BS EN 15063-1:2014

BSI Standards Publication

Copper and copper alloys — Determination of main constituents and impurities by wavelength dispersive X-ray fluorescence spectrometry (XRF)

Part 1: Guidelines to the routine method

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National foreword

This British Standard is the UK implementation of EN 15063-1:2014. It supersedes BS EN 15063-1:2006 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee NFE/34/1, Wrought and unwrought copper and copper alloys.

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

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Copper and copper alloys - Determination of main constituents and impurities by wavelength dispersive X-ray fluorescence spectrometry (XRF) - Part 1: Guidelines to the routine method

Cuivre et alliages de cuivre - Détermination des éléments principaux et des impuretés par spectrométrie de fluorescence X à dispersion de longueur d'onde (FRX) - Partie 1 : Lignes directrices pour la méthode de routine

Kupfer und Kupferlegierungen - Bestimmung von Hauptbestandteilen und Verunreinigungen durch wellenlängendispersive Röntgenfluoreszenzanalyse (RFA) - Teil 1: Leitfaden für das Routineverfahren

This European Standard was approved by CEN on 8 November 2014.

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Foreword

This document (EN 15063-1:2014) has been prepared by Technical Committee CEN/TC 133 “Copper and copper alloys”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2015 and conflicting national standards shall be withdrawn at the latest by June 2015.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 15063-1:2006.

Within its programme of work, Technical Committee CEN/TC 133 requested CEN/TC 133/WG 10 “Methods of analysis” to revise the following standard:

EN 15063-1:2006, *Copper and copper alloys — Determination of main constituents and impurities by wavelength dispersive X-ray fluorescence spectrometry (XRF) — Part 1: Guidelines to the routine method*

This is one of two parts of the standard for the determination of main constituents and impurities in copper and copper alloys. The other part is:

EN 15063-2, *Copper and copper alloys — Determination of main constituents and impurities by wavelength dispersive X-ray fluorescence spectrometry (XRF) — Part 2: Routine method*

In comparison with EN 15063-1:2006, the following changes have been made:

a) Definition 3.1 and 3.2 modified;

b) Clause 5 modified;

c) Editorial modifications have been made.

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

Introduction

Wavelength dispersive X-ray fluorescence spectrometry (XRF) has been used for several decades as an important analytical tool for production analysis. XRF is characterised by its speed and high precision over a wide concentration range and as the XRF-method in most cases is used as a relative method, the limitations are often connected to the quality of the calibration samples. The technique is well established and most of the physical fundamentals are well known.

This guideline is intended to be used for the analysis of copper and copper alloys but it may also be applied to other materials.

1 Scope

This European Standard provides guidance on the concepts and procedures for the calibration and analysis of copper and copper alloys by wavelength dispersive X-ray fluorescence spectrometry.

2 Principle

An appropriately prepared test sample is irradiated by an X-ray beam of high energy. The secondary X-rays produced are dispersed by means of crystals and the intensities are measured by detectors at selected characteristic wavelengths. Concentrations of elements are determined by relating the measured intensities of test samples to calibration curves prepared from reference materials.

3 Terms and definitions

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

3.1
reference material
RM
material, sufficiently homogeneous and stable with respect to one or more specified properties which has been established to be fit for its intended use in a measurement process

[SOURCE: ISO GUIDE 30:1992/Amd.1:2008, definition 2.1]

3.2
certified reference material
CRM
reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate, that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

[SOURCE: ISO GUIDE 30:1992/Amd.1:2008, definition 2.2]

3.3
test sample
representative quantity of material for testing purposes

3.4
calibration samples
series of certified reference materials or if not available, reference materials used for calibration

3.5
drift control samples
series of homogeneous materials that contain all the elements which have been calibrated and that cover the low, mid and high points of the calibration range for each element, used to detect variations over time in these points

Note 1 to entry: Drift control samples can also be used for statistical process control (SPC) of the instrument.

3.6
recalibration samples
samples at both low and high points in the calibration ranges used to recalibrate the spectrometer

Note 1 to entry: These samples are measured during the calibration procedure and the intensities obtained are stored in the computer according to the manufacturer's instructions.

Note 2 to entry: No chemical analyses are necessary, but the homogeneity of these samples should be carefully evaluated.

3.7
calibration

process to establish the curve(s) by measuring and calculating the best fit of net intensities for elemental concentrations of a number of calibration samples

3.8
recalibration

adjusting instrumental output to conform to the calibration

Note 1 to entry: To compensate for day to day instrumental variation, a set of recalibration samples are measured at the minimum low concentration and at a high concentration for each element (two-points recalibration). The measured intensities are compared to the initial measured intensities stored during the calibration procedure and the recalibration coefficients are calculated. Calibration constants are not changed.

3.9
reference measurements

measurements carried out to determine intensities for reference materials

Note 1 to entry: Initial intensities for the reference materials are stored during the calibration procedure and the intensities are updated to compensate for day to day variations.

3.10
spectral background

background caused by radiation energy of a wavelength corrected for its position in the spectrum, but not directly related to the desired observation

Note 1 to entry: For a spectral line, spectral background may consist of other lines, bands or continuous radiation.

3.11
background equivalent concentration

concentration of analyte, which, when it is excited, provides a net intensity equal to the spectral background

Note 1 to entry: See Annex A.

3.12
limit of detection

minimum concentration at which the signal generated by a given element can be positively recognised with a specified confidence level above any background signals

Note 1 to entry: See Annex A.

3.13
lower limit of detection

calculated minimum concentration based on counting statistical error at which the signal generated by a given element can be positively recognised, with a specified confidence level, above any background signals

Note 1 to entry: See Annex A.

3.14
limit of quantification

smallest concentration that can be determined with a specified confidence level related to the limit of detection by a factor dependent on the method

Note 1 to entry: See Annex A.

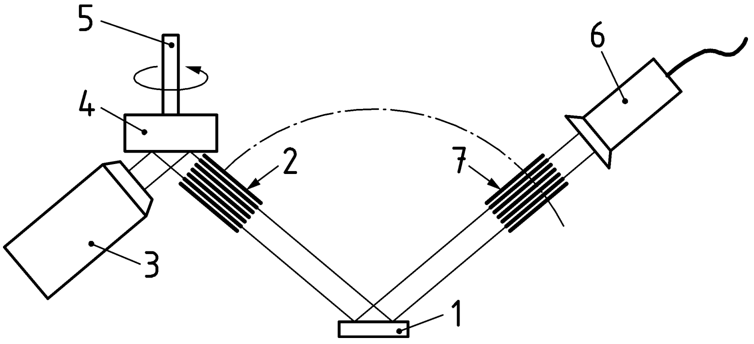
3.15
sensitivity
rate of change of signal with change in concentration

Note 1 to entry: See Annex A. Sensitivity is expressed as counts per second percent, and derived by difference in signals between a sample with a high concentration and one with a low concentration divided by the difference in concentrations.

4 Instrumentation

4.1 Principles of X-ray fluorescence spectrometers

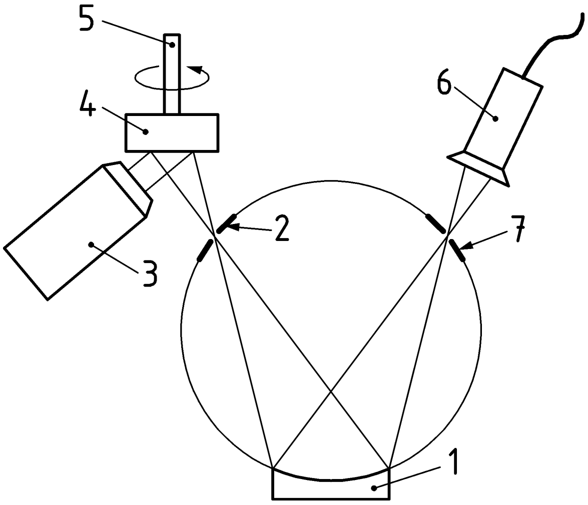
The principles of two different X-ray fluorescence spectrometer concepts are shown in Figures 1 and 2. Each detail is described in the following sub-clauses.



Key

1	Crystal	5	Spinner
2	Primary collimator	6	Counter
3	X-ray tube	7	Secondary collimator
4	Test sample		

Figure 1 — Plane crystal spectrometer geometry, used in sequential instruments



Key

1	Crystal	5	Spinner
2	Source slit	6	Counter
3	X-ray tube	7	Detector slit
4	Test sample		

Figure 2 — Curved crystal spectrometer geometry, used in simultaneous instruments

4.2 X-ray tubes

Two different types of X-ray tubes are used: side-window tubes or end-window tubes. Table 1 compares these two types. More favourable measuring conditions are usually obtained for elements with a low atomic number ($Z < 20$) with an end-window tube due to the thinner window.

Different high purity elements such as Rh, Ag, W, Cr or Au are used as anode materials. For analysing copper and copper alloys, rhodium is usually used as the anode material in a multipurpose tube as it provides good excitation conditions for all elements of interest. If possible, the anode material should not be the same as the element to be determined.

Table 1 — Comparison between end-window and side-window tubes

Feature	End-window tubes	Side-window tubes
Cooling	Two cooling circuits a) Direct cooling with deionised water b) Indirect cooling with tap water	One cooling circuit Direct cooling with tap water
Window	Slight thermal stressing: Thinner window	Greater thermal stressing: Thicker window
Service Life	20 000 h	5 000 h

The applicability of common anode materials is summarised in Table 2.

Table 2 — Anode materials for X-ray tubes and corresponding fields of application

Anode material	Application
Rh	Good excitation conditions for elements with a low or high atomic number.
Cr	Good excitation conditions for elements with a low atomic number, especially for K, Ca and Ti. Not so good for elements with a high atomic number.
Mo	Good excitation conditions for elements with a high atomic number, especially for Rb and Sr.
W	Good excitation conditions for elements with a high atomic number, especially for Fe and Ni.
Au	Good excitation conditions for elements with a high atomic number, especially for Cu and Zn.
Ag	Equivalent to Rh. Ag is used if Rh lines interfere with element of interest.
Double anode	Different applications according to the anode materials.

The X-ray tube produces a continuous spectrum and characteristic spectra depending on the selected anode material. For optimum excitation, a maximum excitation energy lying at least two to three times above the corresponding absorption edge of the element line to be measured, is recommended.

Equipment is available which may be operated with acceleration voltages up to 100 kV and with a maximum power of 3 kW. The applicability of the apparatus is derived from either the high-voltage supply or the X-ray tube used. Using acceleration voltages above 60 kV is only advantageous in a few cases, e.g. to determine traces of elements with a high atomic number.

The fluorescence arising inside a test sample is emitted uniformly in all directions. Only a fraction reaches the test sample surface. The proportion of the fluorescence measured depends on the angle between the test sample surface and the spectrometer. The nearer to perpendicular the beam of radiation is to the test sample, the deeper the layers of the test samples that are measured.

4.3 Vacuum system

The test sample is placed in the spectrometer chamber to be measured. To analyse copper and copper alloys it is recommended, for all elements, to measure under vacuum, to maintain stable conditions in the instrument. A pressure of 13 Pa or less, controlled to ± 3 Pa is required.

4.4 Test sample spinner

Most instruments are equipped with a test sample spinner to avoid effects of inhomogeneities, e. g. grinding striations. If not, the test sample shall be orientated so that the relation between the X-ray beam and the inhomogeneities is always the same from measurement to measurement.

4.5 Filters

If the element to be determined is the same as the anode material, a filter has to be put in front of the exit window of the tube to eliminate the characteristic lines. The efficiency of a filter depends on its material and thickness. A filter made of titanium or aluminium is often used to eliminate the characteristic lines from a chromium anode. When a filter is used, the sensitivity for the element of interest will significantly decrease. Sometimes a filter can be used to increase the peak to background ratio for low concentrations of elements with a high atomic number. Many instruments are supplied with a filter changer containing filters of different materials and thicknesses.

4.6 Collimators of slits

In a plane crystal geometry (Figure 1), only a portion of the secondary radiation is selected by a primary collimator and the parallel beam is allowed to penetrate the plane surface of the crystal. The resolution of the spectrometer is affected not only by the crystal used, but also by the collimation of the radiation. The finer the collimator selected, the better the resolution, but the intensity measured is lower. Most sequential spectrometers of this type are supplied with at least two collimators: coarse and fine.

In a curved crystal geometry (Figure 2), using collimators is not necessary as the radiation is focussed on the detector by a slit system.

4.7 Analysing crystals

Analysing crystals are flat or curved with optimised capability for diffraction of the wavelength of interest.

In order to isolate individual characteristic lines emitted by the test sample, large single crystals are used as dispersion media. To cover the usual wavelength range between 0,2 Å and 15 Å, crystals with different spaces between the atomic layers (d-value) are used. Commonly used analysing crystals are listed in Table 3 for measuring the Kα-lines of particular elements. To cover the whole wavelength range, a minimum of three crystals is required; LiF(200), PET and TIAP or a multi-layer crystal for elements with a low atomic number.

Table 3 — Crystals and their fields of application

Crystal	**Lattice planes**	**2 d-value** nm	**Elements**
Lithium fluoride (LiF)	220	0,284 8	Ti, V, Cr, Mn, Fe, Co, Ni
Lithium fluoride (LiF)	200	0,402 7	K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr
Germanium (Ge)	111	0,653 2	P, S, Cl
Pyrolitic graphite (PG)	002	0,671 5	P, S, Cl
Pentaerythritol (PET)	002	0,874 2	Al, Si, P, S, Cl
Ammonium dihydrogen phosphate (ADP)	101	1,064 2	Mg, Na
Thallium hydrogen phtalate (TIAP)	100	2,575	F, Mg, Na, Al
Synthetic multi-layer crystal (PX, OVO)	—	Variable	Elements Z[a] < 11
[a] Atomic number			

A typical set of crystals used for the analysis of copper and copper materials is shown in Table 4.

Table 4 — Typical set of crystals for the analysis of copper and copper alloys

Channel-No.	**Line**	**Crystal**	***d*-value** nm	**2*θ*** degrees	**Counter** FC/SC[a]	**Foil thickness** µm
1	CKα1, 2	OVO — C	12,0	48,02	FC	1,0
2	MgKα1, 2	OVO 55	5,5	20,70	FC	1,0
3	AlKα1, 2	PET	0,874	144,92	FC	1,5
4	SiKα1, 2	PET	0,874	109,12	FC	1,5
5	PKα1, 2	GE	0,653	141,14	FC	1,5
6	SKα1, 2	GE	0,653	110,74	FC	1,5
7	AgLα1	GE	0,653	79,00	FC	6,0
8	CdLβ1	LiF	0,403	136,32	FC	6,0
9	SbLα1	LiF	0,403	117,31	FC	6,0
10	TeLα1	LiF	0,403	109,50	FC	6,0
11	CrKα1, 2	LiF	0,403	69,36	FC	6,0
12	MnKα1, 2	LiF	0,403	62,98	FC	6,0
13	FeKα1, 2	LiF	0,403	57,51	FC	6,0
14	NiKα1, 2	LiF	0,403	48,65	SC	—
15	ZnKα1, 2	LiF	0,403	41,80	SC	—
16	CuKβ1	LiF	0,403	40,45	SC	—
17	PbLα1	LiF	0,403	33,93	SC	—
18	BiLα1	LiF	0,403	33,01	SC	—
19	SeKα1, 2	LiF	0,403	31,89	SC	—
20	AsKβ1	LiF	0,403	30,44	SC	—
21	ZrKα1	LiF	0,403	22,50	SC	—
22	SnKα1	LiF	0,403	13,99	SC	—

[a] FC = flow counter and SC = scintillation counter.

4.8 Counters

The selected fluorescent radiation in a spectrometer is recorded by means of appropriate counters (flow counter, sealed gas counter, scintillation counter). The sensitivity of the various counters is a function of the radiation energy measured. In simultaneous instruments the most suitable counter should be used for the particular element line. In sequential instruments, flow and scintillation counters are generally used at the same time and are connected in a series (tandem connection). For elements with atomic numbers below 25, the flow counter is used, and with atomic numbers above 30, the scintillation counter is used. For elements with atomic numbers between 25 and 30, both counters are used in tandem if possible. In simultaneous instruments, gas counters filled with Kr or Xe are often used for elements with atomic numbers between 20 and 40.

All counters can record only a limited number of pulses per unit of time because the measuring process for each pulse requires a fixed amount of time, which is in the order of 1 µs to 100 µs. Other pulses cannot be detected in this time, which is defined as dead time τ. Therefore, care shall be taken to ensure that the maximum pre-set pulse rate is not exceeded. This is possible, for example, by connecting attenuation filters (simultaneous equipment) or decreasing the tube current. Otherwise, there will be no linearity between the intensity of the X-ray radiation and the pulse rate measured.

NOTE Normally the number of pulses (counts) is indicated as kilocounts per second (Kc/s).

The dead time of the counters may have an effect from a pulse rate of approximately 10^5 pulses per second, however, higher pulse rates may be used if correction is applied.

The counters used register pulses at different intensities as a function of the energy of the X-ray radiation. Therefore, specific pulses or energies may be filtered out by selecting an electronic “window” (Pulse Height Discriminator), as pulse height discrimination eliminates interference pulses.

4.9 Simultaneous and sequential Instruments

X-ray fluorescence instruments can be subdivided into two categories: simultaneous and sequential. Simultaneous instruments have several fixed goniometers (channels) arranged around the test sample so that the individual element lines can be measured at the same time with the same excitation conditions. Each channel is optimised for each element. In sequential instruments, the user has the flexibility to optimise the measuring conditions independently for all selected elements and their backgrounds. The goniometer can be set to a pre-defined angle (5° to 150°) and the excitation conditions can be optimised separately for all elements.

Simultaneous instruments are often used in a production environment where speed is important and the sample matrix is known. In modern instruments sequential and simultaneous functions can be combined.

5 Sampling and test sample preparation

Test sample preparation is a critical procedure. The test sample required is a flat solid with a diameter of at least 25 mm, and thickness of at least 1 mm, prepared from a sample obtained directly from a melt by pouring the liquid metal rapidly in an appropriately designed mould. The test sample is prepared on a milling machine, without any other mechanical treatment (grinding, etc.). Chips or small pieces of pure copper may be transformed into a suitable test sample by remelting under an inert gas atmosphere followed by the same operations as above.

NOTE Remelting copper alloys will lead to losses of elements, e.g. Zn, Be, Pb.

The measuring surface should be free of defects.

6 Evaluation methods

6.1 General

Measure the intensities of secondary X-rays produced at the selected characteristic wavelengths and apply corrections as described in 6.2 to 6.5.

6.2 Dead time correction

The dead time τ, is a function of a type of counter and can be calculated from the following approximate relationship between the measured pulse rate n, and the corrected pulse rate, n_0.

$$n_0 = \frac{n}{1 - \tau \times n} \tag{1}$$

The dead time τ is generally around 2 µs. With current types of spectrometers, dead time losses are often compensated by means of a built-in correction circuit. If this is not the case, they can be determined by repeatedly measuring the same test sample at a constant high voltage and with different current settings or by measuring the ratio of $I_{K\alpha}/I_{K\beta}$, which is constant.

The pulse rates determined are a linear function of the current as long as the dead time has no effect on the measurement. The numerical value of τ, results from the reciprocal of the pulse rate at which a deviation from the linear function has been established.

6.3 Background correction

The background consists mainly of scattered X-rays from the tube. For very low concentrations of determined elements (trace analysis), it is necessary to take the background into account, i.e. to work with the net intensity. As the background fluctuations from test sample to test sample may assume magnitudes in the range of the line intensities, the background radiation value has to be subtracted from the gross value measured.

6.4 Line interference correction models

The spectral line of the element to be determined can be overlapped by adjacent lines of other elements. This leads to an increased measured value. The increase is corrected by subtracting the interfering proportion from the measured value of the element to be determined.

Two correction methods are common:

$$I_K = I_g - f_1 \times I_{st} \tag{2}$$

$$I_K = I_g - f_2 \times C_{st} \tag{3}$$

Here, I_K and I_g are the corrected and measured intensities, f_1 and f_2 are the interference factors, and I_{st} and C_{st} represent the intensity and mass fraction in percent of the interfering element.

Software solutions to handle line interferences differ between manufacturers. Only the net intensities (corrected for line overlap) are used in regression analysis but in some cases the line interferences are calculated within the regression analysis.

If possible, line interferences should be investigated separately. There are several ways to do this:

- By measuring a set of binary samples where the concentration of the element of interest is zero or constant and the interfering element concentration is increasing, the interference factor can then be calculated.
- Plot the intensities for the element in question on the Y-axis and the intensities for the interfering element on the X-axis.
- Use the equation $Y = AX + B$ to calculate the straight line. The slope A corresponds to the interference factor, see, for example, Annex B.

6.5 Inter-element effects correction models

The result of the fluorescence produced inside the test sample by one of the other alloying or accompanying elements is that the intensity of the analysis line is either too low (absorption effect) or too high (secondary excitation) when measured.

There are two basic types of methods used for correcting these inter-elements effects:

a) “Physical parameter” method (fundamental parameters).

This method assumes that a series of physical magnitudes are known, generally only by the spectrometer manufacturer who informs the user about the correction coefficients. In the model, the correction is made on the basis of the mass fraction, in percent, using the following equations:

$$c_i = \bar{c}_i \times (\sum_j \alpha_{ij} \times c_j) \tag{4}$$

$$\bar{c}_i = a_0 + a_1 \times I_i + a_2 \times (I_i)^2 \tag{5}$$

where

i	is the index of the element to be determined;
j	is the index of the interfering element;
c_i	is the mass fraction in percent (%) of the element i;
$\bar{c}_i$	is the apparent (uncorrected) mass fraction, in percent (%);
α_{ij}	is the correction coefficient of element j for the mass fraction in percent (%) of element i;
c_j	is the mass fraction in percent (%) of the element j;
a_0, a_1, a_2	is the regression coefficients (a_2 is often evaluated as 0);
I_i	is the measured intensity of the element i.

The mass fraction, in percent (%), of unknown samples can be calculated according to Equation (4) using iteration methods that converge so well, that they can be truncated by the computer after a few steps (normally five).

b) "Empirical coefficients" method.

The correction coefficients may be determined using a multi-variable regression method. If the mass fractions in percent (%) are taken as the variables, then a model formally identical to the Equations (4) and (5) is obtained and its solution is identical to that of the "physical parameter" method. If, however, the intensities of the interfering elements are used instead, as a basis for the regression calculation[1], the following correction equation is obtained.

$$c_i = \left[a_0 + a_1 \times I_i + a_2 \times (I_i)^2\right] \times \left(1 + \sum_j \alpha_{ij} \times I_j\right) \tag{6}$$

In this case, in order to determine the mass fraction, in percent (%) of an element of an unknown sample, it is sufficient to insert the intensity of the element to be determined and that of interfering elements in the correct Equation (6).

7 Calibration procedure

7.1 General

Before proceeding to the calibration step, it is necessary to ensure that the instrument is fully optimised to avoid time-consuming mistakes. In this clause some strategic advice is given. Check this advice before performing any measurements. In most cases the basic calibration is performed only once owing to the high stability of the technique.

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[1] The multi-variable non-linear regression methods used here lead to a complex, redundant, non-linear equation system that can only be solved iteratively by computers using a numerical analysis methods. With new types of equipment, the relevant software is generally supplied.

7.2 Optimizing of the diffraction angle (2*θ*)

Since the geometrical configuration is slightly different from one instrument to another it is good practice to experimentally determine the actual peak position for each element. Choose a sample with a concentration of the element as high as possible.

7.3 Selecting optimum conditions for detectors

Follow the instructions in the user's manual for setting the detector high voltage. Pulse High Distribution (PHD) settings (lower level and window) should be set experimentally by measuring samples with concentrations within the actual concentration ranges to be calibrated.

7.4 Selecting optimum tube voltage and current

Depending on the equipment used, it might be possible to increase the sensitivity and peak to a background ratio by modifying the tube voltage and current, especially for elements with a low atomic number.

7.5 Selecting minimum measuring times

The statistical error can be minimised by increasing the measuring time. For practical reasons, the measuring time is fixed between 10 s and 100 s. As a rule of thumb, select a measuring time so that the relative standard deviation (RSD) of the statistical error at a 1 % level of the element concentration is at least less than 0,5 % and that a 10 % level or more, is less than 0,1 %.

RSD for the statistical error is calculated using the following equation:

$$RSD = \frac{1}{\sqrt{N}} \times 100\ \% = \frac{1}{\sqrt{RT}} \times 100\ \% \qquad (7)$$

where

N is the number of counts (c);

T is the measuring time, in seconds (s);

R is the count rate (c/s).

7.6 Selecting calibration samples

The number of samples should be as large as possible. As a rule of thumb, there should be a degree of freedom of 30 for calculating a regression curve from the values corrected in accordance with Clause 6. This means that for p samples and n individual measurements per sample, the requirement of the following equation should be met.

$$n \times p - 2 = 30 \qquad (8)$$

When plotting the calibration curve, the measured intensities are regarded as the ideals. That means that in a graph, the intensity values I are plotted on the ordinate, and the mass fraction values c in percent (%) on the abscissa. Following the correction procedure in Clause 6, the regression function in the following equation is calculated.

$$I = f(c) \qquad (9)$$

The analysis function and evaluation curve used for determining the unknown mass fractions in per cent are obtained by performing the reverse function. A software package for calculating theoretical coefficients is often included in XRF-instruments. Otherwise, they can be calculated by the manufacturer. Using these coefficients, the degrees of freedom will not be affected since they are treated as fixed constants. The number of samples could then be reduced, since the only unknown factors are the line interferences, the slope and the background.

7.7 Selecting drift control and recalibration samples

Instrumental drift is checked by running drift control samples. The instrument should be recalibrated as frequently as performance experience indicates.

To correct for instrumental drift, select at least two recalibration samples per element, one at the higher level of the concentration range and one at the lower. For practical reasons, try to minimise the total number of recalibration samples for an analytical programme.

In order to attain better repeatability, the recalibration samples shall be protected against contamination and stored in a desiccator.

7.8 Measuring the calibration samples

Measure the calibration samples and, in order to get initial intensities for further recalibration stored, measure the recalibration samples according to the instrument user's manual. Keep the time between measurements as short as possible in order to minimize the long term variation.

7.9 Regression calculations

To make the regression calculation, follow the calibration guideline in the instrument user's manual. The criterion for evaluating the accuracy of the various correction methods is a reduction of the residual spread of the mass fractions, in percent (%), for the calibration samples around the analysis function. The residual spread is the standard deviation for the residuals due to differences between reference values and values for samples within the calibration set determined by X-ray spectrometry:

$$SD = \sqrt{\frac{\sum (c - c')^2}{n - p}} \qquad (10)$$

where

SD is the residual spread;

c is the reference value, expressed as mass fraction in per cent (%);

c' is the measured value, expressed as mass fraction in per cent (%);

n is the number of calibration samples;

p is the number of parameters determined by regression calculation (p = 2 for a straight line).

8 Method validation (accuracy and precision)

Validation can be divided into three steps:

1) Calculate the limits of detection and the limits of quantification.

2) Check that the method has no systematic errors by measuring a number of certified reference materials, not used in calibration, covering the calibrated concentration range.

3) Calculate the repeatability (r) and the reproducibility within the laboratory (R_w).

9 Performance criteria

9.1 General

Before starting a calibration or measuring procedure, satisfactory performance of the instrument shall be demonstrated.

Precision of the instrument shall be checked according to the procedure in 9.2 at regular time intervals (every 3, 6 or 12 months), after major repairs or whenever there is reason to suspect that the measuring conditions might have changed.

During routine measurements, SPC-diagrams (control charts) shall be used in regular performance checking, see 9.3.

9.2 Precision test

In order to check the precision of the instrument, a test sample shall be measured under repeatability conditions, in a period of 1 h to 4 h, and the measured intensities shall be stored. The same test sample cup shall be used and not moved between measurements. The relative standard deviations (RSD_{cal}) for each element shall be calculated and compared with the relative statistical standard deviation (RSD_{stat}) calculated by Equation (7) in 7.5.

If all mechanical movements in the instrument are included during the measurements, assuming that the instrumental error is of the same order as the statistical error, RSD_{cal} should be less than or equal to 2 times the RSD_{stat}. If no mechanical movements are involved (simultaneous instrument), then RSD_{cal} should be close to RSD_{stat}. An example of a precision test for a simultaneous instrument is given in Annex C.

9.3 Performance monitoring

It is common practice to use SPC-diagrams (control charts) in the regular checking of both the method and instrument performance (test sample preparation excluded). As a rule of thumb, corrective actions should be based on assessment of the control charts. Automatic drift corrections based only on time intervals should not be used.

The time interval between measurements of the check samples should be based on the experience of the stability of the instrument. Instrument performance should be checked at least every 8 h.

9.4 Maintenance

In order to ensure the operation is as fault-free as possible, a series of checks and maintenance is necessary at regular intervals. Table 5 gives an example for a current type of apparatus. Maintenance may be carried out by the equipment manufacturer or by specially trained laboratory personnel.

Performance monitoring and maintenance should be recorded systematically.

Table 5 — Example of checks and maintenance work to be carried out on X-ray fluorescence spectrometers

System part	Check interval			
	weekly	monthly	every 6 months	every year
Cooling system	Water level, temperature, pressure resistance and connections	—	—	Change or clean water filters
Vacuum system	Oil level, pressure during standby and measurement	—	Change oil	Change dynamic stressed O-rings in the vacuum system and test sample transportation system
Flow detector	—	Check detector resolution and PHD settings	—	Clean detector and change foil
Scintillation detector	—	—	Check resolution and PHD settings	—
Mechanical parts	Test sample holders, test sample rotation and transportation system	—	—	Clean
Electronics and generator	—	—	—	Check power supplies and clean air filters and fans

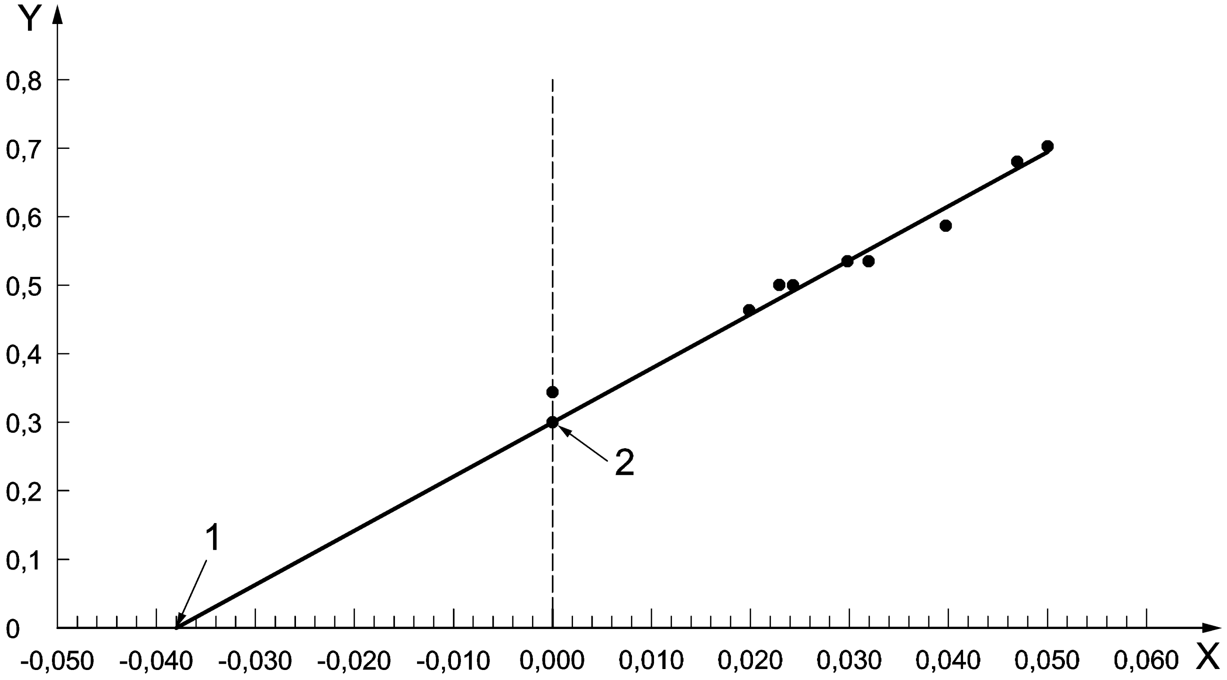
10 Radiation protection

The X-ray fluorescence spectrometers commercially available are generally approved fully-protected apparatus. This means that the user is not subjected to any radiation when operating the apparatus. All apparatus are subject to specific official approval and acceptance conditions.

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

Annex A
(informative)

Example of calculating background equivalent concentration, limit of detection, limit of quantification and lower limit of detection



Key

1	*BEC*	X	Pb (%)
2	*Bg*	Y	Kc/s

Figure A.1 — Calibration curve for lead in copper-aluminium alloys

$$\text{Sensitivity } (S) = \frac{I_{\text{High}} - I_{\text{Low}}}{C_{\text{High}} - C_{\text{Low}}} = \frac{0{,}732\,8 - 0{,}486\,0}{0{,}050 - 0{,}020} = 8{,}227 \text{ Kc/s }\%^{-1} \qquad \text{(A.1)}$$

I_{High}, I_{Low}, C_{High}, C_{Low} are taken from the curve

Background Equivalent Concentration (*BEC*) = 0,038 5 % (absolute value in the curve)

Background *(Bg)* = 0,32 Kc/s (from the curve)

Measuring time *(T)* = 24 s (defined in the measuring programme)

Relative standard deviation *(RSD)* on the background intensity = 1,1 %

The *RSD* value is calculated based on data collected under reproducibility conditions within the laboratory, e.g. different days, different operators and new test sample preparation.

Limit of detection *(LOD)* = 3 × *BEC* × *RSD* = 3 × 0,038 5 × 0,011 = 0,001 3 %

Limit of quantification $(LOQ) = 3 \times LOD = 3 \times 0{,}001\,3\ \% = 0{,}003\,9\ \%$

For practical reasons the LOQ is set to 0,004 %; measured values below 0,004 % should be reported as < 0,004 %.

Another equation for calculating the LOD is often referred in XRF literature. In this guideline, that equation is used to define the lower limit of detection, LLD since it is based only on the counting statistical error.

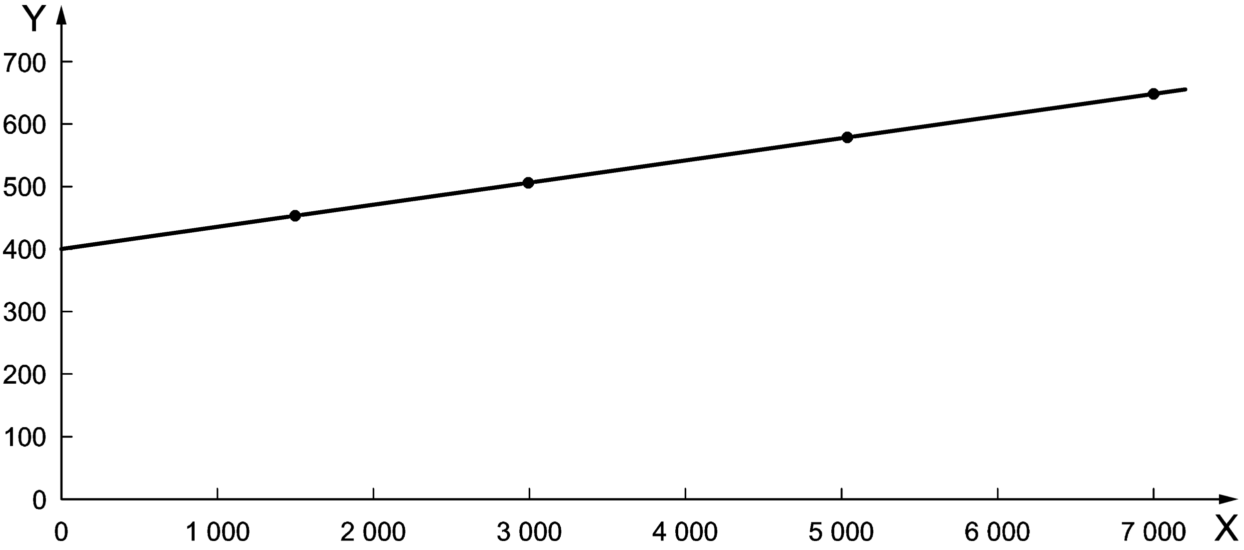
The LLD is a very useful tool in comparing the performances of different XRF equipment.

$$\text{Lower limit of detection}\,(LLD) = \frac{3}{S}\sqrt{\frac{Bg}{T}} = \frac{3}{8\,227}\sqrt{\frac{320}{24}} = 0{,}0013\ \% \qquad \text{(A.2)}$$

Annex B
(informative)

Example of calculating line interference of one element to another

Select a set of samples with a low and constant content of an element A but with an increasing content of an element B. Measure the A spectral line intensity and the B spectral line intensity. Plot the intensities according to the following example: Int A = *f* (Int B).



Key

X	Int B (c/s)
Y	Int A (c/s)

Figure B.1 — Example for a plot of intensities Int A = *f* (Int B)

Calculate the interference factor (f) =

$$\frac{\Delta I_A}{\Delta I_B} = \frac{650 - 450}{7\,000 - 1\,500} = 0{,}036\,7 \tag{B.1}$$

$\Delta\ C_B$ between points 1 and 4 is 4 % in this case.

The difference in A intensities is about 200 c/s.

The sensitivity, S, for A is 8,400 Kc/s $\%^{-1}$.

The influence of 1 % B can be calculated by: 1 % B = 0,006 % A.

Annex C
(informative)

Example of performance criteria obtained under repeatability conditions

A test sample was measured 50 times, with a delay of 10 min between the measurements. No mechanical movements were involved except those of the test sample spinner. The following results were obtained:

Table C.1 — Performance criteria

Element	**Mean intensity** Kc/s	RSD_{cal} %	RSD_{stat} %	**Performance criteria fulfilled**
A	0,37	0,803	0,827	yes
B	4,11	0,276	0,247	yes
C	10,00	0,159	0,158	yes
D	28,05	0,114	0,094	yes
E	96,46	0,065	0,051	yes
F	168,52	0,049	0,039	yes
G	181,07	0,095	0,037	no

The measurements were performed with a simultaneous instrument and the measuring time was fixed for all elements, 40 s.

The results obtained gave satisfactory relative standard deviation (RSD_{cal}) for all elements except element G, which is more than two times higher than the statistical relative standard deviation (RSD_{stat}), indicating a deficiency in that channel. In such circumstances, the procedure should be investigated and repeated.

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