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Microbeam analysis — Electron probe microanalyser (EPMA) — Guidelines for performing quality assurance procedures

Analyse par microfaisceaux — Analyse par microsonde électronique (microsonde de Castaing) — Lignes directrices pour la mise en œuvre des procédures d'assurance qualité

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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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).

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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 202, *Microbeam analysis*, Subcommittee SC 2, *Electron probe microanalysis*.

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

This document was developed to provide a general method for operators of electron probe microanalysers (EPMA) to perform the most complete and reliable instrument diagnostic routine possible in the smallest amount of operator time, instrument time and analysis time. Performing this procedure on their instruments at regularly scheduled intervals will allow the operator to track the quality of an instrument's elemental qualitative and quantitative performance, and alert the operator of the need for instrument service and calibration shortly after it fails to meet its operating specifications for measurement uncertainty. With equal application of this document to the diagnostics procedure of multiple instruments in a single laboratory, or even multiple instruments managed by different operators in separate laboratories, analysis results can be normalized between instruments using the performance comparison, facilitating analytical reproducibility.

The chief product of an analytical laboratory quality assurance (QA) program, ultimately, is confidence – confidence that the analysis of any specimen sent to any laboratory participating in the program will be consistent, correct within tolerance and interchangeable with equivalent analyses of related specimens performed by any other laboratory in the program. In order to maximize confidence, the QA tests and test materials chosen should evaluate the broadest possible range of instrument functionality. In the context of EPMA, this means testing not only the stability of the electron gun and the function of the photon counters, but also the functionality of every component of each wavelength spectrometer mounted to the system. This includes the numerous types of diffracting crystals that disperse the X-rays, the mechanical components that switch the spectrometer from one crystal to another, and the drive mechanisms that scan the crystal through a spectral region of interest. Since these spectrometer components can fail independently of the others, and many such failures will not be noticeable in all measurements, a complete QA test will include materials that generate X-ray lines that span the range of any diffracting crystal and methods to properly analyse them. It will therefore generate the maximum possible information on the instrument's functional integrity. From this information, instrument performance can be optimized, thereby obtaining maximum analytical confidence. The procedures and reference material attributes outlined in this document are designed to achieve these goals.

Microbeam analysis — Electron probe microanalyser (EPMA) — Guidelines for performing quality assurance procedures

1 Scope

This document provides guidelines for performing routine diagnostics and quality assurance procedures on electron probe microanalysers (EPMA). It is intended to be used periodically by an instrument's operator to confirm that the instrument is performing optimally, and to aid in troubleshooting if it is not. It covers the properties of reference materials required and the analysis procedures necessary to independently test and fully evaluate the functionality of the main components of an EPMA system.

The analytical procedure described herein is distinct from single-element diagnostic procedures, which can be performed more rapidly. Such procedures are valid for the diffractor position and conditions under which the test is performed, whereas the procedure described herein is intended to qualify an instrument's capabilities for exploratory analysis of unknowns, trace analysis and non-routine work (such as peak interferences).

This document is applicable to EPMA and other wavelength dispersive spectrometer (WDS) systems in which elemental identification and quantification are performed by analysis of the energy and intensity of the characteristic X-ray lines observed in wavelength-dispersed X-ray spectra. It is not directly applicable to elemental analysis using energy dispersive spectrometry (EDS).

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 3534-2, *Statistics — Vocabulary and symbols — Part 2: Applied statistics*

ISO 14595, *Microbeam analysis — Electron probe microanalysis — Guidelines for the specification of certified reference materials (CRMs)*

ISO 22489, *Microbeam analysis — Electron probe microanalysis — Quantitative point analysis for bulk specimens using wavelength dispersive X-ray spectroscopy*

ISO 23833, *Microbeam analysis — Electron probe microanalysis (EPMA) — Vocabulary*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/IEC Guide 99, ISO 3534-2, ISO 23833 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
electron probe microanalyser
EPMA
instrument for carrying out electron-excited X-ray microanalysis

Note 1 to entry: This instrument is usually equipped with more than one wavelength spectrometer and an optical microscope for precise specimen placement.

[SOURCE: ISO 23833:2013, 3.2]

3.1.1
electron probe microanalysis
EPMA
technique of spatially-resolved elemental analysis based upon electron-excited X-ray spectrometry with a focussed electron probe and an electron interaction volume with micrometer to sub-micrometer dimensions

[SOURCE: ISO 23833:2013, 3.1]

3.2
wavelength dispersive spectrometer
WDS
device for determining X-ray intensity as a function of the wavelength of the radiation, where separation is based upon Bragg's law, $n\lambda = 2d\sin\theta$, where n is an integer, λ is the X-ray wavelength, d is the spacing of the atom planes of the diffracting crystal or the repeated layers of a synthetic diffractor and θ is the angle at which constructive interference takes place

Note 1 to entry: This definition excludes the recent technological development of WDS spectrometers based on diffraction at gratings, which are not as yet in widespread use.

[SOURCE: ISO 23833:2013, 4.6.14, modified — Note 1 to entry replaced.]

3.3
diffracting crystal
dispersion element
X-ray scattering element in a wavelength-dispersive X-ray spectrometer, consisting of a periodic array of atoms obtained either in a natural crystal or in a synthetic multilayer

Note 1 to entry: For the purposes of this document, the term “diffracting crystal” is used rather than the term “dispersion element” in order to avoid confusion when discussion of components of X-ray energy analysers is intermingled with discussion of chemical elements from the periodic table.

[SOURCE: ISO 23833:2013, 4.6.14.3, modified — Note 1 to entry has been added.]

3.3.1
lithium fluoride
LiF
diffracting crystal featuring 2d spacing of 0,402 8 nm[4] used in WDS for dispersion of X-rays

Note 1 to entry: This can also sometimes be written as LiF(200) to denote the most common crystallographic orientation of LiF used. However, it is also available in other less commonly used orientations that feature different 2d spacings; for example, the [220] orientation has a 2d spacing of 0,284 8 nm. Additionally, some instruments could utilize LiF in the [422] or the [420] orientation. If the orientation is not stated, the [200] orientation is assumed. All orientations are typically used to disperse short wavelength/high energy X-rays.

3.3.2
pentaerythritol
PET
diffracting crystal featuring 2d spacing of 0,874 2 nm[4] used in WDS for dispersion of X-rays

Note 1 to entry: PET is typically used to disperse intermediate wavelength/intermediate energy X-rays.

3.3.3
thallium acid phthalate
TAP
diffracting crystal featuring 2*d* spacing of 2,59 nm[4] used in WDS for dispersion of X-rays

Note 1 to entry: TAP is typically used to disperse long wavelength/low energy X-rays.

3.3.4
layered synthetic microstructure
multilayer diffracting element engineered to feature an arbitrary 2*d* spacing used in WDS for dispersion of X-rays

Note 1 to entry: layered synthetic microstructure is typically used to disperse long wavelength/low energy X-rays in the light element region of the spectrum inaccessible by TAP.

3.4
peak energy
peak wavelength
spectrometer position or channel at which the characteristic peak intensity is measured

Note 1 to entry: Due to X-ray counts originating from higher-order Bragg reflections, both of these terms describe the measurand but not the actual measurement; an EPMA instrument counts X-rays from the higher-order reflections and the principle first-order reflection simultaneously. Pulse filtering electronics can be used to preferentially distinguish X-rays at the wavelength or energy of interest; in practice, such strategies reduce but do not eliminate spurious counts.

3.5
peak counting time
time spent measuring X-ray emission at a given characteristic peak energy

3.6
peak counting rate
mean rate at which characteristic peak X-rays are collected by the detector at the peak energy

3.7
background reference
background reference energy
background reference wavelength
spectrometer position or channel at which the continuous background radiation is measured so that an estimate can be made of what portion of the measured intensity at a characteristic peak originates from characteristic photoemission

Note 1 to entry: Multiple background positions are typically chosen to improve the estimate; often, at least one on each side of the characteristic peak of interest.

Note 2 to entry: Due to X-ray counts originating from higher-order Bragg reflections, both of these terms describe the measurand but not the actual measurement; an EPMA instrument counts X-rays from the higher-order reflections and the principle first-order reflection simultaneously. Pulse-filtering electronics can be used to preferentially distinguish X-rays at the wavelength or energy of interest; in practice, such strategies reduce but do not eliminate spurious counts.

3.8
background counting time
time spent measuring X-ray emission at a given background energy

3.9
background counting rate
mean rate at which continuum X-rays are collected by the detector at the background energy

Note 1 to entry: The background counting rate is used to estimate the portion of peak counts due to continuum X-rays; this estimate may be derived by interpolation, extrapolation, or comparison to the background rate generated by a selection of materials characterized by a range of mean atomic numbers.

3.10
beam defocus
condition in which the objective lens of the electron optical column is set such that the size of the incidence of the electron beam on the surface of the specimen (the "beam spot") is expanded to a diameter greater than the diameter of the focal point

Note 1 to entry: Increasing the spot size is a technique used to compensate for specimen heterogeneity when performing a quantitative analysis or to reduce the damage caused to a beam-sensitive specimen by distributing the electron dose over a greater volume.

3.11
quality assurance
QA
<electron probe microanalyser> procedure by which standard measurements of model materials are performed on a periodic basis to confirm that each component of the electron probe microanalyser is functioning such that the instrument's uncertainty specification is attainable

3.12
confidence interval
range of analytical error expected to contain the true value with a stated uncertainty as estimated from a statistical model of the measurement process

[SOURCE: ISO 23833:2013, 5.4.2.1]

3.13
error
natural deviation from the true value in a measured quantity arising from (1) random counting fluctuations in a time-distributed phenomenon (e.g. X-ray photons) and (2) systematic deviations from the true value introduced during application of calculated correction factors (e.g. ZAF matrix correction factors) to convert the measured quantity (e.g. X-ray photons) to a different dimension (e.g. concentration)

[SOURCE: ISO 23833:2013, 5.4.2]

3.14
uncertainty
quantitative statement that provides a value for the expected deviation of a measurement from an estimate of the value of the specific measured quantity

[SOURCE: ISO 23833:2013, 5.5.13]

3.15
detection limit
smallest amount of an element or compound that can be measured under specific analysis conditions

Note 1 to entry: By convention, the detection limit is often taken to correspond to the amount of material for which the total signal for that material minus the background signal is three times the standard deviation of the signal above the background signal. This convention might not be applicable to all measurements and, for a fuller discussion of detection limits, Reference [11] should be consulted.

Note 2 to entry: The detection limit may be expressed in many ways depending on the purpose. Examples of expressions are mass or weight fraction, atomic fraction, concentration, number of atoms, and mass or weight.

Note 3 to entry: The detection limit will generally be different for different materials.

[SOURCE: ISO 23833:2013, 5.2]

3.16
instrument uncertainty specification
<electron probe microanalyser> manufacturer's estimate of the lowest uncertainty attainable by a given instrument based upon physical limitations and construction

3.17
control chart
chart on which some statistical measure of a series of samples is plotted in a particular order to steer the process with respect to that measure and to control and reduce variation

[SOURCE: ISO 3534-2:2006, 2.3.1, modified — Notes 1 and 2 to entry have been removed.]

3.17.1
mean and standard deviation plot
mean and range plot
$\bar{x}$ and R plot
graphical representation of a set of measurements that plots the data means in relation to a certified or targeted value and also plots the standard deviations in relation to a control limit

Note 1 to entry: Mean and standard deviation plots can be used as an aid in determining when and how the data no longer attains the instrument uncertainty specification.

3.17.2
box-and-whisker plot
box plot
graphical representation of a set of measurements that plots the data along with the data mean, median, inner quartiles ("box") and a chosen outlier delimiter (e.g. standard deviation, outer quartiles or other "whiskers")

Note 1 to entry: Box plots can be used as an aid in determining when and how the data no longer attains the instrument uncertainty specification.

3.17.3
bean plot
density plot
graphical representation of a set of measurements that plots the data along with the data mean and a density function

Note 1 to entry: Bean plots can be used as an aid in determining when and how the data no longer conforms to the instrument uncertainty specification.

3.18
failure mode
<electron probe microanalyser> observable deviation from a normal data distribution within the instrument uncertainty specification that is symptomatic of a specific instrument malfunction

3.19
reference material
RM
material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties

Note 1 to entry: For electron probe microanalysis, a material whose overall composition is known from independent, ideally absolute, measurements (e.g. separations and gravimetric analysis) and that is microscopically homogeneous on a sufficiently fine scale that any location measured with an electron probe microanalyser produces the same X-ray intensities, within counting statistics.

[SOURCE: ISO/IEC Guide 99:2007, 5.13, modified — Note 1 to entry has been added.]

3.19.1
certified reference material
CRM
reference material (3.19)accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures

Note 1 to entry: For certified reference materials for electron probe microanalysis, the microscopic heterogeneity at the micrometer scale is certified as well as the composition.

[SOURCE: ISO/IEC Guide 99:2007, 5.14, modified — Note 1 to entry has been added.]

3.19.1.1
challenge material
certified reference material (3.19.1) of known composition that is measured as if it were an unknown sample in the EPMA QA procedure

Note 1 to entry: Challenge materials are selected by the analyst to present an analytical challenge to specific components of an EPMA instrument. Ideally, challenge materials that present an analytical challenge to as many components of a given instrument as possible should be selected.

4 General principles of electron probe microanalyser quality assurance (EPMA QA)

4.1 Objective

When performing analysis of unknown specimens in EPMA, it is crucial for the analyst to know that their instrument is working properly. Herein is described a procedure that should be performed periodically to ensure that analyses performed using EPMA are reliable. The procedure is built upon the analysis of challenge materials.

4.2 Selection of challenge materials

4.2.1 General

Challenge materials and their associated reference materials shall be selected such that they conform to the criteria outlined in the following subsections.

4.2.2 General characteristics of analysed materials

Challenge materials and their associated reference materials shall meet the requirements for certified reference materials as described in ISO 14595. The materials shall:

a) be stable in vacuum;

b) not degrade under interrogation by the electron beam incidence;

c) be characterized by heterogeneity sufficiently less than the instrument's repeatability specification so as to be indistinguishable from the instrument uncertainty specification;

d) be suitably conductive to eliminate electrostatic charging under electron beam interrogation (or be coated with conductive material with a path to instrument ground);

Many types of solids meet these criteria, including a number of pure elemental solids, single-phase alloys, vitreous solids such as glass, natural or synthetic minerals, and pure compounds.