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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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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.

4.2.3 Specific characteristics of challenge materials

The purpose of a challenge material is to provide an analytical challenge for an instrument that requires the proper function of as many instrument components as possible. Therefore, a challenge material should be sufficiently complex such that each diffracting crystal on every WDS in a given EPMA can be used to quantify at least one of the elements of which it is composed. For multi-crystal WDS spectrometers, diffracting crystal switching should be required.

The challenge material should also be sufficiently simple to analyse such that deconvolution of peak overlaps and large absorption or fluorescence corrections are not required to calculate the composition. Secondary standard reference materials should not be necessary to achieve an accurate result. Finally, the elements of interest for evaluating the performance of a given spectrometer should be present in sufficient concentration that uncertainties associated with concentrations approaching the detection limit are not a factor.

In summary, challenge materials should possess the following characteristics, in addition to those identified in 4.2.2:

a) For evaluation of a given diffracting crystal, the challenge material shall contain at least two elements that emit characteristic X-rays that fall within the diffracting crystal's analytical range. Alternatively, a single element is allowable if it emits two well-separated characteristic X-rays that can be independently measured using a single diffracting crystal during the same analysis (e.g. Kα and Kβ transitions for certain high-Z elements), after which the composition of the element shall be evaluated for each X-ray line separately. A single element is also allowable if it emits a single characteristic X-ray that can be measured using at least two different Bragg reflections (e.g. first order and second order reflections) on the same diffracting element (see Annex A for examples).

b) The characteristic X-rays analysed for each element in the challenge material should overlap minimally with any other characteristic X-rays emitted by any other matrix element and with any absorption edge of any matrix element.

c) The composition of each analysed element in the challenge material should be greater than 1 %.

d) Analysis of X-ray lines whose emission energies depend upon chemical bonding effects shall be avoided; for example, the Lα lines of third row transition elements. For further details, see Reference [10].

4.3 QA measurement parameters

4.3.1 General

Upon specification of the challenge material best suited to use in the evaluation of a given instrument's array of spectrometers, and the selection of reference materials best suited to quantitatively analyse the challenge material, a procedure for performing the analysis can be specified. This procedure should be optimized such that a maximum of diagnostic information about the instrument is collected in a minimum amount of time.

4.3.2 Laboratory environment preparation

The long-term stability of the laboratory environment affects instrument stability. In particular, temperature fluctuations can affect the beam current stability and the diffracting crystal lattice constants, thereby contributing to measurement uncertainty. Ideally, room temperature should be held constant for the duration of the QA diagnostic, and should be unchanged between diagnostic tests. The room temperature shall be monitored during the QA diagnostic; at minimum, it may be recorded both before and after each QA diagnostic is performed. If neither the temperature nor its fluctuation conforms to the limits allowed by the instrument's installation specification, the test results shall be deemed invalid and the laboratory environment shall be stabilized before repeating the test.

4.3.3 Instrument parameters

4.3.3.1 General

The instrument parameters identified below are required to perform a diagnostic evaluation of the EPMA electron gun and WDS X-ray spectrometers. Upon selection of the characteristic X-ray lines to be analysed and the spectrometers with which the analysis is to be performed, the greatest value can be extracted from a QA diagnostic experiment if the instrument is finely tuned ahead of time to make the best possible measurement. This fine-tuning includes confirming and readjusting the X-ray peak centres on the diffracting crystals (frequently referred to as "peaking" the spectrometers) and fine-tuning the X-ray counter electronics discriminator settings to maximize noise rejection and higher-order coincidence peak rejection while still collecting the entirety of the signal X-rays. See ISO 14594 for complete details of these procedures.

4.3.3.2 Accelerating voltage

The electron beam energy, or accelerating voltage, shall be set such that it exceeds the excitation energy for the highest characteristic X-ray to be measured during the QA diagnostic by an overvoltage factor of at least 1,5. While higher overvoltage is acceptable, there is usually little benefit to exceeding the highest excitation energy by a factor of three. The beam energy should be held constant for the duration of the diagnostic. Ideally, it should be set where future measurements are expected to be made using this instrument.

The operator may choose to optimize accelerating voltage for analysis of the system by plotting the measured X-ray intensity versus accelerating voltage for both the highest energy characteristic X-ray line and the selected characteristic line emitted by the element with the lowest concentration in the challenge material. The accelerating voltages corresponding to the highest X-ray intensity for each of the curves establish the limits for the range in which the ideal accelerating voltage for analysing this system lies. It might not, however, necessarily correspond to the voltage that is expected to be used for typical measurements on a given instrument.

Should the operator desire performance data for multiple accelerating voltages, a separate QA diagnostic should be planned for each. While using multiple accelerating voltages to perform a single analysis can be advantageous in some circumstances, maintaining a single accelerating voltage is necessary for this exercise in order to assess electron beam stability.

If electron beam damage at higher beam energy is a problem for either the challenge material or for the selected reference materials, this should also be considered when selecting the accelerating voltage.

For low overvoltage or soft X-rays, carbon contamination and surface oxidation should be avoided as much as possible.

4.3.3.3 Probe current

The probe, or electron beam, current shall be set such that the resulting X-ray count rate falls within the proportional counting range for every characteristic X-ray to be analysed from the challenge material and any reference material during the QA diagnostic. Ideally, this current setting will be consistent with the setting at which future measurements are expected to be made. The beam current should be held constant for the duration of the diagnostic measurement. Failure to confirm that the count rate is within proportional counting range for every specimen to be analysed risks the possibility of errors due to detector dead time discrepancies or to counts falling outside of the pulse height analyser (PHA) acceptance window.

If electron beam damage at higher current is a problem for either the challenge material or for the selected reference materials, this fact should also be considered when setting the probe current. Damage caused by high current dose may also be mitigated by defocusing the beam (and thus the beam dose per unit volume) if reducing the beam current itself reduces the X-ray count rate to unacceptable levels. Beam defocus can also mitigate uncertainties arising from specimen heterogeneity on the scale

of the size of the beam incidence. See Annex B for further details. The beam defocus shall not exceed the acceptance angle of the spectrometer.

The operator might find it convenient to collect a full spectrum wave scan using each spectrometer and diffracting crystal selected (see 4.3.3.4) on all reference material and challenge material, and then adjust the probe current to optimize the count rate for the most intense line to be analysed.

Should the operator desire performance data at multiple probe currents, a separate QA diagnostic should be planned for each. While using multiple probe currents to perform a single analysis can be advantageous in some circumstances, maintaining a single probe current is necessary for this QA diagnostic exercise to properly assess electron beam stability.

4.3.3.4 Spectrometer and diffracting crystal selection

Many electron probe microanalysis instruments feature considerable built-in spectrometer redundancy, i.e. multiple spectrometers equipped with identical diffracting crystals. Although this feature affords the analyst considerable versatility in approaches to a given analysis, it also makes it nearly impossible for most configurations to be tested in their entirety during a single diagnostic QA.

EXAMPLE 1 An EPMA instrument configured with five spectrometers each equipped with two diffracting crystals would require a challenge material composed of at least 20 elements each at greater than 1 % mass fraction in order to test each diffracting crystal, each Rowland circle mechanical translation and each diffracting crystal exchange motion.

Given this limitation, the operator should select diffracting crystals and spectrometers for the QA diagnostic that are most likely to be used in future measurements. If the diffracting crystals and spectrometers to be tested exceed what is required to properly analyse the challenge material, the operator should schedule multiple iterations of the QA diagnostic that sequentially tests a subset of the most necessary components.

EXAMPLE 2 An operator wishes to perform a QA diagnostic on an EPMA instrument configured with two spectrometers each equipped with TAP and lead stearate diffracting crystals, and two spectrometers each equipped with PET and LiF diffracting crystals. The challenge material selected for the diagnostic is an alloy composed of six elements: three pairs that can be analysed using TAP, PET and LiF, respectively. The operator determines that for upcoming analyses all spectrometers will be required, but it is unlikely that any unknown will necessitate a diffracting crystal change on any spectrometer. Given the operator's expectations, it is decided that the QA diagnostic will be run twice – once for each TAP spectrometer, with the PET and the LiF on the remaining spectrometers alternated between runs. Using such a procedure, the functionality of all four X-ray counters, all diffracting crystals except the lead stearate, and all diffracting crystal translation mechanisms on each Rowland circle are tested, while none of the mechanisms responsible for changing between diffracting crystals on the same spectrometer are diagnosed.

4.3.3.5 Peak and background energy selection

The measured energy for each analysed X-ray line shall be selected to coincide with the most probable maximum intensity of that line as determined by the spectrometer peaking procedure employed.

For linear interpolation of the background intensity at the peak energy, the background reference energies should be selected such that one energy is chosen on the higher and one on the lower energy sides of each analysed X-ray line. The selected background energies shall be chosen such that they are not coincident (within the specified uncertainty of the instrument) with potential sources of interference, such as other characteristic X-ray lines or photoabsorption edges of the specimen or detector. To minimize the uncertainty in the background intensity, the background energies should be selected such that they are as far as possible from the peak energy, yet not so far that the continuum intensity profile between the background energies no longer approximates a straight line. Furthermore, the product of the background intensity and the distance, in spectrometer units, from the peak energy should ideally be equal for both background energies chosen.

Performing a wave scan of an energy range from the low background through the peak to the high background energy is suggested to best evaluate the background energy choices.

4.3.3.6 Selecting the analysis positions on the challenge material and the reference material

The analysis positions on all specimens measured during the diagnostic shall be located on polished, clean, conductively coated (if necessary) and large (more than two electron beam interaction volume diameters, and more than the mean free path length of fluorescing X-rays, away from any edge of a single-phase homogeneous region of the specimen) regions of the material. At least seven randomly selected positions separated by at least twice the electron beam interaction volume diameter shall be measured on all reference material and challenge material to ensure that the 90 % confidence interval is subsumed as in Formula (1).

$$I \pm 2\,\sigma \tag{1}$$

where

I is the mean measured X-ray intensity expressed in total counts;

σ is the standard deviation of the measurements.

More positions may be selected if more rigorous statistics are desired; consult ISO/IEC Guide 98-3:2008, Annex G, Table G.2 to estimate the number of measurements required to achieve the desired precision.

4.3.3.7 Selecting the optimum X-ray counting times

4.3.3.7.1 General

Once the specimens have been selected, the instrument parameters appropriate for their complete analysis have been determined, and the instrument spectrometers have been properly peaked and tuned, optimized X-ray counting times will enable the operator to obtain the maximum actionable diagnostic information from the EPMA instrument in a minimum of instrument and analysis time.

4.3.3.7.2 Peak counting time

In 4.3.3.3, an electron probe current setting was selected to generate an acceptable X-ray count rate for all analysed lines to be measured during a given QA diagnostic. The optimum X-ray peak counting time, in turn, is governed by this selected beam current and by the repeatability specification of the instrument component to be tested. The peak counting time shall equal or exceed the time required to collect a total number of counts above background that equals or exceeds the total counts needed to match the instrument's repeatability uncertainty specification. Assuming that Poisson counting statistics govern the measurement uncertainty, the target peak counting time, in seconds, is as in Formula (2).

$$t_P \geq \frac{r_P + r_B}{2 \times \left(u_{spec} \times \left(r_P - r_B\right)\right)^2} \tag{2}$$

where

t_P is the target peak counting time, in seconds;

u_{spec} is the instrument's uncertainty specification expressed as a decimal (e.g. 1 % is expressed as 0,01);

r_P is the expected mean peak counting rate in counts/second;

r_B is the interpolated background counting rate in counts/second.

The higher the peak counting time, the greater the likelihood of introducing uncertainties unrelated to Poisson counting statistics, such as beam damage or beam-induced contamination, which would

invalidate this procedure for estimating it. For this reason, specimens with high peak counting rates for an element of interest should be selected.

A simpler estimate for target peak counting time is to divide the peak counting rate from the reciprocal square of the instrument's uncertainty specification. This estimate is valid for background counting rates that are much less than the peak counting rates times the uncertainty specification.

EXAMPLE On an instrument with an uncertainty specification of 1 %, a QA diagnostic is performed on a peak with a counting rate of 400 Hz and an interpolated background counting rate of 4 Hz. The minimum peak counting time to achieve sufficient statistics to challenge the instrument's uncertainty specification is 25,76 s.

4.3.3.7.3 Background counting time

The counting time at each background energy should be selected such that the total uncertainty of peak intensity minus interpolated background intensity is minimized. Assuming that Poisson counting statistics govern the measurement uncertainties, the target of the ratio of the peak counting time to the total background counting time should approximate[6] Formula (3).

$$\frac{t_P}{t_B} \cong \sqrt{\frac{r_P}{r_B}} \tag{3}$$

where

t_P is the peak counting time, in seconds;

t_B is the total background counting time, in seconds;

r_P is the mean peak counting rate in counts/second;

r_B is the interpolated background counting rate in counts/second.

The background counting time should be minimized.

EXAMPLE A simple linear interpolation background with a counting rate of 4 Hz and a peak with a counting rate of 400 Hz will have an optimum total peak counting time to background counting time ratio of 10:1. The example in 4.3.3.7.2 provides a minimum peak counting time of 25,76 s for this peak; the optimum total background collection time in this example is then 2,58 s. This time is divided between the background energies; for background energies of equal intensity that are equidistant (in spectrometer units) from the peak energy, the optimized collection time will be 1,29 s on each background energy.

The validity of this estimate depends upon the background energies being a large and equal distance from the peak energies as described in 4.3.3.5, and the intensities at both background energies being equal. The greater the experiment's deviation from these ideal conditions is, the higher the uncertainty in the interpolated background intensity will be. In these circumstances, the operator should compensate by increasing the peak counting time.

For very intense peaks, the ratio of peak counting time to background counting time could dictate background counting times lower than the minimum allowed by the instrument electronics. In these cases, the lowest allowable counting time may be used.

4.4 Data acquisition

Upon completing the procedure of 4.3, data acquisition shall be performed. Data acquisition is to commence on the specimen positions and energies identified previously. The diagnostic shall be carried out, as closely as possible, under the conditions and by the procedure under which the instrument normally operates, with the following exceptions:

a) In order to track electron beam stability during the measurement, a measurement of the beam current in the Faraday cup shall be performed before and after each analysis point.

b) Data shall be acquired on the reference material positions both before and after the data acquisition on the challenge material positions, so that the data may be used to track spectrometer and detector stability during the experiment.

c) The reference materials shall be measured using the same peak and background collection times as the challenge material on each spectrometer; that is, no abbreviated reference material analysis procedure shall be used. Doing so increases the probability that contamination or other defects in the reference materials will be identified during a QA diagnostic. However, the operator should be aware of using correct dead time correction procedures, if different count rates are expected between the reference and the challenge materials.

4.5 Frequency of QA diagnostic testing

The operator shall repeat the QA diagnostic experiment on a regular schedule. Monthly QA is recommended; however, the time efficiency of the QA diagnostic is largely dependent upon instrument construction and availability of reference materials and challenge materials. For this reason, different laboratories will find that more or less frequent QA schedules integrate better into their production schedules.

5 Test report

Records of the instrument and individual investigations shall be kept so that, if required, a test report may be issued. Reports shall present at least the following information:

a) the designation of the ISO method used;

b) the name and address of the laboratory that performed the QA diagnostic(s);

c) the name and address of the client, where relevant;

d) the instrument type (manufacturer, model number, electron beam emitter specifications, and attached spectrometers' manufacturers, model numbers, integrated diffracting crystals and take-off angles);

e) the laboratory room temperature;

f) the components of the instrument tested during the QA diagnostic(s);

g) the accelerating voltage;

h) the probe current and incident probe diameter;

i) the identity and certified composition of the challenge material and reference materials analysed during the QA diagnostic(s);

j) the X-ray peak(s) analysed in the course of the QA diagnostic(s);

k) the diffracting crystals used and the PHA and discriminator settings used for each diffracting crystal (integral or differential);

l) the raw data file including the raw data uncorrected counts for each analysed peak;

m) the quantitative analysis of the unknown, and the deviation of the composition from the certified composition;

n) an estimate of the uncertainties for each element of the test result;

o) the quantitative matrix correction method used;

p) the additional statistical and graphical analyses used to evaluate the data as outlined in Clause 6 and Annex C, respectively;

q) a summary indicating whether the test indicated that the instrument is performing to specifications and, if not, where the deviations from proper function occur;

r) the name(s), title(s) and signature(s) or equivalent identification of the person(s) accepting responsibility for the result;

s) the content of the certificate or report and the date on which the report was issued.

The test results shall also be collected in a control chart format, so that the time dependence of the data can be monitored and deviations from normal function can be identified. The methods for doing so are discussed in greater detail in Clause 6 and Annex C, while the remedies for certain deviations are discussed in Annex D. Whatever the schedule, operators should report the date and summary results of the most recent QA diagnostic with EPMA results, as well as keep the most recent test report and control chart information readily available to instrument operators.

NOTE Often an instrument can exhibit a malfunction, such as one failed diffracting crystal, that does not render the entire instrument unusable. Particularly in a multiple operator environment, the availability of this information allows operators to find alternative solutions to problems with the instrument (for example, using an equivalent diffracting crystal on an alternative spectrometer) that maximize productivity and minimize failed analyses while repairs are arranged.

6 Data analysis and performance tracking

6.1 General

Once the data has been collected, a variety of analysis procedures can be used to extract actionable information from the experimental output. This clause provides recommended analyses of the QA diagnostic data that will allow the operator to identify specific problems with the instrument.

6.2 Quantitative analysis of the challenge material

A conventional quantitative analysis of the challenge material shall be performed as described in ISO 22489 using the data collected during the QA diagnostic measurement. Results may be, and in most cases are required to be, corrected for matrix effects. However, results shall not be normalized, as doing so provides no probative value with respect to instrument performance. A properly working instrument should generate a consistent result within the uncertainty specification of the instrument every time the diagnostic is performed.

NOTE The diagnostic need not generate a result that agrees with the certified composition in order to provide a valid diagnostic; only consistent results from test to test are required. Many issues could arise either with specimen integrity or with correction procedures that generate a result that does not correspond to the certified compositions of the challenge material or the reference materials. These issues have no bearing on instrument performance.

6.3 Calculation of means and standard deviations

Upon completion of the QA diagnostic experiment, the operator should compute the raw intensity means and standard deviations for each measured element in the challenge material and the reference material. These means and standard deviations should be included in the periodic tracking and control chart.

6.4 Statistical tests performed on data

6.4.1 General

A variety of statistical tests applied to the raw intensity data can be used by the operator to assist in identifying specific malfunctions in an instrument that has failed to generate either a consistent quantitative analysis or a sufficiently narrow intensity standard deviation to remain consistent with the instrument's uncertainty specification. Some tests, such as the normality test, are valuable for

identifying whether a set of measured intensities are statistically consistent with Poisson's statistics for random counting data, as would be expected for a properly functioning X-ray counter. Other tests, such as the variance test, are valuable for comparing independently collected data sets.

6.4.2 Normality test

A normality test determines whether a given set of data are normally distributed about the mean. In the context of the EPMA QA diagnostic, the goal is to determine whether the distribution of intensities collected is consistent with what would be expected from a properly functioning X-ray counter.

A rigorous normality test can be applied using a statistics software package; alternatively, an estimated normality test can be performed by comparing the magnitude of the differences from the mean of the highest and lowest intensity data points to the magnitude of the standard deviation (also known as the data point's z-statistic). For a set of seven measured intensities with a normal distribution, the z-statistics of both extremes should fall between 1σ and 2σ, but only one should exceed 1,5σ, and neither should exceed 2σ. If these conditions are not met, then the intensity data are probably not normally distributed.

NOTE The target standard deviations in this test were derived from the continuous distribution function for a Gaussian distribution as an approximation of the Poisson distribution for a very large number of counts.

EXAMPLE A normality test failure could indicate a skewed or bimodal distribution of intensities.

6.4.3 Variance test

Variance tests determine whether two sets of data have equal variances. In the context of the EPMA QA diagnostic, variance testing can be used as a tool to compare intensity data measured in two separate QA diagnostic runs, thereby evaluating consistency of performance with time. Since reference materials are measured before and after the challenge material, a variance test on the two separate reference material data sets can be used to evaluate instrument stability within a single diagnostic experiment. Variance tests may also be performed to determine if data are consistent with a theoretical model. A variety of variance tests are available in widely available statistical software packages.

Since X-ray count data are governed by Poisson counting statistics, variance is equal to measured intensity. Therefore, failure of a variance test indicates a statistically significant change in intensity. Care should be taken in selecting the variance test used to evaluate data; tests such as the F-test require normal distributions in order to be valid. Furthermore, since the variance regresses to the mean for counting data, a Student's *t*-test to evaluate the means of two independent data sets may also be utilized.

Annex A
(informative)

Examples of challenge materials and reference materials for EPMA WDS QA

A.1 Selected challenge materials and reference materials

Table A.1 lists a selection of challenge material candidates, their elemental compositions, the diffracting crystals that they are most suitable for evaluating and suitable reference materials for their analysis. This list is not exhaustive, and is included for information only. Any materials that fit the requirements described in 4.2 may be used to evaluate WDS spectrometer performance.

Table A.1 — Selected challenge materials

Challenge material	Composition	Diffracting crystals	Reference materials
National Institute of Standards and Technology (NIST) SRM 470[a]	Two glasses composed of O, Mg, Al, Si, Ca, and Fe	TAP	Oxides or pure elements for Mg, Al, Si, and Fe; for Ca, one glass specimen can be used as the reference for the other
NIST SRM 480	Alloy of W and Mo	PET	Pure W and Mo
NIST SRM 481	Alloy of Au and Ag	PET	Pure Au and Ag
NIST SRM 482	Alloy of Au and Cu	TAP, PET, LiF[b]	Pure Au and Cu
NIST SRM 1871[a]	Lead silicate glass	PET	Pure Pb or PbS, pure Si, SiO_2 or other known silicate
NIST SRM 1872[a]	Lead germanate glass	LiF	Pure Pb, or PbS, pure Ge or known germanate
NIST SRM 1873[a]	Barium zinc[c] silicate glass	PET	Known barium-bearing material, pure Si, SiO_2 or other known silicate
NIST SRM 1874[a]	Lithium[d] aluminium borate glass	Long wavelength/low energy diffracting crystals[e]	Al_2O_3, pure B
NIST SRM 1875[a]	Aluminium magnesium phosphate glass	TAP	Pure Al or Al_2O_3, pure Mg or MgO, pure P or other known phosphate

[a] These materials have been discontinued; however, the certificates providing the full description of the materials can be located at https://www.nist.gov/srm by searching for the keyword "microanalysis."

[b] As this is a binary alloy, conventional quantitative analysis affords the ability to perform a QA diagnostic as described in this document on only one type of diffracting crystal during a single QA diagnostic run.

[c] The zinc content of this SRM is lower than that recommended for analysis in a challenge material.

[d] The lithium content of this SRM is lower than that recommended for analysis in a challenge material.

[e] Includes diffraction gratings, layered synthetic microstructures and artificial crystals such as lead stearate.

[f] As this is a quaternary alloy, conventional quantitative analysis affords the ability to perform a QA diagnostic as described in this document on at most two types of diffracting crystals during a single QA diagnostic run.

[g] Complete compositions of the collection of reference materials can be found at https://mineralsciences.si.edu/facilities/standards/datasheets.htm.

Table A.1 *(continued)*

Challenge material	Composition	Diffracting crystals	Reference materials
NIST SRM 2061	Alloy of Ti, Al, Nb and W	TAP, PET, LiF[f]	Pure Ti, Al, Nb and W
NIST SRM 2066	Beads of glass composed of O, Mg, Si, Ca and Fe	TAP	Oxides or pure elements for Mg, Al, Si and Fe
Certain minerals, glasses and compounds from the Smithsonian Microbeam Standards collection[g]	Depends upon specimen chosen	Depends upon specimen chosen	Depends upon specimen chosen

[a] These materials have been discontinued; however, the certificates providing the full description of the materials can be located at https://www.nist.gov/srm by searching for the keyword "microanalysis."

[b] As this is a binary alloy, conventional quantitative analysis affords the ability to perform a QA diagnostic as described in this document on only one type of diffracting crystal during a single QA diagnostic run.

[c] The zinc content of this SRM is lower than that recommended for analysis in a challenge material.

[d] The lithium content of this SRM is lower than that recommended for analysis in a challenge material.

[e] Includes diffraction gratings, layered synthetic microstructures and artificial crystals such as lead stearate.

[f] As this is a quaternary alloy, conventional quantitative analysis affords the ability to perform a QA diagnostic as described in this document on at most two types of diffracting crystals during a single QA diagnostic run.

[g] Complete compositions of the collection of reference materials can be found at https://mineralsciences.si.edu/facilities/standards/datasheets.htm.

Annex B
(informative)

Distinguishing specimen preparation effects from instrument malfunction

B.1 Specimen preparation

B.1.1 Correct specimen preparation for optimal EPMA analysis

Ideally, after all corrections are applied for mass absorption and secondary fluorescence, X-ray compositional analyses should arrive at a total elemental composition of 100 %, within the expected uncertainty for the analytical technique used. While there are exceptions to this (such as hydrogen content not directly measured in an X-ray analysis), corrected compositions not equal to 100 % frequently indicate either an instrument error or that the specimen is not ideal (homogeneous in composition and density, electrically conductive, topographically flat and smooth, and aligned normal to the electron beam incidence within the detector focus) (ISO 14594, ISO 14595).

Analytical totals that deviate from 100 % are not necessarily an indictment of the instrument with which the analysis was performed. The following subclauses describe multiple scenarios in which peculiarities of the specimen preparation could result in non-unity analytical totals, and offer techniques the analyst may use to mitigate uncertainties or identify the origins of non-ideal analytical results.

B.1.2 Elemental composition total is below 100 %

B.1.2.1 General

A variety of specimen properties or analysis regions can result in elemental composition totals less than unity. If the same area of the specimen is analysed multiple times, quantitative results statistics can be obtained that will either conform to the manufacturer's certified instrument uncertainty or will consistently exceed it. If the analyst determines that the total composition is less than 100 %, yet the uncertainty of the results is consistent with the manufacturer's specification, any of the following could be causing the deviation.

B.1.2.2 Deviation from unity at the instrument's uncertainty specification

B.1.2.2.1 Rough specimen

An electron beam impinging on a "valley" in the surface topography creates a longer average path for X-rays leaving the specimen than does a flat polished surface, resulting in a greater probability of X-ray absorption and scattering events. Hard X-rays generally have lower absorption cross-sections for most elements than do soft X-rays; thus, their intensities are usually affected less than soft X-ray emissions. For this reason, variations in topography will have their greatest effect on the low atomic number, or "low-Z", element intensities, and those elements with emission lines that overlap an absorption edge of another matrix element.

Uncertainties due to surface roughness can be mitigated by the analyst in a few ways. If improving the specimen polish is not an option, analysing additional spots on the specimen or increasing the

analytical spot size (so that the interrogating beam captures more “peaks” as well as valleys) could mitigate the analytical deviation from unity.

NOTE While the mean composition might approach 100 % as the surface roughness is “averaged out”, uncertainties for low-Z elements will likely be higher than the instrument’s uncertainty specification due to the measured X-ray intensity changes from point to point.

B.1.2.2.2 Tilted specimen with respect to standard

Depending upon the tilt angle, X-rays can have a longer path through the specimen to the detector, resulting in more absorption and scattering. As discussed, for analysing inside pits or cracks or on protrusions in the specimen, the greatest effect on intensity is observed for X-rays emitted from low-Z elements (and other low-energy X-rays) and those with characteristic lines near the absorption edges of other elements in the matrix. In this case, however, an analysis of multiple locations on the specimen will give the same result at the instrument’s specified uncertainty. If the analyst suspects specimen tilt, the analysis can be double-checked using other spectrometers on the same system. Alternatively, the specimen may be rotated to test for this error.

NOTE A specimen tilt error ought to give a non-unity, but consistent, quantitative result. Usually, high tilt angles are required to produce this result, so it is not often seen.

B.1.2.2.3 Crystalline specimen

When performing quantitative analysis on crystalline specimens, the intensity of emitted X-rays can be modulated as a function of the specimen crystal plane orientation with respect to the orientation of the spectrometer due to polarization effects. In these circumstances, analytical totals might deviate from 100 % but remain within the instrument’s repeatability uncertainty specification. This specimen-dependent analytical anomaly can be identified by either rotating the specimen to different orientations and measuring again, or repeating the measurement with different identical spectrometers on the same system.

B.1.2.3 Deviation from unity above the instrument uncertainty specification

B.1.2.3.1 General

If the analyst determines that the total composition is less than 100 %, yet the uncertainty of the results is higher than the manufacturer’s specification, any of the following could be causing the deviation. This scenario includes some of the more frequent “real world” analysis problems.

B.1.2.3.2 Subsurface voids

Often, the electron beam impinges on a spot directly above an unseen subsurface void. This specimen problem generates a number of curious effects. If the analyst tries to measure several locations on the specimen (some that impinge upon the void and some that do not), they could arrive at a large range of analytical results, with the greatest effect on the highest energy lines (recall that the measured hard X-rays are emitted from deep within the sample, while the soft X-rays only escape from a relatively thin region near the surface). In some cases, X-ray emissions from trapped gases from within the void could be observed. Argon X-rays, for example, are a sign of a trapped bubble under the surface. Localized specimen charging could also increase due to the thinner path to ground formed by the material above the void, contributing to further measurement uncertainty.

Moreover, when analysing the same location, apparent analytical totals will change with beam voltage, since the beam interaction volume is dependent upon accelerating voltage. Thus, changing the beam voltage where a void is suspected can be a useful strategy for confirming that suspicion. If the analytical total changes appreciably, especially if it approaches unity as the accelerating voltage is reduced, then it is likely that analysis is occurring in a region containing a void, and a different location should be chosen for a more reliable analytical total.

B.1.2.3.3 Porous specimen

This specimen artefact results in data similar to that observed for large buried voids, though with some differences. If an electron beam impinges on a specimen with many tiny (compared to the size of the beam incidence) voids, the localized specimen charging, total compositions different from 100 %, undercounted hard X-rays and overcounted soft X-rays at greater-than-specified uncertainty, and trapped gas spectra might all be observed. However, since many closely spaced tiny voids could be distributed throughout the analysis area, compared with much larger bubbles at greater spacing within a dense matrix, the data artefacts are more subtle than those produced over a large void, and techniques such as changing accelerating voltage are not as effective at identifying cause (though apparent analytical totals can change with beam voltage).

B.1.2.3.4 Contaminated specimen

Surface contamination of challenge materials and reference materials of ostensibly known composition frequently results in analytical totals deviating from 100 %. Performing a full wave scan of the specimen can aid the analyst in identifying specimen contaminants previously unaccounted for in the quality assurance measurement.

B.1.2.3.5 Edge effects

Epoxy-mounted challenge materials and reference materials that are not simple cylinders or prisms with sides normal to the surface plane might exhibit edge effects similar to that observed above a subsurface void. At high beam energies, the interaction volume of the electron beam fully penetrates a wedge-shaped or other irregularly shaped specimen shard such that the epoxy mount underneath or adjacent to the shard is sampled by the electron probe, reducing the spectral intensity of the target element and increasing the intensity due to carbon and oxygen. This effect can be avoided if the analyst avoids setting analysis positions at the edge of the specimen. Elemental mapping prior to analysis can help in locating edges or thin regions in the specimen; a reduction in spectral intensity will be observable wherever the defect occurs.

B.1.3 Total elemental composition is above 100 % (within manufacturer's specification for reproducibility or uncertainty)

B.1.3.1 Rough specimen

An electron beam impinging on a "peak" or protrusion in the surface topography creates a shorter average path for X-rays leaving the specimen than does a flat surface, resulting in fewer X-ray absorption and scattering events. Remember that hard X-rays generally have lower absorption cross-sections with most elements than do soft X-rays; thus, their intensities are affected considerably less than soft X-ray emissions. For this reason, variations in topography will have their greatest effect on the low-Z element intensities (and those elements whose emission lines overlap an absorption edge of another matrix element). Expect low-Z elements to be over-weighted when measured in a protrusion from the surface.

Surface roughness issues can be mitigated by the analyst in a few ways. If improving the specimen polish is not an option, analysing additional spots on the specimen or increasing the analytical spot size (so that the interrogating beam captures more valleys as well as peaks) can mitigate the analytical deviation from unity. It should be noted that while the mean composition should approach 100 % as the surface roughness is "averaged out", uncertainties for low-Z elements will likely be higher due to the intensity changes from point to point.

B.1.3.2 Tilted specimen with respect to standard

Depending upon the tilt angle, X-rays might have a shorter path through the specimen to the detector, resulting in less absorption and scattering. The greatest effect on intensity is observed for X-rays emitted from low-Z elements (and other low-energy X-rays) and those with characteristic lines near the absorption edges of other elements in the matrix. In this case, however, an analysis of multiple locations on the specimen will give the same result at the instrument's specified uncertainty. If the

analyst suspects specimen tilt, the analysis can be double-checked using other spectrometers on the same system. Alternatively, the specimen may be rotated to test for this error.

NOTE A specimen tilt error ought to give a non-unity, but consistent, quantitative result. Usually, high tilt angles are required to produce this result, so it is not often seen.

B.1.4 Total elemental composition is 100 % (uncertainties are higher than instrumental uncertainty)

B.1.4.1 Compositionally heterogeneous specimens

Heterogeneities become a factor as the size regime of compositionally and/or morphologically distinct phases approaches the electron beam interaction volume.

B.1.4.2 Multi-phase specimens

Due to secondary fluorescence or absorption, analytical edge effects will be apparent at phase boundaries. Before any boundary effects can be successfully identified, the "stray electron" problem has to be evaluated for the particular instrument (e.g. "in hole" spectrum measured with a Faraday cup, <10 µm in diameter). As the electron beam approaches a phase boundary, the X-ray spectra will frequently exhibit characteristic peaks of elements in the incident phase modified by the mass absorption characteristics and the secondary fluorescence of the neighbouring phase, due to the lateral component of the electron beam interaction volume entering into the neighbouring phase.

Even if the electron beam interaction volume is larger than the phase domains, or if the electron beam is defocused to a larger incidence than the domain size, quantitative uncertainty can be higher due to local mass absorption and secondary fluorescence effects.

B.1.4.3 Variations of composition within a single phase

This specimen artefact includes those instances, such as doping or a diffusion gradient across a phase boundary, in which there is no distinct boundary between two phases in a solid. Compositional line profiles in the region of interest can be used to assess diffusion gradients or gradients due to treatment history.

B.1.5 Summary

Virtually any non-ideal characteristic of a specimen will have consequences for quantitative analysis. If accuracy and precision are to be maximized, it is critical for the analyst to consider the compositional analysis totals and their distribution over several measurements in the context of the specimen's properties and particularly its non-ideal features. While computational methods or adjustments of instrument parameters can be used to reduce uncertainty, it is rare to obtain an ideal analytical result from a non-ideal specimen. Reporting complete information on an analysis, including compositional uncertainties, compositional deviation from unity and the description of the specimen being analysed, affords the greatest chance of performing the most effective corrective action.

Annex C
(informative)

Graphical rendering of data and control charting

C.1 Introduction

While the computed results of data analysis can provide valuable information regarding the functionality of an instrument, a number of plotting strategies and graphical representations of the data within one QA diagnostic or including the relevant statistics of several such experiments completed over a period of time (control charting) can assist the operator in identifying minor instrument malfunctions that are degrading instrument performance quality. For EPMA QA, monitoring the electron beam current with time and monitoring X-ray intensity statistics using quartile (box-and-whisker) or kernel density (bean) plotting with time are convenient methods to utilize when identifying instrument performance problems.

C.2 Electron beam current tracking

The electron beam current as measured in the Faraday cup between acquisitions should be plotted versus time. Visual inspection of such graphs, along with the report of the mean and standard deviation of the beam current, should be used to identify electron emitter instability, such as noise, drift or electrostatic discharge (see D.2).

C.3 Control charting

C.3.1 General

Control charts, which graph relevant statistics from the QA diagnostic data over a period of time, are a convenient way to track instrument performance and identify when performance has degraded[Z]. Depending upon the needs of a given laboratory, a number of methods may be utilized to track instrument performance.

C.3.2 Univariate and multivariate mean and standard deviation ($\bar{x}$ and R) plots

For EPMA QA, plotting the mean and standard deviation ($\bar{x}$ and R) of the intensity for each experiment in relation to the mean intensity for the factory-certified instrument, and using the instrument uncertainty specification as the control limit, is an acceptable method to identify when an instrument fails to function as specified. This information does not necessarily provide a complete picture of instrument functionality, however. For more informative and actionable graphical representation of QA diagnostic data, the operator may choose to utilize quartile plotting or density plotting.

EXAMPLE Figure C.1 is an example of a univariate $\bar{x}$ and R control chart showing four independent seven-position QA diagnostics of a single element on an instrument that has an uncertainty specification of 1 % at 1σ. The seven individual measurements within each of the four tests are marked with small crosshairs. The mean of the measurements within each test (filled circles) is tracked in relation to the certified mean (dashed line) in the top graph, while the standard deviation of those measurements (filled squares) in relation to the uncertainty specification (dash-dotted line) is tracked in the bottom graph. Figure C.2 is a multivariate $\bar{x}$ and R control chart of the same data that were used to produce Figure C.1. The control band is shown in the figure (dotted line). Note that, due to Poisson counting statistics, 1 % uncertainty at 1σ can only be achieved when the square root of the total counts is less than 1 % of the total counts, which occurs at 10 000 counts or higher. In the present example, the mean count for the tests is 25 780; 1 % of this value is 257,8 counts, while 1σ is ~160 counts. The mean values (squares) of all four tests fall within the control limit range, but the 1σ (error bar) of Test 4 exceeds the lower bound of the control band, indicating a potential problem with this spectrometer or diffracting crystal. Comparison of these charts with those of other elements in the same QA run can be used to narrow the problem to a single instrument component or group of components.

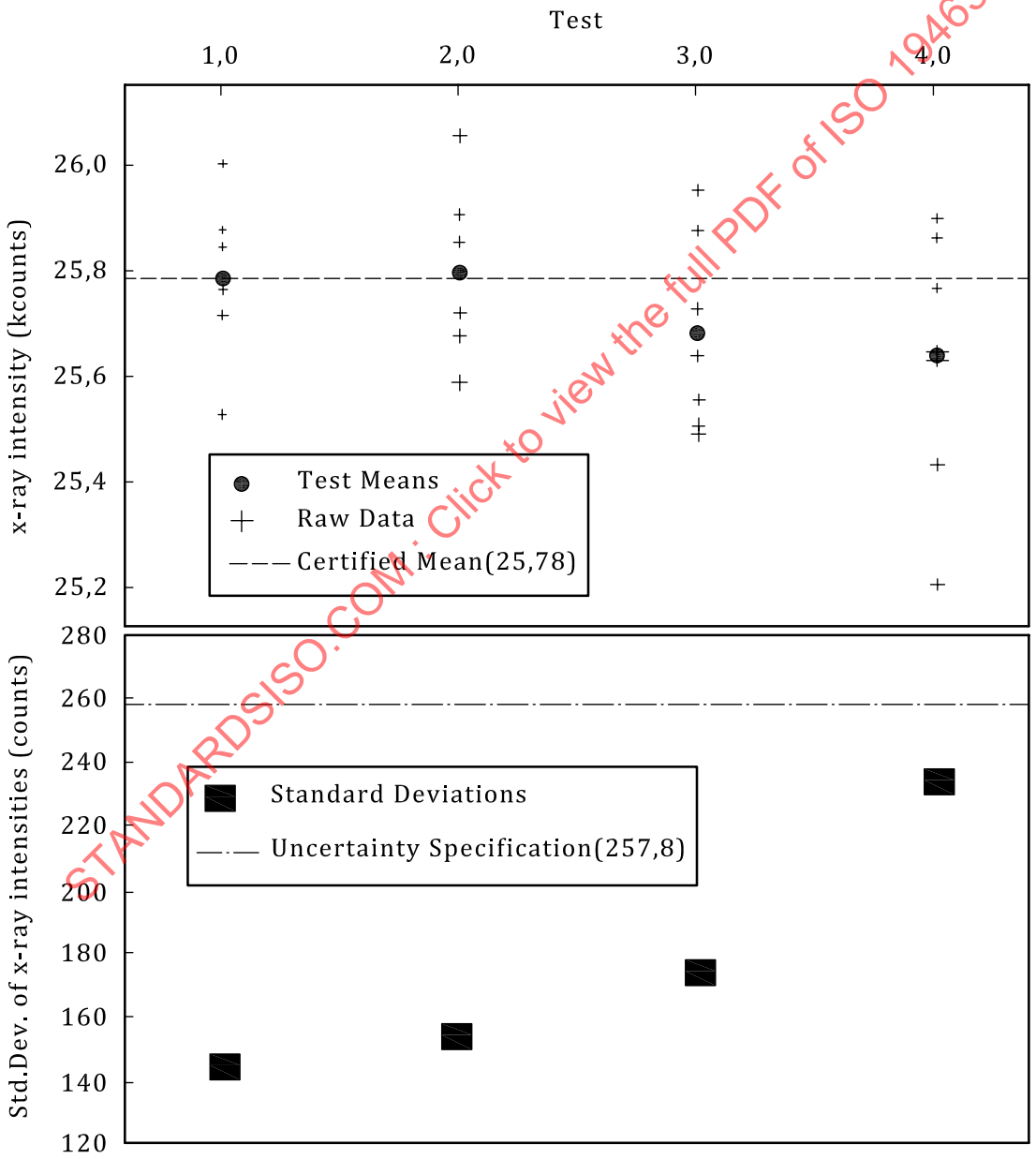

Figure C.1 — Control chart – mean and standard deviation ($\bar{x}$ and R) plot (univariate)

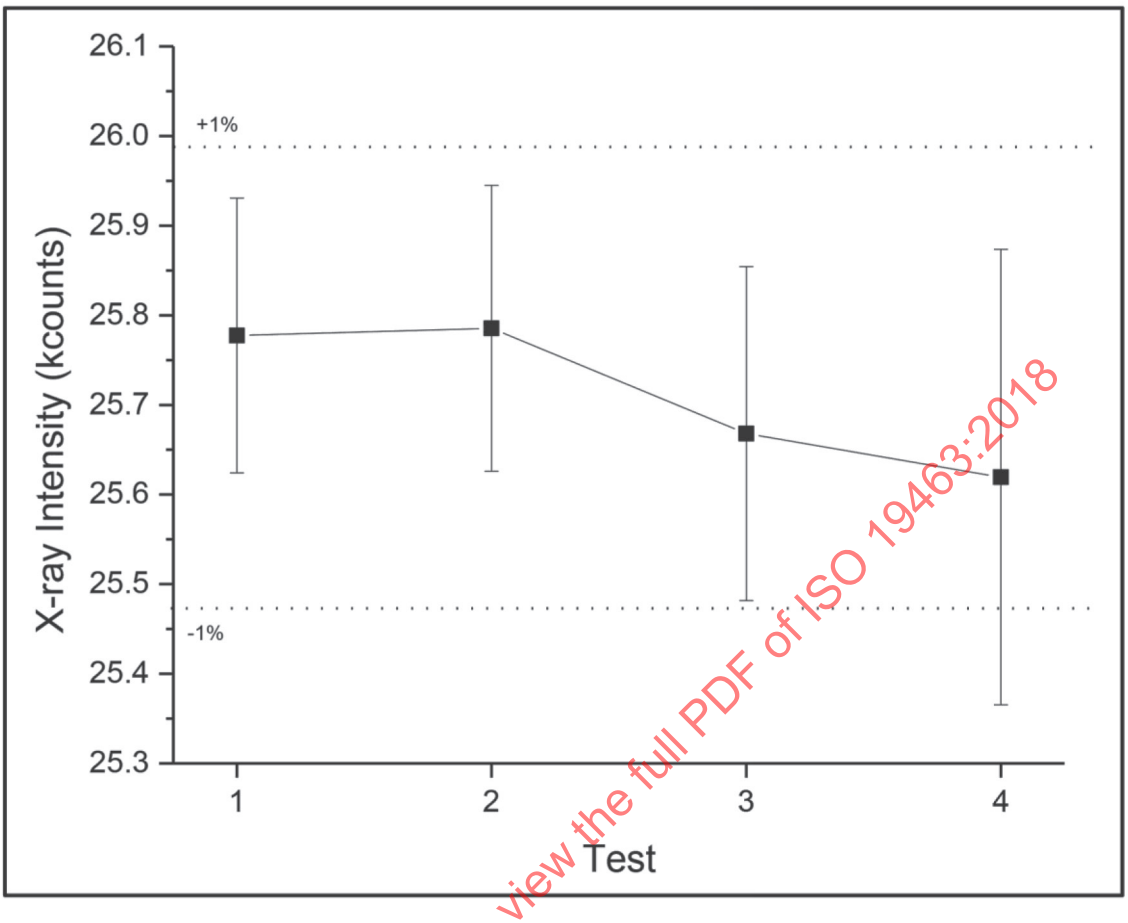

Figure C.2 — Control chart – mean and standard deviation ($\bar{x}$ and R) plot (multivariate)

C.3.3 Quartile ("box-and-whisker") plots

The quartile, or "box-and-whisker" plot, can be a useful visual tool to include in a control chart[8]. The graph is made up of three primary components: a horizontal line at the median of a data set, a rectangle encompassing the centre of the data distribution (the "box") and horizontal lines extended to the range or other limits of the data set (the "whiskers"). Such a graph divides the data into quartiles, which gives an operator a visual estimate of the magnitude of the data spread and the normality of the data set. Multiple such box-and-whiskers plotted over time allow the operator to identify trends in these parameters.

For EPMA QA diagnostic control charting, a quartile plot overlaid with the raw data points and featuring whiskers set to ± 1,5σ allows the operator to identify when data or the data spread exceed the control range as well as perform the simple normality test described in 6.4.2.

EXAMPLE Figure C.3 shows a control chart featuring quartile plots as described above, using the same data as was used to produce Figure C.1. Test 1 and Test 2 exhibit similar analyses to Figures C.1 and C.2, but the additional statistical information provided by the quartile plots of Figure C.3 reveal additional information. Both extremes of the Test 1 data set (diamonds) are outside the 1,5σ whisker (error bar), indicating that the diagnostic apparently fails the simple normality test described in 6.4.2. Test 2, on the other hand, shows results expected from a properly functioning instrument. The inner quartiles (box) on either side of the median are roughly equal in size, the median and mean of the data are nearly coincident and the estimated normality condition is met, as only a single data point is greater than 1,5σ from the mean. Note that although some individual data points exceed the control limit (dotted line) in the first two tests, this is not necessarily cause for concern, since the means and standard deviations are still within control limits (recall Figures C.1 and C.2). The Test 3 data, while also within the control limits, are clearly skewed (note the size difference between the two inner quartiles). By Test 4, the deviation from the instrument specification is more apparent as the spread of the data increases.

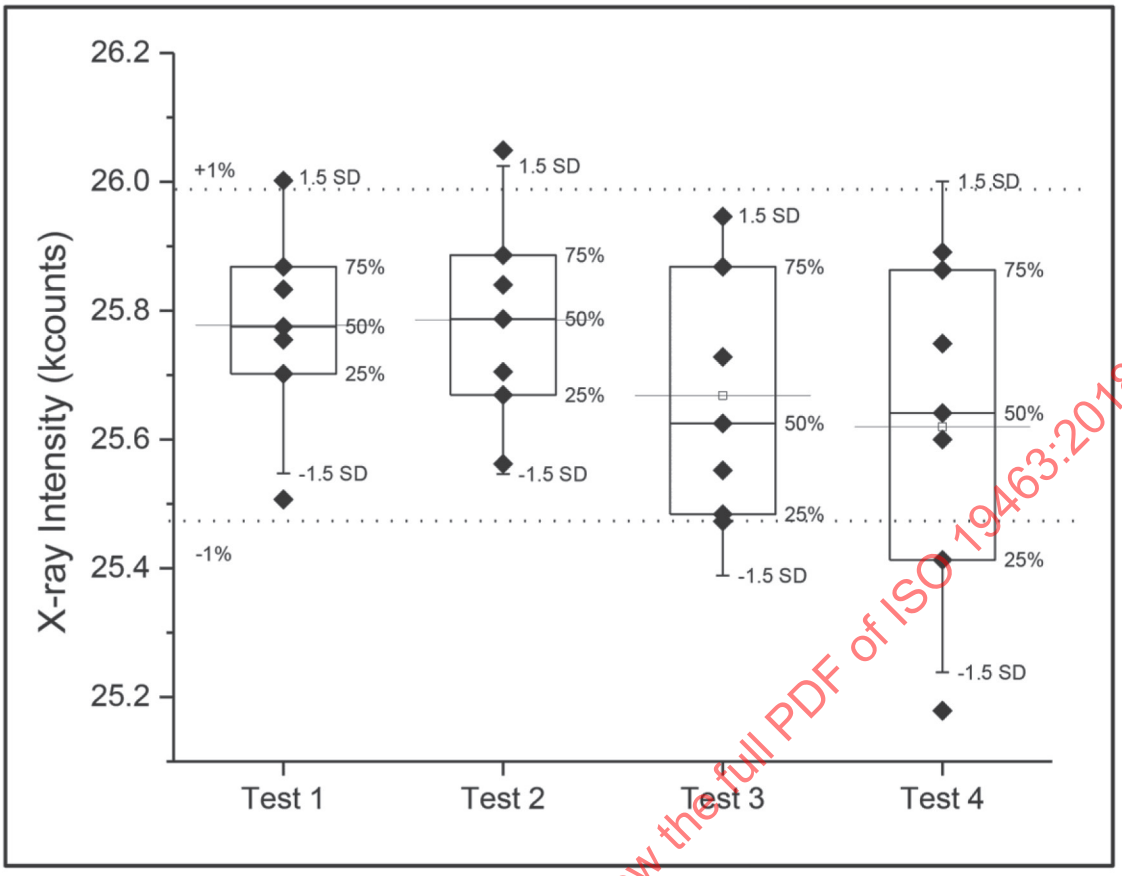

Figure C.3 — Control chart – quartile plot

C.3.4 Density ("bean") plots

The density, or "bean", plot is a recently developed visual tool that can make control charting more valuable[9]. This type of graph shows each raw data point inside a density curve that is a function of the data distribution. Visual inspection alerts the operator to whether the mean is within the control limits and to whether the data are normally distributed, skewed or bimodal. Figure C.4 is a representation of the same data as Figure C.1 using bean plots.