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Koppar och kopparlegeringar – Bestämning av huvudbeståndsdelar och orenheter genom våglängdsskingrande röntgenfluorescencespektrometri (XRF) –
Del 1: Riktlinjer för rutinmetod

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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English Version

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 analyse spectrométrique de fluorescence X à dispersion en longueur d'onde (XRF) - Partie 1: Lignes directrices pour la méthode de routine

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

This European Standard was approved by CEN on 22 September 2006.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.



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EN 15063-1:2006 (E)

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Foreword

This European Standard (EN 15063-1:2006) 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 May 2007, and conflicting national standards shall be withdrawn at the latest by May 2007.

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

EN 15063-1, *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*

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

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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 primarily intended to be used for the analysis of metal alloys but it is also applicable to other materials although the test specimen preparation techniques differ.

1 Scope

This part of 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 cleaned test specimen 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 unknown test specimens to analytical curves prepared from reference materials of known concentrations.

3 Terms and definitions

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

3.1

reference material

material, one or more of whose property values are sufficiently homogeneous and well established to be used for calibrating an apparatus, assessing a measurement method, or for assigning values to materials

3.2

certified reference material

reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realisation of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence

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 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 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 No chemical analyses are necessary, but the homogeneity of the 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

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3.8 recalibration

adjusting instrumental output to conform to the calibration

NOTE 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 ratios of intensities for unknown reference materials

NOTE 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 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 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 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 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 See Annex A.

3.15 sensitivity

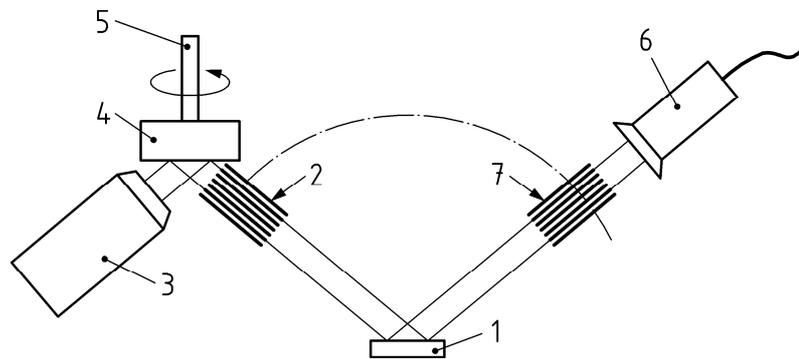
rate of change of signal with change in concentration

NOTE 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

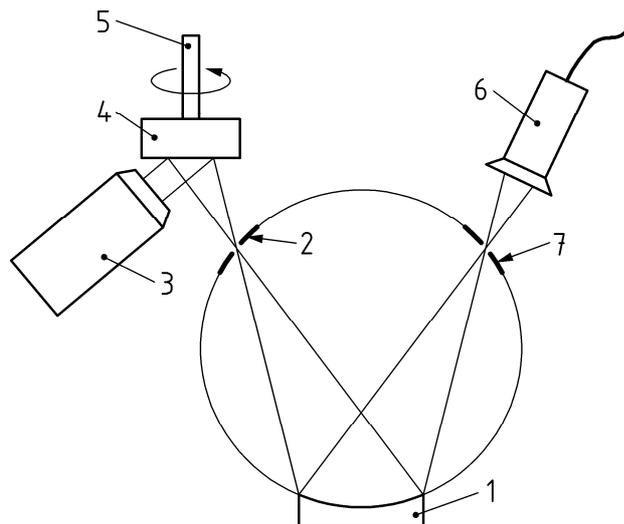
The principles of two different X-ray fluorescence spectrometer concepts are shown in Figures 1 and 2. Each detail is described in the following sub-clauses.



Key

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

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 specimen | |

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

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

4.3 Vacuum system

The test specimen 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 specimen spinner

Most instruments are equipped with a test specimen spinner to avoid effects of inhomogeneities, e. g. grinding striations. If not, the test specimen 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.