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Soil quality — Determination of elemental composition by X-ray fluorescence

Qualité du sol — Détermination de la composition élémentaire par fluorescence X

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Contents

Page

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Foreword

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The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

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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 analysed, the elements to be determined, the detection limits required, and the measuring times. 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 such as waste, it is generally difficult to set up a calibration with matrix-matched reference materials.

Therefore, this International 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 materials as waste, sludge, and soil in Annex A which provides a total element characterization at a semi-quantitative level. The calibration is based on matrix-independent calibration curves, previously set up by the manufacturer.

The technical content of this International Standard is identical with the European Standard EN 15309:2007.

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Soil quality — Determination of elemental composition by X-ray fluorescence

1 Scope

This International 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 International 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 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 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*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

EN 14346:2006, *Characterization of waste — Calculation of dry matter by determination of dry residue or water content*

EN 15002:2006, *Characterization of waste — Preparation of test portions from the laboratory sample*

3 Terms and definitions

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

NOTE See References [11] and [14] 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 the determination of the analyte content

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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 strike 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 monitor
physically stable sample used to correct for instrumental drift

3.7
emitted sample X-ray
radiation emitted by a 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

Note 1 to entry: This is expressed in cm^2/g.

Note 2 to entry: The mass absorption coefficient is a function of the wavelength of the absorbed radiation and the atomic number of the absorbing element.

3.11
polarized excitation X-ray spectrometer
energy dispersive X-ray spectrometer where the excitation is performed by polarized radiation and the emitted X-ray fluorescence radiation is detected along the direction of polarization

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

[SOURCE: ISO 5725-2:1994]

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

3.15
primary X-ray
X-ray by which the sample is radiated

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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 can contain hazardous e.g. toxic, reactive, flammable, and 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 can be produced by microbiological or chemical activity are potentially flammable and pressurize 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 international and national regulations relevant to radiation protection.

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

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5 Principle

After a suitable preparation, if necessary, the sample is introduced into an 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, shall be able to analyse the elements according to the scope of this International 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 (such as 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 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 polarizing 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 can 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 ISO 12677 for compensation for moisture in flux).

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

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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 can be observed for some elements, e.g. Al, As, Ba, Ce, K, Na, and 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, and 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 strongly influences 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 can be difficult or can cause problems in case of waste-like matrices such 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 can 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 can 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.

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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 prEN 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 homogenized with a binder (7.1) in a ratio of sample:binder of 10:1 by weight. For the preparation of 40 mm in diameter pellets, about 10,0 g of sample is taken; for 32 mm in 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 types 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.

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 1 025 °C ± 25 °C until constant mass is reached. Determine the loss on ignition at the chosen 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.

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, and 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, and Tl, can occur during the fusion process. Also, Cu can be volatile if a bromide-releasing agent is used.

The flux (7.2) is added to the ignited material in a dilution ratio of sample:flux of 1:5 by weight. For the preparation of 40 mm in diameter beads, about 1,6 g of ignited sample is taken; for 32 mm in 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 can 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 can contain compounds that can damage the platinum crucibles during fusion.

NOTE 5 Different dilution factors can be used.

After fusion in a platinum-gold crucible (6.6) the melt is poured into a casting mould (6.7) to make a bead.

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

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10 Procedure

10.1 Analytical measurement conditions

10.1.1 Wavelength dispersive instruments

The analytical lines to be used and the suggested operating conditions are given in Table C.1. The settings are strongly dependent on the spectrometer configuration, e.g. the type of X-ray tube (Rh, Cr), tube power, available crystals, and type of collimators.

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:

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

where

I_p is the count rate of the element i, expressed as the number of counts per second;

I_b is the background count rate of the element i, expressed as the number of counts per second.

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, 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 the suggested operating conditions are given in Table C.2. The settings are strongly dependent on the spectrometer configuration, e.g. type of X-ray tube (Rh, Pd), tube power, available targets, and type of filters.

Intensities and background corrections

Deconvolution of the spectra and background correction are needed when analysing the samples with overlapping lines. Usually, XRF instruments are supplied with a specific software module for that purpose.

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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 can 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. Aside from 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.

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10.2.2 General calibration procedure

For calibration purposes, the measurement of analyte lines of samples of known composition is needed. Formula (3) implies a linear relationship between the intensity and the concentration.

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

where

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

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

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

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

Matrix effects have to be taken into account in X-ray spectrometry according to Formula (4):

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

where

M is the correction term due to the matrix effects.

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

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10.2.3 Internal standard correction using Compton (incoherent) scattering method

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

The Compton scatter method can be expressed as:

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

where

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

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

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

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

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

$I_{\mathrm{i,r}}$ is the intensity of the element i of the calibration reference material, expressed in 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 Formulae (6) and (7):

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

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

where

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

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

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

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

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

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

M is the matrix correction term;

α_{ij} is the correction coefficient (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 the 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 Formulae (6) and (7) 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 recognized producers is recommended (see Annex D) or synthetic mixtures of oxides can 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 can be necessary.

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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 (dependent 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.

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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 Kβ	PbLα BrKα	Compton or FP or MAC
Se	Kα		Compton or FP or MAC
Br	Kα	AsKβ	Compton or FP or MAC

Table 1 *(continued)*

Element	Line	Spectral line overlap	Type of matrix correction method
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 Lα	CrKβ	Compton or FP or MAC Alpha or FP
Cd	Kα Lα	AgLβ	Compton or FP or MAC Alpha or FP
Sn	Kα Lα	CoKα	Compton or FP or MAC Alpha or FP or MAC
Sb	Kα Lβ	CoKβ	Compton or FP or MAC Alpha or FP or MAC
Te	Kα Lα	SnLβ	Compton or FP or MAC Alpha or FP or MAC
I	Kα Lα		Compton or FP or MAC Alpha or FP or MAC
Cs	Kα Lα	ZnKα ILβ	Compton or FP or MAC Alpha or FP or MAC
Ba	Kα Lα	TiKα ILβ CuKβ	Compton or FP or MAC Alpha or FP or MAC
Ta	Lα	CuKα NiKβ	Compton or FP or MAC
W	Lα	TaLη	Compton or FP or MAC
Hg	Lα	WLβ	Compton or FP or MAC
Tl	Lβ	PbLβ	Compton or FP or MAC
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

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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 recognized producers is recommended (see Annex D) or synthetic mixtures of oxides can 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 can 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 is higher than those for pressed pellets.

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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 have 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 (dependent 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.

10.2.9 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, and 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.

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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 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 ISO/IEC 17025.

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

a) the description and identification of the laboratory sample;

b) which processes, procedures, and apparatus were used;

c) the results of the determination expressed in mg/kg dry matter or in mass percentages dry matter;

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

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

f) a reference to this International 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.

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Annex A
(informative)

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

A.1 Principle

The principle is identical with that 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 those described in 6.1 can be used; however, a specific software package, suitable to perform the XRF analysis without the use of calibration curves set up with dedicated reference samples, is applied. 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 by 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 optimized 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-dependent and contain two 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, and measurement times. The analytical program is always linked to a selected evaluation and calibration program. Actually, the same measurement conditions have to be applied

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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 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 can 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.

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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 these elements 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 can be possible to enter the matrix compounds, e.g. CH_2 for polymers, H_2O for water samples, and C for coal samples, to optimize 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.

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Annex B
(informative)

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

B.1 General

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 Figures B.1 to B.5 are described in ISO 11464 and EN 15002, explained in the normative part or otherwise given directly.

B.2 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.3 Preparation of powder samples

After milling/grinding of the sample to powder, the homogenized 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.4 Impregnation on powders

B.4.1 Impregnation on aluminium oxide

Place 15,000 g ± 0,005 g of aluminium oxide (pre-calcined 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.4.2 Impregnation on activated carbon

Weigh 4,000 g ± 0,005 g of sample, add 2,000 g ± 0,005 g of active carbon, and homogenize very well the mixture. Empty the active carbon/sample mixture from the bottle to the sample cup. The powder is

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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.

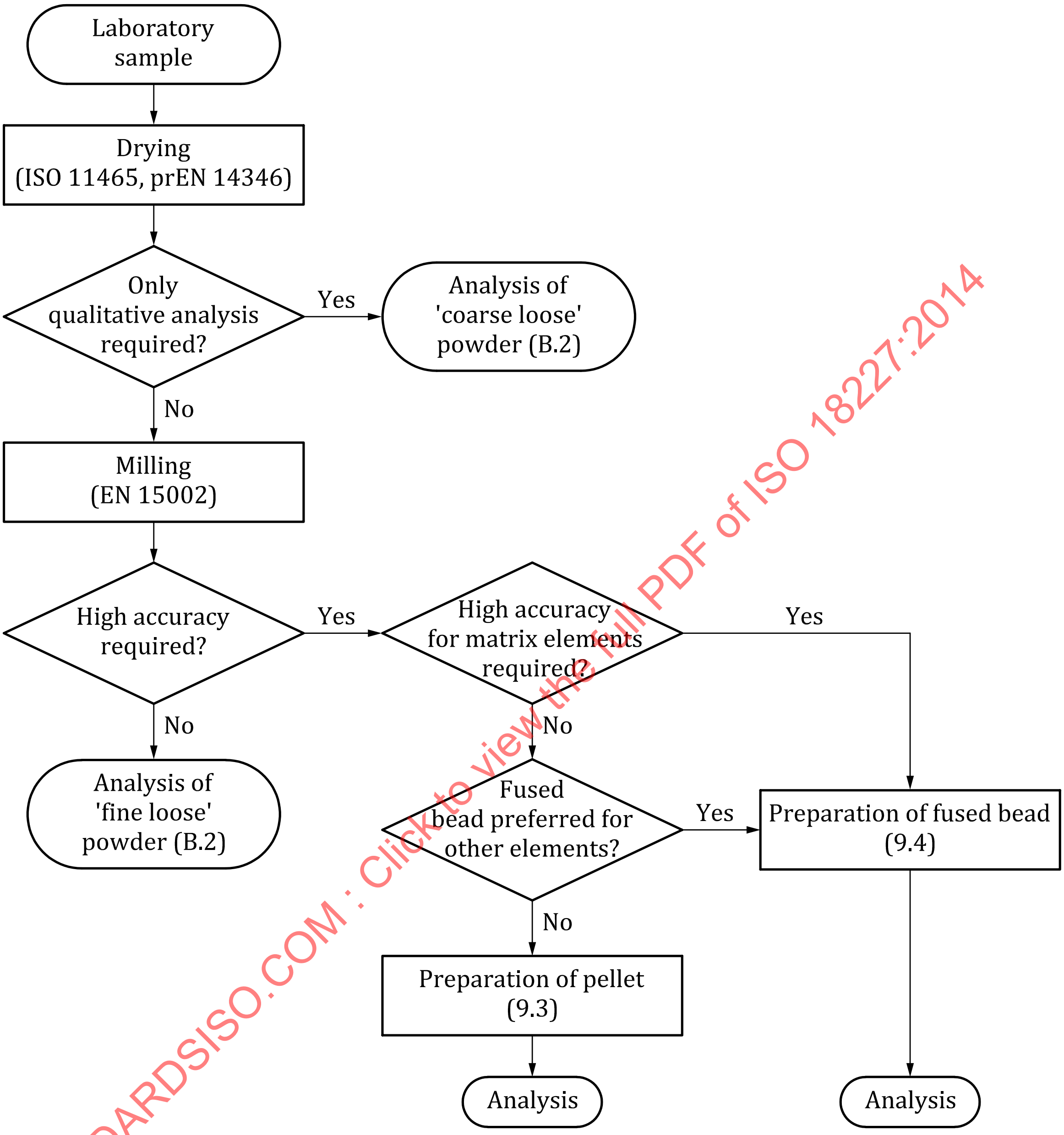

Figure B.1 — Operational steps for the preparation of soil, sediment, fly ash, and sludge samples

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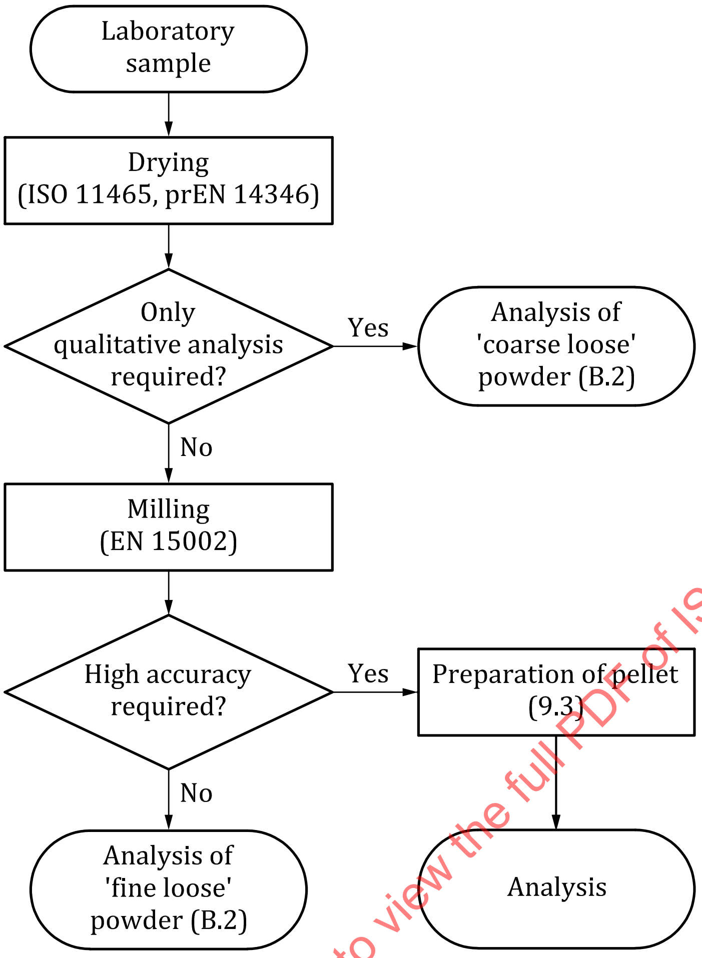

Figure B.2 — Operational steps for the preparation of samples consisting of carbon matrices

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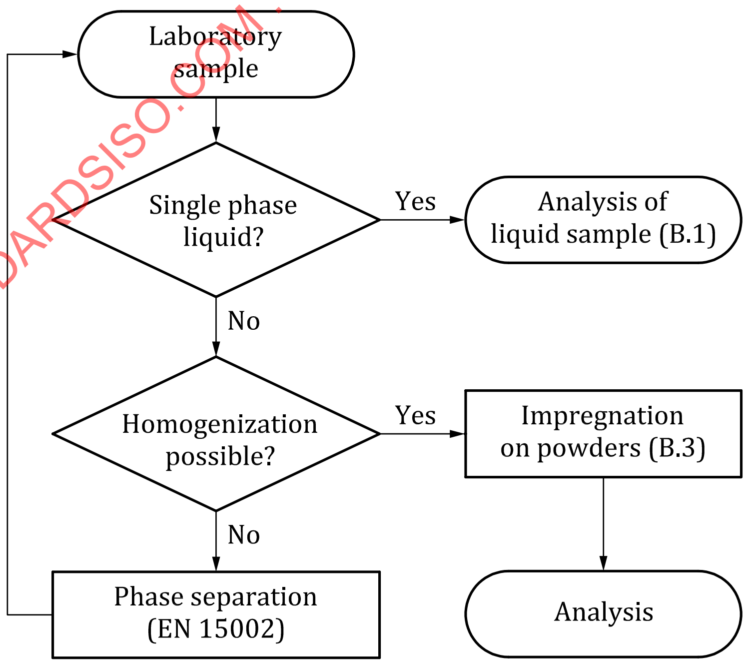

Figure B.3 — Operational steps for the preparation of liquid samples

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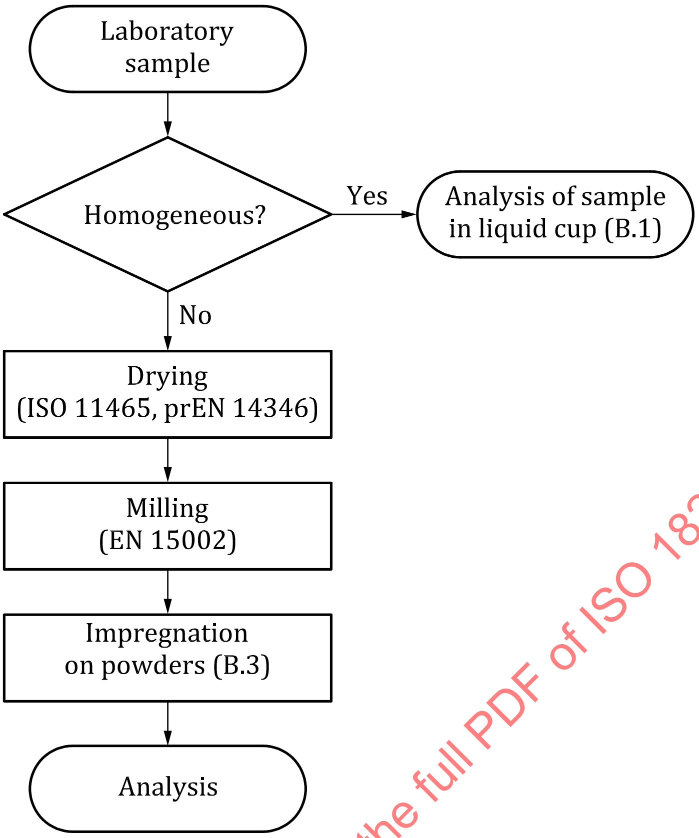

Figure B.4 — Operational steps for the preparation of paste-like materials

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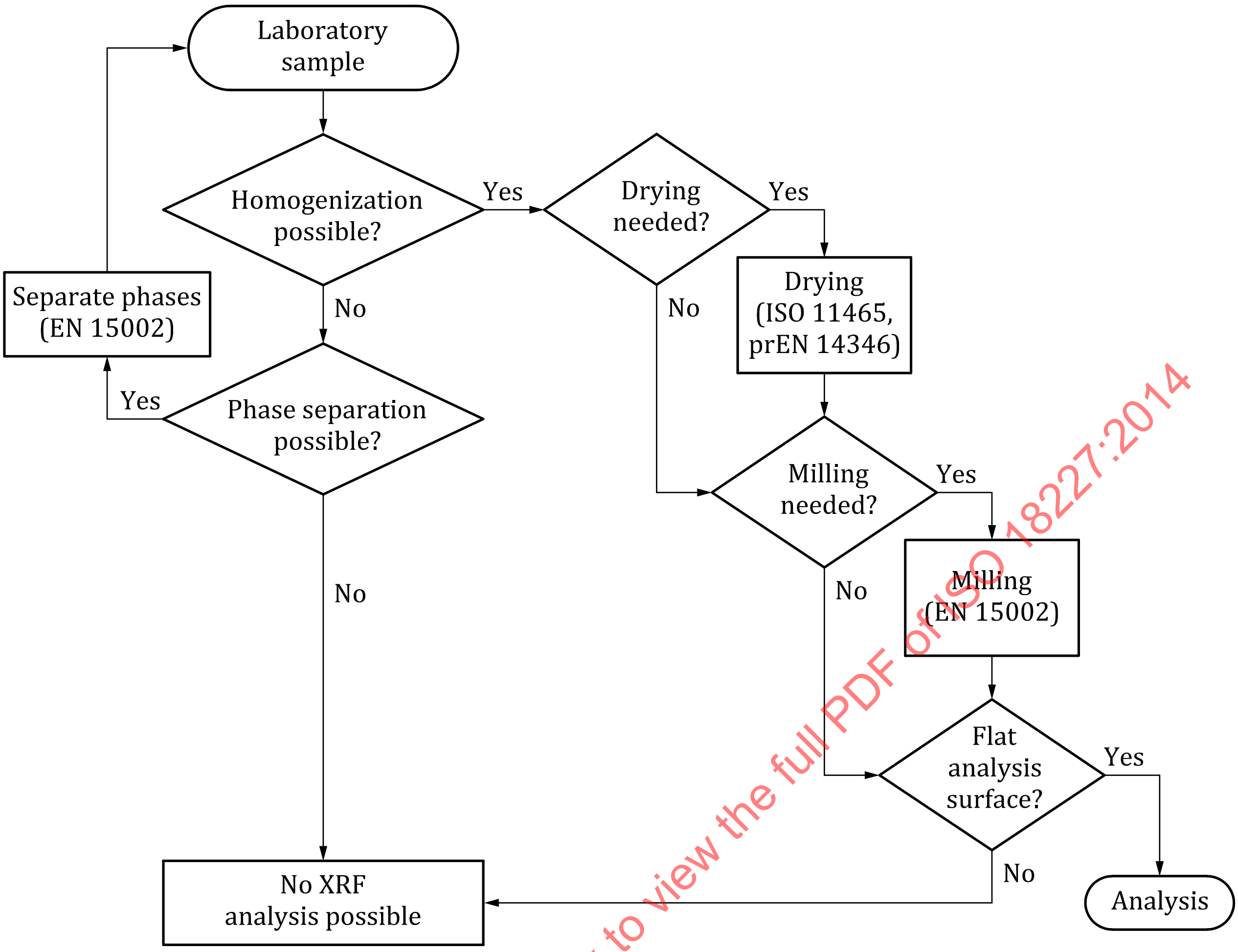

Figure B.5 — Operational steps for the preparation of scrap samples

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Annex C
(informative)

Suggested analytical lines, crystals, and operating conditions

Optimum excitation for element analysis can be realized by applying a suitable crystal. Table C.1 shows a list with potentially usable crystals. For all of these, the tube voltage and current need to be set carefully in order to get optimum results. The number of excitation conditions selected shall be optimized, particularly, with regard to detection sensitivity and required analysis time.

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

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 Kβ	LiF200 LiF200	60/50 60/50	fine fine	SC 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

FC flow counter

SC scintillation counter

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Table C.1 *(continued)*

Element	Line	Crystals	kV/mA	Collimator	Detector
Zr	Kα	LiF220	60/50	fine	FC
Nb	Kα	LiF220	60/50	fine	FC
Mo	Kα	LiF220	60/50	fine	FC
Ag	Ka Lα	LiF220 PET	60/50 30/100	fine coarse	SC FC
Cd	Kα Lα	LiF220 PET	60/50 30/100	fine coarse	SC FC
Sn	Lα	LiF200	30/100	fine	FC
Sb	Lα	LiF200	30/100	fine	FC
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

SC scintillation counter

Optimum excitation for trace element analysis can be realized by applying secondary or polarization targets in to the excitation beam of the spectrometer. Table C.2 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 optimized, particularly, with regard to detection sensitivity and required analysis time.

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

Target	Target type	Elements
Mo	Secondary	Cr – Zr (K) Hf – U (L)
Zr	Secondary	Cr – Sr (K) Hf – Bi (L)
Al_2O_3	Barkla	Mo – Ba (K)
CsI	Secondary	Mo – In (K)
Pd	Secondary	Fe – Mo (K) Hf – U (L)
B_4C	Barkla	Fe – Mo (K) Hf – U (L)
Ge	Secondary	Cr – Zn (K) Hf – Ta (L)
Zn	Secondary	Ti – Ni (K)
Co	Secondary	K – Mn (K) Cd – La (L)
Ti	Secondary	P – Ca (K)
Si	Secondary	Na – Al (K)
Al	Secondary	Na – Mg (K)
HOPG	Bragg	Na – Sr (K) Y – Hf (L)
(K) Kα radiation (L) Lα radiation		

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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	Sediment
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
2709a	National Institute of Standards and Technology (NIST)	Soil
2710a	National Institute of Standards and Technology (NIST)	Soil
2711a	National Institute of Standards and Technology (NIST)	Soil
1633b	National Institute of Standards and Technology (NIST)	Fly ash
2689	National Institute of Standards and Technology (NIST)	Fly ash
2690	National Institute of Standards and Technology (NIST)	Fly ash
2691	National Institute of Standards and Technology (NIST)	Fly ash
188-WT-H	SPEX Certiprep, UK	City Treatment Sewage Sludge
188-WT-M	SPEX Certiprep, UK	City Treatment Sewage Sludge

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Table D.1 *(continued)*

Identification		**Matrix**
188-WT-L	SPEX Certiprep, UK	City Treatment Sewage Sludge
BAM-U110	Federal Institute for Materials Research and Testing	Wetland Soil

NOTE This list can be incomplete.

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Annex E
(informative)

Validation

An inter-laboratory comparison supported by DIN was organized by CEN/TC 292 in May 2006/August 2006 with participants from seven 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 50 m beside a highway in Germany, homogenized 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.[15]
- Sample 3: fly ash sample of a household waste incineration plant, homogenized 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 (International Commission's DG Joint Research Centre) and used for validation of the digestion standards EN 13656 and EN 13657.[16]
- Sample 5: electronic sludge, cited by (3) as SAMPLE CEN9/99, homogeneity-tested by EU DG JRC (International Commission's DG Joint Research Centre) and used for validation of the digestion standards EN 13565 and EN 13657.[16]

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

The samples were analysed using EDXRF and WDXRF 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, two test samples were prepared (pellets or beads) and analysed in duplicate. Finally, for each combination, four 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 laboratories were removed. The maximum number of laboratories providing results for the statistical evaluation was therefore 13.

For the statistical evaluation, the data of the EDXRF and the WDXRF 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.[17]

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

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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.

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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.

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