FINAL
DRAFT

INTERNATIONAL
STANDARD

ISO/FDIS
22940

ISO/TC **300**

Secretariat: SFS

Voting begins on:
2021-05-20

Voting terminates on:
2021-07-15

Solid recovered fuels — Determination of elemental composition by X-ray fluorescence

Combustibles solides de récupération — Détermination de la composition élémentaire par fluorescence de rayons X

ISO/CEN PARALLEL PROCESSING

Reference number
ISO/FDIS 22940:2021(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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 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

X-ray fluorescence spectrometry can be used as a fast method for a qualitative overview of ash forming elements and impurities. When calibration is based on reference materials or on matrix-matched homogeneous solid recovered fuel samples with known content, X-ray fluorescence spectrometry can be used for a quantitative analysis of the total content of the specified elements within different solid recovered fuels.

The quality of the results obtained depends very closely on the type of instrument used, e.g. bench top or high performance, energy-dispersive or wavelength-dispersive instruments. When selecting a specific instrument, several factors need to be considered, such as the matrices to be analysed, elements to be determined, detection limits required and the measuring time.

Due to the wide range of matrix compositions and the lack of suitable reference materials in the case of solid recovered fuels from various origin, it is generally difficult to set up a calibration with matrix-matched reference materials. Therefore, it is important to use several homogenized solid recovered fuel samples with properties that sufficiently match the matrices of interest and whose content has been derived by independent measurement techniques, for example total digestion of solid recovered fuels and characterization of major and minor elements by measurement of digestion solutions with ICP-MS or ICP-OES, or by other techniques such as elemental analysis using combustion technology on sulfur or by combustion and ion chromatographic determination for chlorine.

This document describes two different procedures:

1) Quantitative analytical procedure for major elements of solid recovered fuels. The calibration is based on different reference materials and solid recovered fuel samples with known content.

   The elements described as major elements of solid recovered fuels are in fact major elements of the fuel ashes more than of the fuels. The determination of these elements can be helpful to predict the melting behaviour and slagging of the ashes. Moreover, contamination of fuel with sand or soil is indicated by high values of several elements.

2) Total element characterization at a semiquantitative level for major and minor elements of solid recovered fuels. The calibration is based on matrix-independent calibration curves, previously set up by the manufacturer.

   In general, the sensitivity of X-ray fluorescence is not sufficient for a determination of the content of minor elements (trace metals) in solid recovered fuels. However, it is possible to use determination of minor elements after calibration with solid recovered fuel samples with known content or at a semiquantitative level based on matrix-independent calibration curves to collect data for higher sample numbers, taking into account lower achievable precision. Therefore, it may be used to reveal excessive contents of minor elements in solid recovered fuels.

Solid recovered fuels — Determination of elemental composition by X-ray fluorescence

1 Scope

This document specifies the procedure for a determination of major and minor element concentrations in solid recovered fuel material by energy-dispersive X-ray fluorescence (EDXRF) spectrometry or wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry using a calibration with solid recovered fuel reference materials or solid recovered fuel samples with known content. A semiquantitative determination can be carried out using matrix independent standards.

This document is applicable to the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Mo, Cd, Sb, Sn, Tl and Pb. Concentration levels between approximately 0,000 1 % and 100 % can be determined depending on the element, the calibration materials used and the instrument used.

NOTE X-ray fluorescence spectrometry can be used as a fast method for a qualitative overview of elements and impurities and after suitable calibration it is very useful for determining major elements or even minor elements (except Hg) in order to quickly identify increased concentrations of minor elements in solid recovered fuels (SRF), for example during SRF-production.

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 — Vocabulary*

ISO 21646,[1]*Solid recovered fuels — Sample preparation*

ISO 21660-3, *Solid recovered fuels — Determination of moisture content using the 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 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 http://www.electropedia.org/

3.1

absorption edge
abrupt change in mass absorption coefficient at a specific wavelength or energy

3.2

absorption
loss of intensity of X-rays due to isotropic and homogenous material, as described by the Beer-Lambert law

---

[1] Under preparation. Stage at the time of publication: ISO/DIS 21646:2021.

3.3
analytical line
specific characteristic X-ray spectral line of the atom or ion of the analyte used for determination of the analyte content

3.4
continuous radiation (Bremsstrahlung)
electromagnetic radiation produced by the acceleration of a charged particle, such as an electron, when deflected by another charged particle, such as an atomic nucleus

3.5
Compton line
spectral line due to incoherent scattering (Compton effect), occurring when the incident X-ray photon strikes an atom without promoting fluorescence

Note 1 to entry: Energy is lost in the collision and, therefore, the resulting scattered X-ray photon is of lower energy than the incident X-ray photon.

3.6
drift correction monitors
physically stable samples used to correct for instrumental drift

3.7
emitted radiation
emitted sample X-rays
radiation emitted by sample consisting of *X-ray fluorescence radiation* (3.13) and scattered *primary X-rays* (3.11)

3.8
mass absorption coefficient
constant describing the fractional decrease in the intensity of a beam of X-radiation as it passes through an absorbing medium

Note 1 to entry: It is expressed in cm^2/g.

Note 2 to entry: The mass absorption coefficient is a function of the wavelength of the absorbed radiation and the atomic number of the absorbing element.

3.9
powder sample
analyte sample submitted as a powder for direct measurement in the sample cup

3.10
pressed pellet
analyte sample prepared by pressing milled material into a disk

3.11
primary X-rays
X-rays by which the sample is radiated

3.12
quality control sample
stable sample with known contents, for example (certified) reference material (CRM) or homogenized solid recovered fuel samples from known origin whose contents have been derived by independent analysis used to monitor instrument and calibration performance

3.13
X-ray fluorescence radiation
emission of characteristic X-rays from a sample that has been bombarded by high-energy X-rays or gamma rays

4 Symbols and abbreviated terms

4.1 Symbols

Al	aluminium
As	arsenic
Br	bromine
Ca	calcium
Cd	cadmium
Cl	chlorine
Co	cobalt
Cr	chromium
Cu	copper
Fe	iron
K	potassium
Mg	magnesium
Mn	manganese
Mo	molybdenum
Na	sodium
Ni	nickel
P	phosphorus
Pb	lead
S	sulfur
Sb	antimony
Si	silicon
Sn	tin
Ti	titanium
Tl	thallium
V	vanadium
Zn	zinc

4.2 Abbreviated terms

EDXRF	energy-dispersive x-ray fluorescence
MCA	multi-channel analyser
WDXRF	wavelength-dispersive x-ray fluorescence

5 Safety remarks

The organization shall be aware of applicable legal requirements relating to the X-ray fluorescence spectrometer.

The person responsible for managing or supervising the operation of X-ray equipment shall provide evidence of their knowledge of national regulations relating to radiation protection.

6 Principle

After a suitable preparation, the sample is introduced into an XRF-spectrometer and excited by primary X-rays. The intensities of the secondary fluorescent energy lines specific for each element are measured and the elemental composition of the sample is determined by reference to previously established calibration graphs or equations and applying corrections for inter-element effects. The calibration equations and inter-element corrections are established using pure reagents and/or series of internal or reference materials, provided that they meet all the requirements of the relevant preparation technique.

7 Apparatus

7.1 X-ray fluorescence spectrometer, which shall be able to analyse the elements according to the scope of this document. The following types of X-ray fluorescence spectrometers are applicable:

- EDXRF spectrometer that achieves the dispersion of the emitted X-ray fluorescence radiation by an energy-dispersive detector;
- WDXRF spectrometer that achieves the dispersion of the emitted X-ray fluorescence radiation by diffraction by a crystal or a synthetic multilayer.

The spectrometer consists of the following components:

- primary X-ray source, an X-ray tube with a high-voltage generator;
- sample holder;
- detector unit including electronic equipment;
- source modifiers to modify the shape or intensity of the source spectrum or the beam shape (e.g. source filters, secondary targets, polarizing targets, collimators, focusing optics).

The detector unit is different for WDXRF and for EDXRF spectrometers. WDXRF spectrometers take advantage of the dispersion of the emitted radiation by diffraction by a crystal or a synthetic multilayer. The detector does not need to be capable of energy discrimination. EDXRF spectrometers use an energy-dispersive detector. Pulses of current from the detector, which are a measure of the energy of the incoming X-rays, are segregated into channels according to energy using an MCA.

NOTE 1 The use of a high-energy X-ray tube increases the potential for losses of volatile analytes from samples by heating in the spectrometer during analysis.

NOTE 2 The new generation of EDXRF spectrometers takes advantage of the polarizing target theory. The excitation is performed by polarized radiation. The emitted X-ray fluorescence radiation is detected along the direction of polarization, resulting in a significant decrease of the background scattering, therefore lower limits of detection can be achieved (comparable to WDXRF).

7.2 **Pellet press**, capable of providing a pressure of at least 30 kN. The pellet press may be a cold press or a hot mould press, operating at temperatures not exceeding 180 °C.

8 Interferences and sources of error

Interferences in X-ray fluorescence spectrometry are due to spectral line overlaps, matrix effects, spectral artefacts and particle size or mineralogical effects.

Spectral line overlaps occur when an analytical line cannot be resolved from the line of a different element. Corrections for these interferences are made using the algorithms provided with the instrument software.

Matrix effects occur when the X-ray fluorescence radiation from the analyte element is absorbed or enhanced by other elements in the sample before it reaches the detector. In the case of complex matrices, these effects generally shall be corrected. The correction procedure depends on the X-ray fluorescence spectrometry system (EDXRF or WDXRF) and the apparatus type itself.

Spectral artefacts, for example escape peaks, sum peaks, pulse pile up lines, dead time and continuous radiation (Bremsstrahlung) correction, are accounted for by the provided instrument software. Spectral artefacts differ for energy-dispersive and wavelength-dispersive XRF spectrometry.

9 Sample preparation

9.1 Preparation principles

The sample preparation is very critical for XRF analysis of solid recovered fuels. The quality of sample preparation strongly influences the accuracy of the results. The following different options exist:

- For quantitative analysis of solid recovered fuel samples, the preparation of pressed pellets from prepared general analysis sample material is recommended.
- For semiquantitative analysis of solid recovered fuels, the general analysis material may be used directly (in powder form); concerning samples of solid recovered fuel pellets, the original pellets may be used directly without any sample preparation. It may be used to provide fast basic information about the approximate composition of a sample. Similar results can be obtained using portable XRF instruments for field analysis.

For a given calibration, the same preparation method shall be used throughout, for both samples and standards.

For precise quantitative measurements, homogeneous and representative test portions are necessary. The nominal top size of the material shall be 0,5 mm or less, following the procedure according to ISO 21646.

9.2 Drying of general analysis sample material

Dry a sufficient amount of general analysis sample material in accordance with ISO 21660-3 immediately before pressing pellets for XRF-analysis.

NOTE Concerning some XRF instruments, the applied vacuum will dry the general analysis sample material during the determination, giving the same results as if the sample had been previously dried.

9.3 Preparation of pressed pellet

A pellet is prepared in the pellet press (7.2). Before pressing, the sample shall be mixed and homogenized. Use the same weight for any single set of standards and samples and add binder (e.g. wax or liquid organic binder), if necessary.

For the preparation, follow the manufacturer's instructions.

NOTE 1 Different binders can be used. In the case of organic liquid binders (approximately 0,6 % weight of sample) the pressed pellet will be placed in an oven at between 70 and 100 °C for a minimum of 10 minutes to evaporate the organic solvent or for the formation of long chain polymers formed by heating (e.g. PVP-methylcellulose binders).

NOTE 2 In the case of wax binder, the ratio of the sample weight to wax is around 10:1.

10 Procedure

10.1 Analytical measurement conditions

10.1.1 Wavelength-dispersive instruments

10.1.1.1 General

The analytical lines to be used and suggested operating conditions are given in Table 1. The settings strongly depend on the spectrometer configuration, e.g. the type of X-ray tube (Rh, Cr), tube power, available crystals and type of collimators. The instrument manufacturer's recommendations should be followed in all cases.

10.1.1.2 Intensities and background corrections

For the determination of trace elements, the measured intensities shall be background corrected. The measured background positions should be free of spectral line interferences. The net peak intensity, I, expressed as the number of counts per second of the element of interest (i), is calculated as the difference between the measured peak intensity of the element and the background intensity, as given in Formula (1):

$$I = I_\text{p} - I_\text{b} \tag{1}$$

where

I_p is the count rate of the element i, expressed as the number of counts per second;

I_b is the background count rate of the element i with no analyte present, expressed as the number of counts per second.

10.1.1.3 Counting time

The minimum counting time is the time necessary to achieve an uncertainty ($2\sigma_{\%}$) which is less than the desired precision of the measurement. Choose a reference material or quality control sample with a concentration level in the middle of the working range and measure the count rate. The counting time for each element can be calculated according to Formula (2):

$$T = \left(100 \,/\, 2\sigma_{\%} \times 1 \,/\, \left(\sqrt{I_\text{p}} - \sqrt{I_\text{b}}\right)\right)^2 \tag{2}$$

where

T is the total counting time for the peaks and background, expressed in seconds;

$2\sigma_{\%}$ is the relative target precision at a confidence level of 95 %, expressed as a percentage.

10.1.2 Energy-dispersive instruments

The analytical lines to be used and suggested operating conditions are given in Table 1. The settings strongly depend on the spectrometer configuration, e.g. type of X-ray tube (Rh, Pd), tube power, available targets and types of filters. The instrument manufacturer's recommendations should be followed in all cases.

10.1.3 Intensities and background corrections

Deconvolution of the spectra and background correction are needed when analysing samples with overlapping lines. Usually, XRF instruments are supplied with a specific software module for that purpose.

Table 1 — Suggested analytical lines, spectral line overlaps and correction methods

Element	Line	Spectral line overlap	Type of matrix correction method
Na	Kα	ZnLβ	Alpha or FP
Mg	Kα	AsLα	Alpha or FP
Al	Kα	BrLα	Alpha or FP
Si	Kα		Alpha or FP
P	Kα		Alpha or FP
S	Kα	CoKα PbMα NbLβ	Alpha or FP or MAC
Cl	Kα		Alpha or FP or MAC
K	Kα		Alpha or FP
Ca	Kα		Alpha or FP
Ti	Kα	BaLα ILβ	Alpha or FP
V	Kα	Ti Kβ	Alpha or FP or MAC
Cr	Kα	VKβ PbLα	Alpha or FP or MAC
Mn	Kα	CrKβ	Alpha or FP
Fe	Kα	MnKβ	Alpha or FP
Co	Kα	FeKβ	Alpha or FP or MAC
Ni	Kα	CoKβ	Compton or FP or MAC
Cu	Kα	TaLα ThLβ	Compton or FP or MAC
Zn	Kα	WLα	Compton or FP or MAC
As	Kα Kβ	PbLα BrKα	Compton or FP or MAC
Br	Kα	AsKβ	Compton or FP or MAC
Mo	Kα	ZrKβ ULβ	Compton or FP or MAC
Ag	Kα Lα	CrKβ	Compton or FP or MAC Alpha or FP
Cd	Kα Lα	AgLβ	Compton or FP or MAC Alpha or FP
Sb	Kα Lβ	CoKβ	Compton or FP or MAC Alpha or FP or MAC