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Microbeam analysis — Electron probe microanalysis — Methods for elemental-mapping analysis using wavelength-dispersive spectroscopy

Analyse par microfaisceaux — Analyse par microsonde électronique (microsonde de Castaing) — Méthodes d'analyse par cartographie élémentaire en utilisant la spectrométrie à dispersion de longueur d'onde

Reference number
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Foreword

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ISO 11938 was prepared by Technical Committee ISO/TC 202, *Microbeam analysis*, Subcommittee SC 2, *Electron probe microanalysis*.

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Introduction

Electron probe microanalysis (EPMA) has been developed over the last 50 years[1][2][3][4] and has many areas of application in science and industry. Both qualitative and accurate quantitative analyses are employed extensively in mineralogy and in metallurgical studies, for example. In recent years, with the advances in computers, digital processing techniques have been developed and, instead of X-ray dot images being used to qualitatively observe element distributions, colour mapping techniques[5] are now often employed. These enable products to be compared and evaluated for the purpose of quality control. Particle analysis and/or phase analysis using mapping requires careful selection of the experimental parameters, and it is essential that a standard be available for this purpose in order to achieve consistent and reliable results.

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Microbeam analysis — Electron probe microanalysis — Methods for elemental-mapping analysis using wavelength-dispersive spectroscopy

1 Scope

This International Standard provides procedures for electron microprobe elemental-mapping analysis using wavelength-dispersive spectrometry. The choice between mapping with the electron beam moving digitally across the specimen (electron beam mapping) and mapping with stage movement only (large-area mapping) is assessed. It describes five types of data processing: the raw X-ray intensity data method, the k-value method, the calibration method, the correlation method and the matrix correction method.

2 Normative references

The following referenced documents are indispensable for the application 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 5725-6, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

ISO 14594, *Microbeam analysis — Electron probe microanalysis — Guidelines for the determination of experimental parameters for wavelength dispersive spectroscopy*

ISO 16592:2006, *Microbeam analysis — Electron probe microanalysis — Guidelines for determining the carbon content of steels using a calibration curve method*

ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories*

ISO 17470, *Microbeam analysis — Electron probe microanalysis — Guidelines for qualitative point analysis by wavelength dispersive X-ray spectrometry*

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*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 23833 and the following apply.

3.1
mapping area
orthogonal array of equally spaced pixels in the X and Y directions that define the region of the specimen being mapped

NOTE Each pixel is analysed for the same time period, and the integrity of the data from each pixel is maintained in the stored data such that the graphical display of the data exhibits the distribution for each of the elements analysed.

3.2
beam scanning
time-controlled movement of the electron beam on the specimen surface with the synchronized movement on the display screen

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3.3
pseudo-colour map
false-colour map
grey-level map
element concentration display using different grey levels or colours, where each pixel grey level or colour value represents the magnitude of the measured element intensity at that pixel position

3.4
pixel
single data point in a map

3.5
stage mapping
production of an X-ray map by mechanically moving the stage under a stationary electron beam in a predefined orthogonal-array pattern

4 Procedure of mapping analysis

4.1 General

The experimental parameters to be used during the analysis should be selected using the guidelines detailed in ISO 14594.

In order to carry out mapping analysis, the analysing instrument shall be sufficiently stable for any variation due to instrument drift over the total mapping period to be reasonably expected to be significantly less than the variation due to differences in the measured element intensities. The instrument's stability will be defined from a test of the instrument's performance. The stability should be measured over a time period similar to that used for the mapping analysis.

NOTE 1 An Si wafer is sufficiently homogeneous and suitable to check the stability.

NOTE 2 There are two options for carrying out the background measurement. The first method is to measure both the peak and the background intensities pixel by pixel. This minimizes the effects of stage and/or beam energy drift, but requires the spectrometer to move between the peak and background positions at every pixel, significantly increasing analysis time and introducing potential drift in the spectrometer positioning. The second method is to acquire a complete peak map and a complete background map. This significantly reduces the total analysis time and removes the risk of spectrometer drift, but is more prone to stage and/or beam-energy drift.

4.2 Specimen preparation

The specimen shall be prepared so as to minimize the effects of artefacts and errors on the mapping analysis, but without destroying the integrity of the specimen (see ISO 22489).

The specimens (reference specimen and unknown specimen) shall be clean and free of dust.

The specimen shall be as flat as possible. If necessary, the specimen shall be embedded in a mounting medium and metallographically polished.

The specimen shall have good electrical conductivity. Charging under electron beam irradiation can be avoided by coating the specimen with a conductive layer of a suitable material. The coating shall be as thin as possible whilst still providing sufficient charge dissipation. A conducting path shall be established between the specimen surface and the metallic specimen holder. Carbon coating is generally used but, in particular cases, other materials should be considered (Au, Al, etc.). Carbon to a thickness of around 10 nm to 20 nm is usually sufficient to establish good conduction. It is recommended that both the reference material and unknown specimen be coated with the same element at the same thickness.

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4.3 Measurement procedure

4.3.1 General

Mapping analysis shall be performed as follows:

a) Select the location and size of the required map area on the specimen.

b) Select the number of pixels to meet the required spatial resolution, and the method of acquisition (stage or beam mapping).

c) Select and apply the element and instrument conditions.

d) Collect characteristic peak and background X-rays and any required electron signals (e.g. backscatter, secondary electrons, absorbed current) at each pixel, and store all data in the computer memory point by point[1].

e) Apply the chosen correction method to the X-ray data (see Clause 5).

f) Finally, the data can be displayed as pseudo-colour maps, as shown in Figure 1.

g) The mapping procedure is summarized in Figure 2.

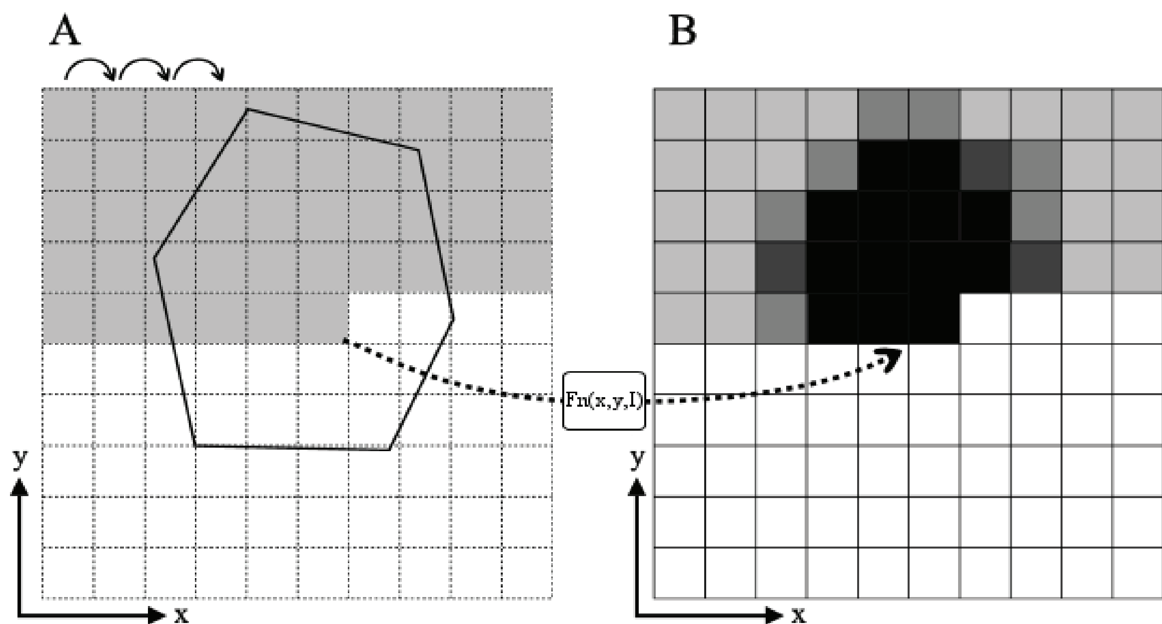

Figure 1 — Procedure for converting mapping data into pseudo-colour maps

The mapping area and resolution are selected on the specimen (grid A) and the mapping is acquired by electron beam movement or stage movement pixel by pixel (solid arrows above grid A). At each pixel position, x,y, the measured X-ray intensity, I, is converted via the chosen correction method, Fn(x,y,I), into a false-colour level at the correlating pixel position in the result map (grid B).

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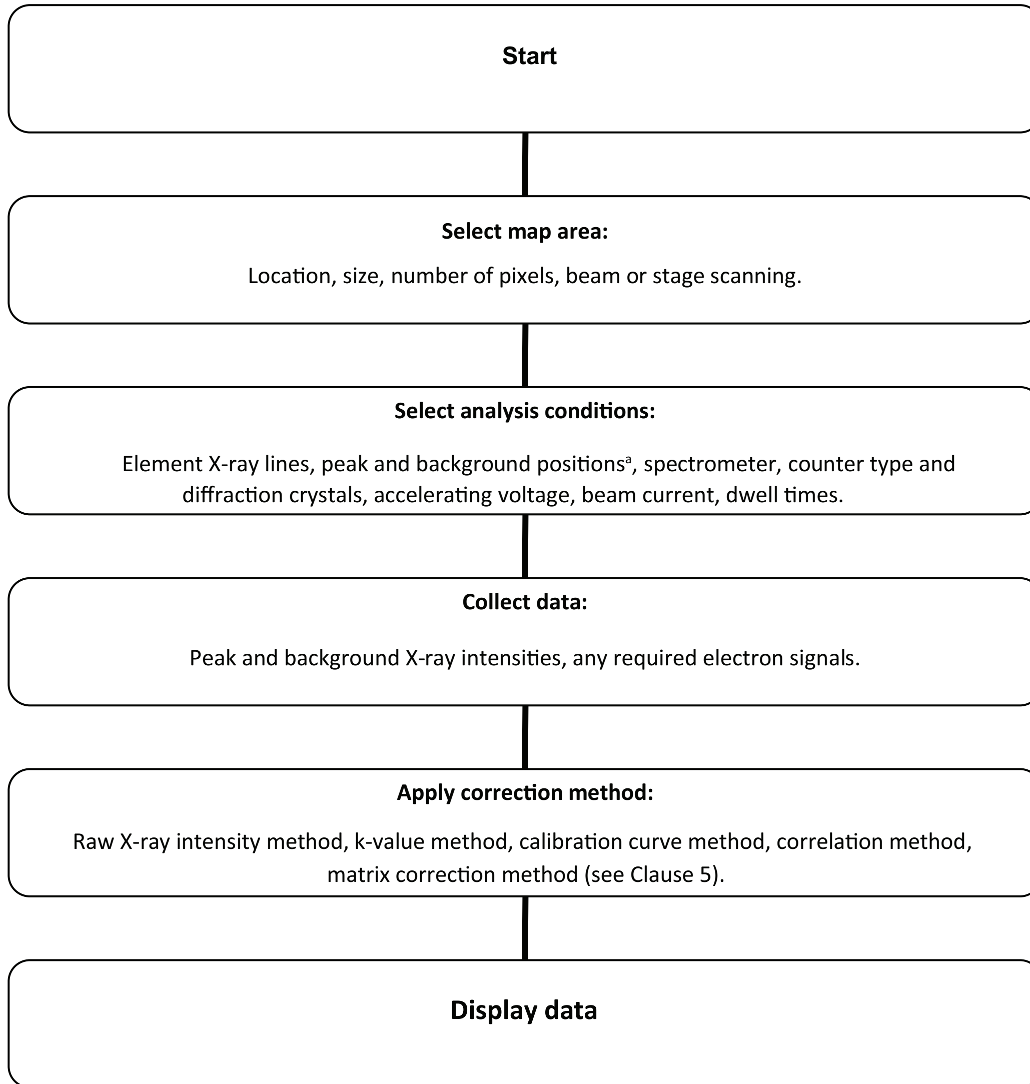

[a] To avoid the peak overlap problem, qualitative analysis is recommended (see ISO 17470).

Figure 2 — Flowchart for the mapping measurement procedure

4.3.2 Probe conditions

The accelerating voltage shall be selected so as to efficiently excite all the elements within the mapping area. For best resolution, the diameter of the excitation volume in the specimen shall be no greater than the pixel spacing.

The probe current and dwell time shall be sufficient to provide a statistically meaningful X-ray peak intensity above that of the background for all the elements measured in the specimen. Beware that light-element and/or trace-element components might require higher count rates or longer counting times. The choice of beam current and/or dwell time might also be limited for beam-sensitive materials, or by saturation of the X-ray detectors when measuring elements present in the specimen in high concentrations.

4.3.3 Stage conditions

To satisfy Bragg's diffraction condition for detecting characteristic X-rays, the geometric relationship between the X-ray source, the analysing crystal and the X-ray detector shall be fixed. Therefore, the working distance (or optical focus) shall be kept constant.

For stage mapping, the specimen surface shall be as flat as possible, in accordance with ISO 22489, and the specimen shall be installed horizontally in the specimen chamber to keep the surface always in optical focus. When the scanned area becomes larger, it might be difficult to maintain optical focus across the specimen.

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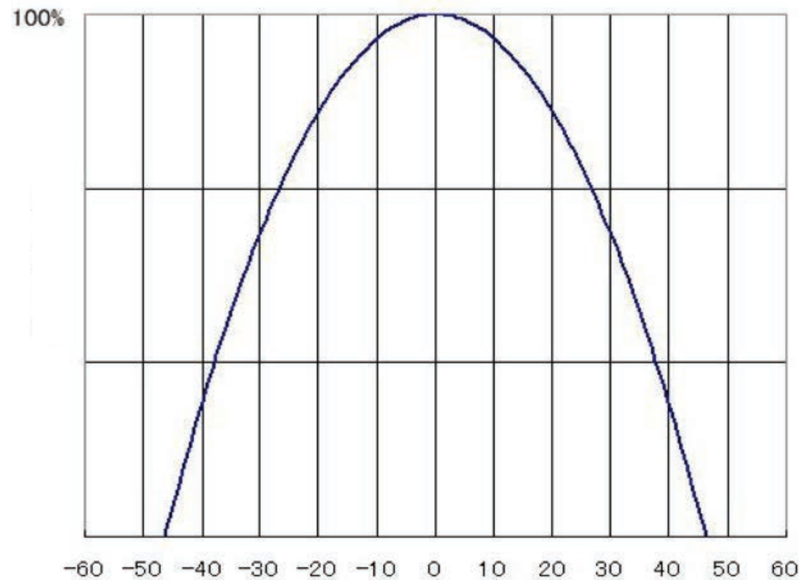
With automation software, the Z positions that correspond to the working distance can be determined as a function of the X and Y locations. This will ensure that optical focus is maintained for the entire map.

4.3.4 Selection of scanning method

Since optimum X-ray emission is dependent upon the geometric relationship between the specimen, the analysing crystal and the detector, defocussing will occur with electron beam mapping when the mapped area exceeds the region of optimum focus (see Figure 3). Beam mapping shall only be selected where there will be insignificant signal loss due to spectrometer defocussing over the entire mapped area. Otherwise, stage mapping shall be used.



Key

X-axis distance, in micrometres, from focus in direction of beam scanning

Y-axis X-ray intensity

Figure 3 — Example of X-ray intensity drop by beam scanning in the case of Fe Kα (LiF)

For beam mapping, using the chosen analysis conditions, the maximum difference in detected intensity due to beam displacement between the centre of the map and the corners shall be determined. This can be achieved, for example, by running test maps either on areas of the specimen known to be homogeneous or on reference materials. Note that the degree of defocussing is also a function of the orientation of the spectrometer relative to the mapping area, and of the diffraction angle, theta, of the diffracting crystal. The degree of defocussing should therefore, as a minimum, be determined for the element/spectrometer/diffraction crystal configuration with the highest rate of intensity reduction due to beam displacement. Ideally, this should be determined for all the elements being analysed. If the maximum difference in the X-ray intensities due to defocussing is larger than is acceptable for the analysis requirements, the stage mapping method should be used.

4.3.5 Probe size and pixel numbers

In response to the purpose, the probe shall be selected so that it is comparable to the pixel size.

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5 Methods for displaying element maps

5.1 General

Element maps can be displayed by using the raw X-ray intensity method, the k-value method, the calibration curve method, the correlation method or the matrix correction method.

5.2 Raw X-ray intensity method

In the raw-intensity method, the uncorrected measured element X-ray intensity data for all pixels are plotted directly on the map.

The main benefits of this method are its speed and the simplicity of data acquisition, since there is no computational overhead for quantification. Analysis times can be further reduced by measuring only selected elements of interest rather than all of the elements present in the specimen. Also, the counting statistics can be relatively poor and still produce a visible element distribution.

One need measure only selected elements of interest rather than all of the elements present in the specimen. This method can be used as a first-step analysis to give an indication of what more detailed analysis might be required, for example to indicate qualitatively the degree of heterogeneity, or the number of phases, present in the specimen.

The limitations of this method are that, since no matrix corrections are carried out, background levels and absorption, fluorescence and atomic-number effects might produce apparent variations in the element maps which do not reflect the true element variations. An example is given in Annex A. Partial correction may be carried out by acquiring element background maps and subtracting these from the respective element peak maps, but this will still not compensate for absorption or fluorescence effects.

NOTE It is not necessary to subtract the background intensity.

5.3 k-value method

When using the k-value method, the measured raw X-ray intensity at each pixel is divided by the intensity value of a stored reference material. After adjusting for the concentration of the element in the reference material, the resulting values are displayed as the element map. Where possible, the X-ray intensity values for both the specimen and the reference material shall be corrected for background.

As with the raw-intensity method, this is a quick and simple method of analysis and does not require all the elements in the specimen to be measured. It can be used as a qualitative first-step analysis, or for beam-sensitive specimens where only single mapping runs can be carried out.

The limitations are also similar to the raw-intensity method, since only a crude correction is carried out. Absorption, fluorescence and atomic-number effects are not corrected for, so this method could lead to misinterpretation of the element distributions.

5.4 Calibration curve method

In the calibration curve method, a series of reference materials with the same matrix as the specimen and encompassing the range of compositions in the specimen is used to generate a correction curve. The curve is used to convert the measured raw intensities into quantitative ratios on the plotted map.

The main benefits of this method are its speed and simplicity, since there is no computational overhead for quantification because no background or matrix corrections are needed as these are automatically compensated for by the reference materials. Analysis times can be further reduced by measuring only selected elements of interest rather than all of the elements present in the specimen. Also, the counting statistics can be relatively poor and still produce a visible element distribution. The main limitations are that it is generally restricted to the study of binary and ternary systems and requires an appropriate range of reference materials, as shown in ISO 16592.

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5.5 Correlation method

Correlation methods, such as the Bence-Albee method, use pre-determined correlation (or alpha) factors to convert the measured raw intensities to quantitative values[6]. It is most commonly applied to the analysis of mineralogical specimens, in particular oxides and silicates.

The method is more accurate than the k-value method, with similar computational times. It can produce accurate results for systems in which the alpha factors have been determined; however, it is generally restricted to the study of binary and ternary systems, and it does require the use of alpha factors, which are characterized only for a limited number of systems and experimental conditions.

5.6 Matrix correction method

For the matrix correction method, a full quantitative correction is carried out at each pixel, using ZAF (atomic-number correction, absorption correction, fluorescence correction) or phi-rho-Z procedures. Quantification of each pixel of the map shall be carried out in accordance with ISO 22489.

The benefit of this method is that, since it is a fully corrected method, it can potentially be applied to any specimen and will fully correct for all matrix effects.

The major drawback of this method is the time required to carry out the analysis, since all the elements present and their backgrounds have to be measured and the matrix correction has to be carried out at every pixel. For specimens with trace elements present, long counting times might be necessary to produce sufficiently good analysis statistics.

6 Evaluation of uncertainty

Validation of the method shall be carried out prior to any analyses being done. This can be accomplished using certified reference materials. The analyst shall establish the repeatability, reproducibility and uncertainty of measurement for typical specimens analysed in the laboratory. The analyst should also validate the method to ensure that it is fit for the purpose (see ISO 5725-6).

Factors that contribute to the uncertainty of measurement shall be identified. Typical factors are those associated with the instrument, changes in ambient conditions, the analytical procedure, the specimen and the operator. Large differences in the chemical composition of the specimen over small areas can also be a major source of uncertainty in the measurement. The repeatability of the measurement shall be obtained from repeat readings obtained by the same operator using the same instrument operating under the same conditions and examining the same area of the specimen during a relatively short time period.

The reproducibility of the measurement shall be established by performing the repeatability tests at intervals. This can involve different operators and different specimen areas. Participation in proficiency-testing schemes or round-robin specimen analyses will provide a useful measure of the reproducibility among laboratories.

A measure of the accuracy of the result can be obtained from the analysis of certified reference materials, using identical operating conditions. This approach will also establish the traceability of the results to recognized standards and identify the occurrence of systematic errors.

An alternative is for the laboratory to establish the accuracy using results obtained by an established analytical method or methods. The uncertainty of values calculated from the calibration curve shall be estimated using the method given in Annex A of ISO 16592:2006.

7 Report

Records of the instrumental and individual investigations shall be kept so that, if required, a test report conforming to ISO/IEC 17025:2005, 5.10, can be issued, including the following items:

a) purpose of analysis;

b) type of instrument;

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c) data correction method;

d) accelerating voltage;

e) analysing crystals;

f) elements analysed;

g) characteristic X-ray lines of elements;

h) number of pixel points.

i) probe current measured in a Faraday cup;

j) probe diameter;

k) size of analysis area;

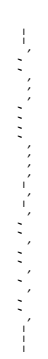
l) pixel size;

m) colour scale;

n) scanning mode;

o) dwell time;

p) grey-level scale and/or pseudo-colour coding scale.



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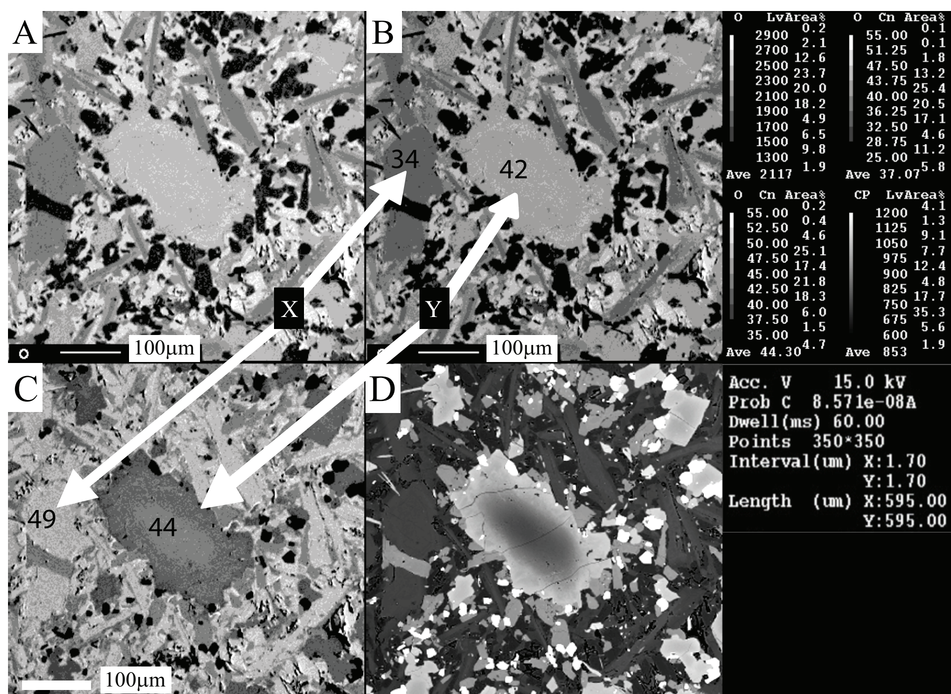
Annex A
(normative)

Comparison of absorption effects for a light element

Figure A.1 is a comparison of three types of map — k-value map, matrix-corrected map, and backscatter electron map — showing the oxygen concentration in a basalt specimen including olivine (centre) and plagioclase (surrounding it). The raw data give a stronger X-ray intensity for oxygen in the plagioclase than in the olivine due to the absorption effect[2]. The O Kα in the plagioclase is more strongly absorbed by the matrix than that in the olivine. For this reason, in the k-value map, the concentration of oxygen in the olivine (42 % by mass) is higher than that in the plagioclase (34 % by mass). However, in the corrected map, the concentration of oxygen in the olivine (44 % by mass) is lower than that in the plagioclase (49 % by mass).



Key

A raw oxygen X-ray counts map

B oxygen k-value map

C corrected oxygen concentration map

D backscatter electron image

X calculated mass percentage of oxygen in the plagioclase

Y calculated mass percentage of oxygen in the olivine

(Images courtesy of Surface Analysis Group of JEOL Ltd.)

Figure A.1 — Four images of the same area of a specimen demonstrating the effect of absorption on the results

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