

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

Feste Biobrennstoffe - Bestimmung der elementaren Zusammensetzung durch Röntgenfluoreszenz-Analyse

Biocombustibles solide - Détermination de la composition élémentaire par fluorescence X

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Foreword

This document (XXX) has been prepared by Technical Committee CEN/TC 335 “Solid Biofuels”, the secretariat of which is held by SIS.

This document is currently submitted to comments.

Introduction

X-ray fluorescence spectrometry is a fast method for a qualitative overview of ash forming elements and impurities, as improved procedures it is a reliable method for the quantitative analysis of the total content of certain elements within different matrices.

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 analyzed, elements to be determined, detection limits required and the measuring time. The quality of the results depends on the element to be determined and on the surrounding matrix.

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 standard describes two different procedures:

- a 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.

- a total element characterisation 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 some cases the minor elements present in solid biofuels can be of environmental concern, e.g. it has been shown that certain energy crops concentrate cadmium in polluted areas other toxic elements may be found at elevated concentrations in the biofuels. This may be a problem if the ash from combustion is used in the forest as a fertilizer.

1 Scope

This CEN/TC document specifies the procedure for a quantitative 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 matrix-matched reference material and matrix independent standards.

This European Standard 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. Concentration levels between approximately 0,000 1 % and 100 % can be determined depending on the element and the instrument used.

2 Normative references

The following referenced documents are indispensable for the application 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.

CEN/TS 14588:2003, *Solid biofuels – Terminology, definitions and descriptions*.

CEN/TS 14774-3, *Solid biofuels – Methods for the determination of moisture content – Oven dry method – Part 3: Moisture in general analysis sample*.

CEN/TS 14775, *Solid biofuels – Methods for the determination of ash content*.

prCEN/TS 14780, *Solid biofuels – Methods for sample preparation*.

prCEN/TS 15296, *Solid biofuels – Calculation of different bases*.

3 Terms and definitions

For the purpose of this CEN/TCXXX, the following terms and definitions and the terms and definitions given in CEN/TS 14588:2003 apply.

3.1

absorption edge

jump of the mass absorption coefficient at a specific wavelength or energy

3.2

absorption of X-rays

loss of intensity of X-rays by an isotropic and homogenous material as described by the Bouger-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

Bremsstrahlung; 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 strike an atom without promoting fluorescence

NOTE 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 and scattered primary X-rays

**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, expressed in units of cm^2/g . 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 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 with a hot mounting press 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 European 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.

5 Symbols and abbreviations

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

5.2 Abbreviations

EDXRF	energy dispersive X-ray fluorescence
MCA	Multi-Channel Analyser
WDXRF	wavelength dispersive X-ray fluorescence

6 Principle

After a suitable preparation, if necessary, 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 providing they meet all the requirements of the relevant preparation technique.

7 Apparatus

7.1 X-ray fluorescence spectrometer

The X-ray fluorescence spectrometer shall be able to analyse the elements according to the scope of this EN **XXX**. 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 a number of components:

- primary X-ray source, an X-ray tube with a high voltage generator;
- a 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, polarising targets, collimators, focussing 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 scattering 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.

NOTE 2 The new generation of EDXRF spectrometers takes advantage of the polarising 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 Sample preparation

For the recommended method with a hot melt pellet, a hot mounting pellet press, capable of providing a pressure of at least 50 kN and a temperature of at least 150°C is required. For other sample preparation methods see Annex B.

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 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.

Spectral artefacts e.g. escape peaks, sum peaks, pulse pile up lines, dead time, Bremsstrahlung correction, are accounted for by the provided software. Spectral artefacts differ for energy dispersive and wavelength dispersive XRF spectrometry.

Particle size effects can be reduced by milling the sample, and both particle size and mineralogical effects can be eliminated by preparing bead samples. It is vital for quantitative analysis that the same sample preparation procedure is applied to both the standards and the samples to be analysed.

9 Sample preparation

9.1 General

XRF spectrometry of solid biofuels is very sensitive regarding sample preparation. The quality of sample preparation strongly influences the accuracy of the results. Different options exist:

- For quantitative analysis of solid biofuel samples, the preparation of pressed pellets is recommended. For most samples stable pellets with smooth surfaces can be prepared by means of a hot mould pellet press. For the quantification of all major and minor elements listed in the scope of the standard, this sample preparation is essential.
- For semi-quantitative analysis of solid biofuel samples, a grinded or milled powder sample can be analysed directly. This preparation method may be used for a fast basic information of 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, the fused bead method may be used applying pre-ashed samples. The use of a fusion apparatus and fluxes like lithium metaborate or lithium tetraborate and heating up the sample >1000°C constrains 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. Pre-treatment and preparation of test portions shall be carried out according to the appropriate clauses of CEN/TS 14780. The particle size of the sample may strongly affect the precision of the measurement. The particle size should preferably be smaller than 500 µm.

9.2 Drying and milling

The sample is dried according to CEN/TS 14774-3 and prepared according to CEN/TS 14780. It is recommended to reduce particle size to <500 µm. The sample should be in equilibrium with the lab atmosphere, a moisture content of 3-5 % is typical.

9.3 Preparation of pressed pellet

The sample prepared according to clause 9.2 is used to prepare the sample pellet in the hot moulding pellet press (7.2). Before pressing, the sample shall be mixed and homogenised. For the preparation of 40 mm diameter pellets, minimum 12,0 g of sample is taken, for 32 mm diameter pellets minimum 7 g of sample is required. A minimum pellet thickness of 5 mm should be achieved. The sample is heated up by temperature/pressure programme to 140°C and is kept at a pressure of 50kN for 4,5 minutes. After cooling down the pellet is removed from the apparatus.

After sample preparation, the pellet should rest in a controlled lab atmosphere e.g. 20/50 or stored in a desiccator. During preparation of the pellet in the hot mould press, some of the remaining moisture evaporates. Adsorption of moisture in the lab atmosphere occurs but is negligible even when storing the pellet for weeks or months in the controlled lab atmosphere.

NOTE 1 It is important to homogenize the sample before loading the press and loading of the press should be done carefully to avoid decomposition effects.

NOTE 2 The pressing condition can be changed if sample material cannot be pressed to stable pellets, but higher temperature and longer pressing time can cause decomposition of sample. The standards for calibration should be treated in the same way as the sample.

NOTE 2 Biomass samples containing oil tend to segregate oil during hot pressing action. Samples showing oily surfaces after removing from the pellet press have to be dried by clean lab wipes. Due to this segregation this sample preparation may not be possible for oil containing samples like oil seeds.

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 B.1. The settings are strongly dependant on the spectrometer configuration, e.g. the type of X-ray tube (Rh, Cr), tube power, available crystals, type of collimators.

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 difference between the measured peak intensity of the element and the background intensity:

$$I = I_p - I_b \tag{1}$$

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 , expressed as the number of counts per second.

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 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:

$$t = \left(\frac{100}{2\sigma_{\%}} \cdot \frac{1}{\sqrt{I_p} - \sqrt{I_b}} \right)^2 \tag{2}$$

where

t is the total counting time for the peaks and background in seconds;

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

10.1.2 Energy dispersive instruments

The analytical lines to be used and suggested operating conditions are given in Table B.2. The settings are strongly dependant on the spectrometer configuration, e.g. type of X-ray tube (Rh, Pd), tube power, available targets, type of filters.

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.

10.2 Calibration

10.2.1 General

The calibration procedure is similar for energy dispersive and wavelength dispersive techniques. In general calibration is established by using matrix-adapted reference materials. The calibration equations and inter-element corrections are calculated by the software of the instrument. An accuracy check is performed with CRMs or samples with known composition.

Since concentration of some elements may vary over more than 4 orders of magnitude between different biomass samples it is recommended to set up different calibrations for samples with low and high contents of elements to improve the accuracy of the method.

Different procedures for correcting matrix effects may be used according to the analytical accuracy required:

- the scattered radiation method is based on the principle that the intensities of the analyte line and of the Compton line are affected in the same proportion due to the overall mass absorption coefficient of the sample. This linear relationship holds when all analytes are at low concentrations (minor elements) and their absorption coefficients are not affected by an adjacent absorption edge. In this case an internal Compton correction can be used. Beside that, a correction method using the Compton intensity with Mass Absorption Coefficients (MAC) is also applicable. In this method, the intensities of the major elements are measured to apply a jump edge correction for the analysed trace elements;
- correction using the fundamental parameter approach;
- correction using theoretical correction coefficients (alphas) taking basic physical principles, instrumental geometry etc. into account;
- correction using empirical correction coefficients (alphas) based on regression analysis of standards with known elemental concentrations.

10.2.2 General calibration procedure

For calibration purposes the measurement of analyte lines of samples of known composition is needed. The basic equation implies a linear relationship between the intensity and the concentration.

$$C_i = a_{i,0} + a_{i,1} \cdot I_i \quad (3)$$

where

C_i is the concentration of the element of interest, expressed as mg/kg or percentage dry matter;

$a_{i,0}$ is the offset of the calibration curve;

$a_{i,1}$ is the slope of the calibration curve;

I_i is the net intensity of the element of interest, expressed as counts per second.

Matrix effects have to be taken into account in X-ray spectrometry according to the following equation:

$$C_i = (a_{i,0} + a_{i,1} \cdot I_i) \cdot M \quad (4)$$

where

M is the correction term due to the matrix effects.

The matrix effect correction term may consist of an internal standard Compton correction method or may be calculated from mathematical models.

10.2.3 Calibration procedure using pressed pellets

The pressed pellet method is used to determine the concentrations of major and minor elements.

Select calibration standards with a similar composition as the samples under investigation containing the elements of interest and covering the concentration range of interest. The use of reference materials from different recognised producers is recommended (for examples see Annex D). The element concentrations shall vary independently in the standards. If the calibration covers many elements in a wide range of concentrations, a large number of calibration samples may be necessary.

Prepare pressed pellets from the selected calibration standards according to 9.3.

Define the analytical measurement method for EDXRF or WDXRF as described in 10.1.

Start up the XRF equipment according to the instrument manufacturer's manual and measure the calibration standards using the defined measurement method. All measurements shall be performed under vacuum.

Follow the guidelines in the instrument manufacturer's manual to perform the regression, the background correction, the line overlap correction and the matrix corrections for all elements under consideration. In Table 1 the possible spectral line overlaps are indicated (dependant on the configuration of the instrument) and also the matrix correction method that can be applied. For minor elements with an absorption edge above the absorption edge of iron, a Compton internal standard correction can be applied. Otherwise a theoretical alpha correction or correction for the absorption edge should be performed (for these corrections all elements in the sample have to be analysed).

Depending on the type of instrument and the software programs available, alternative correction methods can be applied. Validation of the final calibration curves shall demonstrate the accuracy of the method.

Perform the regression calculation and verify that the correlation factors are within the limits of accuracy required.

10.2.4 Internal standard correction using Compton (incoherent) scattering method

The measured intensity of incoherent scattering may be used directly to compensate for matrix effects or indirectly for the determination of the effective mass absorption coefficient μ to correct for matrix effects. The compensation for matrix effects is based on a combination of sample preparation and experimental intensity data but not on fundamental and experimental parameters.

The Compton scatter method can be expressed as:

$$C_{i,u} = (C_{i,r} \cdot \frac{I_{inc,r}}{I_{i,r}}) \cdot (\frac{I_{i,u}}{I_{inc,u}}) \tag{5}$$

where

$C_{i,u}$ is the concentration of the element of interest i of the sample, expressed as mg/kg or percentage dry matter;

$C_{i,r}$ is the concentration of the element of interest i of the calibration reference material, expressed as mg/kg or percentage dry matter;

- $I_{inc,u}$ is the intensity of the incoherent Compton line of the sample, expressed as counts per second;
- $I_{inc,r}$ is the intensity of the incoherent Compton line element of the calibration reference material, expressed as counts per second;
- $I_{i,u}$ is the intensity of the element of interest i of the sample, expressed as counts per second;
- $I_{i,r}$ is the intensity of the element of interest i of the calibration reference material, expressed as counts per second.

10.2.5 Fundamental parameter approach

The fundamental parameter approach uses the physical processes forming the basis of X-ray fluorescence emission and scattering to construct a theoretical model for the correction of matrix effects in practice. The correction term M is calculated from first principle expressions. These are derived from basic X-ray physics and contain physical constants and parameters that include absorption and scattering coefficients, fluorescence yield, primary spectral distributions and spectrometry geometry. The use of scattered radiation (Compton and/or Rayleigh) allows the determination of matrix effects caused by sample elements that cannot be measured directly. The calculation of analyte concentrations in samples is based on making successively better estimates of composition by an iteration procedure. These iteration cycles are performed until the difference between the compared results is below a defined value.

NOTE The algorithm used for the procedure is usually implemented in the manufacturer's software.

10.2.6 Fundamental or theoretical influence coefficient method

The fundamental influence coefficient method encompasses any mathematical expression relating emitted intensities and concentrations in which the influence coefficients are defined and derived explicitly in terms of fundamental parameters.

The calculation of the concentration from the intensities is performed by linear regression whereby the net intensities are corrected for the present matrix effects. For each element the concentration is calculated according to the following equation:

$$C_{i,u} = \left(\frac{C_{i,r}}{I_{i,r} (1 + \sum_j \alpha_{ij} C_{jr})} \right) \cdot I_{i,u} \cdot M \quad (6)$$

$$C_{i,u} = \left(\frac{C_{i,r}}{I_{i,r} (1 + \sum_j \alpha_{ij} C_{jr})} \right) \cdot I_{i,u} \cdot \left(1 + \sum_j \alpha_{ij} C_{ju} \right) \quad (7)$$

where

- $C_{i,u}$ is the concentration of the element of interest i of the sample, expressed as mg/kg or percentage dry matter;
- $C_{i,r}$ is the concentration of the element of interest i of the calibration reference material, expressed as mg/kg or percentage dry matter;
- $I_{i,r}$ is the intensity of the element of interest i of the calibration reference material, expressed as counts per second;

- $I_{i,u}$ is the intensity of the element of interest i of the sample, expressed as counts per second;
- $C_{j,r}$ is the concentration of the matrix element j of the calibration reference material, expressed as mg/kg or percentage dry matter;
- $C_{j,u}$ is the concentration of the matrix element j of the sample, expressed as mg/kg or percentage dry matter;
- M is the matrix correction term;
- α_{ij} is the correction coefficient α_{ij} (called alphas) calculated from theory, although some approximations are involved.

Different types of alpha coefficient exist, but all of them are calculated without reference to experimental data; they are calculated using intensity data resulting from a fundamental parameter expression. The alpha coefficients vary as a function of sample composition and are calculated by an iterative process.

10.2.7 Empirical alpha correction

Empirical alphas are obtained experimentally using regression analysis of data from reference materials in which the elements to be measured are known and the total concentration range is covered. Best results are achieved when the samples and reference materials are of similar composition. Thus, empirical alphas are based strictly on experimental data and do not take fundamental and instrumental parameters into account. Different models can be applied, but generally they are based on the above equation where the correction term for matrix effects is a function of concentrations.

The empirical alphas are only applicable for a limited concentration range and a well-defined analytical method where the matrices of samples and standards are similar. The reference materials used should contain each analyte together with fairly wide concentration ranges of each matrix element. Poor analytical results are obtained when inappropriate combinations of analytes are chosen. A large number of reference materials have to be analysed to define the alphas (rule of thumb: minimum of 3 times the number of parameters to be calculated).

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

Element	Line	Spectral line overlap	Type of matrix correction method
Na	K α	ZnL β	Alpha or FP
Mg	K α	AsL α	Alpha or FP
Al	K α	BrL α	Alpha or FP
Si	K α		Alpha or FP
P	K α		Alpha or FP
S	K α	CoK α PbM α NbL β	Alpha or FP or MAC
Cl	K α		Alpha or FP or MAC
K	K α		Alpha or FP
Ca	K α		Alpha or FP
Ti	K α	BaL α IL β	Alpha or FP
V	K α	Ti K β	Alpha or FP or MAC
Cr	K α	VK β PbL α	Alpha or FP or MAC
Mn	K α	CrK β	Alpha or FP
Fe	K α	MnK β	Alpha or FP
Co	K α	FeK β	Alpha or FP or MAC
Ni	K α	CoK β	Compton or FP or MAC

Element	Line	Spectral line overlap	Type of matrix correction method
Cu	K α	TaL α ThL β	Compton or FP or MAC
Zn	K α	WL α	Compton or FP or MAC
As	K α K β	PbL α BrK α	Compton or FP or MAC
Mo	K α	ZrK β UL β	Compton or FP or MAC
Ag	K α L α	CrK β	Compton or FP or MAC Alpha or FP
Cd	K α L α	AgL β	Compton or FP or MAC Alpha or FP
Sb	K α L β	CoK β	Compton or FP or MAC Alpha or FP or MAC
Pb	L β	ThL α BiL β SnK α	Compton or FP or MAC

10.3 Analysis of the samples

Follow the instrument manufacturer's instructions for set up, conditioning, preparation and maintenance of the XRF spectrometer.

Select the required preparation method and prepare the samples. To analyse the prepared samples, an analytical measurement method has to be defined. The measurement method describes the analytical lines to be measured and the measurement parameters e.g. the XRF generator settings (tube voltage and current), selection of primary beam filters, targets and crystals, detector to be used, measurement time.

The same measurement parameters used for the calibration according to 10.2 are applied to the samples.

Before analysis or at frequent intervals, quality control samples have to be measured to check the instrument stability and the quality of the calibration, in accordance to the manufacturer's instructions.

Introduce the prepared sample into the XRF spectrometer and analyse it in accordance to the manufacturer's instructions.

11 Quality control

11.1 Drift correction procedure

XRF calibrations, once established, tend to be stable over long periods of time. Small amounts of instrumental drift can be corrected by analysing stable monitor samples as frequently as performance experience indicates.

Drift correction monitors are stable beads that should contain all the elements to be determined and at concentration levels comparable to or higher than those from the samples.

The monitor samples shall be measured together with the calibration samples in order to get the initial intensities stored. When drift correction is needed, they are measured again. The initial set and the actual set of intensities are used to adjust the calibration regression. The procedure described is usually part of the instruments software.

For EDXRF spectrometers, an additional energy calibration has to be performed on a regular basis, as defined by the manufacturer's instructions.

11.2 Reference materials

Verify the trueness of the results by applying the procedure to one or more reference materials not used for calibration and covering the concentration range of interest.

The element content of the reference material used shall be in accordance with the concentration range of interest.

11.3 Plausibility check

If all ash forming elements are determined, a plausibility check is recommended. The content of all ash forming elements, calculated as oxides (Ca and Mg as oxides or carbonates; 50 % of S as sulphate) should equal 80-105% of the ash prepared according to CEN/TS 14775.

12 Calculation of the result

Follow the guideline in the instrument manufacturer's manual how to perform the regression, the background correction and the overlap correction.

The concentrations of the analytes are calculated by the software program from the measured intensities using the calibrations curves previously set-up. The results shall be calculated as the mean of duplicate determinations. The results may be calculated to other basis e.g. to an as received basis according to prCEN/TS 15296.

13 Precision of the method

Data for repeatability and reproducibility will be worked out within the BIONORM-Project (with respect to biomass samples).

14 Test report

The test report shall contain at least the following information:

- a) reference to this document (CEN/TS XXXXX);
- b) Type of instrument and method for calculation of element contents
- c) results of the test including the basis in which they are expressed, as indicated in clause 10;
- d) identification of the laboratory performing the test and the date of the test;
- e) identification of product (sample) tested;
- f) any operation not included in this document, or regarded as optional;

any unusual features noted during the test procedure.



Annex A (informative)

Semi-quantitative screening analysis of solid biofuels samples

A.1 Principle

The principle is identical as described in Clause 6, however the elemental composition of the sample is determined by reference to calibration curves, previously set up by the manufacturer. This procedure is often referred to as “standardless” analysis. The method is generally applicable for the semi-quantitative determinations of elements from Calcium to Lead between approximately 0,001 % and 100 %, depending on the element and the instrument used.

NOTE It is important to note that the “standardless” analysis can be optimised to defined matrices and expand the measurement range to 0,0001 and 100%.

During the evaluation and calculation of the element concentration of the sample the various interferences e.g. spectral line overlap, matrix effects, spectral artefacts and sample preparation are all accounted for with the provided analytical program.

A.2 Energy dispersive (ED) or wavelength dispersive (WD) X-ray fluorescence spectrometer

The same instruments as described in 7.1 may be used, however a specific software package is applied suitable to perform the XRF analysis without the use of calibration curves set up with dedicated reference samples. Most of the instruments available are delivered with pre-calibrated analytical methods. These calibrations are set up by the manufacturer with a suite of synthetic calibration samples to cover a wide concentration range on a broad spectrum of matrix types. Improvement of the accuracy can be obtained by additional analyses of sample specific reference materials and extending the calibration for the specific needs.

NOTE Because of the differences between various models of XRF instruments, no detailed operating instructions can be provided.

The validity of the programmed calibration curves can be checked and optimised by using reference materials of a similar composition as the samples under investigation.

A.3 Sample preparation

See clause 9.

NOTE Pay regard to the operating instruction of manufacturer about the sample requirements. Depending on method the use of powder samples can be not allowed.

A.4 Procedure

A.4.1 Analytical measurement conditions and calibration

All X-ray spectrometers are supplied with a spectrometer software program to operate the instrument. The software packages are manufacturer depended and contain 2 major modules:

- analytical measurement program for data collection. This module controls the measurement of a sample using a certain set of measurement parameters e.g. tube setting (kV, mA), targets and crystals, detectors, measurement times. The analytical program is always linked to a selected evaluation and calibration program. Actually, the same measurement conditions have to be applied for both the standards of the calibration curve and the samples. Because in screening analysis the measurements will be performed with the predefined analytical programs, no further detailed descriptions will be given of the analytical measurement parameters. Follow the manufacturer's instruction for further operation and handling of the analytical software package;
- evaluation program for data processing. This module converts the measured intensities of the different element line to elemental concentrations taking all corrections into account. There are various types of evaluation programs available and each manufacturer has set up his own program for data processing based on the XRF principles.

Sensitivity, instrumental detection limits and precision are instrument dependent and should therefore be investigated and established for each individual analyte line on that particular instrument, and, if relevant, in function of matrix type and sample preparation.

A.4.2 Analysis

Follow the instrument's instructions for set up, conditioning, preparation and maintenance of the XRF spectrometer.

To analyse the prepared samples, an analytical measurement method has to be defined. Depending on the type of instrument, the analytical measurement method is immediately applicable, or can be modified starting from a 'master' measurement method or has to be set up using the available pre-calibrated spectral lines. The measurement method describes the analytical lines to be measured and the measurement parameters like the XRF generator settings (tube voltage and current), selection of primary beam filters, targets and crystals, detector to be used, measurement time etc.

The same measurement parameters of the analyte line used for the calibration have to be applied for the samples. The provided software program has to be capable of defining automatically for each analyte the required measurement parameters.

Before analysis, quality control samples have to be measured to check the instrument stability and the quality of the calibration, in accordance to the manufacturer's instruction.

Introduce the prepared sample into the XRF spectrometer and analyse it with the selected analytical measurement method, in accordance to the manufacturer's instruction.

Annex B (informative)

Examples for alternative sample preparation for solid biofuels samples

If the recommended sample preparation method can not be used, alternative procedures of the different sample preparation techniques may be used. Using this alternative methods the loss of precision (powder sample method) or loss of volatile elements (fused beads method) should be regarded.

B.1 Preparation of powder samples

After milling/grinding of the sample to powder, the homogenised powder sample can be poured directly into a sample cup. The bottom of the sample cup is closed by a thin-film support. Close the sample cup. Press the powder slightly with a piston to form a flat and even surface and avoid any air bubbles inside the powder.

B.2 Preparation of fused beads

From the general analysis sample, an ash is prepared according to CEN/TS 14775. With the ash, a fused bead is prepared using the fusion apparatus. For application of alkaline fusion technique (e.g. selection of flux, fusion temperature, additives) ISO 14869-2 or CEN/TR 15018 should be used.

NOTE 1 Fluxes commonly used are lithium metaborate, lithium tetraborate or mixtures of both.

NOTE 2 Loss of volatile elements e.g. Na, K, As, Br, Cd, Cl, Hg, I, S, Sb, Se, Tl may occur during the ignition and fusion processes. Also Cu may be volatile if a bromide releasing agent is used.

Because of the wide applicability of the fused bead technique, various fluxes and modes of calibration are permitted providing they have been demonstrated to be able to meet certain criteria of reproducibility, sensitivity and accuracy.

The flux is added to the sample material. For the preparation of 40 mm diameter beads, about 1,6 g of sample is taken, for 32 mm diameter beads about 0,8 g of sample is required. The amount of flux in the bead shall be taken into account for the dilution factor. The same sample preparation procedure and ratio of sample to flux shall be used for samples and standards. The beads produced should be visually homogeneous and transparent. Different dilution factors may be used. A proportion of sample: flux commonly used is 1:5 by weight.

After fusion in a platinum-gold crucible the melt is poured into a casting mould to make a bead.

NOTE 3 Beads can deteriorate because of adverse temperature and humidity conditions, so it is recommended that beads are stored in desiccators.

(informative)

Suggested analytical lines, crystals and operating conditions

Table B.1 — Suggested analytical lines, crystals and operating conditions for wavelength dispersive XRF

Optimum excitation for element analysis can be realised by applying a suitable crystal. The following table shows a list with potentially usable crystals. For all of these the tube voltage and current needs to be set carefully in order to get optimum results. The number of excitation conditions selected shall be optimised particularly with regard to detection sensitivity and required analysis time.

Element	Line	Crystals	kV/mA	Collimator	Detector
Na	K α	OVO-55/PX-1/ TlAp	30/100	coarse	FC
Mg	K α	OVO-55/PX-1/ TlAp	30/100	coarse	FC
Al	K α	OVO-55/PX-1/ PET	30/100	coarse	FC
Si	K α	OVO-55/PX-1/ PET	30/100	coarse	FC
P	K α	Ge/PET	30/100	coarse	FC
S	K α	Ge/PET	30/100	coarse	FC
Cl	K α	Ge/PET	30/100	coarse	FC
K	K α	LiF200	50/60	fine	FC
Ca	K α	LiF200	50/60	fine	FC
Ti	K α	LiF200	50/60	fine	FC
V	K α	LiF200	30/100	fine	FC
Cr	K α	LiF200	60/50	fine	FC
Mn	K α	LiF200	60/50	fine	FC
Fe	K α	LiF200	60/50	fine	FC
Co	K α	LiF200	60/50	fine	SC
Ni	K α	LiF200	60/50	fine	SC
Cu	K α	LiF200	60/50	fine	SC
Zn	K α	LiF200	60/50	fine	SC
As	K α	LiF200	60/50	fine	SC
	K β	LiF200	60/50	fine	SC
Mo	K α	LiF220	60/50	fine	FC
Cd	K α	LiF220	60/50	fine	SC
	L α	PET	30/100	coarse	FC
Pb	L β	LiF200	60/50	fine	SC
FC flow counter					
SC scintillation counter					

Table B.2 — Suggested analytical lines, targets and operating conditions for energy dispersive XRF

Optimum excitation for trace element analysis can be realised by applying secondary or polarisation targets in to the excitation beam of the spectrometer. The following table shows a list with potentially usable targets. For all of these the tube voltage and current needs to be set carefully in order to get optimum results. The number of excitation conditions selected shall be optimised particularly with regard to detection sensitivity and required analysis time.

Target	Target type	Elements
Mo	Secondary	Cr – Zr (K) Hf – U (L)
Zr	Secondary	Cr – Sr (K) Hf – Bi (L)
Al ₂ O ₃	Barkla	Mo – Ba (K)
Csl	Secondary	Mo – In (K)
Pd	Secondary	Fe – Mo (K) Hf – U (L)
B ₄ C	Barkla	Fe – Mo (K) Hf – U (L)
Ge	Secondary	Cr – Zn (K) Hf – Ta (L)
Zn	Secondary	Ti – Ni (K)
Co	Secondary	K – Mn (K) Cd – La (L)
Ti	Secondary	P – Ca (K)
Si	Secondary	Na – Al (K)
Al	Secondary	Na – Mg (K)
HOPG	Bragg	Na – Sr (K) Y – Hf (L)
(K) K α radiation (L) L α radiation		

Annex C (informative)

List of reference materials applicable for XRF-analysis

Reference materials should be selected containing the elements of interest and covering the total concentration range of interest. Additionally reference materials with a similar composition of the samples under investigation should be selected.

Table C.1 — Reference materials applicable for XRF-analysis

Identification		Matrix	CRM/RM*
WU B112	University of Wageningen	Carnation (Straw)	CRM
WU B211	University of Wageningen	Maize (Plant)	RM
WU B212	University of Wageningen	Gladiolus (Leaf)	RM
WU B213	University of Wageningen	Conifers	RM
WU B214	University of Wageningen	Wheat (Straw)	RM
WU B215	University of Wageningen	Cabbage (Leaf)	RM
WU B223	University of Wageningen	Grass (Mixture)	RM
WU B225	University of Wageningen	Cord Grass	RM
WU B226	University of Wageningen	Sea Aster	RM
WU B227	University of Wageningen	Wheat (Straw)	RM
WU B229	University of Wageningen	Lucerne	RM
WU B230	University of Wageningen	Maize (Stalk)	RM
WU B231	University of Wageningen	Pine Needles	RM
WU B235	University of Wageningen	Curly Kail, Leaves	RM
WU B236	University of Wageningen	Scots Pine, Needles	RM
3 1547	Certified by recognized certifying organization	Pech Leaves	CRM
3 1515	Certified by recognized certifying organization	Apple Leaves	CRM
3 1573a	Certified by recognized certifying organization	Tomato Leaves	CRM
3 1570a	Certified by recognized certifying organization	Spinach Leaves	CRM
H 062	Certified by recognized certifying organization	Olive Leaves	CRM
GB 07602	Certified by recognized certifying organization	Bush Branches	CRM
GB 07603	Certified by recognized certifying organization	Bush Leaves	CRM
GB 07604	Certified by recognized certifying organization	Poplar Leaves	CRM
H 100	Certified by recognized certifying organization	Beech Leaves	CRM
H 101	Certified by recognized certifying organization	Spruce Needles	CRM
3 1575a	Certified by recognized certifying organization	Pine Needles	CRM
AE V10	Certified by recognized certifying organization	Hay Powder	CRM
GB 08513	Certified by recognized certifying organization	Tea Leaves	CRM
IJ INCT-TL1	Certified by recognized certifying organization	Tea Leaves	CRM
3 8412	To be added	Corn Stalk	RM
3 8413	To be added	Corn Kernel	RM
3 8433	To be added	Corn Bran	RM
XXX	BioNorm, To be added	Wood chips	RM
XXX	BioNorm, To be added, etc.	Cynara cardunculus	RM

*CRM... Certified Reference Material

*RM... Referenze Material

NOTE This list may be incomplete.

Examples of calibration set up with CRM and RM of table C1:

To be added

Annex D **(informative)**

Validation

An inter-laboratory comparison within the Bionorm II project was organized in 2009 with participants from few laboratories in different European countries. For the inter-laboratory comparison two different solid biofuels were selected and distributed to the participants. The samples are representing a wide spectrum of contents of elements and a broad variety of the matrix composition.

- Sample 1:wood chips
- Sample 2:olive residues

All the samples were sent to the participating laboratories as powder sample.

The samples were analysed using ED-XRF and WD-XRF instrumentation as well.

Six volunteer laboratories received the samples and all of them transmitted data. The evaluation of the data was done according to ISO 5725-2.

Discussion of the results

Will follow

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