled plasma-Mass Spectrometry
PTFE	polytetrafluorethylene
PFA	perfluoroalkoxy (e.g. PFA liner)
TFM	tetrafluoroethylene, modified (e.g. TFM liner)
XRF	X-ray fluorescence
SRF	Solid recovered fuels
CRM	certified reference material
RM	reference material
dm	dry matter (DM)
HCl	hydrochloric acid
HNO_3	nitric acid
HBF_4	Tetrafluoroboric acid
H_2O_2	hydrogen peroxide
HF	hydrofluoric acid

5 Safety remarks

The safety in handling of potentially hazardous material is dealt with by the relevant (inter-)national 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 and safety instructions described in the manufacturer manual;

— The microwave unit cavity shall be built in a way that even in case of leakage or explosion of the vessels the safety of the operators can be guaranteed. Household instruments are not suitable for laboratory use.

— Most of the reagents used within this document 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 a closed force-ventilated equipment. By the use of strong oxidising reagents the formation of explosive 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.

6 Principle

The test portion is digested using one of the proposed methods with a suitable acid mixture or by addition of a fluxing agent (ashed SRF). The digested sample is then analysed by the most appropriate spectrometric technique, such as Inductively Coupled Plasma with optical or mass detection (ICP-OES, ICP-MS) or atomic absorption (GF-AAS, CV-AAS, HG-AAS). Alternatively specific direct methods can be applied after validation (e.g. for determination of mercury or sulphur or for direct determination of elements by XRF).

For XRF analysis of major elements in the ashed SRF, the sample is ashed at 815 °C (ISO 21656:2021[3]) and the ash is homogenized in a ball mill to obtain a uniform size dimension of the particles. The ash is then pressed in the form of pellets (ISO 22940:2021, EN 15309:2007) or fused with lithiummetaborate (EN 15309:2007). Both techniques are suitable for the analysis by XRF. Coal ash and other ashes of various origins can be used for instrument calibration.

7 Reagents

7.1 General

All reagents and acids used should be of recognized analytical grade or verify the content of the elements to be analysed to avoid high blank values for subsequent analytical measurements. A test blank solution throughout the procedure applying all steps with the same amount of acids or reagents, but without a sample, shall be used.

7.2 Water, e.g. deionized (< 0,055 µS/cm).

7.3 Nitric acid (HNO_3), approximately 15 mol/l, 65 % to 70 % (w/w).

7.4 Hydrofluoric acid (HF), approximately 23 mol/l, 40 % to 45 % (w/w).

7.5 Hydrochloric acid (HCl), approximately 12 mol/l, 35 % to 37 % (w/w).

7.6 Diluted Hydrochloric acid (HCl), approximately 2 mol/l.

Dissolve 166,5 ml of HCl 37 % (7.5) in water and dilute to 1 l with water (7.2).

7.7 Boric acid (H_3BO_3), solid.

7.8 Boric acid (H_3BO_3) solution, e.g. 4 % (w/w).

Dissolve 40 g of boric acid (7.6) in water and dilute to 1 l of water (7.2).

7.9 Hydrogen peroxide (H_2O_2), 30 % (w/w).

7.10 Lithiummetaborat ($LiBO_2$), solid.

7.11 Tetrafluoroboric acid (HBF_4), approximately 6 mol/l, 38 % to 50 % (w/w).

8 Apparatus

8.1 General

Usual laboratory apparatus. All volumetric flasks and digestion vessels shall be adequately cleaned and stored in order to avoid any contamination, particularly with respect to low concentration of the elements of interest.

8.2 Microwave unit, temperature and/or power-controlled, closed vessels

8.2.1 Digestion vessels, for pressurized microwave digestion of appropriate volume, reagent-, temperature- and pressure-resistant and capable of containing the mixture of sample and digest solution. The vessel shall be suitable for the safe application in the temperature and pressure range applied, capable of withstanding pressures of at least 3 000 kPa.

Digestion vessels made of modified polytetrafluorethene (PTFE), e.g. TFM or PFA liner, and equipped with a safety pressure releasing system to avoid explosion of the vessel shall be used. The inner wall of the vessel shall be inert and shall not release contaminations to the digest solutions.

NOTE It can be necessary to periodically clean the digestion vessels with a suitable surfactant to remove persistent deposits.

8.2.2 Microwave unit, temperature-controlled, corrosion resistant and well ventilated.

All electronics shall be protected against corrosion for safe operation. Use a laboratory-grade microwave oven with temperature feedback control mechanisms.

The microwave digestion system shall be able to control the temperature with an accuracy of at least ±5 °C and automatically adjust the microwave field output power within 2 s of sensing. Temperature sensors shall be accurate to ±2 °C, including the final reaction temperature of 190 °C ± 10 °C. Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment (i.e. different vessel types and microwave designs), control of the temperature during digestion is important for reproducible microwave heating and comparable data.

The accuracy of the temperature measurement system shall be periodically tested at an elevated temperature according to the manufacturers' instructions. If the temperature deviates by more than 2 °C from the temperature measured by an external, calibrated temperature measurement system, the microwave temperature measurement system shall be re-calibrated.

8.2.3 Microwave unit, power-controlled, corrosion resistant and well ventilated.

All electronics shall be protected against corrosion for safe operation. A laboratory-grade microwave oven with temperature feedback control mechanisms shall be used.

The microwave unit shall be able to provide programmable power which can be programmed to within ±10 W of the required power. Typical units provide a nominal power of 600 W to 1 200 W. If necessary (referring to manufacturers' specifications) calibration of the microwave unit shall be performed (see Annex A).

The microwave unit shall be designed in a way that guarantees homogeneous heating of the samples.

The microwave unit shall include a temperature and/or pressure control system.

8.3 Sample containers, plastic containers or glass containers (when no free hydrofluoric acid is present)

8.4 Filter, usually with a pore size of 0,45 µm and resistant to the employed acid mixture and of adequate purity

8.5 Centrifuge, minimum 3 000 rpm

8.6 Volumetric flasks, usually of nominal capacity of 50 ml (microwave digestion) or 100 ml, or 250 ml (fluxing agent)

8.7 Magnetic stirrer with heating function and PTFE stirring bone