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

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National foreword

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

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Foreword

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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*.

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.

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

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 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
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.

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

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.

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 difference between the measured peak intensity of the element and the background intensity, as given in Formula (1):

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

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 with no analyte present, expressed as the number of counts per second.

10.1.1.2 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 Formula (2):

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

where

t is the total counting time for the peaks and background, expressed 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 1. The settings strongly depend on the spectrometer configuration, e.g. type of X-ray tube (Rh, Pd), tube power, available targets, types of filters. Instrument manufacturer’s recommendations should be followed in all cases.

10.1.2.1 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

Table 1 *(continued)*

Element	Line	Spectral line overlap	Type of matrix correction method
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
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
Pb	Lβ	ThLα BiLβ SnKα	Compton or FP or MAC

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-matched 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.

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

- 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 true 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. Besides 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. This procedure will normally need more standards than a calibration based on theoretical correction coefficients.

10.2.2 General calibration procedure

The measurements of analyte lines of samples of known composition are needed for calibration purposes. The basic formula implies a linear relationship between the intensity and the concentration, as given in Formula (3):

$$C_\mathrm{i} = a_{\mathrm{i},0} + a_{\mathrm{i},1} \cdot I_\mathrm{i} \tag{3}$$

where

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

$a_{\mathrm{i},0}$ is the intercept of the calibration curve;

$a_{\mathrm{i},1}$ 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 Formula (4):

$$C_\mathrm{i} = \left(a_{\mathrm{i},0} + a_{\mathrm{i},1} \cdot I_\mathrm{i}\right) \cdot M \tag{4}$$

where

M is the correction factor due to the matrix effects.

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

10.2.3 Calibration procedure using the pressed pellet method (recommended method)

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 recognized producers is recommended (see Annex A). 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.

Specify 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 specified measurement method. All measurements shall be performed under vacuum. A minimum of four different calibration samples with different concentration should be used.

Follow the instructions 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.

10.3 Procedures for correcting matrix effect

The use of correcting methods should be performed by users with a high level of expertise. The choice for the different procedures should be taken in compliance with the manufacturer's instructions.

10.3.1 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 Formula (5):

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

where

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

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

$I_{\mathrm{inc,u}}$ is the intensity of the incoherent Compton line of the sample, expressed as counts per second;

$I_{\mathrm{inc,r}}$ is the intensity of the incoherent Compton line element of the calibration reference material, expressed as counts per second;

$I_{\mathrm{i,u}}$ is the intensity of the element of interest i of the sample, expressed as counts per second;

I_{ir} is the intensity of the element of interest i of the calibration reference material, expressed as counts per second.

10.3.2 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.

10.3.3 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 Formula (6) and Formula (7):

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

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

where

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

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

$I_{\mathrm{i,r}}$ is the intensity of the element of interest i of the calibration reference material, expressed as counts per second;

$I_{\mathrm{i,u}}$ is the intensity of the element of interest i of the sample, expressed as counts per second;

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

$C_{\mathrm{j,u}}$ is the concentration of the matrix element j of the sample, expressed as mg/kg or percentage dry matter;

M is the matrix correction factor;

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.

10.3.4 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 formula where the correction factor 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 three times the number of parameters to be calculated).

10.4 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. For the quantification of major and minor elements, the pressed pellet method is recommended and for the semi-quantitative determination of major elements, the powder method can be used.

To analyse the prepared samples, an analytical measurement method has to be specified. 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.

At the beginning of analysis and at frequent intervals, quality control samples have to be measured to check the instrument stability and the quality of the analyses, 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 frequency and performance experience indicate.

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 standard 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 accuracy 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.

NOTE Certified reference materials are available, e.g. from BCR (see Annex A).

12 Calculation of the result

Follow the guideline in the instrument manufacturer's manual on 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 are expressed in terms of weight percent dry basis concerning the major elements and mg/kg dry basis concerning minor elements. The results may be calculated to another basis, e.g. to an as received basis according to EN 15296.

13 Performance characteristics

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) a reference to this Technical Specification, i.e. ISO/TS 16996;

b) results of the test including the basis in which they are expressed, as indicated in Clause 12;

c) identification of the laboratory performing the test and the date of the test;

d) identification of product (sample) tested;

e) any operation not included in this Technical Specification, or regarded as optional;

f) any unusual features noted during the test procedure.

Annex A
(informative)

Publicly available biomass reference materials

- BCR 60. Aquatic plant (Lagarosiphon major) — Trace elements
- BCR 100. Beech leaves — Trace elements
- BCR 129. Elements in hay powder
- BCR 414 Plankton — Trace elements
- NIST 1512. Apple leaves — Trace elements
- NIST 1547. Peach leaves — Trace elements
- NIST 1570a. Spinach leaves — Trace elements
- NIST 1573a. Tomato leaves — Trace elements
- NIST1575a. Pine needles — Trace elements and minor constituents
- NCS DC 73348. Bush Branches and Leaves
- ERM-CD281 Rye grass — Trace elements
- IAEA-V-9 Cotton Cellulose — Trace elements
- IAEA-392. Algae — Trace elements

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