
**Solid biofuels — Determination of
elemental composition by X-ray
fluorescence**

*Biocarburants solides — Détermination de la composition
élémentaire par fluorescence de rayons X*

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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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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).

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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](#).

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

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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 biomass reference materials, X-ray fluorescence spectrometry can be used for a quantitative analysis of the total content of the specified elements within different solid biofuels.

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 have 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 some biomass like olive residues, it is generally difficult to set up a calibration with matrix-matched reference materials.

Therefore, this Technical Specification describes two different procedures.

- Quantitative analytical procedure for major elements of biomass. The calibration is based on different biomass reference materials.

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 may 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.

- Total element characterization at a semi-quantitative level for major elements of biomass. 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 biofuels. However, determination may be used to reveal excessive contents of minor elements in solid biofuels.

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Solid biofuels — Determination of elemental composition by X-ray fluorescence

1 Scope

This Technical Specification specifies the procedure for a determination of major and minor element concentrations in biomass material by energy dispersive X-ray fluorescence (EDXRF) spectrometry or wavelength dispersive X-ray fluorescence (WDXRF) spectrometry using a calibration with biomass reference materials. A semi-quantitative determination may be carried out using matrix independent standards.

This Technical Specification is applicable for 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, and Pb. Concentrations from approximately 0,000 1 % and above can be determined depending on the element, the calibration materials used and the instrument used.

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 16559, *Solid biofuels — Terminology definitions and descriptions*

3 Terms and definitions

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

3.1

absorption edge

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

3.2

absorption of X-rays

loss of intensity of X-rays through absorption by an isotropic and homogenous material as described by the Beer-Lambert law

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

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 sample X-rays**

radiation emitted by sample consisting of *X-ray fluorescence radiation* (3.14) and scattered *primary X-rays* (3.12)

**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 cm²/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
polarised excitation X-ray spectrometer**

energy dispersive X-ray spectrometer where the excitation is performed by polarised radiation and the emitted *X-ray fluorescence radiation* (3.14) is detected along the direction of polarisation

**3.10
powder sample**

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

**3.11
pressed pellet**

analyte sample prepared by pressing milled material into a disk

**3.12
primary X-rays**

X-rays by which the sample is radiated

**3.13
quality control sample**

stable sample with known contents, e.g. certified reference material (CRM) used to monitor instrument and calibration performance

**3.14
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 Safety remarks

The X-ray fluorescence spectrometer shall comply with international and national regulations relevant to radiation protection.

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

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5 Symbols and abbreviated terms

5.1 Symbols

Al	Aluminium
As	Arsenic
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
K	Potassium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
Ni	Nickel
P	Phosphorus
Pb	Lead
Sb	Antimony
Ti	Titanium
V	Vanadium
Zn	Zinc

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5.2 Abbreviated terms

EDXRF	Energy dispersive X-ray fluorescence
MCA	Multi-Channel Analyser
WDXRF	Wavelength dispersive X-ray fluorescence

6 Principle

After a suitable preparation, the sample is introduced into a 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, shall be able to analyse the elements according to the scope of this Technical Specification. The following types of X-ray fluorescence spectrometers are applicable:

- energy dispersive X-ray fluorescence (EDXRF) spectrometer that achieves the dispersion of the emitted X-ray fluorescence radiation by an energy dispersive detector;
- wavelength dispersive X-ray fluorescence (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 (like source filters, secondary targets, polarizing targets, collimators, focusing optics, etc.).

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 a Multi-Channel Analyser (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. [ISO/TS 16996:2015](https://standards.iteh.ai/catalog/standards/sist/7b56e26-b5ee-4816-bffa-7a00c59c378e/iso-ts-16996-2015)

NOTE 2 The new generation of EDXRF spectrometers takes advantage of the polarizing target theory resulting in a significant decrease of the background scattering, and therefore lower limits of detection can be achieved (comparable to WDXRF).

7.2 Pellet press, capable of providing a pressure of at least 50 kN. The pellet press may be a cold press, operating at temperatures not exceeding 150 °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 have to be corrected. The correction procedure depends on the X-ray fluorescence spectrometry system (EDXRF or WDXRF) and the apparatus type itself.

Spectral artefacts, e.g. escape peaks, sum peaks, pulse pile up lines, dead time, 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 biofuels. The quality of sample preparation strongly influences the accuracy of the results. The following different options exist.

- For quantitative analysis of solid biofuel samples, the preparation of pressed pellets from prepared general analysis sample material is recommended.
- For semi-quantitative analysis of solid biofuels, the general analysis material may be used directly (in powder form) and concerning samples of biofuel 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 may be obtained using portable XRF instruments for field analysis.
- For the quantitative determination of some elements, especially in inhomogeneous samples or elements with very low concentrations in solid biofuels, the fused bead method may be used for pre-ashed samples. The use of a fusion apparatus and fluxes like lithium meta borate or lithium tetra borate and heating up the sample >1 000°C limits the application of this method for the determination of non-volatile elements.

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. According to EN 14780, the nominal top size of the material shall be 1 mm or less. Regarding the use of a hot mould pellets press, the material should be further comminute to a nominal top size of 0,5 mm or less.

9.2 Drying of general analysis sample material

Dry a sufficient amount of general analysis sample material according to EN 14774-3 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 was 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. For the preparation, follow the manufacturer's instructions.

10 Procedure

10.1 Analytical measurement conditions

10.1.1 Wavelength 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. the type of X-ray tube (Rh, Cr), tube power, available crystals, type of collimators. Instrument manufacturer's recommendations should be followed in all cases.

10.1.1.1 Intensities and background corrections

For the determination of trace elements, the measured intensities have to 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, is calculated as the