

---

---

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

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

STANDARDSISO.COM : Click to view the full PDF of ISO/TS 16996:2015



STANDARDSISO.COM : Click to view the full PDF of ISO/TS 16996:2015



**COPYRIGHT PROTECTED DOCUMENT**

© ISO 2015, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

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

# Contents

Page

<b>Foreword</b> .....	<b>iv</b>
<b>Introduction</b> .....	<b>v</b>
<b>1 Scope</b> .....	<b>1</b>
<b>2 Normative references</b> .....	<b>1</b>
<b>3 Terms and definitions</b> .....	<b>1</b>
<b>4 Safety remarks</b> .....	<b>2</b>
<b>5 Symbols and abbreviated terms</b> .....	<b>3</b>
5.1 Symbols.....	3
5.2 Abbreviated terms.....	3
<b>6 Principle</b> .....	<b>3</b>
<b>7 Apparatus</b> .....	<b>4</b>
<b>8 Interferences and sources of error</b> .....	<b>4</b>
<b>9 Sample preparation</b> .....	<b>5</b>
9.1 Preparation principles.....	5
9.2 Drying of general analysis sample material.....	5
9.3 Preparation of pressed pellet.....	5
<b>10 Procedure</b> .....	<b>5</b>
10.1 Analytical measurement conditions.....	5
10.1.1 Wavelength dispersive instruments.....	5
10.1.2 Energy dispersive instruments.....	6
10.2 Calibration.....	7
10.2.1 General.....	7
10.2.2 General calibration procedure.....	8
10.2.3 Calibration procedure using the pressed pellet method (recommended method).....	8
10.3 Procedures for correcting matrix effect.....	9
10.3.1 Internal standard correction using Compton (incoherent) scattering method.....	9
10.3.2 Fundamental parameter approach.....	9
10.3.3 Fundamental or theoretical influence coefficient method.....	9
10.3.4 Empirical alpha correction.....	10
10.4 Analysis of the samples.....	11
<b>11 Quality control</b> .....	<b>11</b>
11.1 Drift correction procedure.....	11
11.2 Reference materials.....	11
<b>12 Calculation of the result</b> .....	<b>11</b>
<b>13 Performance characteristics</b> .....	<b>12</b>
<b>14 Test report</b> .....	<b>12</b>
<b>Annex A (informative) Publicly available biomass reference materials</b> .....	<b>13</b>
<b>Bibliography</b> .....	<b>14</b>

## 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](http://www.iso.org/directives)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation 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.

STANDARDSISO.COM : Click to view the full PDF of ISO/TS 16996:2015

# 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  $\text{cm}^2/\text{g}$ .

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	K $\alpha$	ZnL $\beta$	Alpha or FP
Mg	K $\alpha$	AsL $\alpha$	Alpha or FP
Al	K $\alpha$	BrL $\alpha$	Alpha or FP
Si	K $\alpha$		Alpha or FP
P	K $\alpha$		Alpha or FP
S	K $\alpha$	CoK $\alpha$ PbM $\alpha$ NbL $\beta$	Alpha or FP or MAC
Cl	K $\alpha$		Alpha or FP or MAC
K	K $\alpha$		Alpha or FP
Ca	K $\alpha$		Alpha or FP
Ti	K $\alpha$	BaL $\alpha$ IL $\beta$	Alpha or FP
V	K $\alpha$	Ti K $\beta$	Alpha or FP or MAC

Table 1 (continued)

Element	Line	Spectral line overlap	Type of matrix correction method
Cr	K $\alpha$	VK $\beta$ PbL $\alpha$	Alpha or FP or MAC
Mn	K $\alpha$	CrK $\beta$	Alpha or FP
Fe	K $\alpha$	MnK $\beta$	Alpha or FP
Co	K $\alpha$	FeK $\beta$	Alpha or FP or MAC
Ni	K $\alpha$	CoK $\beta$	Compton or FP or MAC
Cu	K $\alpha$	TaL $\alpha$ ThL $\beta$	Compton or FP or MAC
Zn	K $\alpha$	WL $\alpha$	Compton or FP or MAC
As	K $\alpha$ K $\beta$	PbL $\alpha$ BrK $\alpha$	Compton or FP or MAC
Mo	K $\alpha$	ZrK $\beta$ UL $\beta$	Compton or FP or MAC
Ag	K $\alpha$ L $\alpha$	CrK $\beta$	Compton or FP or MAC Alpha or FP
Cd	K $\alpha$ L $\alpha$	AgL $\beta$	Compton or FP or MAC Alpha or FP
Sb	K $\alpha$ L $\beta$	CoK $\beta$	Compton or FP or MAC Alpha or FP or MAC
Pb	L $\beta$	ThL $\alpha$ BiL $\beta$ SnK $\alpha$	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):

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

where

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

$a_{i,0}$  is the intercept 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 Formula (4):

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

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,  $\mu$ , 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):

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

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.

#### 10.3.2 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):

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

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

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 factor;
- $\alpha_{ij}$  is the correction coefficient  $\alpha_{ij}$  (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.