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

*Analyse par microfaisceaux — Analyse par microsonde de Castaing —
Analyse quantitative ponctuelle d'échantillons massifs par spectrométrie
X à dispersion de longueur d'onde*



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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Introduction

Electron microanalysis is widely used for the quantitative analysis of elemental composition in materials. It is a typical instrumental analysis and the electron probe microanalyser has been greatly improved to be user-friendly. Obtaining accurate results with this powerful tool requires that it be properly used. In order to obtain reliable data, however, optimum procedures must be followed. These procedures, such as preparation of specimens, measurement of intensities of characteristic X-rays and calculation of concentrations from X-ray intensities, are given, for use as standard procedures, in this International Standard.

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

1 Scope

This International Standard specifies requirements for the quantification of elements in a micrometre-sized volume of a specimen identified through analysis of the X-rays generated by an electron beam using a wavelength-dispersive spectrometer (WDS) fitted either to an electron probe microanalyser or to a scanning electron microscope (SEM).

It describes:

- the principle of the quantitative analysis;
- the general coverage of this technique in terms of elements, mass fractions and reference specimens;
- the general requirements for the instrument;
- the fundamental procedures involved, such as specimen preparation, selection of experimental conditions, the measurements, the analysis of these and the report.

This International Standard is intended for the quantitative analysis of a flat and homogeneous bulk specimen using a normal incidence beam. It does not specify detailed requirements for either the instruments or the data reduction software. Operators should obtain information such as installation conditions, detailed procedures for operation and specification of the instrument from the makers of any products used.

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

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

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 22309:2006, *Microbeam analysis — Quantitative analysis using energy-dispersive spectrometry (EDS)*

3 Abbreviated terms

EPMA electron probe microanalyser

PHA pulse height analyser

P/B peak-to-background ratio

4 Procedure for quantification

4.1 General procedure for quantitative microanalysis

4.1.1 Principle and procedure of quantitative microanalysis

The characteristic X-ray intensities from electron beam interactions with a solid are approximately proportional to the mass fraction of the elements contained within the interaction volume. By measurement of characteristic X-ray intensities, the mass fractions of the elements that compose a specimen can be determined.

Quantitative analysis is performed by comparing the intensity of a characteristic X-ray line of an element in the specimen with that from a reference material containing a known mass fraction of the element, the measurements being performed under identical experimental conditions. The relationship between intensity and mass fraction is not linear over a wide mass fraction range; correction calculations for both specimen and reference material are therefore required.

X-ray absorption within the specimen and the reference material results in the emitted intensities being less than the generated intensities therefore a correction is made for this. A correction is also made for characteristic X-ray fluorescence in the analytical volume, and the effect of loss of X-ray production due to electron backscattering. When electrons enter the specimen, they lose energy due to the interactions with the constituent atoms. As well as being dependent on electron energy, the rate of energy loss is a function of the mean atomic number. The matrix correction procedure thus has three components, corresponding to the atomic number (Z), the absorption (A) and the characteristic fluorescence (F).

The accuracy of the quantitative analysis depends upon the selection of the reference materials, the specimen preparation process, the measurement conditions/method, the stability and calibration of the instrument and the use of models for quantitative correction.

4.1.2 The coverage of the quantitative analysis

Reference materials and unknown specimens shall fulfil the following conditions:

- be stable under the action of the electron beam and stable in a vacuum;
- have a flat surface perpendicular to the electron beam;
- be homogeneous over the analysis volume;
- have no magnetic domains.

For the analysis volume, see ISO 14594 (analysis area and depth and volume).

It is possible to perform quantitative elemental analysis for elements with an atomic number greater than or equal to 4 (beryllium).

The detection limit for quantitative analysis depends on many parameters, such as the X-ray line selected, the matrix and the operating conditions (beam intensity, accelerating voltage and counting parameters). It varies from a few ppm to a few hundred ppm.

NOTE 1 Detection limits are covered in ISO 17470.

NOTE 2 For light-element analysis or strong X-ray absorption conditions, the detection limit may be above 1 % (i.e. B K α in a silicon matrix).

The accuracy obtainable is governed by the mass fraction of the element, the measurement conditions and the correction calculation. It is generally considered that the relative precision and relative accuracy for major elements can be better than 1 % and 2 %, respectively.

NOTE 3 For analysis of elements in a strongly absorbing matrix with a reference material not matched to the specimen in composition, accuracy may be significantly worse than 2 %.

4.1.3 Selection of reference materials

The reference materials shall be in accordance with the specifications of ISO 14595.

In general, pure elements are used, but corrections for matrix effects are minimized when the composition of the reference material is close to that of the unknown specimen.

When coating of the specimen is required (see 4.2), the reference material shall be coated under the same conditions.

4.2 Specimen preparation

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

The specimen surface shall be flat. If necessary, the specimen shall be embedded in a conducting medium and metallographically polished.

The specimen must have good electrical conductivity. Charging under electron beam irradiation can be avoided by coating the specimen with a very thin conductive layer of a suitable material. A conducting path shall be established between the specimen surface and the metallic specimen holder.

Carbon coating is generally used but in particular cases (e.g. light-element analysis) other materials should be considered (Au, Al, etc.). Carbon to a thickness of about 20 nm can be used.

It is recommended that both the reference material and unknown specimen be coated with the same element at the same thickness.

4.3 Calibration of the instrument

4.3.1 Accelerating voltage

It is important to check that the accelerating voltage is correct for the quantitative analysis to be accurate.

Quantification errors will occur if the accelerating voltage is not known accurately and if it is not stable. The accelerating voltage shall therefore be calibrated and stable.

NOTE If an EDS system is attached to the EPMA, the true voltage may be determined through measurement of the Duane-Hunt limit ^[6]. If an EDS system is not attached, there is no generally available calibration method. It is advisable to request that the manufacturer periodically checks the voltage values.

4.3.2 Probe current

Quantification errors will occur if the probe current is not known accurately and if its stability is low. The probe current shall therefore be accurately monitored and stable.

The probe current is normally measured using a Faraday cup.

4.3.3 X-ray spectrometer

It is necessary to confirm the accurate adjustment of the X-ray spectrometer prior to its use for measurement. This should be done for all spectrometers and all crystals by following the instructions given by the manufacturer of the instrument.

The proportionality of the X-ray detector shall be checked.

NOTE The proportionality of the X-ray detector is covered in ISO 14594.

4.3.4 Dead time

It is necessary to correct for the loss of X-ray counts due to the counting-chain dead time. A dead-time calibration curve shall be determined as specified in ISO 14594.

4.4 Analysis conditions

4.4.1 Accelerating voltage

The accelerating voltage, typically between 5 kV and 30 kV, shall be selected to meet the following criteria:

- the accelerating voltage shall exceed 1,5 times the critical ionization energy of the most energetic X-ray line used in the analysis;
- the volume to be analysed shall be larger than the ionization volume;
- the accelerating voltage shall not be so high as to induce heat or electrostatic damage or make large absorption corrections necessary.

For every element, the measurements on the reference and unknown specimen should be performed at the same accelerating voltage. In particular cases, however, it is possible to carry out quantitative analysis using different accelerating voltages to optimize the X-ray intensities of elements in the same energy range.

4.4.2 Probe current

The probe current shall be selected to meet the following criteria:

- the X-ray intensity shall be high enough for an accurate result to be obtained;
- the X-ray intensity shall not be so high that it saturates the X-ray detector;
- contamination and thermal and electrostatic damage shall be minimized.

The stability of the probe current shall be checked before making a measurement.

Glasses and some minerals (e.g. plagioclases) contain alkali metals such as Na, K, etc., which migrate under a focused beam and they should therefore be analysed using a defocused beam.

4.4.3 Analysis position

If the instrument has an optical microscope, the feature requiring analysis shall be positioned in the centre of the optical field and the height of the specimen adjusted until it is in focus. In addition, the operator shall ensure that the position of the probe is stable.

The focal point of the spectrometer shall be adjusted to be the same as the focal point of the optical microscope, at the centre of the optical microscope and the centre of the electron image.

With vertically mounted spectrometers, the spectrometer sensitivity falls rapidly if the specimen height is incorrect. Therefore it is essential to use the instrument's optical microscope because its small depth of focus ensures that, when a sharp image is obtained, the specimen is correctly positioned. With inclined

spectrometers usually fitted to SEM's, the sensitivity is much less dependent upon vertical variations and it is sufficient to locate the specimen to within 100 μm .

In an SEM/WDS having no optical microscope, one can proceed as follows. First select a place in the reference specimen (specimen holder) that is known to be at the focal point of the WDS at the analysis working distance, then drive the holder to that working distance, select the secondary or back-scattered electron imaging mode and bring the image into focus at fairly high magnification. Then bring the unknown specimen under the electron beam and focus the electron image by adjusting the height of the specimen only.

4.4.4 Probe diameter

The probe diameter shall be as small as possible for accurate results, while being consistent with the aim of the analysis. The same probe diameter shall be used during the measurement on the reference and the unknown specimen. If necessary, the probe diameter can be enlarged to prevent specimen damage and to reduce contamination.

NOTE The probe diameter and analysis volume are covered in ISO 14594.

As alkali metals such as Na, K, etc., migrate under a focused electron beam, a defocused electron beam should be used for analysis of these elements.

4.4.5 Scanning the focused electron beam

When wishing to analyse an area larger than the normal spot size, either enlarge the spot or use the microscope in the scanning mode. If using the latter, the same procedures for spot analysis shall be considered with the same limitations.

The area analysed should fall within the area of maximum sensitivity of the spectrometer. If the scanning raster is too large, the spectrometer sensitivity will fall off at the extremes of the raster. Thus spot mode analysis is preferable for high accuracy.

4.4.6 Specimen surface

In quantitative microanalysis, the specimen surface shall be planar and perpendicular to the axis of the electron beam. The specimen shall be polished so that it is as flat and scratch-free as possible. The specimens (reference specimen and unknown specimen) shall be clean and free of dust. The specimen shall be analysed in the unetched condition so as not to alter its topography or surface chemistry.

NOTE It is possible to perform a quantitative analysis on tilted specimens, if the correction model is dedicated to this application and the tilt angle is accurately known.

4.4.7 Selection of X-ray line

In selecting the X-ray line to be used for the analysis, the instructions given hereafter shall be followed:

- a) a peak with a high intensity and high P/B ratio shall be chosen;
- b) a background shall be selected with which measurement of the continuum is possible;
- c) whenever possible, the peak selected should be free of overlapping peaks.

If overlapping peaks cannot be avoided, the following instructions are useful:

- when the overlapping peaks are of higher order, the pulse height analyser should be operated to eliminate these overlaps (for PHA operation, see ISO 17470 and ISO 14594);
- in the event of first-order overlap, a specific programme can be used for peak deconvolution; this procedure can, however, influence the accuracy of the results ^[7].

4.4.8 Spectrometer

The spectrometer, the analysing crystal and the detector shall be selected according to the elements and X-ray lines of analytical interest. This shall be done in accordance with the manufacturer's specifications unless extraordinary conditions make following those specifications inappropriate.

The analysing crystal should be selected with reference to materials accompanying the instrument. Efforts should be made to efficiently group elements to be measured by using a common diffracting crystal to minimize spectrometer positioning reproducibility errors.

If the X-ray detector is equipped with an adjustable entrance slit, it should be set to the slit size appropriate to the analytical problem. Light-element measurement may require the use of a wide slit, whereas high-resolution X-ray spectroscopy measurements require the use of the narrowest slit.

4.4.9 Method of measurement of X-ray peak intensity

4.4.9.1 Wavelength position

For the measurement of X-ray peak intensity with an unknown specimen, the spectrometer shall be positioned at the maximum intensity of the peak measured with the reference material.

In the analysis of low-energy peaks (< 1 keV), the position and the shape of the peak can be different with an unknown specimen and with a reference material. In this case, an appropriate procedure shall be applied (see Annex C).

4.4.9.2 Counting time

The counting times for the peak and the background are determined by the sensitivity, detection limit and statistical accuracy required. All three can be improved by increasing the counting time. However, there are restrictions due to beam damage and contamination.

For minor- and trace-element analysis, the counting time needs to be longer than that for major elements, and the counting time for the peak and the background should be as close to equal as possible.

The counting time can be selected in order to reduce the statistical error in the counting process. Since the distribution of the X-ray counts is Poissonian, the standard deviation (σ) of the distribution of N counts is $\sqrt{N}$.

Since N , the net counts, is derived from the number of counts for the peak (P) and that for the background (B), the standard deviation for N counts ($N = P - B$) is

$$\sigma_N = \sqrt{(\sigma_P)^2 + (\sigma_B)^2} = \sqrt{P + B}$$

The term "beam damage" refers to element migration and carbon contamination. Counting time should be adjusted to limit the consequences of element migration and contamination. For this reason, the peak measurement should be done prior to the background measurement.

4.4.10 Method for measurement of background intensity

The procedures for background measurement given in ISO 14594 shall be followed.

4.5 Correction method based on analytical models

4.5.1 Principles

To a first approximation, the measured X-ray intensities are roughly proportional to the mass fractions of the emitting elements:

$$k_A = I_A^{\text{unk}} / I_A^{\text{std}} \cong C_A^{\text{unk}} / C_A^{\text{std}} \quad (1)$$

where I_A^{unk} and I_A^{std} are the measured intensities of the characteristic X-ray emission of element A emitted from the unknown and the reference specimen, respectively. I_A^{unk} and I_A^{std} correspond to the difference between the peak intensity and the background intensity. C_A^{unk} and C_A^{std} are the mass fraction of element A in the unknown and in the reference specimens, respectively. k_A is the X-ray intensity ratio, usually called the k -ratio.

Equation (1) is only valid when both the unknown and the reference specimen have mass fractions and atomic numbers close to each other. For common applications where these mass fractions may be quite different, the measured intensities shall be corrected for matrix effects by terms called correction coefficients. The k -ratio expression then becomes

$$k_A = C_A^{\text{unk}} / C_A^{\text{std}} \times ZAF_A^{\text{unk}} / ZAF_A^{\text{std}} \quad (2)$$

where ZAF_A^{unk} and ZAF_A^{std} represent the correction coefficients for the unknown and the reference specimen, respectively. ZAF is the generic term usually employed to denote the correction coefficients. It is also the first model developed for matrix effect correction by Castaing in 1951 [2].

Correction coefficients are based on the physical theory of the interactions between the electron beams and the solid specimens (see Annex A). The most commonly used correction models are the ZAF , φ - ρ - Z (phi-rho-Z) and Bence and Albee (B-A) procedures. Depending on the model selected, or the programme used within the same procedure, results may differ. Generally, relative accuracy of modern models is better than 2 %. The correction models are applicable to a wide range of X-ray energies (100 eV to 30 keV) and beam energies (1 keV to 50 keV).

4.5.2 Correction models

Matrix effects correction coefficients are calculated from three parameters: the atomic number term (Z), the absorption term (A) and the fluorescence term (F) (see Annex A). In the ZAF method, these three effects are calculated separately and applied to Equation (2), and mass fractions are derived from the measured k -ratios through an iterative procedure.

In the φ - ρ - Z method, the X-ray intensities generated in the target, i.e. the $\varphi(\rho Z)$ functions, are determined by combining the atomic number term (Z) and the absorption term (A) [3]. Several φ - ρ - Z models have been developed since the 1980s. They are considered a more suitable approach to the physical phenomena involved than the ZAF method, particularly when light elements are being analysed.

The Bence-Albee method was originally proposed for oxide components of silicate minerals. It is based on the assumption that a simple hyperbolic relationship exists between the mass fractions and the k -ratios for a binary oxide system in which fluorescence effects are negligible. The correction factors are called α -factors. For ternary or more complicated oxide systems, the relationship between mass fraction and k -ratio can be determined by a linear combination of α -factors. α -factors can be determined either experimentally, by analysing a well-characterized set of silicate and oxide reference specimens, or theoretically from ZAF or φ - ρ - Z models.

4.6 Calibration curve method

4.6.1 Principle

This method is usually used to analyse minor or trace elements in a given matrix. The mass fractions are directly deduced from the characteristic X-ray intensity emitted by the element of interest through the use of calibration curves. These curves are constructed from a set of reference specimens containing the element of interest in varying mass fractions close to that of the unknown in the same matrix material as the unknown. The intensity of the characteristic X-ray for each of these reference specimens is plotted against the reference mass fraction. Applying this method requires neither correction calculations nor background subtraction.

4.6.2 Selection of reference materials

The reference specimens selected for constructing the calibration curves shall meet the specifications of ISO 14595. The composition of the major elements in the reference specimens shall be similar to the composition of the major elements in the unknown specimen.

Reference specimens with at least three different nominal mass fractions are required to construct a calibration curve. The mass fraction range of the reference specimens for the element of interest shall be chosen so that the mass fraction of the unknown is between the reference mass fractions.

4.6.3 Procedure

The counting time selected for each available reference specimen should be calculated to reduce uncertainty. In the calibration curve, short error bars covering the experimental plots indicate high accuracy.

The calibration curve is obtained by fitting a straight line, low-order polynomial or other analytical function to these experimental plots with an acceptable value for regression trend lines. (An ideal fit would have a value of 100 %.) Low regression coefficient values indicate unsuitable reference specimens and/or a lack of statistical precision in the measurement of the X-ray intensity.

The unknown composition shall be determined by measuring the intensity of the characteristic X-ray and using the calibration curve to determine the corresponding mass fraction.

The measurements on the reference and the unknown specimen shall be performed under the same analytical conditions (probe current, spot size, accelerating voltage and counting parameters).

4.7 Uncertainty

Specimen preparation, calibration of the instrument, analytical conditions, selection of reference materials, correction method, and other factors offer information on the uncertainties in such measurements. For a list of factors, see ISO 22309:2006, Annex C.

5 Test report

Records of the instrument and individual investigations shall be kept so that, if required, a test report conforming to ISO/IEC 17025:2005, 5.10, 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 calibration(s) or test(s) and the address where the calibration(s) or test(s) were carried out if that address is different from the address of the laboratory;
- c) the name and address of the client, where relevant;
- d) the date of receipt of the calibration item or test item and the date(s) that the calibration(s) or test(s) were performed, where relevant;
- e) the instrument type;

- f) identification of the sampling procedure, where relevant;
- g) the accelerating voltage;
- h) the probe current;
- i) the X-ray peak(s) detected;
- j) the crystal used and the PHA settings (integral or differential);
- k) the take-off angle of the instrument;
- l) the method of estimation of the analysis volume, where relevant;
- m) an estimate of the uncertainty of the calibration or test result, where relevant;
- n) the correction method used;
- o) the name(s), title(s) and signature(s) or equivalent identification of the person(s) accepting responsibility for the content of the certificate or report, and the date on which the report was issued.

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Annex A (informative)

Physical effects and correction

A.1 General

The k -ratio, k_A , measured for an element A is related to the mass fraction C_A by three correction parameters that are calculated in taking into account matrix effects.

A.2 Atomic number term, Z

Z is divided into two factors: the stopping power factor denoted S and the backscatter correction factor denoted R . S can be derived from Bethe's theory^[15]. It depends on (1) the ionization cross-section Q_j^A of the atomic level j involved in the production of the measured X-ray line and (2) the energy loss of beam electrons along their path to the target. R takes into account the loss in ionization due to the backscattered electrons that leave the target with an energy higher than the ionization energy of the atomic level j . Analytical expressions for R have been proposed by Duncumb and Reed and by Bishop^{[11], [12]}; in particular Z is given by:

$$Z = R/S$$

A.3 Absorption term, A

The intensity of X-rays emerging from the target and measured by the spectrometer is a fraction of the intensity generated in the target. The difference is due to absorption of X-rays in the target. The absorption term A is often preponderant in the correction process. A is given by the function $f(\chi)$:

$$f(\chi) = \left[\int \varphi(\rho Z) \exp(-\chi \cdot \rho Z) d(\rho Z) \right] / \int \varphi(\rho Z) d(\rho Z) \quad (\text{A.1})$$

$$\text{with } \chi = (\mu/\rho) \csc \theta \quad (\text{A.2})$$

where $\varphi(\rho Z)$ represents the intensity generated in a layer of thickness $d(\rho Z)$ at depth ρZ in the target compared with the intensity of an isolated thin film of thickness $d(\rho Z)$, θ is the take-off angle and (μ/ρ) is the average mass absorption coefficient for the measured X-ray energy in the target.

Several analytical expressions for $f(\chi)$ are available; among them, those deduced from Philibert's absorption model are widely used^[4].

A.4 Fluorescence term, F

A characteristic X-ray from element A may be produced as a result of excitation by a characteristic X-ray from a neighbouring element, leading to secondary fluorescence emission of A. In theory, this phenomenon is important when the ratio of the energy of the companion element peak over the threshold energy of the atomic level j associated with the element A peak is between 1 and 1,25. A good example is the secondary fluorescence emission of the Cr $K\alpha$ line excited by the K-emission lines of Fe and Ni in stainless-steel specimens. The background emission is also the source of secondary fluorescence emission, but it is generally weak and neglected for bulk specimen analyses. The secondary fluorescence emission is generally corrected for by the fluorescence correction factor F established by Reed^[11].

Annex B (informative)

Outline of various correction techniques

B.1 ZAF model

In this model, the Z , A and F terms described above are calculated separately. The k -ratios are related to the mass fraction by the relationship

$$k_A = (C_A^{\text{unk}}/C_A^{\text{std}}) \cdot G_Z \cdot G_A \cdot G_F \quad (\text{B.1})$$

where

$$G_Z = (R/S)^{\text{unk}}/(R/S)^{\text{std}};$$

$$G_A = f(\chi)^{\text{unk}}/f(\chi)^{\text{std}};$$

$$G_F \quad \text{is in general weak (a few \% at most).}$$

Various analytical expressions for R , S , $f(\chi)$ and G_F can be found in the literature.

B.2 φ - ρ - Z (phi-rho-Z) model

The starting point of the method is to represent as accurately as possible the depth distribution of the X-ray intensity, i.e. function $\varphi(\rho Z)$ in Equation (A.1). The shape of $\varphi(\rho Z)$ is generally approached by a simple analytical function such as two parabola branches (Pouchou and Pichoir) [5], a Gaussian curve (Packwood & Brown) [9] and (Bastin) [6], or double Gaussian curves (Merlet) [7]. Parameters of these different analytical functions (e.g. parameters γ and α for the Gaussian function $\gamma \exp[-\alpha^2(\rho Z)^2]$ used in Bastin's model) are dependent on the physical parameters constituting the atomic number term Z and the surface ionization value $\varphi(0)$. A refined shape of the $\varphi(\rho Z)$ function can be achieved by comparing models with experimental data derived from tracer experiments or from theoretical data deduced from Monte-Carlo simulations. A point of interest to note about the $\varphi(\rho Z)$ approach is that it does not require a separation of the G_Z and G_A factors. The k -ratios can be expressed as

$$k_A = (C_A^{\text{unk}}/C_A^{\text{std}}) \cdot \left[\int \varphi_A^{\text{unk}}(\rho Z) \cdot \exp(-\chi_A^{\text{unk}} \cdot \rho Z) d(\rho Z) \right] / \left[\int \varphi_A^{\text{std}}(\rho Z) \cdot \exp(-\chi_A^{\text{std}} \cdot \rho Z) d(\rho Z) \right]$$

with the above equation numerically integrated, a task easily performed by modern microcomputers.

B.3 Bence and Albee method

For a simple binary system AB where secondary fluorescence is not severe, the relationship between the mass fraction of element A, C_A^{AB} , and the related k -ratio, k_A^{AB} , is

$$C_A^{\text{AB}}/k_A^{\text{AB}} = \alpha_A^{\text{AB}} + (1 - \alpha_A^{\text{AB}})C_A^{\text{AB}}$$

where α_A^{AB} represents an empirical correction deduced from measurements on numerous reference specimens of varying A and B compositions. Alternatively, α_A^{AB} may be calculated from ZAF or φ - ρ - Z models. α_A^{AB} is, in effect, the sum of the matrix effects.