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

Analyse par microfaisceaux — Microanalyse par sonde à électrons — Lignes directrices pour les spécifications des matériaux de référence certifiés (CRM)

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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 document 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*.

This third edition cancels and replaces the second edition (ISO 14595:2014), which has been technically revised.

The main changes are as follows:

- formulae to calculate the uncertainty of the mean mass fraction in 5.6 has been modified by adding a power of 1/2;
- the requirement of the dead time for the energy dispersive spectrometer test has been removed;
- editorial changes have been made to improve the consistency of terms and definitions used throughout the document.

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

For electron probe microanalysis (EPMA), which is a comparative quantitative analytical method used globally, certified reference materials (CRMs) play a crucial role in the analytical accuracy.

This document has been developed to facilitate international exchange and compatibility of analysis data in EPMA.

It aims to give guidance on evaluating and selecting reference materials (RMs), on evaluating the extent of heterogeneity and stability of RMs. It gives recommendations for the determination of the chemical composition of RMs for production as EPMA-certified reference materials.

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

1 Scope

This document specifies recommendations for single-phase certified reference materials (CRMs) used in electron probe microanalysis (EPMA). It also provides guidance on the use of CRMs for the microanalysis of flat, polished specimens. It does not cover organic or biological materials.

This document supplements ISO 17034. A producer of CRM must also comply with ISO 17034. In case of conflict, ISO 17034 takes precedence.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

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

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

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

3.1
heterogeneity
measured variation in compositions of elements measured from a group of specimens

Note 1 to entry: The contributions to heterogeneity include the uncertainties in the measurements from specimen to specimen, from micrometre to micrometre within each specimen, and from the test procedure itself.

3.2
research material
material that appears to have the physical and chemical characteristics required of a CRM, but which is to be examined in detail, including the determination of chemical composition, stability, and micro-heterogeneity and macro-heterogeneity, before certification as a CRM

3.3
stability
<general>resistance of a specimen to chemical and physical change during long-term storage at normal temperature and pressure

3.4
stability
<EPMA>resistance of the material to changes in chemical composition during electron bombardment, i.e. the resistance to change of the intensity of the relevant characteristic X-rays observed during the time the specimen is exposed to the electron beam

3.5
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

4 Preparation of the research material

4.1 Selection of material

The research material used for the preparation of a CRM should exhibit little or no heterogeneity on a micrometre scale, should be free from unwanted inclusions, and should be sufficiently dense (such that voids, if present, can be readily avoided during testing and analysis) and stable under prolonged electron bombardment.

The mounted research material should be of sufficient size to provide several areas suitable for point beam analysis; each area should be approximately 20 µm or more in diameter. At a minimum, the size should be at least twice the area of X-ray emission.

The quantity of research material should be adequate for the preparation of certified specimens.

In the case of a synthetic RM, a detailed description of the preparation technique should be provided. In the case of minerals, the geographic origin, the source, and the separation process should be specified.

4.2 Preliminary inspection of the material

Initial inspection of a possible research material for a CRM should be made using an optical microscope to evaluate the material for the presence of unwanted inclusions, voids, or other phases, and if these are found to be sufficiently abundant to interfere with EPMA of the major phase of interest, i.e. to prevent a clean sampling of the major phase at multiple points with a 1 µm electron beam, the material should be rejected.

Further inspection for the possible presence of very small inclusions or other phases should be carried out on polished sections in reflected and/or transmitted light. An electron microprobe or a scanning electron microscope with secondary electron and backscatter electron detectors can be needed. Material of known composition with inclusions or other phases should only be considered suitable if the inclusions or other phases can be easily identified and clearly marked on accompanying documentation so that they can be avoided during use.

Material found suitable after preliminary inspection should subsequently be processed for further determination of heterogeneity and stability.

5 Heterogeneity of material

5.1 Sample preparation

The CRM should be stable under the electron beam. It should not charge under required test conditions, though in some cases, a conductive coating can be required. It should be in such a physical state that it can be mounted and polished if necessary, without rapid surface deterioration on exposure to the atmosphere or vacuum.

The research material should be in the same or similar physical orientation as that proposed for the CRM, e.g. if the CRM is to be cut or cleaved so that flat surfaces are to be used by the analyst for EPMA, then the research material should be mounted in the same manner as that used to obtain heterogeneity data.

5.2 Sample size

The number of specimens selected for testing will depend upon the number, size, and composition of the individual specimens in the sample group.

For a large number of specimens, such as 200 or more seemingly identical specimens already cut or cleaved and ready for distribution, testing of all specimens would be prohibitively time consuming. A statistically representative number of randomly selected specimens should be selected for testing. If the measured heterogeneity between and/or within specimens is observed to be greater than 1 % relative after taking account of counting statistics for the elements being certified, testing of more specimens can be needed.

Where there are fewer specimens, typically 5 to 20, which can be tested before being cut into smaller specimens for distribution, each specimen should be analysed before being cut, provided that the preparation process does not change the composition in any way.

Consultation with an experienced statistician is strongly recommended before data acquisition is begun. Detailed rules regarding the sample size are avoided here to allow the analyst flexibility in designing the testing procedures since decisions will depend upon the characteristics of the material and the number of specimens available.

5.3 Test conditions

If the extent of heterogeneity is being determined on the micrometre scale, a 1 µm (point) beam should be used for the analysis. In some cases, where there might be damage to the specimen by the electron beam, a defocused beam, typically 5 µm diameter, may be used. Such samples should, therefore, be certified for use only with a defocused beam.

Wavelength-dispersive X-ray spectroscopy (WDS) is the preferred method for heterogeneity determinations because the high X-ray peak rates obtainable with the technique expedite the acquisition of statistically useful data. Energy-dispersive X-ray spectroscopy (EDS) can be applied by using integrated X-ray peak intensities, but the data acquisition process is significantly longer. For specimens sensitive to the high current needed for WDS, EDS can be the only choice.

Ideally, the excitation voltage used for the analysis should be about two and a half times the critical excitation energy of the X-ray line of the element being analysed, although this can be difficult if several elements are analysed simultaneously. As a compromise, the selected excitation voltage should be sufficient to excite the X-ray lines of the elements used in the testing with an adequate overvoltage of at least 1,5 times the critical excitation potential.

The selected X-ray lines used to acquire the heterogeneity data should not overlap any X-ray lines of other elements in the specimen. This can be ascertained from wavelength dispersive spectroscopy scans of the pure elements (or appropriate well-characterized compound specimen in which overlap does not present a problem) and of the RM.

The current used will depend upon element concentrations, the stability of the specimen to the electron beam, and the count rate desired.

The count rate should provide acceptable counting statistics. The count rate should not be so high that the dead time of the WDS proportional counter will increase beyond the normal working range. A normal proportional counter dead time is 1 µs ~ 2 µs or less.

NOTE Acceptable count rates will also depend upon tolerable counting uncertainties. From Poisson counting statistics, the standard uncertainty in the counts obtained from an X-ray measurement is equal to the square root of the total number of X-ray counts, $\sqrt{N}$. A 1 % error can be obtained when the total number of counts is 10 000, but this relative error can be reduced by increasing the number of counts. At 100 000 counts, the relative error is reduced to 0,3 %. For an EDS, the number of counts refers to the counts in the window of interest or integrated peak counts, not the total spectrum counts. This test uncertainty will be present regardless of the extent of heterogeneity and can be minimized by increasing the integral number of counts through increased current and/or counting time at a given excitation voltage. Both ultimately depend on the specimen stability, while the counting time will also be limited by test practicality.

Knowing the estimated count rate, R, and the desired relative error, σ, the counting time, T, required to achieve that relative error can be calculated from the equation $T = 1/(\sigma^2 R)$. This formula is derived from the Poisson estimate of the relative error due to counting statistics, $1/\sqrt{(N)} = 1/\sqrt{(RT)}$.

5.4 Test procedure

Before heterogeneity testing is begun, the edges of bulk specimens should be analysed and compared to the specimen interior to determine whether there might be a consistent difference in element concentrations in the two locations. Occasionally, differences can result from the manufacturing process of materials such as metal alloys or synthetic crystals. If the edges are different from the specimen interior, they should be removed before samples are taken for bulk quantitative analysis and before specimens are mounted and polished for heterogeneity studies. In some specimens, differences can also be due to mounting and polishing procedures; if this occurs and cannot be remedied, the certificate should include instructions to the analyst to avoid using the material within a specified minimum distance from the edge.

Specimens that are being compared should be mounted together in the same sample mount or block, if possible. Carbon coating, if necessary, should be applied to all specimens simultaneously.

Tests should be designed to efficiently acquire the data needed to determine the extent of the within-specimen and between-specimen heterogeneity, to determine the experimental uncertainty, and to look for gradual increasing or decreasing concentration changes on the micrometre scale using 50 µm to 100 µm line scans. Examples of tests are given in the next two paragraphs, but they may be modified depending upon the individual material or group of specimens being analysed. The beam current should be monitored to provide a value corresponding to each data reading enabling subsequent current drift corrections to be carried out, if necessary.

For each specimen being tested, X-ray counts for several randomly selected points (typically 7 to 10 or more depending upon the size of the specimen) should be acquired. These data should be acquired at least in duplicate i.e. integral X-ray counts should be acquired and recorded at least twice on each point without moving the specimen or electron beam between acquisitions. Specimens should be analysed in a random order and preferably, each specimen should be analysed twice, each time in a different order. It may be worthwhile for different operators to take data for duplicate analyses, using a different random sampling plan for each. Refer to ISO Guide 35[1] for sampling procedures and methods of evaluating results. The data from this type of test is used to calculate the within-specimen and between-specimen uncertainties, as well as the test uncertainty after beam current drift corrections are made. When background data are obtained for each element, the uncertainties can be expressed as a mass fraction. The formulae used for these calculations are given in 5.5.

To test for the presence of concentration trends within each specimen, which might not be detected by random sampling, line profiles of the points less than 5 µm apart and 50 µm to 100 µm in length should be prepared. Two-line profiles normal to one another are recommended. For specimens of 1 cm to 2 cm, a set of two-line profiles should be prepared from at least two different locations on the specimen. After current corrections, data should be plotted (distance against X-ray counts) for each element to expose variations in concentrations that can be present. Such trends might not preclude the certification process if they are within the 99 % confidence limits or ±3 times the Poisson counting error (square root of the integral number of X-ray counts).

5.5 Statistical evaluation of data

The uncertainties in the element concentrations resulting from heterogeneity within specimens and between specimens and in the test, acquisition can be obtained from the procedures described in 5.4

using the following calculations. Other validated test and statistical procedures may be used, provided that they are described in full in the CRM certificate.

NOTE There are several examples[2][3][4][5] of the use of test procedures and calculations similar to those described here; the statistical notation has been simplified for this document to facilitate its usage. The statistical approach used here is called a nested design that is described in detail in other references [1][6][7]. The procedures described have been developed in collaboration between the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA and the National Physical Laboratory (NPL), Teddington, Middlesex, UK and have been used successfully.

Let w_0 be the true mass fraction of a particular element in the RM. Any single micrometre scale measurement, w, expressed in weight percent taken from a randomly selected point of a randomly selected specimen will deviate from w_0 because of the variation between specimens (macroheterogeneity), variation within specimens (microheterogeneity), and the measurement error. The deviation, $w - w_0$, may be viewed as a sum of random effects, as shown in Formula (1):

$$w = w_0 + \mathrm{S} + \mathrm{P} + \mathrm{E} \tag{1}$$

where

$w_0 + \mathrm{S}$ is the true mass fraction in the selected specimen;

$w_0 + \mathrm{S} + \mathrm{P}$ is the true micrometre scale mass fraction concentration at the selected point of the selected specimen;

E is the measurement error.

The components of variance $\sigma^2_{S_w}$, $\sigma^2_{P_w}$, and $\sigma^2_{E_w}$ are the variances of the random effects S, P, and E, respectively. The variance, σ^2_w, of the measurement *w* is given by Formula (2):

$$\sigma^2_w = \sigma^2_{S_w} + \sigma^2_{P_w} + \sigma^2_{E_w} \tag{2}$$

If n_E independent measurements are made at each of n_P randomly selected points of each of n_S randomly selected specimens and if w_{ijk} denotes the k th replicated measurement at point *j* of specimen *i*, then the grand mean given by Formula (3):

$$\bar{w} = \frac{1}{\left(n_P n_S n_E\right)} \sum_{i=1}^{n_S} \sum_{j=1}^{n_P} \sum_{k=1}^{n_E} w_{ijk} \tag{3}$$

has a variant, given by Formula (4):

$$\sigma^2_{\bar{w}} = \frac{\sigma^2_{S_w}}{n_S} + \frac{\sigma^2_{P_w}}{n_S n_P} + \frac{\sigma^2_{E_w}}{n_S n_P n_E} \tag{4}$$

assuming the design is balanced. Thus, the uncertainty in the mean measurement $\bar{w}$ can be determined from estimates of $\sigma^2_{S_w}$, $\sigma^2_{P_w}$, and $\sigma^2_{E_w}$. An approximate 95 % or 99 % confidence interval for the mean micrometre scale concentration is respectively

$$\bar{w} \pm 2 \left[\frac{\sigma^2_{S_w}}{n_S} + \frac{\sigma^2_{P_w}}{n_S n_P} + \frac{\sigma^2_{E_w}}{n_S n_P n_E} \right]^{\frac{1}{2}} \tag{5}$$

or

$$\bar{w} \pm 3 \left[\frac{\sigma^2_{S_w}}{n_S} + \frac{\sigma^2_{P_w}}{n_S n_P} + \frac{\sigma^2_{E_w}}{n_S n_P n_E} \right]^{\frac{1}{2}} \tag{6}$$

Estimates of $\sigma^2_{S_w}$, $\sigma^2_{P_w}$, and $\sigma^2_{E_w}$ can be obtained from the raw count data as follows.

Let Y_{ijk} denote the k th count measured at point j of specimen i, and let B_{ijk} represent the background count associated with the measured count Y_{ijk}. Assuming a linear relationship between the number of counts above the background count and the mass fraction on the micrometre scale, $Y_{ijk} - B_{ijk}$ can be used to determine a mass fraction measurement, as given in Formula (7):

$$w_{ijk} = \frac{\left(Y_{ijk} - B_{ijk}\right)}{C} \tag{7}$$

where *C* is a conversion factor which depends on test conditions such as the operating voltage, counting time, etc.

If $\bar{B}$ is the mean background count:

$$\bar{Y}_{ij} = \frac{1}{n_E} \sum_{k=1}^{n_E} Y_{ijk} \tag{8}$$

is the mean count at point j in specimen i;

$$\overline{Y}_i = \frac{1}{n_P}\sum_{j=1}^{n_P}\overline{Y}_{ij} \tag{9}$$

is the mean count for specimen i;

$$\overline{Y} = \frac{1}{n_S}\sum_{i=1}^{n_S}\overline{Y}_i \tag{10}$$

is the grand mean count;

$$S_S = n_P n_E \sum_{i=1}^{n_S}\left(\overline{Y}_i - \overline{Y}\right)^2 \tag{11}$$

is the between-specimen sum of squares;

$$S_P = n_E \sum_{i=1}^{n_S}\sum_{j=1}^{n_P}\left(\overline{Y}_{ij} - \overline{Y}_i\right)^2 \tag{12}$$

is the between-points within-specimen sum of squares;

$$S_E = \sum_{i=1}^{n_S}\sum_{j=1}^{n_P}\sum_{k=1}^{n_E}\left(Y_{ijk} - \overline{Y}_{ij}\right)^2 \tag{13}$$

is the error and baseline sum of squares.

The corresponding mean squares are

$$S_{MS} = \frac{S_S}{n_S - 1} \tag{14}$$

between-specimen;

$$S_{MP} = \frac{S_P}{n_S\,(n_P - 1)} \tag{15}$$

between-points within specimen;

$$S_{ME} = \frac{S_E}{n_S n_P\,(n_E - 1)} \tag{16}$$

residual.

Assuming Poisson variation for the background count and for replicated counts at each point of each specimen, it follows that

a) $\dfrac{\sum_{i=1}^{n_S}\sum_{j=1}^{n_P}\sum_{k=1}^{n_E}\left(Y_{ijk} - \overline{Y}_{ij}\right)^2}{n_S n_P\left(n_E - 1\right)} = S_{ME}$ is an unbiased estimate of $C^2\sigma_{E_w}^2 - \sigma_B^2$;

b) $\dfrac{n_E\sum_{i=1}^{n_S}\sum_{j=1}^{n_P}\left(\overline{Y}_{ij} - \overline{Y}_i\right)^2}{n_S\left(n_P - 1\right)} = S_{MP}$ is an unbiased estimate of $C^2\left(\sigma_{E_w}^2 + n_E\sigma_{P_w}^2\right) - \sigma_B^2$;

c) $\dfrac{n_P n_E \sum\limits_{i=1}^{n_S} \left(\overline{Y}_i - \overline{Y}\right)^2}{\left(n_S - 1\right)} = S_{MS}$ is an unbiased estimate of $C^2\left(\sigma^2_{E_w} + n_E \sigma^2_{P_w} + n_P n_E \sigma^2_{S_w}\right) - \sigma^2_B$.

Where σ^2_B is the variance of the background noise.

The estimated components of variance are thus taken to be

$$\hat{\sigma}^2_{E_w} = \frac{S_{ME} + \overline{B}}{\hat{C}^2} = \frac{\left\{\dfrac{S_E}{n_S n_P \left(n_E - 1\right)}\right\} + \overline{B}}{\hat{C}^2} \tag{17}$$

$$\hat{\sigma}^2_{P_w} = \frac{S_{MP} - S_{ME}}{n_E \hat{C}^2} = \frac{\left\{\dfrac{S_P}{n_S \left(n_P - 1\right)} - \dfrac{S_E}{n_S n_P \left(n_E - 1\right)}\right\}}{n_E \hat{C}^2} \tag{18}$$

$$\hat{\sigma}^2_{S_w} = \frac{S_{MS} - S_{MP}}{n_P n_E \hat{C}^2} = \frac{\left\{\dfrac{S_S}{n_S - 1} - \dfrac{S_P}{n_S \left(n_P - 1\right)}\right\}}{n_P n_E \hat{C}^2} \tag{19}$$

where the conversion factor, C, is estimated using Formula (20):

$$\hat{C} = \left(\overline{Y} - \overline{B}\right) / \widehat{w}_0 \tag{20}$$

where w_0 is equal to the certified mass fraction concentration determined by chemical analysis of the original bulk specimen. The variance of the mean mass fraction, $\overline{w}$, can be calculated directly using Formula (21):

$$\hat{\sigma}^2_{\overline{w}} = \frac{1}{n_S n_P n_E \hat{C}^2}\left[\frac{S_S}{n_S - 1} + \overline{B}\right] \tag{21}$$

With $n_S - 1$ degrees of freedom. This equation is preferred in practice to Formula (4) because, in general, fewer potentially negative substitutions have to be made to calculate the variance. Since the components of variance approach depends on taking differences to estimate the individual components, difficulties arise when either $\hat{\sigma}^2_{S_w}$ or $\hat{\sigma}^2_{P_w}$ are negative. Use of Formula (21), rather than Formula (4), avoids the need to equate a negative variance to zero.

It is essential to the above computations that the conversion factor, C, remain constant throughout the test. If current drift, etc. induces changes in C, there might be practical limitations on the number of measurements that can be taken for any one test. Data should, in that case, be acquired in separate tests, and an estimate of each variance component determined for each test. A weighted average can then be determined from the individual tests to obtain a final estimate for certification.

An example of the use of a spreadsheet for making these calculations is given in Annex A. Detailed instructions are included.

5.6 Criteria for certification

A research material is an acceptable candidate for certification if the relative uncertainty at the 95 % or 99 % confidence interval

$$\pm 2\left\{\frac{1}{n_S n_P n_E \hat{C}^2}\left[\frac{S_S}{(n_S-1)}+\overline{B}\right]\right\}^{\frac{1}{2}} \text{ or } \pm 3\left\{\frac{1}{n_S n_P n_E \hat{C}^2}\left[\frac{S_S}{(n_S-1)}+\overline{B}\right]\right\}^{\frac{1}{2}},$$

for the mean micrometre scale concentration, $\overline{w}$, due to specimen heterogeneity, is less than 1 % or 2 %, respectively. A larger relative uncertainty may, in some cases, be acceptable, particularly if high count rates are not achievable in the testing procedure, which can be due to such factors as the sensitivity of the specimen to the beam, the element concentration in the specimen, or the X-ray line used for testing. The potential usage of the CRM can also influence the acceptance of larger uncertainties. Such factors should be discussed in the certificate.

An example of a spreadsheet for the statistical evaluation of heterogeneity data are given in Annex A.

6 Stability of the research material

The stability of a research material should be determined as a preliminary step in evaluating a material for certification. For specimens that are sensitive to electron bombardment, the specimen stability might influence the choice of test parameters such as the excitation voltage, the beam current, the acquisition time, and the electron beam size.

The stability of a specimen is measured by exposing it to the electron beam without stage or beam movement for a time period that would be used in routine EPMA, such as 10 s to 100 s, while measuring the X-ray peak count rates of the elements present. The count rates can be measured on a ratemeter or on a recorder using a direct display of the ratemeter signal or on a periodic integral trace[4] in which pen excursions are changed after X-ray counts have been collected for a discrete time interval such as 10 s.

If the element X-ray count rates consistently increase or decrease beyond about 0,5 % relative, or beyond the acceptable 1-sigma Poisson counting statistics error during a reasonable time interval, the test parameters cited above should be modified until stability is observed for all elements while also providing the count rates needed for the analysis. Often, the excitation voltage and/or beam current can be reduced (while still maintaining the overvoltage needed for the X-ray lines being used) and the acquisition time can be increased to avoid specimen instability and maintain the counting statistics needed for good test precision. In some cases, the electron beam can be defocused if a point beam resolution is not needed in the analysis. A 5 µm to 10 µm diameter beam is recommended if defocusing is used. The analyst should determine acceptable conditions through trial and error and such recommendations should be clearly specified in the CRM certificate.

7 Determination of the chemical composition of CRMs

7.1 Classification of CRMs

The chemical composition of material for CRMs should be determined and the accuracy and precision of both the analysis method and the test results for the particular material tested should be described on the certificate. The class to which the CRM should be designated is determined by the extent of testing carried out. Requirements for testing for each class are given in Annex B.

7.2 Determination of classification of CRMs

The determination of the chemical composition should be carried out by at least two independent laboratories and the mean or weighted mean[1][8]of their results used as the certified value. If possible, the laboratories should avoid replication of method-dependent systematic errors by using different analytical methods. For class 1 CRMs, these analyses should be carried out in more than one country and should include methods other than EPMA.

In cases where the difference between the results of two laboratories is larger than the accuracy of the analytical method, the results of interlaboratory tests may be used to achieve a preferred value. If this is not possible, a third laboratory should be involved as an arbitrator. This laboratory should be affiliated to a national or international accreditation body.

7.3 Selection of analytical method

An International Standard analytical method should preferably be used for the chemical composition determination. If an International Standard method is not available, a classical method should be used. The method used should have internationally acceptable accuracy and should be described in the certificate.

7.4 CRM material tested by EPMA only

If only a small amount of material is available and the only way to test it is by EPMA, the laboratories participating in the analysis should have well-established expertise in the analysis of that particular type of material and ideally be part of an accreditation programme. These will not be class 1 CRMs.

8 CRM specimen preparation, packaging, transportation, and storage

8.1 Preparation of CRM specimen

The CRM material should be mounted in a holder with its flat, polished surface perpendicular to the electron beam. Non-conducting materials require a suitable conductive coating on the surface.

The polished surface of the CRM should have areas large enough for analysis, which are free from defects when viewed with an optical microscope at ×400 magnification. For the size requirement of these areas, see 5.2.

8.2 Packaging

The CRM specimen should be packaged in a suitable container to protect its working surface and prevent damage.

8.3 Storage

The CRM should be stored under conditions designed to prevent deterioration. For most materials, an air-tight desiccator or cabinet are considered suitable. Certain materials can need special conditions of storage and this should be clearly stated on the certificate.

8.4 Repolishing and recoating of CRMs

CRMs will have to be repolished and recoated from time to time. This time interval will vary according to the type of material. Hard non-reactive materials might only need recoating every two years while soft reactive metals, oxides, and minerals might need repolishing and recoating every time they are used. The certificate should state a time period after which repolishing and/or recoating is recommended.

9 CRM certificate

9.1 Classification of CRM

The CRM shall be classified in one of the three classes of CRMs in accordance with the criteria given in Annex B and the class should be indicated on the certificate.

9.2 Contents of the certificate

The CRM certificate should be written in accordance with ISO Guide 31.[9] It should include the name of the CRM, the source of the RM, the producer, the batch number, a description of its properties, its preparation, instructions for use, and relevant references. The heterogeneity testing procedures and results, the stability, and chemical determinations should be described in detail. A typical example of a certificate is given in Annex C. The amount of information required will depend on the CRM class.

Annex A
(informative)

Spreadsheet instructions for the statistical evaluation of heterogeneity data

A.1 General

This annex gives a step-by-step description of the use of a spreadsheet for calculating components of variance in 5.5. An annotated spreadsheet that begins from step 3 below follows these instructions. These calculations can also be done with a computer program.

A.2 Procedure

A.2.1 Put the data into a spreadsheet so that the name of the data point includes i, the specimen number or code, j, the number of the point analysed on the specimen, and k, the replicate measurement on point j. The beam current, recorded before each data acquisition, should be placed in a single column followed by the data (X-ray peak height or peak integral) for each element tested in respective columns. The statistical notation is that n_E replicated independent measurements are made at each of n_P randomly selected points on each of n_S randomly selected specimens. The integrated X-ray count for a single data point is defined as Y_{ijk} that is the reading for the k th replicate measurement taken from point j of specimen i.

A.2.2 Make current corrections to all data choosing a single current value for evaluating all data from a single experiment.

A.2.3 For each point, j, in each specimen, i, calculate the mean count $\overline{Y}_{ij}$ for that point from the replicated measurements for each element on that specimen.

A.2.4 Group all data for each specimen and calculate the mean count for specimen, i, $\overline{Y}_i$, from all points, j, including the repetitions, for each element.

A.2.5 Calculate the grand average, $\overline{Y}$, for each element from all points and repetitions in all specimens in the experiment.

A.2.6 For each specimen, i, calculate the difference between the mean count at point j and the mean count from all analysed points of specimen i, $\overline{Y}_{ij} - \overline{Y}_i$, for each element.

A.2.7 Calculate the square of this difference, $\left(\overline{Y}_{ij} - \overline{Y}_i\right)^2$, for each element.

A.2.8 Sum the squares of these differences over all points, n_P, in all specimens, n_S, for each of the elements, as shown in Formula (A.1):

$$S_P = n_E \sum_{i=1}^{n_S} \sum_{j=1}^{n_P} \left(\overline{Y}_{ij} - \overline{Y}_i\right)^2 \tag{A.1}$$

A.2.9 Calculate the difference between the specimen mean and the grand average, $\left(\overline{Y}_i - \overline{Y}\right)$, for each element in each specimen.

A.2.10 Calculate the square of this difference, $\left(\overline{Y}_i - \overline{Y}\right)^2$, for each element in each specimen.

A.2.11 Calculate the "between specimen" sum of squares, S_S, for each element knowing the values for n_P and n_E as given in Formula (A.2):

$$S_S = n_P n_E \sum_{i=1}^{n_S} \left(\overline{Y}_i - \overline{Y}\right)^2 \tag{A.2}$$

A.2.12 For each element in each tested point in each specimen, calculate $\left(Y_{ijk} - \overline{Y}_{ij}\right)$, the difference between each single point measurement, and the average of the replicate measurements on that point.

A.2.13 Calculate the square of the difference, $\left(Y_{ijk} - \overline{Y}_{ij}\right)^2$, for each element at each point in each specimen.

A.2.14 For each element, calculate the error sum of the squares, as given in Formula (A.3):

$$S_E = \sum_{i=1}^{n_S} \sum_{j=1}^{n_P} \sum_{k=1}^{n_E} \left(Y_{ijk} - \overline{Y}_{ij}\right)^2 \tag{A.3}$$

A.2.15 Knowing the measured background, $\overline{B}$, in counts/s for each element, calculate the terms $\left(\overline{Y} - \overline{B}\right)$.

A.2.16 Then, from the certified weight fraction concentration, $\widehat{w}_0$, of each element determined by chemical analysis of the bulk specimen, calculate the estimated conversion factor, $\widehat{C}$, using Formula (A.4):

$$\widehat{C} = \left(\overline{Y} - \overline{B}\right) / \widehat{w}_0 \tag{A.4}$$

where $\widehat{w}_0$ is the certified mass fraction value of the original bulk specimen as determined by chemical analysis.

A.2.17 The estimates of the variances $\sigma^2_{E_w}$, $\sigma^2_{P_w}$, and $\sigma^2_{S_w}$ can then be calculated using Formula (A.5), Formula (A.6), and Formula (A.7):

$$\hat{\sigma}^2_{E_w} = \frac{S_{ME} + \overline{B}}{\widehat{C}^2} = \frac{\left\{\dfrac{S_E}{n_S n_P \left(n_E - 1\right)}\right\} + \overline{B}}{\widehat{C}^2} \tag{A.5}$$

$$\hat{\sigma}^2_{P_w} = \frac{S_{MP} - S_{ME}}{n_E \widehat{C}^2} = \frac{\left\{\dfrac{S_P}{n_S \left(n_P - 1\right)} - \dfrac{S_E}{n_S n_P \left(n_E - 1\right)}\right\}}{n_E \widehat{C}^2} \tag{A.6}$$