**BRITISH STANDARD**

**BS EN 15309:2007**

# Characterization of waste and soil — Determination of elemental composition by X-ray fluorescence

ICS 13.030.10; 13.080.10

British Standards

# National foreword

This British Standard is the UK implementation of EN 15309:2007.

The UK participation in its preparation was entrusted to Technical Committee B/508/3, Characterization of waste.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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**EN 15309**

May 2007

ICS 13.030.10; 13.080.10

English Version

# Characterization of waste and soil - Determination of elemental composition by X-ray fluorescence

Caractérisation des déchets et du sol - Détermination de la composition élémentaire par fluorescence X

Charakterisierung von Abfällen und Böden - Bestimmung der elementaren Zusammensetzung durch Röntgenfluoreszenz-Analyse

This European Standard was approved by CEN on 22 March 2007.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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# Contents

# Foreword

This document (EN 15309:2007) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste“, the secretariat of which is held by NEN.

This document has been prepared in coordination with ISO/TC 190 “Soil quality”.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2007, and conflicting national standards shall be withdrawn at the latest by November 2007.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom

# Introduction

X-ray fluorescence spectrometry is a fast and 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 inhomogeneous matrices like waste, 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 homogeneous solid waste, soil and soil-like material in the normative part. The calibration is based on matrix-matched standards;
- an XRF screening method for solid and liquid material as waste, sludge and soil in the informative Annex A which provides a total element characterisation at a semi-quantitative level. The calibration is based on matrix-independent calibration curves, previously set up by the manufacturer.

## 1 Scope

This European Standard specifies the procedure for a quantitative determination of major and trace element concentrations in homogeneous solid waste, soil and soil-like material by energy dispersive X-ray fluorescence (EDXRF) spectrometry or wavelength dispersive X-ray fluorescence (WDXRF) spectrometry using a calibration with matrix-matched 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, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ta, W, Hg, Tl, Pb, Bi, Th and U. 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.

EN 14346, *Characterisation of waste — Calculation of dry matter by determination of dry residue or water content*

EN 15002, *Characterisation of waste — Preparation of test portions from the laboratory sample*

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:1999)*

ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

## 3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

NOTE See [13] and [10] for non specified terms.

### 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**
**fused bead**
analyte sample prepared by dissolution in a flux

**3.9**
**liquid sample**
analyte sample submitted as a solution for direct measurement in the sample cup

**3.10**
**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

**3.11**
**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

**3.12**
**powder sample**
analyte sample submitted as a powder for direct measurement in the sample cup

**3.13**
**precision**
closeness of agreement of results obtained by applying the method several times under prescribed conditions [ISO 5725-2:1994]

**3.14**
**pressed pellet**
analyte sample prepared by pressing milled material into a disk

**3.15**
**primary X-rays**
X-rays by which the sample is radiated

**3.16**
**quality control sample**
stable sample with known contents, e.g. certified reference material (CRM) used to monitor instrument and calibration performance

**3.17**
**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

Anyone dealing with waste and sludge analysis has to be aware of the typical risks that this kind of material presents irrespective of the parameter to be determined. Waste and sludge samples may contain hazardous e.g. toxic, reactive, flammable, infectious substances, which could potentially undergo biological and/or chemical reaction. Consequently it is recommended that these samples should be handled with special care. The gases that may be produced by microbiological or chemical activity are potentially flammable and will pressurise sealed bottles. Bursting bottles are likely to result in hazardous shrapnel, dust and/or aerosol. National regulations should be followed with respect to all hazards associated with this method.

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 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.

## 6 Apparatus

### 6.1 X-ray fluorescence spectrometer

The X-ray fluorescence spectrometer shall be able to analyse the elements according to the scope of this European Standard. 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).

**6.2** Mill, preferable with walls made of agate, corundum or zircon.

**6.3** Pellet preparation equipment: manual or automatic pellet press, capable of providing a pressure of at least 100 kN.

**6.4** Aluminium cup: supporting backing cup for pressed pellets.

**6.5** Fusion apparatus: electric, gas or high frequency induction furnace that can be heated up to a fixed temperature of between 1 050 °C and 1 250 °C.

**6.6** Fusion crucibles: crucibles made of non-wetting platinum alloy (Pt 95 %; Au 5 % is suitable).

Lids, if used, shall be made from platinum alloy.

NOTE Certain metal sulphides (so called platinum poisons) affect the platinum crucibles in which the sample is melted.

**6.7** Casting moulds: non-wetting platinum alloy (Pt 95 %; Au 5 % is suitable).

## 7 Reagents

The reagents mentioned are used as carrier material.

**7.1** Binder: liquid or solid binder free of analytes of interest. Solid materials can contain a certain amount of moisture, which shall be compensated for.

NOTE Different type of binders may be used. A binder commonly used is wax.

**7.2** Flux: solid flux free of analytes of interest. Solid materials can contain a certain amount of moisture, which shall be compensated for (see EN ISO 12677 for compensation for moisture in flux).

NOTE Different type of fluxes may be used. Fluxes commonly used are lithium metaborate, lithium tetraborate or mixtures of both.

## 8 Interferences and sources of error

The container in which the sample is delivered and stored can be a source of error. Its material shall be chosen according to the elements to be determined.

NOTE Elemental Hg can penetrate polyethylene walls very rapidly in both directions. In the case of glass containers, contamination may be observed for some elements e.g. Al, As, Ba, Ce, K, Na, Pb.

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

In analysis by XRF spectrometry the sample preparation step is crucial as the quality of the sample preparation will strongly influence the accuracy of the results.

For quantitative analysis of solid samples, pressed pellets or fused beads have to be prepared. The application of the pressed pellet method is recommended for the quantification of trace elements and mandatory for the quantification of volatile elements, and the fused bead method for the determination of non-volatile major and minor elements.

NOTE 1 The preparation of fused beads eliminates effects due to particle size and mineralogy.

The conditions of the preparation of fused beads shall be adapted to the matrix properties. Otherwise the preparation of fused beads may be difficult or cause problems in case of waste like matrices as sludges.

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

NOTE 2 Depending on the sample type other sample preparation methods may be applied according to Annex B.

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 ISO 11464 and EN 15002. The particle size of the sample may strongly affect the precision of the measurement. The particle size should preferably be smaller than 150 µm.

NOTE 3 Particle size smaller than 80 µm is recommended for the analysis of low atomic mass elements when using the pressed pellet method.

## 9.2 Drying and determination of dry mass

Prepare and dry the sample according to ISO 11464 or EN 15002. Determine the dry mass according to ISO 11465 or EN 14346.

## 9.3 Preparation of pressed pellet

After drying and milling or grinding the sample, a pellet is prepared in the pellet press (6.3). Before pressing, the sample shall be mixed and homogenised with a binder (7.1). For the preparation of 40 mm diameter pellets, about 10,0 g of sample is taken, for 32 mm diameter pellets about 4,5 g of sample is required. The amount of binder in the pellet shall be taken into account for the dilution factor. It is recommended to press the sample in an aluminium cup (6.4) as support.

NOTE 1 Different type of binders can be used. A binder commonly used is wax. In the case of a liquid binder the pellet is placed in an oven to evaporate organic solvent.

NOTE 2 Different dilution factors can be used. A proportion of sample: binder commonly used is 10:1 by weight.

### 9.4 Preparation of fused beads

After drying and milling or grinding the sample, a fused bead is prepared using the fusion apparatus (6.5).

Ignite the sample at an appropriate temperature until constant mass is reached. Determine the loss on ignition at the same temperature to correct for volatile elements and/or compounds being released during ignition of the sample.

NOTE 1 The ignition temperature can vary depending on the sample matrix. A temperature commonly used is 1025°C ± 25°C.

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.

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

NOTE 3 Loss of volatile elements e.g. 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.

The flux (7.2) is added to the ignited material. For the preparation of 40 mm diameter beads, about 1,6 g of ignited sample is taken, for 32 mm diameter beads about 0,8 g of ignited 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.

NOTE 4 Non ignited material may be used to prepare beads but, nevertheless, loss of ignition needs to be determined and needs to be taken into account in the calculation of the results. It should be noted that non ignited material may contain compounds that can damage the platinum crucibles during fusion.

NOTE 5 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 (6.6) the melt is poured into a casting mould (6.7) to make a bead.

NOTE 6 Beads can deteriorate because of adverse temperature and humidity conditions, so it is recommended that beads are stored in desiccators.

## 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 C.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:

$$I = I_\mathrm{p} - I_\mathrm{b} \qquad (1)$$

where

$I_\mathrm{p}$ is the count rate of the element i, expressed as the number of counts per second;

$I_\mathrm{b}$ 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:

$$t = \left( \frac{100}{2\sigma_{\%}} . \frac{1}{\sqrt{I_\mathrm{p}} - \sqrt{I_\mathrm{b}}} \right)^2 \qquad (2)$$

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 C.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.

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 (trace 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.

$$C_\mathrm{i} = a_{\mathrm{i},0} + a_{\mathrm{i},1} \,.\, I_\mathrm{i} \qquad (3)$$

where

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

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

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

$I_\mathrm{i}$ 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:

$$C_\mathrm{i} = (a_{\mathrm{i},0} + a_{\mathrm{i},1} \,.\, I_\mathrm{i}).M \qquad (4)$$

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 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:

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

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;

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

### 10.2.4 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.

### 10.2.5 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:

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

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

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 term; |
| $\alpha_{\mathrm{ij}}$ | is the correction coefficient $\alpha_{\mathrm{ij}}$ (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.

### 10.2.6 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).

### 10.2.7 Calibration procedure for trace elements using the pressed pellet method

The pressed pellet method is used to determine the concentrations of trace 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 (see Annex D) or synthetic mixtures of oxides may be prepared. 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.

NOTE It is important to note that the pressed pellet method is not ideal for the determination of major elements, but these elements are measured so that alpha corrections can be applied to some elements of interest.

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 trace 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.

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

| Element | Line | Spectral line overlap | Type of matrix correction method |
|---|---|---|---|
| Na | Kα | ZnLβ | Alpha or FP |
| Mg | Kα | AsLα | Alpha or FP |
| Al | Kα | BrLα | Alpha or FP |
| Si | Kα | | Alpha or FP |
| P | Kα | | Alpha or FP |
| S | Kα | CoKα PbMα NbLβ | Alpha or FP or MAC |
| Cl | Kα | | Alpha or FP or MAC |
| K | Kα | | Alpha or FP |
| Ca | Kα | | Alpha or FP |
| Ti | Kα | BaLα ILβ | Alpha or FP |
| V | Kα | Ti Kβ | Alpha or FP or MAC |
| Cr | Kα | VKβ PbLα | Alpha or FP or MAC |
| Mn | Kα | CrKβ | Alpha or FP |
| Fe | Kα | MnKβ | Alpha or FP |
| Co | Kα | FeKβ | Alpha or FP or MAC |
| Ni | Kα | CoKβ | Compton or FP or MAC |
| Cu | Kα | TaLα ThLβ | Compton or FP or MAC |
| Zn | Kα | WLα | Compton or FP or MAC |
| As | Kα | PbLα | Compton or FP or MAC |
| | Kβ | BrKα | |
| Se | Kα | | Compton or FP or MAC |
| Br | Kα | AsKβ | Compton or FP or MAC |
| Rb | Kα | ULα BrKβ | Compton or FP or MAC |
| Sr | Kα | ULα | Compton or FP or MAC |
| Y | Kα | RbKβ | Compton or FP or MAC |
| Zr | Kα | SrKβ | Compton or FP or MAC |
| Nb | Kα | YKβ ULβ | Compton or FP or MAC |
| Mo | Kα | ZrKβ ULβ | Compton or FP or MAC |
| Ag | Kα | | Compton or FP or MAC |
| | Lα | CrKβ | Alpha or FP |
| Cd | Kα | | Compton or FP or MAC |
| | Lα | AgLβ | Alpha or FP |
| Sn | Kα | | Compton or FP or MAC |
| | Lα | CoKα | Alpha or FP or MAC |
| Sb | Kα | | Compton or FP or MAC |
| | Lβ | CoKβ | Alpha or FP or MAC |
| Te | Kα | | Compton or FP or MAC |
| | Lα | SnLβ | Alpha or FP or MAC |
| I | Kα | | Compton or FP or MAC |
| | Lα | | Alpha or FP or MAC |
| Cs | Kα | | Compton or FP or MAC |
| | Lα | ZnKα ILβ | Alpha or FP or MAC |
| Ba | Kα | | Compton or FP or MAC |
| | Lα | TiKα ILβ CuKβ | Alpha or FP or MAC |
| Ta | Lα | CuKα NiKβ | Compton or FP or MAC |
| W | Lα | TaLn | Compton or FP or MAC |
| Hg | Lα | WLβ | Compton or FP or MAC |
| Tl | Lβ | PbLβ | Compton or FP or MAC |

| Element | Line | Spectral line overlap | Type of matrix correction method |
|---|---|---|---|
| Pb | Lβ | ThLα BiLβ SnKα | Compton or FP or MAC |
| Bi | Lα | TaLγ | Compton or FP or MAC |
| Th | Lα | BiLβ PbLβ | Compton or FP or MAC |
| U | Lα | BrKβ RbKα | Compton or FP or MAC |

#### 10.2.8 Calibration procedure for major and minor oxides using the fused bead method

The fused bead 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 total concentration range of interest. The use of reference materials from different recognised producers is recommended (see Annex D) or synthetic mixtures of oxides may be prepared. The element concentrations shall vary independently in the samples. If the calibration covers many elements in a wide range of concentrations, a large number of calibration samples may be necessary.

Prepare fused beads from the selected calibration standards according to 9.4.

NOTE Due to a higher dilution factor for fused beads the limit of detection of the different elements will be higher than those for pressed pellets.

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.

In the calibration program all the elements of the reference materials has to be defined as oxides and the concentrations are reported as oxides.

Follow the guidelines in the instrument manufacturer's manual how 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). For all elements an alpha correction method using theoretical alphas should be applied.

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 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 trace elements the pressed pellet method is recommended and for the determination of major and minor elements the fused bead method should be used.

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, 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 frequency 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 Blank test

To assess the level of impurities in the flux, carry out a blank test by preparing and analysing a blank sample using the same sample preparation procedure and the same quantities of reagents.

### 11.3 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.

## 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 are expressed as elements in terms of mg/kg dry matter for trace elements and as oxides in mass percentages dry matter for major and minor elements.

## 13 Test report

The work carried out by the testing laboratory shall be covered by a report which accurately, clearly and unambiguously presents the test results and all other relevant information as specified in EN ISO/IEC 17025.

In addition to test results the test report shall include at least the following information:

a) description and identification of the laboratory sample;

b) which processes, procedures and apparatus were used;

c) results of the determination expressed as mg/kg dm or mass percentages dm;

d) any details not specified in this European Standard or which are optional, and any other factors which may have affected the results;

e) date of receipt of laboratory sample and date(s) of performance of test;

f) a reference to this European Standard, i.e. EN 15309.

Corrections or additions to a test report after issue shall be made only by a further document suitably marked, e.g. "Amendment/Addendum to test report serial number (or as otherwise identified)", and shall meet the relevant requirements of the preceding paragraphs.

# Annex A
(informative)

# Semi-quantitative screening analysis of waste, sludge and soil samples

## A.1 Principle

The principle is identical as described in Clause 5, 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 sodium to uranium except noble gases at levels between approximately 0,01 % and 100 %, depending on the element and the instrument used.

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 6.1 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

The sample preparation determines significantly the obtained quality of the XRF results. For detailed information on sample preparation procedures, refer to the flowcharts and the sample preparation techniques in Annex B.

## 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 Validation

Prior to analysis of a sample, the available pre-calibrated analytical method has to be validated by using reference samples with a similar composition as the samples under investigation. If no reference materials with a comparable matrix are available, only a qualitative analysis with indicative concentration values can be performed.

The reference sample can consist of:

- in-house or commercially available reference materials - if possible certified - with matrices similar to that of the sample;
- synthetic samples, made by weighing the appropriate amount of each pure reagent;
- site specific or batch specific samples, similar to the matrix of the sample;
- standard addition method or spiked samples may also be used to create standards for which appropriate reference materials are not available for an element of interest. The matrix material needs to match that of the sample.

The element concentrations of these reference samples have to be known by certification or by determination with a different analytical technique.

The reference samples have to be analysed under the same analytical conditions as the sample, meaning the same sample preparation (pellet, powder etc.), the same analytical measurement method etc.

### A.4.3 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.

## A.5 Calculation and evaluation

The software program from the measured intensity calculates the element concentrations, expressed in mg/kg dry matter for trace and minor elements and m/m % dry matter for major elements.

The effective matrix corrections have to account for low atomic mass elements like hydrogen, carbon or oxygen. As they are easily absorbed they have a strong influence on the matrix effects. Different approaches are applied in commercial software packages for this effect. First of all, automated correction using mass absorption coefficients can be performed. Secondly, it may be possible to enter the matrix compounds e.g. $CH_2$ for polymers, $H_2O$ for water samples, and C for coal samples, to optimise the calculation process. All these methods allow the use of one calibration for different matrices.

NOTE In some cases, it is possible to optimize the iterative calculation process for the element concentration by inserting concentration values of specific compounds, obtained with another analytical technique.

## A.6 Quality control

The quality control has to be done according to Clause 11.

## A.7 Safety remarks

The safety remarks are the same as described in Clause 4.

## A.8 Test report

The test report has to be done according to Clause 13.

# Annex B
(informative)

# Examples for operational steps of the sample preparation for soil and waste samples

As waste samples can consist of different material types, various sample preparations have to be applied prior to the XRF screening analysis. The operational steps for different matrices are given in the flow diagrams in Figures B.1 to B.5:

- Figure B.1: Operational steps for the preparation of soil, sediment, fly ash and sludge samples;
- Figure B.2: Operational steps for the preparation of samples consisting of carbon matrices;
- Figure B.3: Operational steps for the preparation of liquid samples;
- Figure B.4: Operational steps for the preparation of paste-like materials;
- Figure B.5: Operational steps for the preparation of scrap samples.

The procedures of the different sample preparation techniques as mentioned in the pictures are described in ISO 11464, EN 15002, explained in the normative part or otherwise given directly.

## B.1 Preparation of liquid samples

If the liquid sample is homogeneous, it is poured directly into a sample cup. The bottom of the sample cup is closed by a thin-film support. Close the sample cup.

## B.2 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.3 Impregnation on powders

### B.3.1 Impregnation on aluminium oxide

Place 15,000 g ± 0,005 g of aluminium oxide (precalcined at 1 500°C) into a HDPE bottle. Add 5,000 g ± 0,005 g of the homogeneous sample and two mixing balls. Close the bottle and shake vigorously for approximately 30 s. Empty the aluminium oxide / sample mixture from the bottle to 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.3.2 Impregnation on activated carbon

Weight 4,000 g ± 0,005 g of sample, add 2,000 g ± 0,005 g of active carbon and homogenise very well the mixture. Empty the active carbon / sample mixture from the bottle to the sample cup. The powder is slightly pressed with a piston to form a good surface to avoid any air holes on the bottom. High volatile liquids can be impregnated on active carbon.

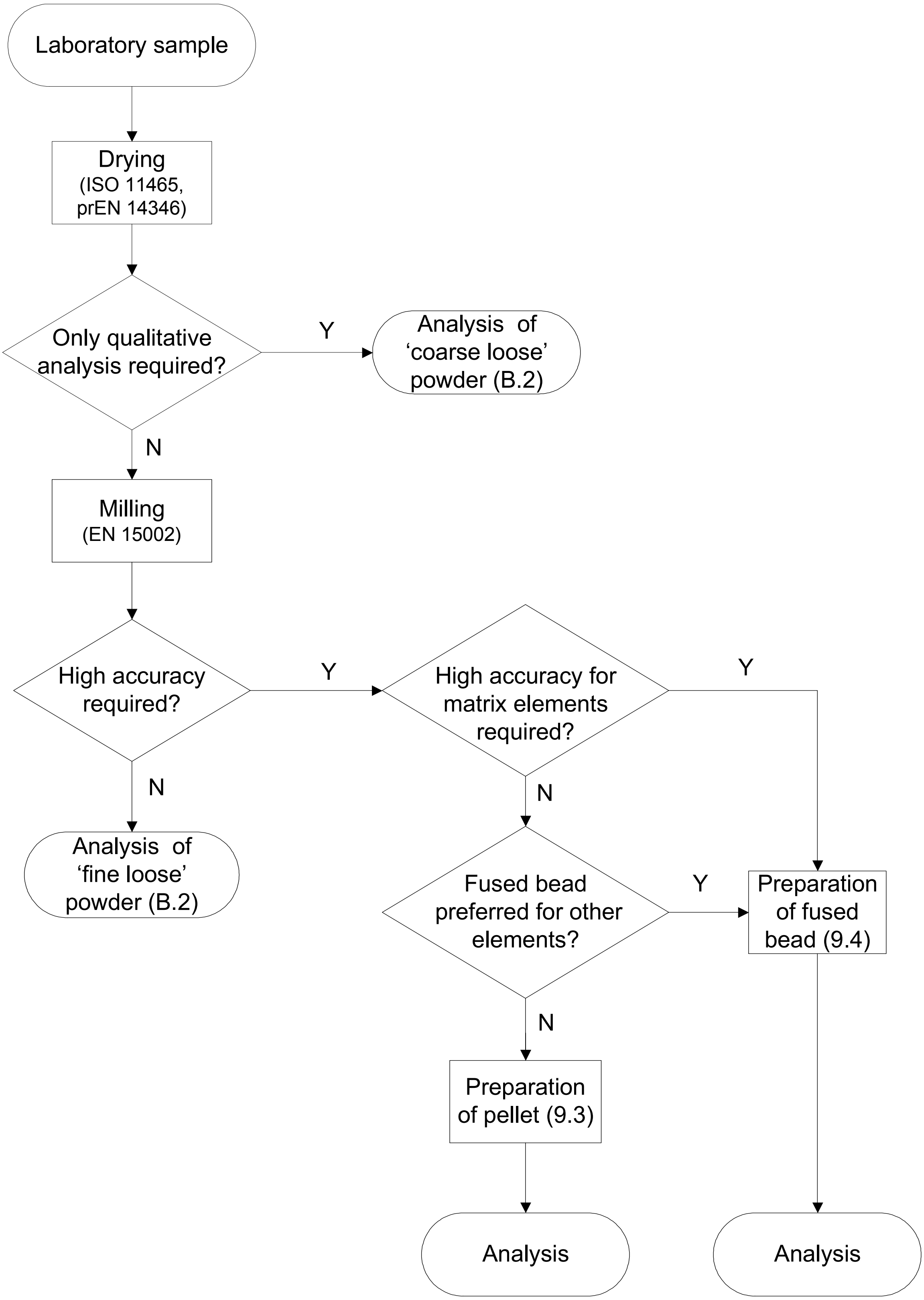

**Figure B.1 — Operational steps for the preparation of soil, sediment, fly ash and sludge samples**

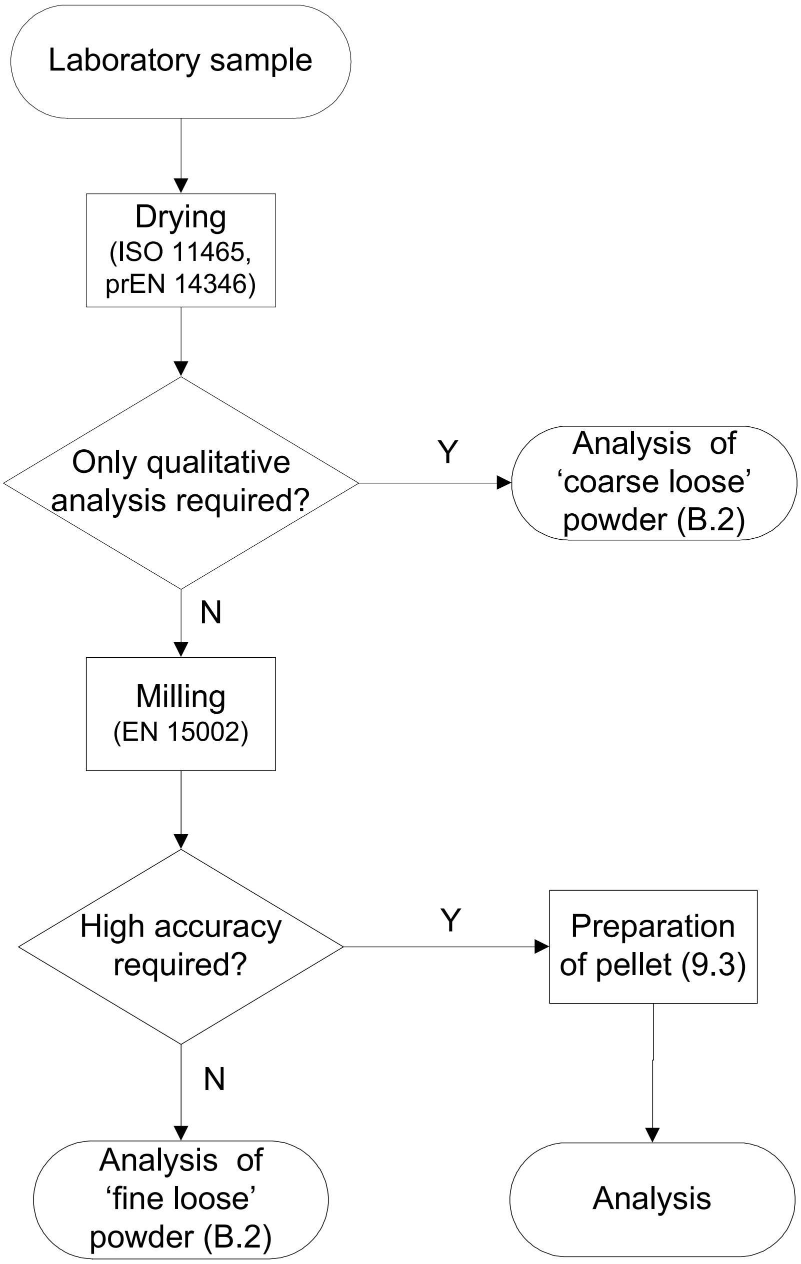

**Figure B.2 — Operational steps for the preparation of samples consisting of carbon matrices**

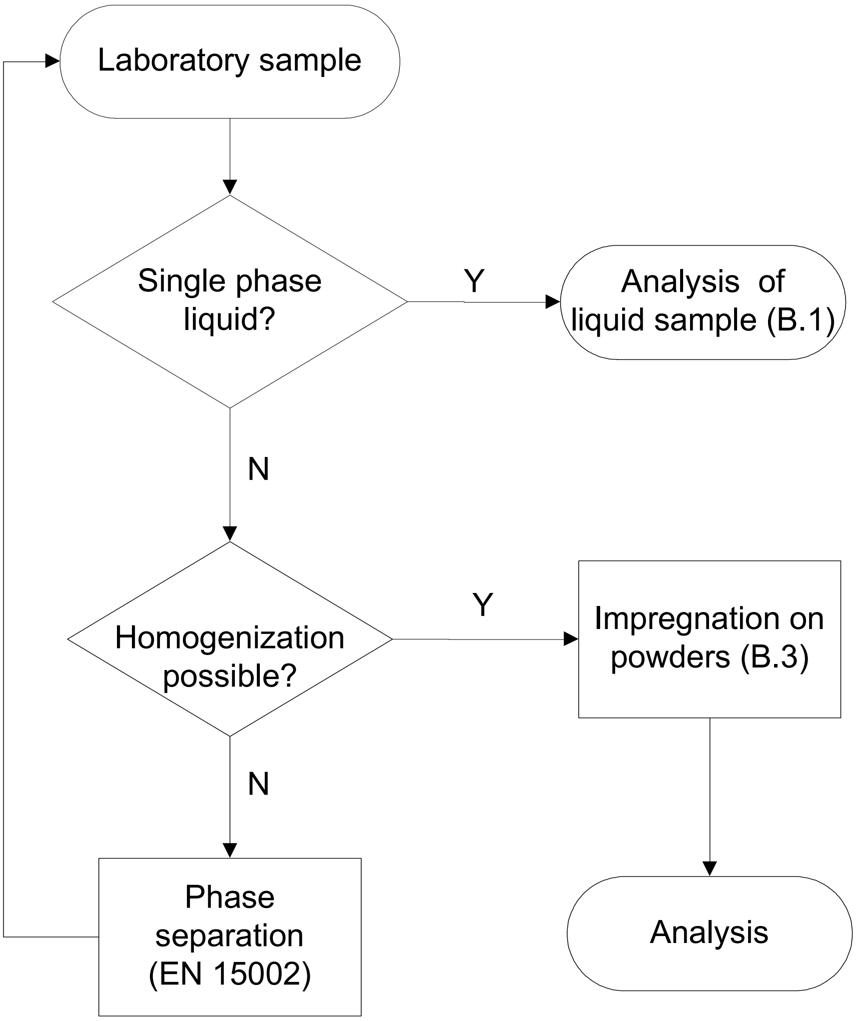

**Figure B.3 — Operational steps for the preparation of liquid samples**

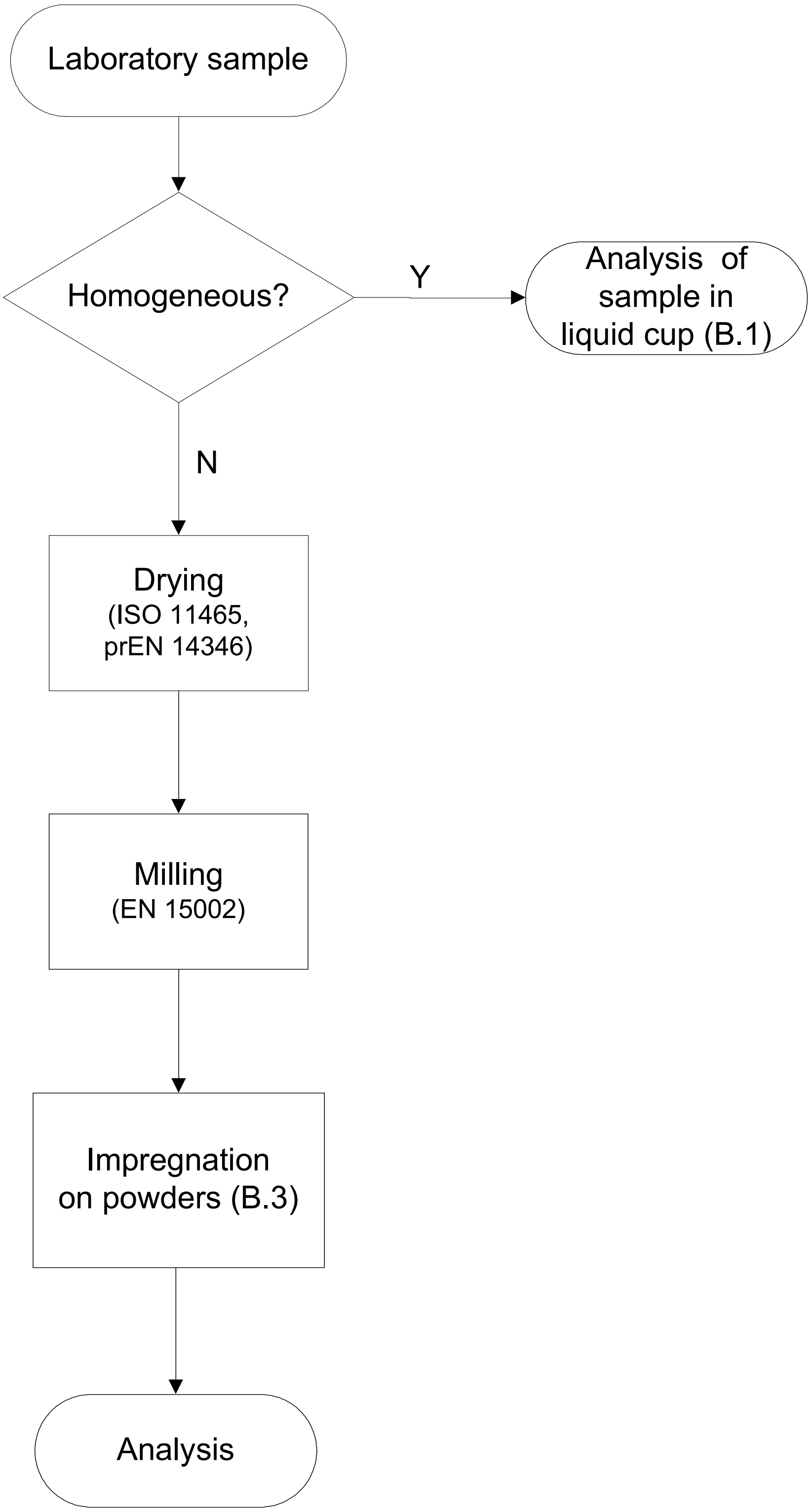

**Figure B.4 — Operational steps for the preparation of paste-like materials**

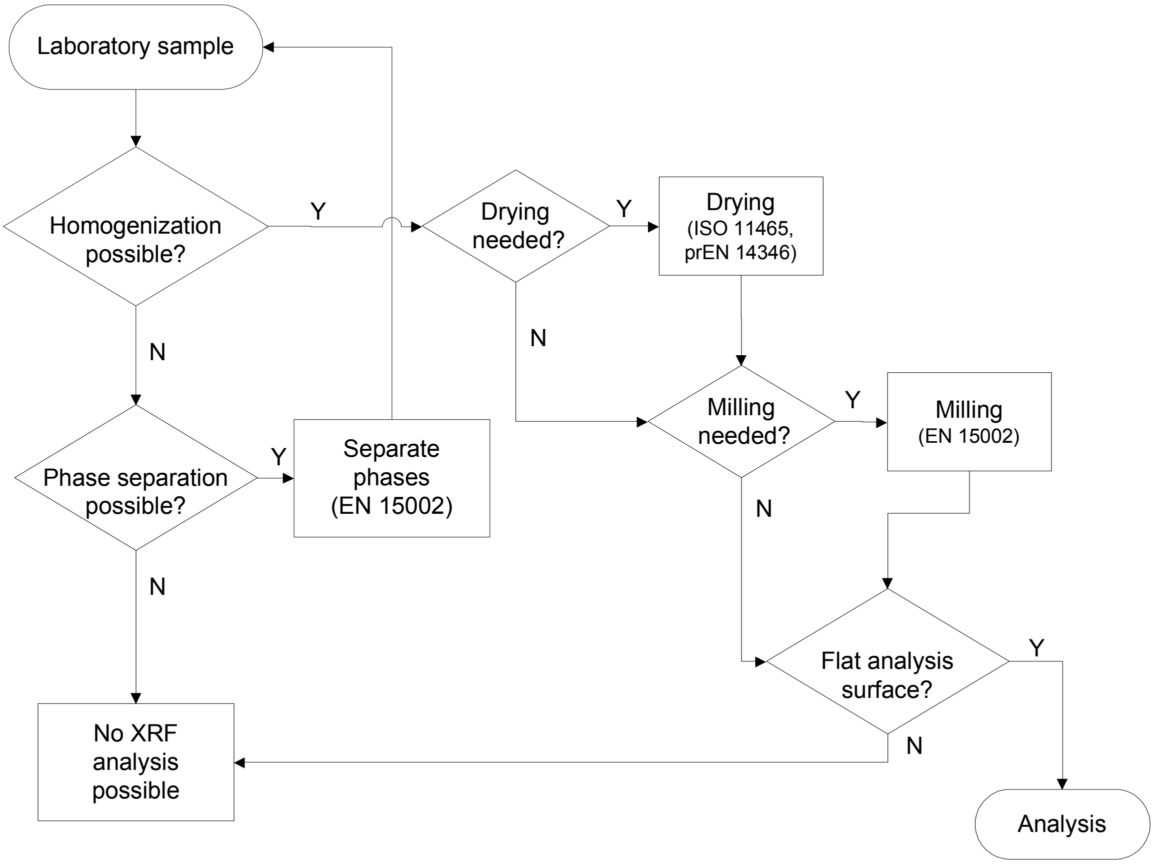

Figure B.5 — Operational steps for the preparation of scrap samples

# Annex C
(informative)

# Suggested analytical lines, crystals and operating conditions

**Table C.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 | Kα | OVO-55/PX-1/ TlAp | 30/100 | coarse | FC |
| Mg | Kα | OVO-55/PX-1/ TlAp | 30/100 | coarse | FC |
| Al | Kα | OVO-55/PX-1/ PET | 30/100 | coarse | FC |
| Si | Kα | OVO-55/PX-1/ PET | 30/100 | coarse | FC |
| P | Kα | Ge/PET | 30/100 | coarse | FC |
| S | Kα | Ge/PET | 30/100 | coarse | FC |
| Cl | Kα | Ge/PET | 30/100 | coarse | FC |
| K | Kα | LiF200 | 50/60 | fine | FC |
| Ca | Kα | LiF200 | 50/60 | fine | FC |
| Ti | Kα | LiF200 | 50/60 | fine | FC |
| V | Kα | LiF200 | 30/100 | fine | FC |
| Cr | Kα | LiF200 | 60/50 | fine | FC |
| Mn | Kα | LiF200 | 60/50 | fine | FC |
| Fe | Kα | LiF200 | 60/50 | fine | FC |
| Co | Kα | LiF200 | 60/50 | fine | SC |
| Ni | Kα | LiF200 | 60/50 | fine | SC |
| Cu | Kα | LiF200 | 60/50 | fine | SC |
| Zn | Kα | LiF200 | 60/50 | fine | SC |
| As | Kα<br>Kβ | LiF200<br>LiF200 | 60/50<br>60/50 | fine<br>fine | SC<br>SC |
| Se | Kα | LiF200 | 60/50 | fine | SC |
| Br | Kα | LiF220 | 60/50 | fine | FC |
| Rb | Kα | LiF220 | 60/50 | fine | FC |
| Sr | Kα | LiF200 | 60/50 | fine | FC |
| Y | Kα | LiF220 | 60/50 | fine | FC |
| Zr | Kα | LiF220 | 60/50 | fine | FC |
| Nb | Kα | LiF220 | 60/50 | fine | FC |
| Mo | Kα | LiF220 | 60/50 | fine | FC |
| Ag | Ka<br>Lα | LiF220<br>PET | 60/50<br>30/100 | fine<br>coarse | SC<br>FC |
| Cd | Kα<br>Lα | LiF220<br>PET | 60/50<br>30/100 | fine<br>coarse | SC<br>FC |
| Sn | Lα | LiF200 | 30/100 | fine | FC |
| Sb | Lα | LiF200 | 30/100 | fine | FC |

| **Element** | **Line** | **Crystals** | **kV/mA** | **Collimator** | **Detector** |
|---|---|---|---|---|---|
| Te | Lα | LiF200 | 30/100 | fine | FC |
| I | Lα | LiF200 | 30/100 | fine | FC |
| Cs | Lα | LiF200 | 30/100 | fine | FC |
| Ba | Lα | LiF200 | 30/100 | fine | FC |
| Ta | Lα | LiF200 | 60/50 | fine | SC |
| W | Lα | LiF200 | 60/50 | fine | SC |
| Hg | Lα | LiF200 | 60/50 | fine | SC |
| Tl | Lβ | LiF200 | 60/50 | fine | SC |
| Pb | Lβ | LiF200 | 60/50 | fine | SC |
| Bi | Lα | LiF200 | 60/50 | fine | SC |
| Th | Lα | LiF220 | 60/50 | fine | SC |
| U | Lα | LiF220 | 60/50 | Fine | SC |
| FC flow counter<br>SC scintillation counter | | | | | |

**Table C.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)<br>Hf – U (L) |
| Zr | Secondary | Cr – Sr (K)<br>Hf – Bi (L) |
| $Al_2O_3$ | Barkla | Mo - Ba (K) |
| CsI | Secondary | Mo – In (K) |
| Pd | Secondary | Fe – Mo (K)<br>Hf – U (L) |
| $B_4C$ | Barkla | Fe – Mo (K)<br>Hf – U (L) |
| Ge | Secondary | Cr – Zn (K)<br>Hf – Ta (L) |
| Zn | Secondary | Ti – Ni (K) |
| Co | Secondary | K – Mn (K)<br>Cd – La (L) |
| Ti | Secondary | P – Ca (K) |
| Si | Secondary | Na – Al (K) |
| Al | Secondary | Na – Mg (K) |
| HOPG | Bragg | Na – Sr (K)<br>Y – Hf (L) |
| (K) Kα radiation<br>(L) Lα radiation | | |

# Annex D
(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 D.1 — Reference materials applicable for XRF-analysis**

| **Identification** | | **Matrix** |
|---|---|---|
| BCR-141R | Institute for Reference Materials and Measurements | Calcareous loam soil |
| BCR-142R | Institute for Reference Materials and Measurements | Light sandy soil |
| BCR-143R | Institute for Reference Materials and Measurements | Sewage sludge soil |
| BCR-667 | Institute for Reference Materials and Measurements | Estuarine sediment |
| ERM-CC690 | Institute for Reference Materials and Measurements | Calcareous soil |
| BCR-144R | Institute for Reference Materials and Measurements | Sewage sludge |
| BCR-145R | Institute for Reference Materials and Measurements | Sewage sludge |
| BCR-146R | Institute for Reference Materials and Measurements | Sewage sludge |
| BCR-038 | Institute for Reference Materials and Measurements | Fly ash |
| GSS-1 up to 16 | National Research Centre for Certified Reference Materials (NRCCRM), China | Soil |
| SO-1 up to 4 | Canadian Certified Reference Materials (CCRMP) | Soil |
| SARM 42 | SACCRM, South Africa | Soil |
| GSD-1 up to 12 | National Research Centre for Certified Reference Materials (NRCCRM), China | Sediments |
| SARM 51 | SACCRM, South Africa | Sediment |
| SARM 52 | SACCRM, South Africa | Sediment |
| LKSD-1 up to 4 | Canadian Certified Reference Materials (CCRMP) | Sediment |
| STSD-1 up to 4 | Canadian Certified Reference Materials (CCRMP) | Sediment |
| TILL-1 up to 3 | Canadian Certified Reference Materials (CCRMP) | Soil |
| N2709 | National Institute of Standards & Technology (NIST) | Soil |
| N2710 | National Institute of Standards & Technology (NIST) | Soil |
| N2711 | National Institute of Standards & Technology (NIST) | Soil |
| N1633b | National Institute of Standards & Technology (NIST) | Fly ash |
| N2689 | National Institute of Standards & Technology (NIST) | Fly ash |
| N2690 | National Institute of Standards & Technology (NIST) | Fly ash |
| N2691 | National Institute of Standards & Technology (NIST) | Fly ash |
| 188-WT-H | SPEX Certiprep, UK | City Treatment Sewage Sludge |
| 188-WT-M | SPEX Certiprep, UK | City Treatment Sewage Sludge |
| 188-WT-L | SPEX Certiprep, UK | City Treatment Sewage Sludge |
| BAM-U110 | Federal Institute for Materials Research and Testing | Wetland Soil |

NOTE This list may be incomplete.

# Annex E
(informative)

# Validation

An inter-laboratory comparison supported by DIN was organized by CEN/TC 292 WG 3 in May 2006/August 2006 with participants from 7 member countries. For the inter-laboratory comparison two soil and three waste samples 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: soil sample of a sandy-loamy arable soil taken fifty meters beside a highway in Germany, homogenised and homogeneity tested by UBA (Federal Environment Agency).
- Sample 2: sample of contaminated soil of an area subject to periodic flooding of the Saale river in Germany, sandy silt, certified as soil reference material BAM-U110 [14].
- Sample 3: fly ash sample of a household waste incineration plant, homogenised and homogeneity tested by BAM (Federal Institute for Materials Research and Testing).
- Sample 4: ink waste sample, cited by (3) as SAMPLE CEN8/99, homogeneity tested by EU DG JRC (European Commission’s DG Joint Research Centre) and used for validation of the digestion standards EN 13656 and EN 13657 [15].
- Sample 5: electronic sludge, cited by (3) as SAMPLE CEN9/99, homogeneity tested by EU DG JRC (European Commission’s DG Joint Research Centre) and used for validation of the digestion standards EN 13565 and EN 13657 [15].

All the samples were sent to the participating laboratories as dried, fine grinded less than 90 µm, and homogenised material.

The samples were analysed using ED-XRF and WD-XRF instrumentation as well. As sample preparation methods the pressed pellet and the fused bead technique were applied depending on the available laboratory equipment. For each type of sample and each preparation method 2 test samples were prepared (pellets or beads) and analysed in duplicate. Finally, for each combination 4 results were reported.

Fifteen volunteer laboratories received the samples and all of them transmitted data. For sample 4 and 5 no data from the fused bead preparation method were reported because the commonly used fused bead method was not applicable for this type of samples.

The evaluation of the data was done according to ISO 5725-2, the principal steps of Figure 3 were followed strictly. According to this procedure, the data of two labs were removed. The maximum number of laboratories providing results for the statistical evaluation was therefore thirteen.

For the statistical evaluation the data of the ED-XRF and the WD-XRF technique were combined resulting in up to 14 different data sets for each element. For each sample and preparation method, i.e. pressed pellet or fused bead, the data were evaluated separately. Outliers were determined and eliminated according to ISO 5725-2 using the test of Mandel statistics combined with Grubbs test. The program used for statistical evaluation of the data and calculation of the performance characteristics was written in SPSS [16].

Tables E.1 through E.8 show the performance characteristics of the 5 samples. Results obtained by the pressed pellet preparation method are presented for sample 1 through 5, while for the fused bead method only results from sample 1, 2 and 3 are available. Repeatability and reproducibility were calculated according to the definitions given by ISO 5725-2.

**Table E.1 — Validation data of sample 1 (soil) – pressed pellet method**

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|
| Na | 12 | 40 | 4 | 8 182 | 2 402 | 29 % | 492 | 6 % | 8 100 |
| Mg | 12 | 40 | 4 | 3 930 | 947 | 24 % | 238 | 6 % | 3 800 |
| Al | 12 | 44 | 4 | 45 039 | 3 469 | 8 % | 784 | 2 % | 38 000 |
| Si | 13 | 46 | 0 | 317 432 | 44 283 | 14 % | 4 204 | 1 % | n.d. |
| P | 11 | 44 | 4 | 1 111 | 409 | 37 % | 26 | 2 % | 820 |
| S | 13 | 46 | 0 | 1 011 | 358 | 35 % | 47 | 5 % | n.d. |
| Cl | 12 | 29 | 4 | 103 | 53 | 51 % | 25 | 24 % | n.d. |
| K | 12 | 46 | 4 | 18 000 | 2 200 | 12 % | 240 | 1 % | 17 000 |
| Ca | 14 | 48 | 0 | 5 353 | 1 617 | 30 % | 149 | 3 % | 6 400 |
| Ti | 13 | 46 | 0 | 1 824 | 368 | 20 % | 37 | 2 % | 1 800 |
| V | 13 | 50 | 0 | 38 | 14 | 38 % | 4 | 10 % | 35 |
| Cr | 12 | 50 | 2 | 64 | 20 | 31 % | 10 | 16 % | 50 |
| Mn | 12 | 46 | 4 | 362 | 40 | 11 % | 6 | 2 % | 390 |
| Fe | 12 | 46 | 4 | 12 190 | 974 | 8 % | 135 | 1 % | 11 000 |
| Co | 12 | 27 | 4 | 6 | 4 | 62 % | 2 | 27 % | n.d. |
| Ni | 12 | 47 | 4 | 15 | 5 | 31 % | 1 | 9 % | 14 |
| Cu | 12 | 49 | 4 | 25 | 7 | 28 % | 2 | 7 % | 34 |
| Zn | 12 | 48 | 0 | 99 | 15 | 15 % | 3 | 3 % | 120 |
| As | 12 | 44 | 4 | 8 | 4 | 47 % | 1 | 13 % | 14 |
| Br | 12 | 42 | 4 | 11 | 3 | 31 % | 2 | 21 % | n.d. |
| Rb | 12 | 50 | 4 | 97 | 9 | 10 % | 1 | 1 % | 97 |
| Sr | 12 | 50 | 4 | 79 | 9 | 11 % | 1 | 1 % | 80 |
| Y | 13 | 48 | 0 | 16 | 4 | 27 % | 1 | 7 % | 9 |
| Zr | 12 | 50 | 4 | 205 | 19 | 9 % | 8 | 4 % | 320 |
| Nb | 11 | 44 | 8 | 8 | 3 | 35 % | 1 | 8 % | 18 |
| Sn | 12 | 28 | 4 | 6 | 2 | 35 % | 1 | 25 % | n.d. |
| Cs | 12 | 26 | 4 | 10 | 5 | 47 % | 3 | 26 % | 8 |
| Ba | 12 | 50 | 4 | 404 | 64 | 16 % | 13 | 3 % | 360 |
| W | 12 | 31 | 4 | 12 | 15 | 125 % | 2 | 17 % | 8 |
| Pb | 12 | 50 | 4 | 78 | 11 | 14 % | 3 | 3 % | 86 |
| Th | 12 | 40 | 4 | 8 | 3 | 37 % | 1 | 13 % | n.d. |

**Table E.2 — Validation data of sample 1 (soil) – fused bead method**

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|
| Na | 5 | 20 | 4 | 10 075 | 836 | 8 % | 518 | 5 % | 8 100 |
| Mg | 5 | 20 | 4 | 3 054 | 347 | 11 % | 89 | 3 % | 3 800 |
| Al | 5 | 20 | 0 | 42 233 | 980 | 2 % | 775 | 2 % | 38 000 |
| Si | 5 | 20 | 0 | 350 701 | 7 042 | 2 % | 3 069 | 1 % | n.d. |
| P | 5 | 20 | 0 | 707 | 203 | 29 % | 58 | 8 % | 820 |
| K | 5 | 20 | 4 | 19 282 | 464 | 2 % | 187 | 1 % | 17 000 |
| Ca | 6 | 24 | 4 | 4 952 | 215 | 4 % | 67 | 1 % | 6 400 |
| Ti | 5 | 20 | 0 | 1 849 | 109 | 6 % | 45 | 2 % | 1 800 |
| V | 5 | 10 | 2 | 35 | 2 | 6 % | 4 | 11 % | 35 |
| Cr | 5 | 11 | 0 | 67 | 15 | 22 % | 5 | 7 % | 50 |
| Mn | 5 | 16 | 0 | 362 | 50 | 14 % | 14 | 4 % | 390 |
| Fe | 5 | 20 | 0 | 12 013 | 2 058 | 17 % | 275 | 2 % | 11 000 |
| Cu | 5 | 10 | 0 | 69 | 14 | 21 % | 5 | 7 % | 34 |
| Ba | 5 | 12 | 4 | 344 | 73 | 21 % | 25 | 7 % | 360 |
| Pb | 5 | 10 | 2 | 82 | 1 | 1 % | 2 | 2 % | 86 |

**Table E.3 — Validation data of sample 2 (contaminated soil) – pressed pellet method**

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] | $m_{CERT}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|---|
| Na | 13 | 34 | 4 | 4 564 | 1 478 | 32 % | 549 | 12 % | 4 700 | n.d. |
| Mg | 14 | 44 | 0 | 10 338 | 1 812 | 18 % | 963 | 9 % | 11 000 | *8 380* |
| Al | 12 | 47 | 8 | 55 589 | 3 792 | 7 % | 583 | 1 % | 67 000 | *50 382* |
| Si | 13 | 51 | 4 | 239 921 | 26 488 | 11 % | 1 720 | 1 % | n.d. | n.d. |
| P | 12 | 47 | 4 | 5 305 | 1 078 | 20 % | 78 | 1 % | 4 800 | n.d. |
| S | 13 | 50 | 4 | 13 665 | 2 181 | 16 % | 314 | 2 % | n.d. | n.d. |
| Cl | 13 | 51 | 4 | 1 782 | 395 | 22 % | 103 | 6 % | n.d. | n.d. |
| K | 12 | 51 | 8 | 20 451 | 1 648 | 8 % | 195 | 1 % | 19 000 | *20 381* |
| Ca | 14 | 55 | 4 | 46 924 | 7 751 | 17 % | 1 065 | 2 % | 47 000 | *40 638* |
| Ti | 14 | 51 | 0 | 3 474 | 521 | 15 % | 50 | 1 % | 3 300 | *3 206* |
| V | 14 | 52 | 0 | 65 | 28 | 42 % | 12 | 18 % | 62 | *68* |
| Cr | 14 | 55 | 0 | 257 | 37 | 15 % | 8 | 3 % | 220 | 230 |
| Mn | 14 | 51 | 0 | 681 | 112 | 17 % | 10 | 2 % | 680 | 621 |
| Fe | 14 | 51 | 0 | 30 840 | 3 976 | 13 % | 404 | 1 % | 25 000 | *28 229* |
| Co | 14 | 43 | 0 | 23 | 9 | 39 % | 3 | 13 % | 14 | 16 |
| Ni | 13 | 55 | 4 | 108 | 14 | 13 % | 4 | 3 % | 87 | 101 |
| Cu | 13 | 55 | 4 | 265 | 28 | 10 % | 7 | 3 % | 240 | 263 |
| Zn | 12 | 51 | 4 | 992 | 52 | 5 % | 14 | 1 % | 1 000 | 1 000 |
| As | 12 | 44 | 8 | 14 | 4 | 30 % | 2 | 11 % | 20 | 16 |
| Se | 12 | 19 | 3 | 2 | 1 | 27 % | 1 | 25 % | n.d. | n.d. |
| Br | 12 | 48 | 5 | 17 | 4 | 25 % | 1 | 5 % | n.d. | n.d. |
| Rb | 13 | 52 | 4 | 92 | 6 | 7 % | 2 | 2 % | 91 | n.d. |
| Sr | 13 | 52 | 4 | 277 | 22 | 8 % | 5 | 2 % | 280 | *277* |
| Y | 13 | 52 | 4 | 24 | 4 | 16 % | 1 | 4 % | 17 | n.d. |
| Zr | 14 | 52 | 0 | 306 | 43 | 14 % | 8 | 3 % | 190 | n.d. |
| Nb | 13 | 44 | 4 | 14 | 4 | 30 % | 1 | 5 % | 23 | n.d. |
| Mo | 13 | 28 | 4 | 4 | 1 | 28 % | 1 | 20 % | n.d. | n.d. |
| Ag | 12 | 26 | 2 | 5 | 2 | 33 % | 1 | 26 % | 7 | n.d. |
| Cd | 14 | 24 | 0 | 8 | 2 | 29 % | 1 | 17 % | n.d. | 7 |
| Sn | 13 | 45 | 1 | 23 | 7 | 31 % | 3 | 13 % | 51 | n.d. |
| Sb | 12 | 27 | 4 | 7 | 2 | 30 % | 2 | 26 % | n.d. | n.d. |
| I | 13 | 16 | 1 | 7 | 2 | 29 % | 4 | 62 % | n.d. | n.d. |
| Cs | 13 | 20 | 4 | 15 | 4 | 28 % | 6 | 40 % | 8 | n.d. |
| Ba | 14 | 55 | 0 | 1 545 | 276 | 18 % | 44 | 3 % | 1 400 | *1 488* |
| Hg | 12 | 47 | 8 | 52 | 11 | 21 % | 2 | 4 % | 37 | 52 |
| Tl | 13 | 16 | 4 | 3 | 1 | 33 % |  |  | n.d. | n.d. |
| Pb | 14 | 55 | 0 | 197 | 33 | 17 % | 5 | 3 % | 210 | 197 |
| Bi | 14 | 19 | 0 | 2 | 1 | 52 % | 1 | 76 % | n.d. | n.d. |
| Th | 12 | 43 | 8 | 10 | 2 | 20 % | 1 | 15 % | n.d. | n.d. |
| U | 12 | 31 | 7 | 7 | 3 | 46 % | 2 | 30 % | 6 | n.d. |

**Table E.4 — Validation data of sample 2 (contaminated soil) – fused bead method**

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] | $m_{CERT}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|---|
| Na | 4 | 19 | 3 | 5 958 | 582 | 10% | 236 | 4 % | 4 700 | n.d. |
| Mg | 5 | 19 | 0 | 8 658 | 789 | 9 % | 340 | 4 % | 11 000 | *8 380* |
| Al | 5 | 19 | 0 | 50 039 | 1 004 | 2 % | 487 | 1 % | 67 000 | *50 382* |
| Si | 5 | 19 | 0 | 257 753 | 3 623 | 1 % | 1 435 | 1 % | n.d. | n.d. |
| P | 4 | 19 | 3 | 3 555 | 177 | 5 % | 47 | 1 % | 4 800 | n.d. |
| K | 4 | 19 | 4 | 19 968 | 733 | 4 % | 125 | 1 % | 19 000 | *20 381* |
| Ca | 5 | 23 | 4 | 41 361 | 1 061 | 3 % | 430 | 1 % | 47 000 | *40 638* |
| Ti | 5 | 19 | 0 | 3 397 | 205 | 6 % | 36 | 1 % | 3 300 | *3 206* |
| Cr | 5 | 12 | 0 | 246 | 28 | 12 % | 7 | 3 % | 220 | 230 |
| Mn | 5 | 16 | 0 | 623 | 14 | 2 % | 15 | 2 % | 680 | 621 |
| Fe | 5 | 19 | 0 | 28 921 | 2 144 | 7 % | 2 150 | 7 % | 25 000 | *28 229* |
| Cu | 5 | 11 | 0 | 263 | 81 | 31 % | 32 | 12 % | 240 | 263 |
| Zn | 4 | 7 | 0 | 1 024 | 178 | 17 % | 17 | 2 % | 1 000 | 1 000 |
| Ba | 5 | 11 | 0 | 1 780 | 495 | 28 % | 132 | 7 % | 1 400 | *1 488* |

**Table E.5 — Validation data of sample 3 (fly ash) – pressed pellet method**

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|
| Na | 13 | 43 | 4 | 14 548 | 3 484 | 24 % | 515 | 4 % | 15 000 |
| Mg | 13 | 44 | 4 | 13 218 | 2 650 | 20 % | 1 385 | 10 % | 12 000 |
| Al | 13 | 47 | 4 | 53 651 | 6 836 | 13 % | 680 | 1 % | 48 000 |
| Si | 13 | 51 | 4 | 176 582 | 25 716 | 15 % | 1 778 | 1 % | n.d. |
| P | 12 | 47 | 4 | 5 257 | 1 036 | 20 % | 112 | 2 % | 4 100 |
| S | 12 | 47 | 8 | 14 592 | 2 483 | 17 % | 185 | 1 % | n.d. |
| Cl | 13 | 51 | 4 | 5 088 | 831 | 16 % | 147 | 3 % | n.d. |
| K | 14 | 51 | 0 | 13 109 | 1 486 | 11 % | 202 | 2 % | 12 000 |
| Ca | 14 | 55 | 4 | 124 013 | 14 792 | 12 % | 3 144 | 3 % | 100 000 |
| Ti | 14 | 51 | 0 | 5 829 | 829 | 14 % | 99 | 2 % | 5 100 |
| V | 13 | 45 | 4 | 46 | 14 | 29 % | 6 | 13 % | 46 |
| Cr | 12 | 55 | 7 | 291 | 31 | 11 % | 8 | 3 % | 190 |
| Mn | 14 | 51 | 0 | 1 161 | 189 | 16 % | 23 | 2 % | 1200 |
| Fe | 14 | 51 | 0 | 45 995 | 3 994 | 9 % | 498 | 1 % | 43 000 |
| Co | 13 | 42 | 4 | 28 | 14 | 49 % | 6 | 20 % | 17 |
| Ni | 13 | 55 | 4 | 104 | 19 | 19 % | 4 | 4 % | 100 |
| Cu | 12 | 55 | 8 | 1 528 | 114 | 7 % | 17 | 1 % | 1 600 |
| Zn | 11 | 51 | 8 | 4 342 | 273 | 6 % | 81 | 2 % | 4 400 |
| As | 13 | 22 | 4 | 12 | 8 | 62 % | 3 | 27 % | 16 |
| Br | 13 | 31 | 4 | 10 | 2 | 18 % | 1 | 7 % | n.d. |
| Rb | 13 | 52 | 4 | 51 | 5 | 10 % | 2 | 4 % | 50 |
| Sr | 12 | 52 | 8 | 337 | 23 | 7 % | 7 | 2 % | 350 |
| Y | 13 | 44 | 4 | 16 | 4 | 22 % | 1 | 5 % | 11 |
| Zr | 13 | 52 | 4 | 225 | 28 | 13 % | 9 | 4 % | 170 |
| Nb | 13 | 36 | 4 | 11 | 2 | 22 % | 1 | 8 % | 19 |
| Mo | 12 | 34 | 6 | 14 | 3 | 24 % | 3 | 23 % | 10 |
| Ag | 13 | 30 | 1 | 10 | 3 | 35 % | 1 | 13 % | 11 |
| Cd | 14 | 33 | 0 | 12 | 4 | 34 % | 2 | 16 % | 12 |
| Sn | 13 | 55 | 4 | 283 | 42 | 15 % | 8 | 3 % | 200 |
| Sb | 13 | 54 | 4 | 47 | 17 | 36 % | 3 | 7 % | 47 |
| Ba | 13 | 55 | 4 | 1 867 | 231 | 12 % | 50 | 3 % | 1 800 |
| W | 13 | 23 | 4 | 42 | 34 | 81 % | 37 | 88 % | 25 |
| Pb | 12 | 51 | 8 | 1 210 | 131 | 11 % | 29 | 2 % | 1 400 |
| Bi | 14 | 21 | 0 | 3 | 2 | 48 % | 1 | 30 % | 5 |
| Th | 13 | 34 | 2 | 14 | 6 | 44 % | 3 | 19 % | n.d. |

**Table E.6 — Validation data of sample 3 (fly ash) – fused bead method**

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|
| Na | 5 | 20 | 4 | 17 940 | 1 402 | 8 % | 666 | 4% | 15 000 |
| Mg | 5 | 20 | 0 | 12 848 | 744 | 6 % | 400 | 3% | 12 000 |
| Al | 5 | 20 | 0 | 54 578 | 2 426 | 4 % | 1 786 | 3% | 48 000 |
| Si | 5 | 20 | 0 | 197 167 | 5 562 | 3 % | 3 194 | 2% | n.d. |
| P | 5 | 20 | 4 | 4 695 | 220 | 5 % | 89 | 2% | 4 100 |
| K | 5 | 20 | 0 | 12 719 | 761 | 6 % | 294 | 2% | 12 000 |
| Ca | 6 | 24 | 4 | 114 789 | 5 223 | 5 % | 1 961 | 2% | 100 000 |
| Ti | 5 | 20 | 0 | 6 021 | 401 | 7 % | 119 | 2% | 5 100 |
| V | 5 | 11 | 0 | 47 | 26 | 54 % | 8 | 18% | 46 |
| Cr | 5 | 12 | 0 | 302 | 28 | 9 % | 24 | 8% | 190 |
| Mn | 5 | 16 | 0 | 1 240 | 41 | 3 % | 20 | 2% | 1 200 |
| Fe | 5 | 20 | 1 | 46 690 | 2 101 | 4 % | 563 | 1% | 43 000 |
| Cu | 5 | 12 | 0 | 1 631 | 226 | 14 % | 58 | 4% | 1 600 |

### Table E.7 — Validation data of sample 4 (ink waste) – pressed pellet method

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] | $m_{EUJRC}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|---|
| Na | 13 | 32 | 6 | 6 119 | 2 146 | 35 % | 341 | 6 % | 4 200 | 6787 |
| Mg | 13 | 39 | 12 | 1 192 | 557 | 47 % | 90 | 8 % | 960 | 960 |
| Al | 13 | 41 | 9 | 2 536 | 683 | 27 % | 194 | 8 % | 3 200 | 2 111 |
| Si | 13 | 48 | 4 | 15 980 | 4 186 | 26 % | 364 | 2 % | n.d. | n.d. |
| P | 12 | 44 | 4 | 17 004 | 5 006 | 29 % | 240 | 1 % | 12 000 | 14 005 |
| S | 13 | 44 | 8 | 35 353 | 5 774 | 16 % | 478 | 1 % | n.d. | 33 032 |
| Cl | 13 | 48 | 4 | 4 630 | 1 961 | 42 % | 1 436 | 31 % | n.d. | n.d. |
| K | 13 | 44 | 8 | 1 032 | 388 | 38 % | 44 | 4 % | 510 | 965 |
| Ca | 14 | 52 | 4 | 124 307 | 57 376 | 46 % | 5 685 | 5 % | 110 000 | 107 315 |
| Ti | 13 | 44 | 0 | 318 | 112 | 35 % | 11 | 3 % | 340 | 232 |
| V | 13 | 32 | 0 | 23 | 13 | 55 % | 5 | 23 % | 20 | 15 |
| Cr | 13 | 52 | 4 | 5 005 | 1770 | 35 % | 138 | 3 % | 3 400 | 3 612 |
| Mn | 13 | 48 | 4 | 717 | 320 | 45 % | 18 | 2 % | 580 | 530 |
| Fe | 13 | 48 | 4 | 105 308 | 37 749 | 36 % | 1 364 | 1 % | 74 000 | 74 271 |
| Co | 13 | 38 | 8 | 30 | 14 | 49 % | 5 | 19 % | 13 | 14 |
| Ni | 13 | 37 | 6 | 25 | 12 | 50 % | 3 | 12 % | 19 | 23 |
| Cu | 13 | 52 | 4 | 16 530 | 6 586 | 40 % | 163 | 1 % | 11 000 | 12 429 |
| Zn | 12 | 48 | 4 | 1 504 | 584 | 39 % | 28 | 2 % | 1 200 | 1 203 |
| Br | 13 | 26 | 2 | 16 | 4 | 28 % | 2 | 11 % | n.d. | n.d. |
| Rb | 13 | 19 | 3 | 11 | 3 | 24 % | 2 | 14 % | <5 | n.d. |
| Sr | 13 | 52 | 4 | 152 | 61 | 40 % | 6 | 4 % | 120 | 117 |
| Y | 13 | 14 | 2 | 10 | 2 | 18 % | 3 | 31 % | <5 | n.d. |
| Zr | 13 | 47 | 4 | 30 | 13 | 43 % | 5 | 16 % | 41 | n.d. |
| Mo | 13 | 28 | 3 | 5 | 2 | 46 % | 1 | 21 % | 6 | 5 |
| Sn | 13 | 16 | 2 | 5 | 2 | 46 % | 2 | 42 % | 19 | 2 |
| Ba | 13 | 40 | 0 | 121 | 39 | 32 % | 10 | 9 % | 100 | 101 |
| Pb | 13 | 52 | 4 | 6 735 | 3 287 | 49 % | 105 | 2 % | 5 900 | 5 894 |
| Th | 13 | 20 | 4 | 26 | 17 | 67 % | 3 | 10 % | n.d. | n.d. |

### Table E.8 — Validation data of sample 5 (electronic sludge) – pressed pellet method

| Element | L | N | O | m [mg/kg] | $S_R$ [mg/kg] | $V_R$ [%] | $S_r$ [mg/kg] | $V_r$ [%] | $m_{ICPMS}$ [mg/kg] | $m_{EUJRC}$ [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|---|
| Na | 12 | 36 | 0 | 16 970 | 7 880 | 46 % | 1 445 | 9% | 19 000 | 13 207 |
| Mg | 12 | 32 | 4 | 2 712 | 1 649 | 61 % | 1 564 | 58 % | 2 000 | 2 163 |
| Al | 12 | 40 | 0 | 114 509 | 20 552 | 18 % | 1 926 | 2 % | 77 000 | 75 505 |
| Si | 12 | 44 | 4 | 26 278 | 5 565 | 21 % | 598 | 2 % | n.d. | n.d. |
| P | 11 | 40 | 0 | 5 776 | 1 383 | 24 % | 186 | 3 % | 4 100 | 4 864 |
| S | 12 | 40 | 4 | 73 081 | 12 698 | 17 % | 1 114 | 2 % | n.d. | 68 041 |
| Cl | 12 | 44 | 0 | 7 684 | 2 536 | 33 % | 130 | 2 % | n.d. | n.d. |
| K | 12 | 44 | 4 | 3 025 | 790 | 26 % | 71 | 2 % | 2 700 | 3 130 |
| Ca | 12 | 44 | 4 | 68 820 | 9 948 | 14 % | 766 | 1 % | 75 000 | 54 808 |
| Ti | 12 | 44 | 4 | 132 | 41 | 31 % | 6 | 5 % | 110 | 116 |
| V | 12 | 17 | 5 | 7 | | | 5 | 67 % | 11 | 6 |
| Cr | 12 | 44 | 0 | 101 | 28 | 28 % | 8 | 8 % | 110 | 85 |
| Mn | 12 | 44 | 4 | 777 | 245 | 31 % | 54 | 7 % | 610 | 622 |
| Fe | 12 | 44 | 4 | 7 016 | 1 150 | 16 % | 170 | 2 % | 6 100 | 5 055 |
| Ni | 12 | 48 | 0 | 2 133 | 514 | 24 % | 59 | 3 % | 1 700 | 1 730 |
| Cu | 12 | 48 | 0 | 106 900 | 29 992 | 28 % | 1 246 | 1 % | 78 000 | 95 369 |
| Zn | 11 | 44 | 8 | 255 | 102 | 40 % | 7 | 3 % | 230 | 249 |
| Br | 12 | 36 | 4 | 91 | 15 | 17 % | 5 | 6 % | n.d. | n.d. |
| Rb | 12 | 33 | 0 | 28 | 11 | 40 % | 1 | 4 % | 20 | n.d. |
| Sr | 12 | 48 | 4 | 203 | 50 | 25 % | 4 | 2 % | 210 | 175 |
| Zr | 12 | 44 | 4 | 33 | 17 | 52 % | 5 | 16 % | 34 | n.d. |
| Nb | 12 | 19 | 0 | 23 | 27 | 115 % | 1 | 5 % | 5 | n.d. |
| Mo | 12 | 35 | 4 | 9 | 5 | 59 % | 2 | 22 % | 8 | 4 |
| Cd | 12 | 17 | 3 | 21 | 27 | 125 % | 7 | 31 % | n.d. | 1 |
| Sn | 12 | 48 | 4 | 22 385 | 4 661 | 21 % | 397 | 2 % | 17 000 | 16 565 |
| I | 12 | 17 | 1 | 77 | 73 | 95 % | 17 | 23 % | n.d. | n.d. |
| Ba | 12 | 39 | 0 | 78 | 31 | 40 % | 8 | 10 % | 86 | 68 |
| Ta | 12 | 21 | 5 | 244 | 135 | 55 % | 26 | 11 % | n.d. | n.d. |
| Pb | 12 | 48 | 0 | 9 754 | 2 646 | 27 % | 171 | 2 % | 10 000 | 9 380 |
| Th | 12 | 26 | 4 | 34 | 26 | 77 % | 3 | 10 % | n.d. | n.d. |

| | |
|---|---|
| L | number of accepted laboratories |
| N | number of accepted results |
| O | number of outliers removed |
| $m_{XRF}$ | mean content of elements specified calculated from N data sets, in mg/kg dry matter |
| $S_R$ | reproducibility standard deviation |
| $S_r$ | repeatability standard deviation |
| $V_R$ | relative reproducibility standard deviation |
| $V_r$ | relative repeatability standard deviation |
| $m_{ICPMS}$ | content of elements specified determined by ICP/MS technique after HNO3/HCL/HF-digestion, in mg/kg dry matter |
| $m_{cert}$ | certified content of elements according [14], in mg/kg dry matter |
| $m_{EUJRC}$ | mean content of elements specified as given by [15], in mg/kg dry matter |
| n.d. | not determined |

NOTE Numbers given in italics indicate informative data according the certification report [2].

### Discussion of the results

The validation data show that in general the standard is fit for purpose. In some cases, there are rather high standard deviations (up to 50 %), especially in case low elemental contents below 100 ppb. The fused bead sample preparation technique has been proved to be more accurate. Matrix-specific calibration will increase the accuracies of the results.

Comparison of the means of the two preparation methods of sample 1 and 2 (soil) and 3 (fly ash) show comparable results for most elements within the calculated reproducibility. The results of sample 2 obtained by method EN 15309 are in good agreement with the certified values [14].

Mean concentrations and reproducibility standard deviations of sample 4 (ink waste) are in most cases evidently higher than those reported in EN 13656 due to the results of three labs which have not been identified as outliers according to ISO 5725. The high loss on ignition (around 60 %) of this sample and the matrix properties are possible explanations.

The validation clearly indicates that for soil like matrices the fused bead sample preparation is the method of choice for main group elements, whereas the pressed pellet method is generally applicable with good results for all elements. On the other hand the validation proves that the fused bead sample preparation technique is not be used in case of waste like matrices as sludges.

# Bibliography

[1] ASTM D 6052-97, *Standard Test Method for Preparation and Elemental Analysis of Liquid Hazardous Waste by Energy-Dispersive X-Ray Fluorescence*

[2] DIN 51418-1, *Röntgenspektralanalyse — Röntgenemissions- und Röntgenfluoreszenz-Analyse (RFA) — Teil 1: Allgemeine Begriffe und Grundlagen*

[3] DIN 51418-2, *Röntgenspektralanalyse — Röntgenemissions- und Röntgenfluorenszenz-Analyse (RFA) — Teil 2: Begriffe und Grundlagen zur Messung, Kalibrierung und Auswertung*

[4] EN 13656, *Characterization of waste — Microwave assisted digestion with hydrofluoic (HF), nitric ($HNO_3$) and hydrochloric (HCl) acid mixture for subsequent determination of elements*

[5] EN 13657, *Characterization of waste — Digestion for subsequent determination of aqua regia soluble portion of elements*

[6] IEC 111/24/CD, *Procedures for the Determination of Levels of Regulated Substances in Electrotechnical Products*

[7] ISO 9516-1:2003, *Iron ores — Determination of various elements by X-ray fluorescence spectrometry — Part 1: Comprehensive procedure*

[8] ISO 12980:2000, *Carbonaceous material used in the production of aluminium — Green coke and calcined coke for electrodes — Analysis using an X-ray fluorescence method*

[9] ISO Guide 32, *Calibration in analytical chemistry and use of certified reference materials*

[10] ISO Guide 33, *Use of certified reference materials*

[11] ISO Guide 34, *General requirements for the competence of reference material producers*

[12] ISO TC 183 N691 E, XRF Analysis of Cu, Pb, Zn, Ni ores and their related products

[13] G.R. Lachance and F. Claisse, Quantitative X-ray fluorescence analysis – Theory and application, ISBN 0-471-95167-6, John Wiley & Sons, West Sussex, England, 1995.

[14] Certification Report CRM BAM-U110; BERICHT zur Zertifizierung der Gesamtgehalte und der mit Königswasser extrahierbaren Gehalte der Elemente As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb und Zn in einer Bodenprobe - Zertifiziertes Referenzmaterial BAM - U110), Bundesanstalt für Materialforschung und -prüfung (BAM) ( http://www.bam.de/index_en.htm ), FG I.1 - Anorganisch-chemische Analytik; Referenzmaterialien, Richard-Willstätter-Str. 11, D - 12489 Berlin, September 2006

[15] H. Muntau, M.I. Kisser, C. Yuste, A. Giove and M. Bianchi, The validation of CEN draft standards for the analysis of wastes, JRC, EUR 19680 EN, 2000.

[16] A. Bühl and P. Zöfel, SPSS 11 Einführung in die moderne Datenanalyse unter Windows, Scientific Tools, Pearson Studium, Munich, ed. 8, 2002.

[17] CEN/TR 15018, *Characterisation of waste — Digestion of waste samples using alkali-fusion techniques*

[18] EN ISO 12677, *Chemical analysis of refractory products by XRF — Fused cast bead method (ISO 12677:2003)*

[19] ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[20] ISO 14869-2:2002, *Soil quality — Dissolution for the determination of total element content — Dissolution of alkaline fusion*

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