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Solid recovered fuels — Determination of elemental composition by X-ray fluorescence

Combustibles solides de récupération — Détermination de la composition élémentaire par fluorescence de rayons X

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 300, *Solid recovered materials, including solid recovered fuels*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 343, *Solid Recovered Fuels*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

X-ray fluorescence spectrometry can be used as a fast method for a qualitative overview of ash forming elements and impurities. When calibration is based on reference materials or on matrix-matched homogeneous solid recovered fuel samples with known content, X-ray fluorescence spectrometry can be used for a quantitative analysis of the total content of the specified elements within different solid recovered fuels.

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 need to be considered, such as the matrices to be analysed, elements to be determined, detection limits required and the measuring time.

Due to the wide range of matrix compositions and the lack of suitable reference materials in the case of solid recovered fuels from various origin, it is generally difficult to set up a calibration with matrix-matched reference materials. Therefore, it is important to use several homogenized solid recovered fuel samples with properties that sufficiently match the matrices of interest and whose content has been derived by independent measurement techniques, for example total digestion of solid recovered fuels and characterization of major and minor elements by measurement of digestion solutions with ICP-MS or ICP-OES, or by other techniques such as elemental analysis using combustion technology on sulfur or by combustion and ion chromatographic determination for chlorine.

This document describes two different procedures:

1) Quantitative analytical procedure for major elements of solid recovered fuels. The calibration is based on different reference materials and solid recovered fuel samples with known content.

   The elements described as major elements of solid recovered fuels are in fact major elements of the fuel ashes more than of the fuels. The determination of these elements can be helpful to predict the melting behaviour and slagging of the ashes. Moreover, contamination of fuel with sand or soil is indicated by high values of several elements.

2) Total element characterization at a semiquantitative level for major and minor elements of solid recovered fuels. The calibration is based on matrix-independent calibration curves, previously set up by the manufacturer.

   In general, the sensitivity of X-ray fluorescence is not sufficient for a determination of the content of minor elements (trace metals) in solid recovered fuels. However, it is possible to use determination of minor elements after calibration with solid recovered fuel samples with known content or at a semiquantitative level based on matrix-independent calibration curves to collect data for higher sample numbers, taking into account lower achievable precision. Therefore, it may be used to reveal excessive contents of minor elements in solid recovered fuels.

Solid recovered fuels — Determination of elemental composition by X-ray fluorescence

1 Scope

This document specifies the procedure for a determination of major and minor element concentrations in solid recovered fuel material by energy-dispersive X-ray fluorescence (EDXRF) spectrometry or wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry using a calibration with solid recovered fuel reference materials or solid recovered fuel samples with known content. A semiquantitative determination can be carried out using matrix independent standards.

This document is applicable to the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Mo, Cd, Sb, Sn, Tl and Pb. Concentration levels between approximately 0,000 1 % and 100 % can be determined depending on the element, the calibration materials used and the instrument used.

NOTE X-ray fluorescence spectrometry can be used as a fast method for a qualitative overview of elements and impurities and after suitable calibration it is very useful for determining major elements or even minor elements (except Hg) in order to quickly identify increased concentrations of minor elements in solid recovered fuels (SRF), for example during SRF-production.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 21637, *Solid recovered fuels — Vocabulary*

ISO 21646,[1)] *Solid recovered fuels — Sample preparation*

ISO 21660-3, *Solid recovered fuels — Determination of moisture content using the oven dry method — Part 3: Moisture in general analysis sample*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21637 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
absorption edge
abrupt change in mass absorption coefficient at a specific wavelength or energy

3.2
absorption
loss of intensity of X-rays due to isotropic and homogenous material, as described by the Beer-Lambert law

1) Under preparation. Stage at the time of publication: ISO/DIS 21646:2021.

3.3
analytical line
specific characteristic X-ray spectral line of the atom or ion of the analyte used for determination of the analyte content

3.4
continuous radiation (Bremsstrahlung)
electromagnetic radiation produced by the acceleration of a charged particle, such as an electron, when deflected by another charged particle, such as an atomic nucleus

3.5
Compton line
spectral line due to incoherent scattering (Compton effect), occurring when the incident X-ray photon strikes an atom without promoting fluorescence

Note 1 to entry: Energy is lost in the collision and, therefore, the resulting scattered X-ray photon is of lower energy than the incident X-ray photon.

3.6
drift correction monitors
physically stable samples used to correct for instrumental drift

3.7
emitted radiation
emitted sample X-rays
radiation emitted by sample consisting of *X-ray fluorescence radiation* (3.13) and scattered *primary X-rays* (3.11)

3.8
mass absorption coefficient
constant describing the fractional decrease in the intensity of a beam of X-radiation as it passes through an absorbing medium

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

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

3.9
powder sample
analyte sample submitted as a powder for direct measurement in the sample cup

3.10
pressed pellet
analyte sample prepared by pressing milled material into a disk

3.11
primary X-rays
X-rays by which the sample is radiated

3.12
quality control sample
stable sample with known contents, for example (certified) reference material (CRM) or homogenized solid recovered fuel samples from known origin whose contents have been derived by independent analysis used to monitor instrument and calibration performance

3.13
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 Symbols and abbreviated terms

4.1 Symbols

Al	aluminium
As	arsenic
Br	bromine
Ca	calcium
Cd	cadmium
Cl	chlorine
Co	cobalt
Cr	chromium
Cu	copper
Fe	iron
K	potassium
Mg	magnesium
Mn	manganese
Mo	molybdenum
Na	sodium
Ni	nickel
P	phosphorus
Pb	lead
S	sulfur
Sb	antimony
Si	silicon
Sn	tin
Ti	titanium
Tl	thallium
V	vanadium
Zn	zinc

4.2 Abbreviated terms

EDXRF energy-dispersive x-ray fluorescence

MCA multi-channel analyser

WDXRF wavelength-dispersive x-ray fluorescence

5 Safety remarks

The organization shall be aware of applicable legal requirements relating to the X-ray fluorescence spectrometer.

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

6 Principle

After a suitable preparation, 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, provided that they meet all the requirements of the relevant preparation technique.

7 Apparatus

7.1 X-ray fluorescence spectrometer, which shall be able to analyse the elements according to the scope of this document. The following types of X-ray fluorescence spectrometers are applicable:

— EDXRF spectrometer that achieves the dispersion of the emitted X-ray fluorescence radiation by an energy-dispersive detector;

— WDXRF spectrometer that achieves the dispersion of the emitted X-ray fluorescence radiation by diffraction by a crystal or a synthetic multilayer.

The spectrometer consists of the following components:

— primary X-ray source, an X-ray tube with a high-voltage generator;

— sample holder;

— detector unit including electronic equipment;

— source modifiers to modify the shape or intensity of the source spectrum or the beam shape (e.g. source filters, secondary targets, polarizing targets, collimators, focusing optics).

The detector unit is different for WDXRF and for EDXRF spectrometers. WDXRF spectrometers take advantage of the dispersion of the emitted radiation by diffraction by a crystal or a synthetic multilayer. The detector does not need to be capable of energy discrimination. EDXRF spectrometers use an energy-dispersive detector. Pulses of current from the detector, which are a measure of the energy of the incoming X-rays, are segregated into channels according to energy using an 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. The excitation is performed by polarized radiation. The emitted X-ray fluorescence radiation is detected along the direction of polarization, resulting in a significant decrease of the background scattering, therefore lower limits of detection can be achieved (comparable to WDXRF).

7.2 Pellet press, capable of providing a pressure of at least 30 kN. The pellet press may be a cold press or a hot mould press, operating at temperatures not exceeding 180 °C.

8 Interferences and sources of error

Interferences in X-ray fluorescence spectrometry are due to spectral line overlaps, matrix effects, spectral artefacts and particle size or mineralogical effects.

Spectral line overlaps occur when an analytical line cannot be resolved from the line of a different element. Corrections for these interferences are made using the algorithms provided with the instrument software.

Matrix effects occur when the X-ray fluorescence radiation from the analyte element is absorbed or enhanced by other elements in the sample before it reaches the detector. In the case of complex matrices, these effects generally shall be corrected. The correction procedure depends on the X-ray fluorescence spectrometry system (EDXRF or WDXRF) and the apparatus type itself.

Spectral artefacts, for example escape peaks, sum peaks, pulse pile up lines, dead time and continuous radiation (Bremsstrahlung) correction, are accounted for by the provided instrument software. Spectral artefacts differ for energy-dispersive and wavelength-dispersive XRF spectrometry.

9 Sample preparation

9.1 Preparation principles

The sample preparation is very critical for XRF analysis of solid recovered fuels. The quality of sample preparation strongly influences the accuracy of the results. The following different options exist:

— For quantitative analysis of solid recovered fuel samples, the preparation of pressed pellets from prepared general analysis sample material is recommended.

— For semiquantitative analysis of solid recovered fuels, the general analysis material may be used directly (in powder form); concerning samples of solid recovered fuel pellets, the original pellets may be used directly without any sample preparation. It may be used to provide fast basic information about the approximate composition of a sample. Similar results can be obtained using portable XRF instruments for field analysis.

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

For precise quantitative measurements, homogeneous and representative test portions are necessary. The nominal top size of the material shall be 0,5 mm or less, following the procedure according to ISO 21646.

9.2 Drying of general analysis sample material

Dry a sufficient amount of general analysis sample material in accordance with ISO 21660-3 immediately before pressing pellets for XRF-analysis.

NOTE Concerning some XRF instruments, the applied vacuum will dry the general analysis sample material during the determination, giving the same results as if the sample had been previously dried.

9.3 Preparation of pressed pellet

A pellet is prepared in the pellet press (7.2). Before pressing, the sample shall be mixed and homogenized. Use the same weight for any single set of standards and samples and add binder (e.g. wax or liquid organic binder), if necessary.

For the preparation, follow the manufacturer's instructions.

NOTE 1 Different binders can be used. In the case of organic liquid binders (approximately 0,6 % weight of sample) the pressed pellet will be placed in an oven at between 70 °C and 100 °C for a minimum of 10 minutes to evaporate the organic solvent or for the formation of long chain polymers formed by heating (e.g. PVP-methylcellulose binders).

NOTE 2 In the case of wax binder, the ratio of the sample weight to wax is around 10:1.

10 Procedure

10.1 Analytical measurement conditions

10.1.1 Wavelength-dispersive instruments

10.1.1.1 General

The analytical lines to be used and suggested operating conditions are given in Table 1. The settings strongly depend on the spectrometer configuration, e.g. the type of X-ray tube (Rh, Cr), tube power, available crystals and type of collimators. The instrument manufacturer's recommendations should be followed in all cases.

10.1.1.2 Intensities and background corrections

For the determination of trace elements, the measured intensities shall 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 (i), is calculated as the difference between the measured peak intensity of the element and the background intensity, as given in Formula (1):

$$I = I_{\mathrm{p}} - I_{\mathrm{b}} \tag{1}$$

where

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

I_{b} is the background count rate of the element i with no analyte present, expressed as the number of counts per second.

10.1.1.3 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 or quality control sample 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):

$$T = \left(100 \,/\, 2\sigma_{\%} \times 1 \,/\, \left(\sqrt{I_{\mathrm{p}}} - \sqrt{I_{\mathrm{b}}}\right)\right)^2 \tag{2}$$

where

T is the total counting time for the peaks and background, expressed in seconds;

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

10.1.2 Energy-dispersive instruments

The analytical lines to be used and suggested operating conditions are given in Table 1. The settings strongly depend on the spectrometer configuration, e.g. type of X-ray tube (Rh, Pd), tube power, available targets and types of filters. The instrument manufacturer's recommendations should be followed in all cases.

10.1.3 Intensities and background corrections

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

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

Element	Line	Spectral line overlap	Type of matrix correction method
Na	Kα	ZnLβ	Alpha or FP
Mg	Kα	AsLα	Alpha or FP
Al	Kα	BrLα	Alpha or FP
Si	Kα		Alpha or FP
P	Kα		Alpha or FP
S	Kα	CoKα PbMα NbLβ	Alpha or FP or MAC
Cl	Kα		Alpha or FP or MAC
K	Kα		Alpha or FP
Ca	Kα		Alpha or FP
Ti	Kα	BaLα ILβ	Alpha or FP
V	Kα	Ti Kβ	Alpha or FP or MAC
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
Br	Kα	AsKβ	Compton or FP or MAC
Mo	Kα	ZrKβ ULβ	Compton or FP or MAC
Ag	Kα Lα	CrKβ	Compton or FP or MAC Alpha or FP
Cd	Kα Lα	AgLβ	Compton or FP or MAC Alpha or FP
Sb	Kα Lβ	CoKβ	Compton or FP or MAC Alpha or FP or MAC

Table 1 *(continued)*

Element	Line	Spectral line overlap	Type of matrix correction method
Sn	Kα	CoKα	Compton or FP or MAC
	Lβ		Alpha or FP or MAC
Tl	Lβ	PbLβ	Compton or FP or MAC
Pb	Lβ	ThLα BiLβ SnKα	Compton or FP or MAC

NOTE See 10.2.1 for additional information on the type of matrix correction methods.

10.2 Calibration

10.2.1 General

The calibration procedure is similar for energy-dispersive and wavelength-dispersive techniques.

In general, calibration is established by using matrix-matched reference materials (if available) or samples with known content of minor and major elements. The calibration equations and inter-element corrections are calculated by the software of the instrument. An accuracy check is performed with CRMs (if available for the matrix) or samples with known composition.

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

— Scattered radiation method is based on the principle that the intensities of the analyte line and of the Compton line are affected in the same proportion due to the overall mass absorption coefficient of the sample. This linear relationship holds true when all analytes are at low concentrations (minor elements) and their absorption coefficients are not affected by an adjacent absorption edge. In this case, an internal Compton correction can be used. Besides that, a correction method using the Compton intensity with mass absorption coefficients (MAC) is also applicable. In this method, the intensities of the major elements are measured to apply a jump edge correction for the analysed trace elements.

— Correction using the fundamental parameter approach (FP).

— Correction using theoretical correction coefficients (alphas), taking basic physical principles, instrumental geometry and so on into account.

— Correction using empirical correction coefficients (alphas) based on regression analysis of standards with known elemental concentrations. This procedure will normally need more standards than a calibration based on theoretical correction coefficients.

10.2.2 General calibration procedure

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

$$C_i = a_{i,0} + a_{i,1} \times I_i \tag{3}$$

where

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

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

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

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

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

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

where M is the correction factor due to the matrix effects.

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

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

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

Select calibration standards with a similar composition as the samples under investigation containing the elements of interest and covering the concentration range of interest. The use of reference materials from different recognized producers is recommended, if available for the matrix (see Annex A). Otherwise, solid recovered fuel samples shall be used whose composition has been assessed by independent analysis techniques (total contents of major and minor elements). 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 will possibly be necessary.

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

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

Start up the XRF equipment according to the instrument manufacturer's manual and measure the calibration standards using the specified measurement method. All measurements shall be performed under vacuum or inert atmosphere. A minimum of four different calibration samples with different concentration should be used.

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

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

NOTE In the case of determination of minor elements it can be sufficient to take into account higher measurement uncertainties.

10.3 Procedures for correcting matrix effects

10.3.1 General

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

10.3.2 Internal standard correction using Compton (incoherent) scattering method

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

The Compton scattering method can be expressed as Formula (5):

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

where

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

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

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

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

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

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

10.3.3 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, Rayleigh or both) allows the determination of matrix effects caused by sample elements that cannot be measured directly. The calculation of analyte concentrations in samples is based on making successively better estimates of composition by an iteration procedure.

These iteration cycles are performed until the difference between the compared results is below a defined value.

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

10.3.4 Fundamental or theoretical influence coefficient method

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

The calculation of the concentration from the intensities is performed by linear regression whereby the net intensities are corrected for the present matrix effects. For each element, the concentration is calculated according to Formula (6) and Formula (7):

$$C_{i,u} = \left(C_{i,r} \middle/ \left(I_{i,r} \times \left(1 + \sum \alpha_{ij} C_{jr}\right)\right)\right) \times I_{i,u} \times M \quad (6)$$

$$C_{i,u} = \left(C_{i,r} \middle/ \left(I_{i,r} \times \left(1 + \sum \alpha_{ij} C_{jr}\right)\right)\right) \times I_{i,u} \times \left(1 + \sum \alpha_{ij} C_{ju}\right) \quad (7)$$

where

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

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

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

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

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

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

M is the matrix correction factor;

α_{ij} is the correction coefficient α_{ij} (called alphas) calculated from theory, although some approximations are involved.

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

10.3.5 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 Formula (6) and Formula (7) where the correction factor for matrix effects is a function of concentrations.

The empirical alphas are only applicable for a limited concentration range and a well-defined analytical method where the matrices of samples and standards are similar. The reference materials used should contain each analyte together with fairly wide concentration ranges of each matrix element.

Poor analytical results are obtained when inappropriate combinations of analytes are chosen. A large number of reference materials shall be analysed to define the alphas (as a rule of thumb, a minimum of three times the number of parameters to be calculated).

10.4 Analysis of the samples

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

Select the required preparation method and prepare the samples. For the quantification of major and minor elements, the pressed pellet method is recommended; for the semiquantitative determination of major elements, the powder method can be used.

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

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

At the beginning of analysis and at frequent intervals, quality control samples shall be measured to check the instrument stability and the quality of the analyses, in accordance with the manufacturer's instructions.

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

11 Quality control

11.1 Drift correction procedure

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

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

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

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

11.2 Reference materials and quality control samples

Verify the accuracy of the results by applying the procedure to one or more reference materials or stable quality control samples with known content not used for calibration and covering the concentration range of interest.

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

NOTE 1 Certified reference materials are available, for example from BCR (see Annex A).

NOTE 2 As it can be difficult to find certified reference materials for solid recovered fuels other than sludges, homogenized quality control samples (real samples) with known content for minor and major elements are recommended.

12 Calculation of the result

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

The concentrations of the analytes are calculated by the software program from the measured intensities using the calibration curves previously set up. The results are expressed in terms of weight percentage dry basis or mg/kg dry basis. The results may be calculated on another basis, for example on an as-received basis.

13 Performance characteristics

Data for repeatability and reproducibility for predefined solid recovered fuel samples (with respect to sludges and typical solid recovered fuel mixtures) are shown in Annex B.

14 Test report

The test report shall contain at least the following information:

a) a reference to this document, i.e. ISO 22940:2021;

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

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

d) identification of product (sample) tested;

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

f) any unusual features noted during the test procedure.

Annex A
(informative)

Publicly available solid recovered fuel reference materials

— BCR-143R. Sewage sludge amended soil — Trace elements.

— BCR-145R. Sewage sludge (mixed origin) — Trace elements.

— BCR-146R. Sewage sludge (industrial origin) — Trace elements.

— BCR-597. Sewage sludge — Trace elements (Cr).

— ERM-CC144. Sewage sludge — Trace elements.

— NIST SRM 2781. Domestic sludge.

— NIST SRM 2782. Industrial sludge.

NOTE This list is possibly incomplete.

Annex B
(informative)

Validation

B.1 General

An interlaboratory comparison study on elements of solid recovered fuels (SRF) by X-ray fluorescence (XRF) was organized by Umweltbundesamt Austria in 2019 and participants from 10 countries (UK, IT, AT, JP, ES, SE, DE, HU, SK, NL) registered (sample dispatch: 5 November 5, 2019; closing time for the submission of results 3 December, 2019; extension by 20 January, 2020, at the latest).

For the interlaboratory comparison for SRF by XRF, three real samples were selected and distributed to the registered participants. Sample preparation for all samples according to EN 15443 and EN 15413, homogenization and homogeneity testing by Umweltbundesamt Austria.

— SRF A: high-calorific waste fraction from non-hazardous municipal solid waste [1 bottle (50 g) per sample for each participant per selected variant (sample/preparation and analysis method); particle size: < 0,5 mm].

— SRF B: high-calorific waste fraction from commercial waste [1 bottle (50 g) per sample for each participant per selected variant (sample/preparation and analysis method); particle size: < 0,5 mm].

— SRF C: municipal sewage sludge [1 bottle (50 g) per sample for each participant per selected variant (sample/preparation and analysis method); finely ground].

The provided samples were real samples as described and contained the elements of interest as they occur in their original composition (no spiking was performed). SRF A and SRF B are more heterogeneous matrices, whereas SRF C is very homogeneous (see Table B.1).

Table B.1 — Materials, variants (sample preparation method/analysis method) and analytes

Material	**Method/variant(s)**		
Solid recovered fuels (SRF)	**Sample preparation**	**Analysis method**	**Type of X-ray fluorescence spectrometer**
SRF A: high-calorific waste fraction from non-hazardous municipal solid waste	Cold press and/or hot mould press and/or (powder)	Quantitative: calibration with reference material and/or reference samples and/or semiquantitative: fundamental approach (pre-calibrated analytical methods by manufacturer) and/or screening: fundamental approach	energy-dispersive EDXRF and/or wavelength-dispersive WDXRF
SRF B: high-calorific waste fraction from commercial waste			
SRF C: municipal sewage sludge			
Analytes	Al Aluminium, As Arsenic, Br Bromine, Ca Calcium, Cd Cadmium, Cl Chlorine, Co Cobalt, Cr Chromium, Cu Copper, Fe Iron, K Potassium, Mg Magnesium, Mn Manganese, Mo Molybdenum, Na Sodium, Ni Nickel, P Phosphorus, Pb Lead, Sb Antimony, Si Silicon, Sn Tin, S Sulfur, Ti Titanium, Tl Thallium, V Vanadium, Zn Zinc		

The samples were sent to all registered laboratories for XRF (n = 20). Unfortunately, not all laboratories transmitted data according to their registration. Therefore, fewer data than expected were reported for each of the variants.

The participants were advised to follow the procedures for preparing the samples and measurement by XRF according to this document. Per variant, two independent sample preparations per sample and duplicate analysis of the prepared samples by XRF under repeatability conditions should be performed.

Data evaluation was performed according to ISO 5725-2 using R-Studio. For the statistical evaluation the results per each variant were treated separately, only measurements by WDXRF and EDXRF were combined. As not all laboratories transmitted data according to the registration, up to nine different data sets were evaluated. Variant cold press/semiquantitative was most commonly applied by the participating laboratories.

Outliers were determined according to ISO 5725-2 (Grubbs test) after plausibility check outliers were eliminated for statistical treatment. Repeatability and reproducibility were calculated according to ISO 5725-2.

The full data set for each variant is shown in Tables B.2 to B.16. Values below the limit of quantification (LOQ) are expressed as '< LOQ' and the calculated statistical data '< LOQ' are provided as values within brackets, if available.

Table B.2 — Validation data of sample SRF A cold press/quantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	2	8	0	9 302	778	8	2	8	0	9 302	758	8	882	9	30 206	5 275	17	31
As	3	9	0	5	1	12	2	8	0	5	0,3	8	0,4	8	< 7 (2)	2	78	242
Br	3	12	0	138	28	20	3	12	0	138	26	19	13	9	< 100 (88)	NA	NA	157
Ca	2	8	0	17 653	8 856	50	2	8	0	17 653	11 712	66	344	2	18 085	2 415	13	98
Cd	4	13	0	4	2	51	3	12	0	4	2	56	1	13	4	1	30	88
Cl	3	12	0	17 169	4 134	24	3	12	0	17 169	4 720	27	1 475	9	17 333	NA	NA	99
Co	3	9	0	8	1	18	2	8	0	7	2	24	0,3	4	6	3	48	135
Cr	3	12	0	69	11	16	3	12	0	69	11	16	6	9	55	10	18	126
Cu	4	13	0	136	47	34	3	12	0	135	46	34	28	21	682	996	146	20
Fe	2	8	0	2 497	688	28	2	8	0	2 497	901	36	152	6	2 278	415	18	110
K	2	8	2	1 226	691	56	1	4	0	781	NA	NA	34	4	1 011	533	53	121
Mg	2	8	0	1 104	560	51	2	8	0	1 104	611	55	308	28	1 454	396	27	76
Mn	4	13	0	157	33	21	3	12	0	157	38	24	6	4	171	34	20	92
Mo	3	9	1	1	1	114	2	8	0	1	1	142	0,1	11	< 5 (2,6)	1	47	27
Na	1	4	0	1 413	474	34	1	4	0	1 413	NA	NA	193	14	3 908	2 130	54	36
Ni	4	13	0	17	2	10	3	12	0	17	8	1	1	7	27	16	59	61
P	2	8	0	565	301	53	2	8	0	565	393	70	76	14	464	68	15	122
Pb	4	13	0	99	17	17	3	12	0	100	19	19	11	11	110	33	30	90
S	2	8	0	1 103	587	53	2	8	0	1 103	776	70	12	1	1 129	385	34	98
Sb	4	13	0	54	15	29	3	12	0	56	16	28	7	12	78	23	30	69
Si	2	8	0	9 833	4 727	48	2	8	0	9 833	6 145	62	1 606	16	24 218	10 360	43	41
Sn	4	13	1	31	3	10	3	12	0	31	3	11	3	9	51	13	26	61
Ti	2	8	0	3 442	1 368	40	2	8	0	3 442	1 809	53	48	1	3 083	197	6	112
Tl	3	9	0	1	1	80	2	8	0	1	0,2	41	0,2	37	< 1 (0,53)	NA	NA	151
V	3	12	4	7	1	14	2	8	0	7	1	14	1	11	6	1	21	113
Zn	4	13	0	352	95	27	3	12	0	340	96	28	25	7	670	785	117	53

Table B.3 — Validation data of sample SRF A cold press/semiquantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	8	33	1	11 128	5 740	52	8	32	0	11 128	5 976	54	2 081	19	30 206	5 275	17	37
As	3	8	0	3	2	54	2	7	0	3	2	62	1	21	< 7 (2)	2	78	172
Br	6	24	0	114	35	31	6	24	0	114	37	32	16	14	< 100 (88)	NA	NA	129
Ca	8	33	5	13 297	3 284	25	7	28	0	13 297	3 454	26	665	5	18 085	2 415	13	74
Cd	2	8	0	8	2	29	2	8	0	8	3	36	1	11	4	1	30	192
Cl	7	29	1	10 471	5 986	57	7	28	0	10 471	6 302	60	2 105	20	17 333	NA	NA	60
Co	2	8	0	7	2	32	2	8	0	7	3	42	1	10	6	3	48	119
Cr	8	29	0	62	21	34	7	28	0	62	23	37	3	6	55	10	18	113
Cu	7	28	0	144	86	59	7	28	0	144	90	62	20	14	682	996	146	21
Fe	8	29	1	1 847	985	53	7	28	0	1 847	1 042	56	109	6	2 278	415	18	81
K	8	29	1	929	382	41	7	28	0	929	404	43	65	7	1 011	533	53	92
Mg	8	33	0	1 786	1 496	84	8	32	0	1 653	1 374	83	102	6	1 454	396	27	123
Mn	7	28	0	93	40	43	7	28	0	93	42	45	6	7	171	34	20	54
Mo	4	10	0	10	9	97	2	8	0	9	13	143	3	29	< 5 (2,6)	1	47	365
Na	8	29	1	2 408	1 167	48	7	28	0	2 408	1 235	51	134	6	3 908	2 130	54	62
Ni	7	28	0	22	12	55	7	28	0	22	13	59	1	5	27	16	59	80
P	8	33	1	626	276	44	8	32	0	626	289	46	25	4	464	68	15	135
Pb	6	23	0	67	24	36	6	23	0	65	26	40	13	20	110	33	30	60
S	6	25	1	976	276	28	6	24	0	976	295	30	57	6	1 129	385	34	86
Sb	2	8	0	76	43	57	2	8	0	76	57	75	10	13	78	23	30	97
Si	8	33	1	6 777	2 885	43	8	32	0	6 777	3 022	45	499	7	24 218	10 360	43	28
Sn	2	5	1	24	1	4	1	4	0	24	NA	NA	0,3	1	51	13	26	47
Ti	7	32	0	3 642	1 692	46	8	32	0	3 642	1 773	49	200	5	3 083	197	6	118
Tl	2	8	0	1	1	82	2	8	0	1	1	106	0,2	19	< 1 (0,53)	NA	NA	215
V	1	4	0	4	1	15	1	4	0	4	NA	NA	0,3	8	6	1	21	67
Zn	7	32	0	342	170	50	8	32	0	342	178	52	31	9	670	785	117	51

Table B.4 — Validation data of sample SRF A hot mould press/quantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	2	12	0	22 066	3 371	15	3	12	0	22 066	3 462	16	1 603	7	30 206	5 275	17	73
As	4	15	0	2	1	36	4	15	0	2	1	36	1	30	< 7 (2)	2	78	103
Br	3	12	0	126	25	20	3	12	0	126	26	20	28	22	< 100 (88)	NA	NA	143
Ca	2	12	4	14 855	2 333	16	2	8	0	14 855	3 033	20	745	5	18 085	2 415	13	82
Cd	4	16	0	3	1	44	4	16	0	3	1	47	0,3	9	4	1	30	73
Cl	2	8	0	17 520	3 476	20	2	8	0	17 520	4 508	26	1 211	7	17 333	NA	NA	101
Co	4	16	0	8	3	42	4	16	0	8	3	43	1	8	6	3	48	145
Cr	4	16	0	52	7	14	4	16	0	52	8	16	3	6	55	10	18	95
Cu	4	16	0	164	37	23	4	16	0	164	39	24	18	11	682	996	146	24
Fe	3	16	0	3 136	1 378	44	4	16	0	3 136	1 532	49	187	6	2 278	415	18	138
K	2	12	0	1 905	1 184	62	3	12	0	1 905	1 388	73	40	2	1 011	533	53	188
Mg	2	12	0	2 056	451	22	3	12	0	2 056	519	25	103	5	1 454	396	27	141
Mn	4	16	0	117	15	13	4	16	0	117	15	13	16	13	171	34	20	68
Mo	2	8	0	5	4	81	2	8	0	5	5	101	1	16	< 5 (2,6)	1	47	209
Na	2	12	0	2 820	1 395	49	3	12	0	2 820	1 626	58	254	9	3 908	2 130	54	72
Ni	4	16	0	21	7	34	4	16	0	21	7	36	3	12	27	16	59	75
P	2	12	0	904	513	57	3	12	0	904	600	66	52	6	464	68	15	195
Pb	4	16	0	96	12	13	4	16	0	96	13	13	9	10	110	33	30	87
S	2	12	0	960	158	16	3	12	0	960	181	19	25	3	1 129	385	34	85
Sb	4	16	0	67	12	17	4	16	0	67	12	18	8	11	78	23	30	85
Si	2	12	0	11 724	2 442	21	3	12	0	11 724	2 757	24	459	4	24 218	10 360	43	48
Sn	4	15	0	36	11	30	4	15	0	36	11	30	12	34	51	13	26	70
Ti	2	12	0	5 708	2 724	48	3	12	0	5 708	3 115	55	371	7	3 083	197	6	185
Tl	2	8	0	1	1	107	2	8	0	1	1	141	0	0	< 1 (0,53)	NA	NA	188
V	4	16	0	4	3	66	4	16	0	4	2	37	0,5	11	6	1	21	68

Table B.4 *(continued)*

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Zn	4	16	0	370	39	10	4	16	0	370	36	10	29	8	670	785	117	55

Table B.5 — Validation data of sample SRF A hot mould press/semiquantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	2	8	0	9 876	994	10	2	8	0	9 876	922	9	1 185	12	30 206	5 275	17	33
As	1	4	0	3	0,2	6	1	4	0	3	NA	NA	0,05	2	< 7 (2)	2	78	141
Br	2	8	0	124	17	14	2	8	0	124	16	13	21	17	< 100 (88)	NA	NA	140
Ca	2	8	0	14 015	1 297	9	2	8	0	14 015	1 508	11	682	5	18 085	2 415	13	77
Cd	1	4	0	5	0,4	8	1	4	0	5	NA	NA	0,03	1	4	1	30	118
Cl	2	8	0	12 308	982	8	2	8	0	12 308	861	7	932	8	17 333	NA	NA	71
Co	1	4	0	7	1	7	1	4	0	7	NA	NA	1	8	6	3	48	128
Cr	2	8	0	56	9	16	2	8	0	56	9	17	10	18	55	10	18	103
Cu	2	8	0	116	12	11	2	8	0	116	10	9	15	13	682	996	146	17
Fe	2	8	0	1 444	105	7	2	8	0	1 444	107	7	62	4	2 278	415	18	63
K	2	8	0	1 110	140	13	2	8	0	1 110	172	16	68	6	1 011	533	53	110
Mg	2	8	0	1 205	209	17	2	8	0	1 205	169	14	80	7	1 454	396	27	83
Mn	2	8	0	96	26	27	2	8	0	96	33	34	4	4	171	34	20	56
Mo	2	5	1	1	0,1	9	1	4	0	1	NA	NA	0,1	10	< 5 (2,6)	1	47	40
Na	2	8	0	2 894	555	19	2	8	0	2 894	437	15	455	16	3 908	2 130	54	74
Ni	2	8	0	19	3	14	2	8	0	19	2	13	2	13	27	16	59	68
P	2	8	0	606	43	7	2	8	0	606	32	5	37	6	464	68	15	130
Pb	2	8	0	84	7	8	2	8	0	84	6	7	6	7	110	33	30	76
S	2	8	0	1 114	96	9	2	8	0	1 114	67	6	83	7	1 129	385	34	99
Sb	1	4	0	38	1	4	1	4	0	38	NA	NA	2	5	78	23	30	48
Si	2	8	0	6 694	750	11	2	8	0	6 694	664	10	939	14	24 218	10 360	43	28
Sn	1	4	0	29	0,3	1	1	4	0	29	NA	NA	0,2	1	51	13	26	57
Ti	2	8	0	3 274	183	6	2	8	0	3 274	117	4	151	5	3 083	197	6	106
Tl	1	4	0	1	0,2	33	1	4	0	1	NA	NA	0,1	23	< 1 (0,53)	NA	NA	110
V	1	4	0	9	2	17	1	4	0	9	NA	NA	1	12	6	1	21	152

Table B.5 *(continued)*

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Re-flab)}$ mg/kg dm	$V_{R\ (Re-flab)}$ %	Recovery %
Zn	2	8	0	343	21	6	2	8	0	343	20	6	26	8	670	785	117	51

Table B.6 — Validation data of sample SRF A powder/semiquantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	4	13	0	19 910	6 657	33	3	12	0	20 461	7 219	35	2 436	12	30 206	5 275	17	66
As	1	4	4	NA	NA	NA	0	0	0	NA	NA	NA	NA	NA	< 7 (2)	2	78	NA
Br	5	17	1	110	39	35	4	16	0	110	37	33	15	13	< 100 (88)	NA	NA	125
Ca	5	17	4	20 148	4 425	22	3	12	0	20 277	5 167	25	1 170	6	18 085	2 415	13	111
Cd	0	0	0	NA	NA	NA	0	0	0	NA	NA	NA	NA	NA	4	1	30	NA
Cl	5	17	4	14 948	1 448	10	3	12	0	15 119	1 237	8	1 404	9	17 333	NA	NA	86
Co	2	8	0	33	6	19	2	8	0	33	8	25	0,2	1	6	3	48	583
Cr	4	13	0	71	15	21	3	12	0	71	15	21	9	12	55	10	18	129
Cu	5	17	0	163	86	53	4	16	0	158	79	50	58	37	682	996	146	24
Fe	5	17	0	3 261	2 123	65	4	16	0	3 350	2 410	72	104	3	2 278	415	18	143
K	5	17	0	2 055	1 076	52	4	16	0	2 094	1 221	58	60	3	1 011	533	53	203
Mg	4	13	0	4 374	3 184	73	3	12	0	4 643	3 703	80	311	7	1 454	396	27	301
Mn	5	17	4	110	33	30	3	12	0	111	38	34	3	2	171	34	20	64
Mo	1	4	0	20	0	0	1	4	0	20	NA	NA	0	0	< 5 (2,6)	1	47	766
Na	3	9	0	6 748	2 408	36	2	8	0	7 234	2 480	34	175	2	3 908	2 130	54	173
Ni	4	13	0	34	18	53	3	12	0	36	20	55	6	15	27	16	59	126
P	4	13	4	902	360	40	2	8	0	954	446	47	63	7	464	68	15	194
Pb	5	17	1	77	19	24	4	16	0	77	20	26	8	11	110	33	30	70
S	3	9	4	2 908	239	8	1	4	0	2 935	NA	NA	156	5	1 129	385	34	258
Sb	2	8	1	54	27	51	2	8	1	57	36	63	1	2	78	23	30	68
Si	5	17	1	15 405	8 293	54	4	16	1	14 925	9 683	65	1 091	7	24 218	10 360	43	64
Sn	2	8	4	56	2	3	1	4	0	56	NA	NA	1	1	51	13	26	110
Ti	5	17	0	3 482	1 987	57	4	16	0	3 439	2 273	66	257	7	3 083	197	6	113
Tl	0	0	0	NA	NA	NA	0	0	0	NA	NA	NA	NA	NA	< 1 (0,53)	NA	NA	NA
V	1	4	0	30	4	13	1	4	0	30	NA	NA	4	12	6	1	21	491

Table B.6 *(continued)*

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Zn	5	17	0	482	221	46	4	16	0	491	249	51	73	15	670	785	117	72

Table B.7 — Validation data of sample SRF B cold press/quantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	2	8	0	7 949	1 256	16	2	8	0	7 949	1 583	20	706	9	14 447	2 452	17	55
As	3	9	0	2	1	42	2	8	0	2	0,5	26	0,4	19	< 5 (2,9)	1	33	60
Br	3	12	0	123	18	14	3	12	0	123	20	16	6	5	< 100 (92,5)	NA	NA	133
Ca	2	8	0	24 729	11 488	46	2	8	0	24 729	15 172	61	1 191	5	23 366	2 770	12	106
Cd	4	13	0	6	3	42	3	12	0	6	3	41	2	26	6	2	38	101
Cl	3	12	0	11 059	1 135	10	3	12	0	11 059	1 131	10	1 337	12	15 000	NA	NA	74
Co	3	9	0	8	1	19	2	8	0	8	2	26	0,3	4	6	3	52	131
Cr	4	13	0	147	22	15	3	12	0	145	24	17	8	6	134	41	31	109
Cu	4	13	0	209	58	28	3	12	0	201	60	30	28	14	1 416	937	66	15
Fe	2	8	0	3 401	900	26	2	8	0	3 401	1 181	35	171	5	3 364	525	16	101
K	2	8	0	1 898	950	50	2	8	0	1 898	1 253	66	128	7	1 787	306	17	106
Mg	2	8	0	2 194	536	24	2	8	0	2 194	526	24	91	4	2 690	402	15	82
Mn	4	13	0	210	35	17	3	12	0	207	39	19	16	8	309	154	50	68
Mo	3	9	2	3	0,2	7	2	8	1	3	0,2	6	0,3	9	< 5(4)	1	21	78
Na	1	4	0	2 010	132	7	1	4	0	2 010	NA	NA	127	6	3 381	980	29	59
Ni	4	13	0	21	4	20	3	12	0	20	2	11	1	7	45	26	57	46
P	2	8	0	438	179	41	2	8	0	438	230	52	12	3	441	52	12	99
Pb	4	13	0	226	39	17	3	12	0	227	47	21	10	4	247	52	21	91
S	2	8	0	2 238	1 035	46	2	8	0	2 238	1 367	61	103	5	2 067	278	13	108
Sb	4	13	0	49	18	38	3	12	0	51	20	39	3	5	74	21	28	66
Si	2	8	0	13 857	6 113	44	2	8	0	13 857	7 994	58	1 715	12	23 364	10 912	47	59
Sn	4	13	0	29	7	23	3	12	0	31	6	20	2	6	44	14	32	68
Ti	2	8	0	3 432	584	17	2	8	0	3 432	767	22	109	3	3 088	218	7	111
Tl	3	9	0	1	0,4	73	2	8	0	1	0,5	87	0,2	45	< 1 (0,5)	NA	NA	121
V	4	13	4	7	2	33	2	8	0	7	1	16	0,4	5	7	2	22	106
Zn	4	13	0	417	95	23	3	12	0	408	108	26	28	7	468	125	27	89

Table B.8 — Validation data of sample SRF B cold press/semiquantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Re-flab)}$ mg/kg dm	$S_{R\ (Re-flab)}$ mg/kg dm	$V_{R\ (Re-flab)}$ %	Recovery %
Al	9	37	1	8 457	3 470	41	9	36	0	8 457	3 602	43	1 578	19	14 447	2 452	17	59
As	3	6	0	2	1	51	1	4	0	2	NA	NA	1	54	< 5 (2,9)	1	33	56
Br	7	28	4	108	29	27	6	24	0	108	30	28	20	18	< 100 (92,5)	NA	NA	117
Ca	9	37	5	18 640	7 267	39	8	32	0	18 640	7 630	41	630	3	23 366	2 770	12	80
Cd	2	8	0	9	3	29	2	8	0	9	3	36	1	14	6	2	38	155
Cl	8	33	1	8 057	5 308	66	8	32	0	8 057	5 563	69	1 609	20	15 000	NA	NA	54
Co	2	7	0	8	1	13	2	7	0	8	1	14	0,5	6	6	3	52	138
Cr	8	32	4	118	35	30	7	28	0	118	37	31	7	6	134	41	31	88
Cu	8	32	4	213	92	43	7	28	0	213	97	45	26	12	1 416	937	66	15
Fe	9	33	5	2 213	871	39	7	28	0	2 213	923	42	100	5	3 364	525	16	66
K	9	33	1	1 816	1 701	94	8	32	0	1 816	1 789	98	125	7	1 787	306	17	102
Mg	9	35	1	2 330	1 430	61	8	32	0	2 400	1 520	63	87	4	2 690	402	15	87
Mn	8	32	4	133	56	42	7	28	0	133	59	44	18	13	309	154	50	43
Mo	4	15	2	11	9	79	3	15	0	10	9	92	1	10	< 5 (4)	1	21	302
Na	8	29	1	2 486	1 113	45	7	28	0	2 486	1 178	47	105	4	3 381	980	29	74
Ni	7	28	4	21	4	21	6	24	0	21	4	20	4	20	45	26	57	46
P	9	37	1	564	280	50	9	36	0	564	290	51	43	8	441	52	12	128
Pb	7	28	4	141	40	28	6	24	0	141	43	30	10	7	247	52	21	57
S	7	25	1	2 556	1 654	65	6	24	0	2 556	1 774	69	92	4	2 067	278	13	124
Sb	3	12	4	67	36	54	2	8	0	67	47	70	12	17	74	21	28	91
Si	9	33	1	10 718	4 354	41	8	32	0	10 718	4 565	43	1 198	11	23 364	10 912	47	46
Sn	1	4	0	30	5	17	1	4	0	30	NA	NA	6	21	44	14	32	69
Ti	8	36	4	2 810	918	33	8	32	0	2 810	961	34	210	7	3 088	218	7	91
Tl	2	8	0	2	1	74	2	8	0	2	2	95	0,2	8	< 1 (0,5)	NA	NA	386
V	3	6	0	12	5	44	1	4	0	12	NA	NA	3	22	7	2	22	168
Zn	8	36	4	398	152	38	8	32	0	398	159	40	29	7	468	125	27	85

Table B.9 — Validation data of sample SRF B hot mould press/quantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	2	12	0	12 563	1 007	8	3	12	0	12 563	1 126	9	432	3	14 447	2 452	17	87
As	4	14	0	1	0,4	41	3	12	0	1	0,3	29	0,2	26	< 5 (2,9)	1	33	31
Br	3	12	0	113	13	11	3	12	0	113	14	12	10	9	< 100 (92,5)	NA	NA	122
Ca	2	12	4	18 179	253	1	2	8	0	18 179	280	2	148	1	23 366	2 770	12	78
Cd	4	16	0	4	2	37	4	16	0	4	2	40	0,4	9	6	2	38	72
Cl	2	8	0	10 636	1 751	16	2	8	0	10 636	2 261	21	660	6	15 000	NA	NA	71
Co	4	16	0	8	2	22	4	16	0	8	2	23	1	13	6	3	52	133
Cr	4	16	0	116	30	26	4	16	0	116	33	28	16	13	134	41	31	86
Cu	3	12	0	278	103	37	3	12	0	278	120	43	14	5	1 416	937	66	20
Fe	3	16	0	4 234	1 867	44	4	16	0	4 234	2 082	49	183	4	3 364	525	16	126
K	2	12	0	2 109	1 136	54	3	12	0	2 109	1 332	63	14	1	1 787	306	17	118
Mg	2	12	0	2 936	464	16	3	12	0	2 936	542	18	26	1	2 690	402	15	109
Mn	4	16	0	176	29	16	4	16	0	176	30	17	27	16	309	154	50	57
Mo	2	8	0	7	5	72	2	8	0	7	6	87	2	29	< 5 (4)	1	21	191
Na	2	12	4	3 205	695	22	2	8	0	3 205	908	28	160	5	3 381	980	29	95
Ni	4	16	0	22	7	31	4	16	0	22	8	35	3	12	45	26	57	50
P	2	12	0	667	401	60	3	12	0	667	469	70	4	1	441	52	12	151
Pb	4	16	0	226	31	14	4	16	0	226	34	15	18	8	247	52	21	91
S	2	12	0	1 822	174	10	3	12	0	1 822	198	11	33	2	2 067	278	13	88
Sb	4	16	0	62	12	19	4	16	0	62	13	21	3	5	74	21	28	83
Si	2	12	0	14 048	2 397	17	3	12	0	14 048	2 725	19	302	2	23 364	10 912	47	60
Sn	4	13	1	37	6	17	3	12	0	37	7	20	1	3	44	14	32	85
Ti	2	12	0	4 876	2 387	49	3	12	0	4 876	2 793	57	134	3	3 088	218	7	158
Tl	2	8	0	1	1	69	2	8	0	1	1	87	0,3	18	< 1 (0,5)	NA	NA	280
V	4	16	0	9	5	62	4	16	0	9	4	43	1	14	7	2	22	121
Zn	4	16	0	420	40	9	4	16	0	420	42	10	31	7	468	125	27	90

Table B.10 — Validation data of sample SRF B hot mould press/semiquantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	2	8	0	7 408	291	4	2	8	0	7 408	303	4	139	2	14 447	2 452	17	51
As	1	4	0	1	0,3	49	1	4	0	1	NA	NA	0,1	16	< 5 (2,9)	1	33	22
Br	2	8	0	114	11	10	2	8	0	114	12	10	8	7	< 100 (92,5)	NA	NA	123
Ca	2	8	0	17 353	1 171	7	2	8	0	17 353	1 498	9	316	2	23 366	2 770	12	74
Cd	1	4	0	6	0,3	5	1	4	0	6	NA	NA	0,3	4	6	2	38	105
Cl	2	8	0	7 898	601	8	2	8	0	7 898	484	6	684	9	15 000	NA	NA	53
Co	1	4	0	7	0,5	6	1	4	0	7	NA	NA	0,3	4	6	3	52	125
Cr	2	8	0	124	14	11	2	8	0	124	13	11	17	14	134	41	31	92
Cu	2	8	0	176	10	5	2	8	0	176	7	4	9	5	1 416	937	66	12
Fe	2	8	0	1 888	99	5	2	8	0	1 888	128	7	19	1	3 364	525	16	56
K	2	8	0	1 321	145	11	2	8	0	1 321	190	14	27	2	1 787	306	17	74
Mg	2	8	0	2 030	107	5	2	8	0	2 030	126	6	78	4	2 690	402	15	75
Mn	2	8	0	143	34	24	2	8	0	143	44	31	5	4	309	154	50	46
Mo	2	8	0	5	3	67	2	8	0	5	4	85	0,5	10	< 5 (4)	1	21	120
Na	2	8	0	2 871	132	5	2	8	0	2 871	145	5	71	2	3 381	980	29	85
Ni	2	7	0	19	5	27	2	7	0	19	6	33	2	9	45	26	57	42
P	2	8	0	459	19	4	2	8	0	459	17	4	8	2	441	52	12	104
Pb	2	8	0	186	16	9	2	8	0	186	19	10	6	3	247	52	21	75
S	2	8	0	2 140	63	3	2	8	0	2 140	53	2	37	2	2 067	278	13	104
Sb	1	4	0	35	1	3	1	4	0	35	NA	NA	0,3	1	74	21	28	48
Si	2	8	0	9 863	355	4	2	8	0	9 863	310	3	432	4	23 364	10 912	47	42
Sn	1	4	0	27	6	21	1	4	0	27	NA	NA	4	15	44	14	32	62
Ti	2	8	0	2 814	152	5	2	8	0	2 814	181	6	84	3	3 088	218	7	91
Tl	1	4	0	1	1	99	1	4	0	1	NA	NA	0,02	3	< 1 (0,5)	NA	NA	108
V	1	4	0	8	5	62	1	4	0	8	NA	NA	5	72	7	2	22	107
Zn	2	8	0	358	29	8	2	8	0	358	38	11	1	0,4	468	125	27	77

Table B.11 — Validation data of sample SRF B powder/semiquantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	4	13	0	14 122	4 361	31	3	12	0	14 718	3 896	26	3 547	24	14 447	2 452	17	98
As	3	9	8	10	NA	NA	0	0	0	NA	NA	NA	NA	NA	< 5 (2,9)	1	33	342
Br	5	17	1	147	85	58	4	16	0	147	81	55	24	16	< 100 (92,5)	NA	NA	159
Ca	5	17	4	26 139	7 427	28	3	12	0	26 025	7 372	28	3 141	12	23 366	2 770	12	112
Cd	0	0	0	NA	NA	NA	0	0	0	NA	NA	NA	NA	NA	6	2	38	
Cl	5	17	0	12 554	7 616	61	4	16	0	12 768	8 120	64	1 750	14	15 000	NA	NA	84
Co	2	8	0	41	10	25	2	8	0	41	10	25	2	6	6	3	52	706
Cr	5	17	0	168	90	54	4	16	0	167	99	59	28	17	134	41	31	125
Cu	5	17	0	285	141	49	4	16	0	285	148	52	15	5	1 416	937	66	20
Fe	5	17	0	3 626	1 307	36	4	16	0	3 642	1 406	39	381	10	3 364	525	16	108
K	5	17	0	2 428	920	38	4	16	0	2 459	976	40	284	12	1 787	306	17	136
Mg	4	13	0	3 608	1 463	41	3	12	0	3 745	1 650	44	317	8	2 690	402	15	134
Mn	5	17	0	203	81	40	4	16	0	202	89	44	32	16	309	154	50	66
Mo	1	4	0	20	0	0	1	4	0	20	NA	NA	0	0	< 5 (4)	1	21	533
Na	4	13	0	3 612	1 997	55	3	12	0	3 702	2 268	61	808	22	3 381	980	29	107
Ni	5	14	0	46	25	54	3	12	0	50	27	54	9	17	45	26	57	104
P	4	13	0	934	354	38	3	12	0	973	355	36	128	13	441	52	12	212
Pb	5	17	1	163	37	23	4	16	0	163	31	19	11	7	247	52	21	66
S	4	13	1	3 418	2 662	78	3	12	0	3 712	3 396	91	277	7	2 067	278	13	165
Sb	3	12	0	51	23	46	3	12	0	51	21	42	2	3	74	21	28	69
Si	5	17	1	15 690	7 085	45	4	16	1	15 095	8 230	55	1 841	12	23 364	10 912	47	67
Sn	2	8	4	68	6	9	1	4	0	68	NA	NA	1	1	44	14	32	155
Ti	4	16	0	5 534	2 917	53	4	16	0	5 534	3 072	56	537	10	3 088	218	7	179
Tl	0	0	0	NA	NA	NA	0	0	0	NA	NA	NA	NA	NA	< 1 (0,5)	NA	NA	
V	1	4	0	43	1	1	1	4	0	43	NA	NA	1	1	7	2	22	608
Zn	5	17	0	468	182	39	4	16	0	435	133	31	54	12	468	125	27	100

Table B.12 — Validation data of sample SRF C cold press/quantitative

Element	L	N	O	m_{all} mg/kg dm	SD_{all} mg/kg dm	V_{all} %	L (5725-2)	N (5725-2)	O (5725-2)	m mg/kg dm	S_R mg/kg dm	V_R %	S_r mg/kg dm	V_r %	$m_{(Reflab)}$ mg/kg dm	$S_{R\ (Reflab)}$ mg/kg dm	$V_{R\ (Reflab)}$ %	Recovery %
Al	2	8	0	10 484	345	3	2	8	0	10 484	266	3	133	1	9 666	888	9	108
As	4	13	0	2	1	57	3	12	0	2	1	68	0,3	15	< 5 (4,5)	1	24	52
Br	4	16	0	38	3	9	4	16	0	38	4	10	1	2	< 100 (67,5)	NA	NA	56
Ca	2	8	0	43 729	8 475	19	2	8	0	43 729	11 159	26	506	1	37 629	3 133	8	116
Cd	5	17	0	12	2	17	4	16	0	12	2	15	1	5	14	2	11	86
Cl	3	12	0	5 031	483	10	3	12	0	5 031	557	11	79	2	3 392	NA	NA	148
Co	4	13	0	3	1	22	3	12	0	3	1	22	0,4	12	2	1	70	176
Cr	5	17	0	38	15	40	4	16	0	39	16	42	1	2	28	3	9	137
Cu	5	17	0	38	3	8	4	16	0	38	3	9	0,3	1	45	3	7	85
Fe	3	12	0	4 845	625	13	3	12	0	4 845	727	15	62	1	3 786	211	6	128
K	2	8	0	2 800	405	14	2	8	0	2 800	532	19	59	2	2 449	170	7	114
Mg	2	8	0	6 652	4 514	68	2	8	0	6 652	5 958	90	314	5	6 440	636	10	103
Mn	4	13	0	5 962	384	6	3	12	0	5 977	462	8	17	0,3	5 285	211	4	113
Mo	3	9	1	3	0,1	3	2	8	0	3	0	2	0,03	1	< 5 (3)	0,2	7	84
Na	1	4	0	9 175	318	3	1	4	0	9 175	NA	NA	7	0,1	6 358	636	10	144
Ni	5	17	0	16	1	8	4	16	0	16	1	9	0,2	1	16	3	18	102
P	2	8	0	12 817	3 125	24	2	8	0	12 817	4 125	32	202	2	10 454	392	4	123
Pb	5	17	0	38	3	9	4	16	0	38	3	9	1	2	30	6	19	126
S	2	8	0	12 758	231	2	2	8	0	12 758	134	1	155	1	12 992	454	3	98
Sb	3	12	0	4	5	124	3	12	0	4	6	145	0,2	4	< 4 (1)	NA	NA	397
Si	2	8	0	19 329	5 779	30	2	8	0	19 329	7 617	39	294	2	22 226	8 609	39	87
Sn	5	17	0	8	3	33	4	16	0	9	3	32	1	10	10	7	69	86
Ti	2	8	0	441	107	24	2	8	0	441	140	32	5	1	341	51	15	129
Tl	3	9	0	1	1	119	2	8	0	0,3	0,3	100	0,03	9	< 5(4)	NA	NA	12
V	4	13	0	11	2	18	3	12	0	11	2	19	1	7	10	1	7	105
Zn	5	17	0	783	59	8	4	16	0	786	67	9	13	2	701	90	13	112