International
Standard

ISO 18118

Third edition
2024-02

Surface chemical analysis — Auger electron spectroscopy and X-ray photoelectron spectroscopy — Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials

Analyse chimique des surfaces — Spectroscopie des électrons Auger et spectroscopie de photoélectrons — Lignes directrices pour l'utilisation de facteurs expérimentaux de sensibilité relative pour l'analyse quantitative de matériaux homogènes

Reference number
ISO 18118:2024(en)

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

Published in Switzerland

Contents

Page

Foreword iv
Introduction v
1 Scope 1
2 Normative references 1
3 Terms and definitions 1
4 Symbols and abbreviated terms 4
5 General information 5
6 Measurement conditions 6
  6.1 General 6
  6.2 Excitation source 7
  6.3 Energy resolution 7
  6.4 Energy step and scan rate 7
  6.5 Signal intensity 7
  6.6 Gain and time constant (for AES instruments with analogue detection systems) 7
  6.7 Modulation to generate a derivative spectrum 7
7 Data-analysis procedures 7
8 Spectrometer response function 8
9 Determination of chemical composition using relative sensitivity factors 8
  9.1 Calculation of chemical composition 8
    9.1.1 General 8
    9.1.2 Composition determined from elemental relative sensitivity factors 9
    9.1.3 Composition determined from atomic relative sensitivity factors or average matrix relative sensitivity factors 9
  9.2 Uncertainties in calculated compositions 9
Annex A (informative) **Formulae for relative sensitivity factors** 10
Annex B (informative) **Information on uncertainty of the analytical results** 16
Bibliography 19

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.

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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

This third edition cancels and replaces the second edition (ISO 18118:2015), which has been technically revised.

The main changes are as follows:

- The main equation for the use of sensitivity factors for analysis has been moved from Annex A to the main text
- Defined symbols and abbreviated terms from the Annexes have been consolidated to Clause 4.
- Several terms have been modified for formatting purposes, and some have been removed due to no longer being required.
- Several formulae have been removed from Annex A and replaced by references to formulae and databases of parameters that are more accurate. Such databases are now the recommended source for the parameters calculated using the removed formulae.
- Annex A has been redefined as an informative Annex.
- Multiple small additions have been made to provide new and updated sources for information.
- Editorial changes have been made throughout.

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

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are surface-analytical techniques that are sensitive to the composition in the surface region of a material to depths of, typically, a few nanometres (nm). Both techniques yield a surface-weighted signal, averaged over the analysis volume. Most samples have compositional variations, both laterally and with depth, and quantification is often performed with approximate methods since it can be difficult to determine the magnitude of any compositional variations and the distance scale over which they can occur. The simplest sample for analysis is one that is homogeneous. Although this situation occurs infrequently, it is often assumed, for simplicity in the analysis, that the sample material of interest is homogeneous. This document provides guidance on the measurement and use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials by AES and XPS.

Surface chemical analysis — Auger electron spectroscopy and X-ray photoelectron spectroscopy — Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials

1 Scope

This document gives guidance on the measurement and use of experimentally-determined relative sensitivity factors for the quantitative analysis of homogeneous materials by Auger electron spectroscopy and X-ray photoelectron spectroscopy. The methods described only apply to polycrystalline and amorphous materials, as effects inherent to single-crystal samples are not addressed.

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 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

ISO 21270, *Surface chemical analysis — X-ray photoelectron and Auger electron spectrometers — Linearity of intensity scale*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115-1 and the following 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
absolute elemental sensitivity factor
coefficient for an element by which the measured intensity for that element is divided to yield the atomic concentration or atomic fraction of the element present in the sample

Note 1 to entry: See *relative elemental sensitivity factor*.

Note 2 to entry: The choice of atomic concentration or atomic fraction should be made clear.

Note 3 to entry: The type of sensitivity factor utilized should be appropriate for the formulae used in the quantification process and for the type of sample analysed, for example homogeneous samples or segregated layers.

Note 4 to entry: The source of sensitivity factors should be given to ensure that the correct *matrix factors* or other parameters are used.

Note 5 to entry: Sensitivity factors depend on parameters of the excitation source, the spectrometer, and the orientation of the sample to these parts of the instrument. Sensitivity factors also depend on the matrix being analysed, and in *SIMS* this has a dominating influence.

[SOURCE: ISO 18115-1]

3.2

elemental relative sensitivity factor

<AES, XPS> coefficient proportional to the *absolute elemental sensitivity factor* (3.1), where the constant of proportionality is chosen such that the value for a selected element and transition is unity

Note 1 to entry: Elements and transitions commonly used are C 1s or F 1s for *XPS* and Ag $M_{4,5}$VV for *AES*.

Note 2 to entry: The type of sensitivity factor used should be appropriate for the type of sample analysed, for example homogeneous samples or segregated layers.

Note 3 to entry: The source of sensitivity factors should be given to ensure that the correct *matrix factors* or other parameters are used.

Note 4 to entry: Sensitivity factors depend on parameters of the excitation source, the spectrometer, and the orientation of the sample to these parts of the instrument. Sensitivity factors also depend on the matrix being analysed, and in *SIMS* this has a dominating influence.

[SOURCE: ISO 18115-1]

3.3

average matrix relative sensitivity factor

AMRSF

<AES, XPS> coefficient, proportional to the intensity, calculated for an element in an average matrix, by which the measured intensity for that element is divided in calculations to yield the atomic concentration or atomic fraction of the element present in the sample

Note 1 to entry: See sensitivity factor, *elemental relative sensitivity factor* (3.2) and *pure element relative sensitivity factor* (3.4).

Note 2 to entry: The choice of atomic concentration or atomic fraction should be made clear.

Note 3 to entry: The type of sensitivity factor utilized should be appropriate for the formulae used in the quantification process and for the type of sample analysed, for example homogeneous samples or segregated layers.

Note 4 to entry: The source of sensitivity factors should be given. *Matrix factors* are taken to be unity for average matrix relative sensitivity factors.

Note 5 to entry: Sensitivity factors depend on parameters of the excitation source, the spectrometer, and the orientation of the sample to these parts of the instrument. The numerical values of the sensitivity factors can also depend on the method used to measure the peak intensities.

[SOURCE: ISO 18115-1]

3.4

pure-element relative sensitivity factor

PERSF

<AES, XPS> coefficient, proportional to the intensity measured for a pure sample of an element, by which the measured intensity for that element is divided in calculations to yield the atomic concentration or atomic fraction of the element present in the sample

Note 1 to entry: See sensitivity factor, *elemental relative sensitivity factor* (3.2), and *average matrix relative sensitivity factor* (3.3).

Note 2 to entry: The choice of atomic concentration or atomic fraction should be made clear.

Note 3 to entry: The type of sensitivity factor used should be appropriate for the formulae used in the quantification process and for the type of sample analysed, for example homogeneous samples or segregated layers.

Note 4 to entry: The source of sensitivity factors should be given to ensure that the correct *matrix factors* or other parameters are used. Matrix factors are significant and should be used with pure-element relative sensitivity factors.

Note 5 to entry: Sensitivity factors depend on parameters of the excitation source, the spectrometer, and the orientation of the sample to these parts of the instrument. The numerical values of the sensitivity factors can also depend on the method used to measure the peak intensities.

[SOURCE: ISO 18115-1]

3.5
spectrometer response function

quotient of the number of particles detected with a spectrometer by the number of such particles per solid angle and per interval of the dispersing parameter available for measurement as a function of the dispersing parameter

Note 1 to entry: See *spectrometer étendue*.

Note 2 to entry: The dispersing parameter is commonly energy, mass, or wavelength.

Note 3 to entry: The units of the spectrometer response function can be sr·eV, sr·amu, or sr·m.

Note 4 to entry: The spectrometer response function is similar to the *spectrometer transmission function* (3.6) or étendue but includes the efficiencies of all other components of the measurement chain, such as detectors and the electronic processing and recording equipment.

Note 5 to entry: For some methods of *quantitative analysis*, the energy dependence of the response function is needed in order to use *relative sensitivity factors*. For these cases, a function is determined which is proportional to the absolute response function, where the proportionality constant is not necessarily important.

[SOURCE: ISO 18115-1]

3.6
spectrometer transmission function

analyser transmission function

quotient of the number of particles transmitted by the analyser by the number of such particles per solid angle and per interval of the dispersing parameter (e.g. energy, mass, or wavelength) available for measurement as a function of the dispersing parameter

Note 1 to entry: See *spectrometer response function* (3.5).

Note 2 to entry: The units of transmission can be sr·eV, sr·amu, or sr·m.

Note 3 to entry: Often, an incomplete use of the term occurs where just the solid angle of acceptance of the spectrometer, in sr, or a fraction of the 2π solid angle of available space is given. This usage is deprecated, cf. *solid angle of analyser*.

Note 4 to entry: This term is often used incorrectly instead of spectrometer response function, which includes contributions from the detector and the signal-processing system.

[SOURCE: ISO 18115-1]

3.7
atomic relative sensitivity factor

ARSF

coefficient, proportional to the intensity measured for a single atom of an element, by which the measured intensity for that element is divided in calculations to yield the atomic concentration or atomic fraction of the element present in the sample.

Note 1 to entry: See *elemental relative sensitivity factor* (3.2).

Note 2 to entry: The choice of atomic concentration or atomic fraction should be made clear.

Note 3 to entry: The type of sensitivity factor utilized should be appropriate for the formulae used in the quantification process and for the type of sample analysed, for example homogeneous samples or segregated layers.

Note 4 to entry: The source of sensitivity factors should be given to ensure that the correct *matrix factors* or other parameters are used.

Note 5 to entry: Sensitivity factors depend on parameters of the excitation source, the spectrometer, and the orientation of the sample to these parts of the instrument. Sensitivity factors also depend on the matrix being analysed, and in *SIMS* this has a dominating influence.

4 Symbols and abbreviated terms

AES	Auger electron spectroscopy
A_i	atomic mass of element *i*
$E_{\mathrm{b},i}$	binding energy of core level for element *i*
E_g	band-gap energy
E_i	kinetic energy of an auger electron or photoelectron from element *i*
E_p	free-electron plasmon energy
E_pr	primary electron energy
F_i	matrix correction factor for element *i*
F_j	matrix correction factor for element *j*
$H(\cos\alpha, \omega_i)$	Chandrasekhar function for parameters $\cos\alpha$ and ω_i
I_key	measured intensity of the chosen peak in the key material
C_i	number of atoms of element *i* in the molecular formula of the compound
$I_{i,\mathrm{ref}}$	measured intensity of element *i* in the reference sample
$I_{i,\mathrm{unk}}$	measured intensity of element *i* in the unknown sample
$I_{j,\mathrm{ref}}$	measured intensity of element *j* in the reference sample
$I_{j,\mathrm{unk}}$	measured intensity of element *j* in the unknown sample
J	excitation beam intensity
M_i	molecular mass of the compound containing element *i*
n	number of identified elements in the unknown sample
N_A	Avogadro constant
N_av	atomic density for the average matrix sample
N_i	atomic density of element *i*
N_ref	atomic density of the reference sample
N_key	atomic density of the key element
N_unk	atomic density of the unknown sample
N_v	number of valence electrons per atom or molecule
Q_av	elastic-scattering correction factor for the average matrix sample at the electron energy E_i for the particular Auger-electron or photoelectron peak of interest
Q_i	elastic-scattering correction factor for element *i* at the electron energy E_i for the particular Auger-electron or photoelectron peak of interest
$Q_i(0)$	elastic-scattering correction factor for element *i* at emission angle $\alpha = 0$ with respect to the surface normal

$Q_{i,\mathrm{ref}}$	elastic-scattering correction factor for element *i* in the reference sample
$Q_{i,\mathrm{unk}}$	elastic-scattering correction factor for element *i* in the unknown sample
R_{av}	backscattering correction factor for the average matrix sample
R_i	backscattering correction factor for element *i*
$R_{i,\mathrm{ref}}$	backscattering correction factor for element *i* in the reference sample (these terms are unity for XPS)
$R_{i,\mathrm{unk}}$	backscattering correction factor for element *i* in the unknown sample (these terms are unity for XPS)
RSF	relative sensitivity factor
$S_{i,\mathrm{At}}$	atomic relative sensitivity factor for element *i*
$S_{i,\mathrm{Av}}$	average matrix relative sensitivity factor for element *i*
$S_{i,\mathrm{Ec}}$	elemental relative sensitivity factor for element *i* in a specified compound
$S_{i,\mathrm{Ep}}$	pure-element relative sensitivity factor for element *i*
$S_{i,\mathrm{RSF}}$	relative sensitivity factor for element *i*
$S_{i,\mathrm{E}}$	elemental relative sensitivity factor for element *i*
$S_{j,\mathrm{RSF}}$	relative sensitivity factor for element *j*
T	spectrometer response function (SRF)
XPS	X-ray photoelectron spectroscopy
Z	atomic number
Z_{av}	atomic number of the average matrix sample
α	emission angle with respect to the surface normal
θ	angle of incidence of electron beam
$X_{i,\mathrm{ref}}$	atomic fraction of element *i* in the reference sample
$X_{i,\mathrm{unk}}$	atomic fraction of element *i* in the unknown sample
$\lambda_{i,\mathrm{ref}}$	electron inelastic mean free path for element *i* in the reference sample
$\lambda_{i,\mathrm{unk}}$	electron inelastic mean free path for element *i* in the unknown sample
λ_{av}	electron inelastic mean free path for the average matrix sample
λ_i	electron inelastic mean free path for element *i*
ρ	density of the solid ($\mathrm{kg \cdot m^{-3}}$)

5 General information

It is convenient in many quantitative applications of AES and XPS to utilize relative sensitivity factors (RSFs) for quantitative analyses. Three types of RSF have been used for this purpose: elemental relative sensitivity factors (ERSFs), atomic relative sensitivity factors (ARSFs), and average matrix relative sensitivity factors (AMRSFs). Formulae defining these three types of RSF are given in A.2 and the principles on which these formulae are based on are given in A.2.

While the ERSFs are the simplest and easiest to apply, they are the least accurate because no account is taken of matrix correction factors (as described in A.2). The matrix correction factors for AES can vary between 0,1 and 8[1] while they can vary between 0,3 and 3[2] for XPS. The ARSFs are more accurate than ERSFs in that they take account of differences in atomic densities, generally the largest single matrix correction. The AMRSFs are the most reliable RSFs in that there is almost complete correction of matrix effects. It is recommended that ERSFs be used only for semi-quantitative analyses (that is, rough estimates of composition) and that ARSFs or preferably, AMRSFs be used for quantitative analyses. For the latter applications, ARSFs shall be used only in situations for which it is not possible to make use of AMRSFs (for example, measurements involving Auger electrons or photoelectrons at energies for which inelastic mean free paths cannot be reliably determined).

In analytical applications of AES and XPS, it is essential that Auger-electron and photoelectron intensities be measured using exactly the same procedure as that used for measurement of the RSFs. For some applications of AES (e.g. sputter depth profiles), it is convenient to use peak-to-peak heights of Auger-electron signals in the differential mode as measures of Auger-electron intensities. For other applications of AES (e.g. scanning Auger microscopy), the Auger-electron intensity can be determined from the difference between the intensity at a peak maximum in the direct spectrum and the intensity of a nearby background signal. Finally, for many applications in XPS and for some applications of AES, areas of peaks in direct spectra are used as measures of photoelectron or Auger-electron intensities.

Relative sensitivity factors depend on the parameters of the excitation source (for example, the incident electron energy in AES and the choice of X-ray energy in XPS), the spectrometer configuration (for example, the angle of incidence of the electron beam in AES, the angle between the X-ray source and the analyser axis in XPS, the sample area viewed by the analyser, and the acceptance solid angle of the analyser), and the orientation of the sample to these parts of the instrument.[3] The sample area viewed by the analyser and the analyser acceptance solid angle can depend on analyser settings (for example, selection of apertures, whether the analyser is operated in the constant analyser energy mode or the constant retardation ratio mode, and the corresponding choices of analyser pass energy or retardation ratio). Finally, the measured Auger-electron or photoelectron intensities can depend on the instrumental parameters described in Clause 6. Therefore, it is essential that Auger-electron and photoelectron intensities be determined using exactly the same instrumental settings and the same sample orientation as those employed for the ERSF measurements. It is also essential that the same data-analysis procedures (described in Clause 7) be used in measurements of signal-electron intensities for the unknown sample as those used in the ERSF measurements.

Commercial AES and XPS instruments are generally supplied with a set of ERSFs for one or more common operating conditions. These ERSFs were typically determined on an instrument of the same type or, in some cases, on similar instruments. It is recommended that an analyst check the ERSFs supplied with the instrument for those elements expected to be of analytical interest to ensure that the supplied ERSFs are correct. In addition, the spectrometer response function (SRF) of the instrument can change with time, as described in Clause 8. Such changes can be detected and corrective actions be taken by regular measurement of the SRF using appropriate reference materials.[5][6] Alternatively, an analyst can check for possible changes in SRF with time by measuring selected ERSFs as described in Clause 8.

6 Measurement conditions

6.1 General

The same measurement conditions (for example, instrumental configuration, sample orientation, and instrumental settings) shall be used for the measurement with the unknown sample as those chosen for the ERSF measurements. Particular attention shall be given to the following parameters.

6.2 Excitation source

The incident-electron energy in AES and the X-ray source in XPS shall be the same for the measurement of the unknown sample as that chosen for the measurement of the ERSFs.

6.3 Energy resolution

Unless peak areas are used to measure the signal intensities, the energy resolution of the electron-energy analyser (that is determined by choice of aperture sizes, pass energy, or retardation ratio) shall be the same for the unknown-sample measurement as for the measurement used to generate the ERSFs[7].

6.4 Energy step and scan rate

The size of the energy step (energy per channel) used to acquire spectral data and the spectral scan rate shall be chosen so that there is negligible spectral distortion in the acquired data for the selected energy resolution.

6.5 Signal intensity

The incident-electron current (in AES) or the X-ray intensity (in XPS) shall be adjusted together with the voltage applied to the detector so that the measured signal intensity is proportional to the incident current or X-ray intensity to within 1 % as described in ISO 21270. Alternatively, the measured signal intensity that is corrected for counting losses, as described in ISO 21270, shall be proportional to the incident current or X-ray intensity to within 1 %.

6.6 Gain and time constant (for AES instruments with analogue detection systems)

The settings of the detector system shall be the same in the unknown-sample measurement as in the measurement used to generate the ERSFs. The time constant[8] in the measurements shall be sufficiently short so that shapes of spectral features are not significantly distorted during data acquisition. The gain of the detector system shall be adjusted so that the intensities measured for the relevant peaks are within the range for linear detector response.

Procedures to check for linear detector response in pulse-counting systems are described in ISO 21270. The first method described there(ISO 21270:2004, 6.6) can be used for analogue AES systems if there are sufficient instrumental controls.

6.7 Modulation to generate a derivative spectrum

It is often convenient in AES to utilize the differential spectrum. The derivative spectrum can be acquired by applying a modulation voltage to the analyser[9][10] or by numerical processing of a measured direct spectrum[11][12]. For this purpose, a modulation or numerical differential of between 2 eV and 10 eV (peak-to-peak) is commonly used. The same modulation energy shall be used for the measurements with the unknown sample as that used to determine the ERSFs.

NOTE 1 The details of the peak attenuation in numerical differentiation and of the Savitzky and Golay differentiation method in AES can be obtained from Reference [9] and Reference [10]. Discussion of improvements to this method, and the effects of the number of points used in this method can be obtained from Reference [68]

NOTE 2 Corrections for the effects of analyser modulation on peak intensity in derivative Auger spectra can be obtained from Reference [69].

7 Data-analysis procedures

The same procedures shall be used for the analysis of the spectra measured for the unknown sample and for the ERSF measurements.

To obtain a peak area or a peak height from a measured direct spectrum, a background shall be chosen and subtracted from the measured spectrum (see Reference [11]). The backgrounds most commonly used for this purpose[14] are a linear background, a Shirley background,[15] or a Tougaard background[16].

In AES, it is often convenient to measure a peak-to-peak height or a peak-to-background height in a differential spectrum. The differential spectrum can be recorded (in analogue detection instruments) or a measured direct spectrum can be numerically differentiated for this purpose. The same numerical procedure and choices shall be made in the differentiation of the spectra for the unknown sample and for the reference samples used to determine the ERSFs[13][17]. See also 6.7.

NOTE 1 Details of background-subtraction procedures are given in Reference [11].

NOTE 2 Details of peak attenuation in numerical differentiation and of the Savitzky and Golay differentiation method in AES can be obtained from Reference [9] and Reference [10].

NOTE 3 Reference [16] gives information on procedures to obtain consistent results in the use of differentiation for measurements with different chemical states of an element. This reference provides similar information for the determination of peak areas.

8 Spectrometer response function

The spectrometer response function (SRF) is a measure of the efficiency of the electron-energy analyser in transmitting electrons and of the detector system in detecting them as a function of electron energy.[1][19][20] In general, the SRF will change if the analyser pass energy, retardation ratio, and aperture sizes are modified. In addition, different instruments of the same type (and from the same manufacturer) can have different SRFs for the same instrumental settings because the detector efficiency as a function of energy will often change during its service life. As a result, it is recommended that the intensity scale be calibrated at regular intervals (for example, every six months) using an appropriate method[5][6] or that ERSFs be measured for selected elements (having Auger-electron or photoelectron peaks over the working range of the energy scale). Such checks should also be made if the detector surface has been exposed to any environment that could affect its efficiency and if insulating films (e.g. from sputtering of non-conducting samples) have been deposited on analyser surfaces. Local measurements of ERSFs for selected elements shall be recorded in the log book for the instrument and plotted as a function of time so that changes can be easily detected. For NAP-XPS systems, due to the additional attenuation of the signal potentially changing the effective SRF, any set of RSFs should only be considered valid for measurements taken under identical NAP conditions.

9 Determination of chemical composition using relative sensitivity factors

9.1 Calculation of chemical composition

9.1.1 General

The chemical composition of an unknown sample can be determined using Formula (A.6) and Formula (1) or one of the other formulae given in Annex A. Formula (1) is commonly used but ignores matrix terms. For some types of relative sensitivity factor, these matrix terms are effectively unity, and can be ignored but, when other types of sensitivity factor are used, the matrix factors can be as high as 8 in AES[1] and 3 in XPS.[2] The accuracy of calculated chemical compositions thus depends significantly on the type of sensitivity factor used. This is discussed in Annex A.

NOTE AES and XPS cannot directly detect hydrogen or helium. A quantitative analysis of an unknown sample that is likely to contain one of these elements (e.g. organic compounds) will have a systematic error unless some method is devised to overcome this limitation.

In some applications, it can be satisfactory to determine the composition of an unknown sample if a reference sample of similar composition is available. For this situation, measurements are made of signal-electron intensities from the unknown samples and reference samples, and the composition is calculated using Formula (A.5). If the two materials are close in composition, matrix correction factors can be ignored and Formula (A.5) is valid. The analyst should nevertheless be aware that it can be difficult to prepare reference samples of known composition; for example, compounds cleaned by ion sputtering will generally have a surface composition different from the bulk composition due to preferential-sputtering effects. This can be helpful if the sample to be analysed has been similarly sputtered. However, artefacts due to sputtering are beyond the scope of this document. Scraping, fracturing, or cleaving of the reference sample, where feasible, can be a suitable means of generating a suitable surface for comparisons with the unknown sample.

9.1.2 Composition determined from elemental relative sensitivity factors

The composition of the unknown sample can be obtained from Formula (1) using ERSFs, $S_{i,\mathrm{E}}$, supplied by the instrument manufacturer or as measured by the analyst.

$$X_{i,\mathrm{unk}} = \frac{\left(\dfrac{I_{i,\mathrm{unk}}}{S_{i,RSF}}\right)}{\sum_{j=1}^{n}\left(\dfrac{I_{j,\mathrm{unk}}}{S_{j,\mathrm{RSF}}}\right)} \tag{1}$$

9.1.3 Composition determined from atomic relative sensitivity factors or average matrix relative sensitivity factors

The composition of the unknown sample can be obtained from Formula (1) using ARSFs, $S_{i,\mathrm{At}}$, or AMRSFs, $S_{i,\mathrm{Av}}$.

NOTE 1 The ARSFs can be supplied by the instrumental manufacturer or be calculated by the analyst using Formula (A.9).

NOTE 2 The AMRSFs can be obtained using methods described in A.2.4.

9.2 Uncertainties in calculated compositions

Many factors can contribute to the uncertainty of a chemical composition determined from RSFs.[21] Information on possible uncertainties in such measurements is given in Annex B.

Annex A
(informative)

Formulae for relative sensitivity factors

A.1 Principles

Quantitative analysis of a homogeneous sample can be accomplished through comparison of an Auger-electron or photoelectron peak intensity, $I_{i,\mathrm{unk}}$, from an unknown sample (the sample material whose surface composition is to be determined) with the corresponding peak intensity, $I_{i,\mathrm{ref}}$, from a reference sample with known surface composition (either a pure element or a suitable compound) in order to remove instrumental and, in some cases, matrix factors. This comparison can only be made if the analytical conditions for both measurements are identical. In the simplest analytical case, when the sample surface is assumed to consist of a single phase and to be atomically flat, the measured intensity is given by Formula (A.1), and the intensity ratio is given by Formula (A.2)[1][22][23][24][25][26]:

$$I_{i,\mathrm{unk}} = JTX_{i,\mathrm{unk}} N_{\mathrm{unk}} Q_{i,\mathrm{unk}} R_{i,\mathrm{unk}} \lambda_{i,\mathrm{unk}} \tag{A.1}$$

$$\frac{I_{i,\mathrm{unk}}}{I_{i,\mathrm{ref}}} = \frac{X_{i,\mathrm{unk}} N_{\mathrm{unk}} Q_{i,\mathrm{unk}} R_{i,\mathrm{unk}} \lambda_{i,\mathrm{unk}}}{X_{i,\mathrm{ref}} N_{\mathrm{ref}} Q_{i,\mathrm{ref}} R_{i,\mathrm{ref}} \lambda_{i,\mathrm{ref}}} \tag{A.2}$$

where

J	is the X-ray photon (for XPS) or electron beam (for AES) intensity on the sample, which should be identical for both the reference and unknown samples
T	is the spectrometer response function (SRF) which should be identical for both the reference and unknown samples
$X_{i,\mathrm{unk}}$	is the atomic fraction of the element *i* in the unknown samples;
$X_{i,\mathrm{ref}}$	is the atomic fraction of the element *i* in the reference samples;
N_{unk}	is the atomic density of the unknown sample;
N_{ref}	is the atomic density of the reference sample;
$Q_{i,\mathrm{unk}}$	is the elastic-scattering correction factor for element *i* in the unknown sample;
$Q_{i,\mathrm{ref}}$	is the elastic-scattering correction factor for element *i* in the reference sample;
$R_{i,\mathrm{unk}}$	is the backscattering correction factor for element *i* in the unknown sample (these terms are unity for XPS);
$R_{i,\mathrm{ref}}$	is the backscattering correction factor for element *i* in the reference sample (these terms are unity for XPS);
$\lambda_{i,\mathrm{unk}}$	is the electron inelastic mean free path for element *i* in the unknown sample;
$\lambda_{i,\mathrm{ref}}$	is the electron inelastic mean free path for element *i* in the reference sample.

From Formula (A.2), $X_{i,\mathrm{unk}}$ can be obtained using Formula (A.3):

$$X_{i,\mathrm{unk}} = \left(\frac{I_{i,\mathrm{unk}}}{I_{i,\mathrm{ref}}}\right)\frac{X_{i,\mathrm{ref}} N_{\mathrm{ref}} Q_{i,\mathrm{ref}} R_{i,\mathrm{ref}} \lambda_{i,\mathrm{ref}}}{N_{\mathrm{unk}} Q_{i,\mathrm{unk}} R_{i,\mathrm{unk}} \lambda_{i,\mathrm{unk}}} = X_{i,\mathrm{ref}}\left(\frac{I_{i,\mathrm{unk}}}{I_{i,\mathrm{ref}}}\right)F_i \tag{A.3}$$

where F_i is the matrix correction factor for element *i* in the comparison of measurements made with a particular unknown sample and a particular reference sample.

The atomic fraction of the element *i* in an unknown sample with *n* identified elements is then given by Formula (A.4)[1][26]:

$$X_{\mathrm{i,unk}} = \frac{X_{i,\mathrm{ref}}\left(\dfrac{I_{i,\mathrm{unk}}}{I_{i,\mathrm{ref}}}\right)}{\sum_{j=1}^{n} X_{j,\mathrm{ref}}\left(\dfrac{I_{j,\mathrm{unk}}}{I_{j,\mathrm{ref}}}\right)} \tag{A.4}$$

This formula should be solved iteratively since the matrix factors depend on the composition of the material. This composition is, of course, unknown until Formula (A.4) is solved. If, for simplicity, it is assumed that the atomic densities, elastic-scattering correction factors, backscattering correction factors, and inelastic mean free paths are the same for the two samples considered in Formula (A.3) and the reference sample is pure elemental solids, the matrix correction factors $F_i = 1$, and the reference atomic fractions $X_{i,\mathrm{ref}} = 1$. For these assumptions, if the unknown sample consists of *n* elements, the atomic fractions X_i of these elements can be obtained from Formula (A.5)[26]:

$$X_{i,\mathrm{unk}} = \frac{\left(\dfrac{I_{i,\mathrm{unk}}}{I_{i,\mathrm{ref}}}\right)}{\sum_{j=1}^{n}\left(\dfrac{I_{j,\mathrm{unk}}}{I_{j,\mathrm{ref}}}\right)} \tag{A.5}$$

While Formula (A.5) is simple and is often used for quantitative surface analysis by AES and XPS, it should be emphasized that it is based on the simplifying assumption that the matrix correction factors F_i for the elements in the unknown sample are unity. In reality, F_i values (calculated using pure elements) range from 0,1 to 8 (with one-third of the values outside the range 0,5 to 1,5)[1] for AES. The F_i values range from 0,3 to 3[2] for XPS.

Values of $I_{i,\mathrm{ref}}$ are needed for a quantitative analysis to obtain the fractional compositions $X_{i,\mathrm{unk}}$ from measured values of $I_{i,\mathrm{unk}}$ for an unknown sample using Formula (A.4) or Formula (A.5). The $I_{i,\mathrm{ref}}$ values can be obtained from a series of measurements for those elements that can be conveniently prepared as solids with a sufficiently high degree of purity (generally better than 99 %) and with clean surfaces in an AES or XPS instrument. For other elements (e.g. the alkali metals and elements such as oxygen, nitrogen, and the halogens that are gases at room temperature), the $I_{i,\mathrm{ref}}$ values can be estimated from similar measurements with compounds containing the desired elements. Unless corrections can be made for matrix effects [the matrix correction factor F_i in Formula (A.4) and the additional matrix effects discussed in B.2], values of $I_{i,\mathrm{ref}}$ for the same element *i* from different compounds can be different[28][29].

It is generally convenient in practice to make use of $I_{i,\mathrm{ref}}$ values that have been normalized to unity for a particular peak from a selected element, hereafter referred to as the key element[1][9],[30][31][32][33][34][35]. In XPS, the 1s photoelectron line of fluorine in lithium fluoride has been generally used for this purpose while the silver M4,5VV Auger-electron line has been commonly used in AES.

A.2 Relative sensitivity factors

A.2.1 Introduction

Defining formulae are given here for three different types of relative sensitivity factor (RSF) that can be obtained from $I_{i,\mathrm{ref}}$ values. The RSFs, $S_{i,\mathrm{RSF}}$, for an element *i* in an unknown material containing *n* elements, can be used to evaluate the atomic fraction, $X_{i,\mathrm{unk}}$, of the element *i* from Formula (A.6):

$$X_{i,\mathrm{unk}} = \frac{\left(\dfrac{I_{i,\mathrm{unk}} F_i}{S_{i,\mathrm{RSF}}}\right)}{\sum_{j=1}^{n} \left(\dfrac{I_{j,\mathrm{unk}} F_j}{S_{j,\mathrm{RSF}}}\right)} \tag{A.6}$$

Formula (A.6) can be obtained from Formula (A.4) by equating $S_{i,\mathrm{RSF}}$ with normalized values of $I_{i,\mathrm{ref}}$. If, for simplicity, the matrix correction factors are neglected, Formula (A.6) becomes Formula (1), as given in Clause 9.

The three types of RSF defined below (elemental RSFs, atomic RSFs, and average matrix RSFs that are designated $S_{i,\mathrm{E}}$, $S_{i,\mathrm{At}}$, and $S_{i,\mathrm{Av}}$, respectively) give analytical results of increasing accuracy. These RSFs can be used for surface analyses in place of $S_{i,\mathrm{RSF}}$ in Formula (1).

It should be emphasized that the values of all RSFs depend on how the line intensities are measured and on the experimental conditions such as the parameters of the excitation source, the spectrometer configuration, and the orientation of the sample with respect to these parts of the instrument. Surface analyses made with particular sets of RSFs shall be based on AES or XPS measurements that were made with the same method of intensity measurement and with identical experimental conditions. Also, a consistent set of RSFs ($S_{i,\mathrm{E}}$, $S_{i,\mathrm{At}}$, or $S_{i,\mathrm{Av}}$) shall be used in an analysis.

A.2.2 Elemental relative sensitivity factors (with no correction for matrix effects)

A.2.2.1 General

As noted in A.2, elemental RSFs can be obtained from measurements made with pure elements or with compounds containing the desired element, as indicated in A.2.2.2 and A.2.2.3, respectively. The elemental RSFs are calculated by normalizing values of $I_{i,\mathrm{ref}}$ to a chosen element/peak combination (e.g. C 1s; Ag M4,5VV) for a key material. A key material refers to a material of known composition that is chosen as a benchmark when calculating values of $S_{i,\mathrm{E}}$. The measured intensity of a chosen peak from an element in the key material is defined as I_{key}.

A.2.2.2 Pure-element relative sensitivity factors

The pure-element relative sensitivity factor (PERSF), $S_{i,\mathrm{Ep}}$, can be obtained from measurements of $I_{i,\mathrm{ref}}$ for the selected peak in a pure-element material normalised to a measurement of the peak intensity for the chosen peak in the selected key material, I_{key}, as given in Formula (A.7):

$$S_{i,\mathrm{Ep}} = \frac{I_{i,\mathrm{ref}}}{I_{\mathrm{key}}} \tag{A.7}$$

The use of these $S_{i,\mathrm{Ep}}$ in Formula (A.6) would require that the F_i terms given in Formula (A.3) are evaluated for pure elements. The use of these sensitivity factors in Formula (1) leads to errors in calculation atomic fractions stemming from the unaccounted-for F_i values which are between 0,1 and 8 in AES[1] and 0,3 and 3 in XPS[2].

A.2.2.3 Elemental relative sensitivity factors from measurements with compounds

The elemental relative sensitivity factor for element *i* in a specified compound, $S_{i,Ec}$, can be obtained from measurements of $I_{i,\mathrm{ref}}$ for the selected element in that compound and of I_{key} for the particular key material as given in Formula (A.8):

$$S_{i,\mathrm{Ec}} = \frac{X_{\mathrm{key}} I_{i,\mathrm{ref}}}{X_{i,\mathrm{ref}} I_{\mathrm{key}}} \tag{A.8}$$

where $X_{i,\mathrm{ref}}$ is the atomic fraction of element *i* in the compound, and X_{key} is the atomic fraction of the key element in the key material (required for cases where the key material is a compound).

As noted in A.1, values of $S_{i,\mathrm{Ec}}$ for the same element *i* in different compounds can be different due in part to uncorrected matrix factors and in part to limitations of the experimental measurements

The use of $S_{i,\mathrm{Ec}}$ in Formula (A.6) requires that the F_i terms given in Formula (A.3) are evaluated for compounds where, in each matrix factor, the $X_{i,\mathrm{ref}}$ values can differ.

A.2.2.4 Sets of elemental relative sensitivity factors

Measurements of $S_{i,\mathrm{Ep}}$ and $S_{i,\mathrm{Ec}}$ for a particular instrument and for particular experimental conditions have often been combined to yield a set of elemental RSFs, $S_{i,\mathrm{E}}$.

NOTE Instrument suppliers can provide a set of elemental RSFs.

A.2.3 Atomic relative sensitivity factors (with partial correction of matrix effects)

The ratio of atomic densities in Formula (A.3) is generally the most important contribution to the matrix correction factor F_i.[22][33] Atomic relative sensitivity factors (ARSFs) can be defined that include ratios of atomic densities to provide in this way a partial correction of matrix effects.[22][33] The ARSFs, $S_{\mathrm{i,At}}$, can be obtained from the elemental relative sensitivity factors obtained from pure elements and from compounds, $S_{i,\mathrm{E}}$, using Formula (A.9):

$$S_{i,\mathrm{At}} = \left(\frac{N_{\mathrm{key}}}{N_i}\right) S_{i,\mathrm{E}} \tag{A.9}$$

where

N_{key} is the atomic densities for the key element;

N_i is the atomic densities for element *i*.

N_i and N_{key} can be calculated using Formula (A.11) and Formula (A.12) in A.2.4. These sensitivity factors are used with Formula (1) with errors significantly lower than those for pure-element relative sensitivity factors.

A.2.4 Average matrix relative sensitivity factors (with nearly complete correction of matrix effects)

Additional corrections for matrix effects can be made by consideration of all of the parameters in Formula (A.2). In order to determine average matrix values for these parameters, a nominal average matrix material can be chosen. The specific choice of average matrix parameters is relatively unimportant, given it is used consistently. The relevant parameters can be determined for the chosen material, either by calculation or use of the appropriate database[45][53] and applied using Formula (A.10) to determine the

AMRSFs. AMRSFs generated in this fashion should be provided with details of the selected matrix and means by which the relevant parameters were determined.

NOTE When choosing a nominal average matrix material, it is most appropriate to choose elements with moderate atomic number, for example Nb (Z = 41) or to use the mean parameter values from a range of materials. Appropriate average matrix parameters can also be obtained from published material[1][2].

The average matrix relative sensitivity factors (AMRSFs), $S_{i,Av}$, are obtained from elemental RSFs, $S_{i,\mathrm{E}}$, with Formula (A.10)[1][2]:[38]

$$S_{i,\,\mathrm{Av}} = \left(\frac{N_{\mathrm{av}} Q_{\mathrm{av}} R_{\mathrm{av}} \lambda_{\mathrm{av}}}{N_i Q_i R_i \lambda_i} \right) S_{i,\,\mathrm{E}} \tag{A.10}$$

where

N_{av} is the atomic density of the average matrix;

Q_{av} is the elastic-scattering correction factor for the average matrix at the electron energy E_i for the particular Auger-electron or photoelectron peak of interest;

R_{av} is the backscattering correction factor for the average matrix;

λ_{av} is the inelastic mean free path for an electron of energy E_i for the particular Auger-electron or photoelectron peak of interest in the average matrix;

N_{i} is the atomic density of element i;

Q_{i} is the elastic-scattering correction factor for element i at the electron energy E_i for the particular Auger-electron or photoelectron peak of interest;

R_{i} is the backscattering correction factor for element i;

λ_{i} is the inelastic mean free path for an electron of energy E_i for the particular Auger-electron or photoelectron peak of interest in element i.

Values for the parameters in Formula (A.10) for an Auger electron or photoelectron of energy E_i can be obtained as follows[1][2][38].

A.2.4.1 Calculating atomic density

N_i and N_{av} can be calculated separately using either Formula (A.11) or Formula (A.12). For a pure elemental solid, the atomic density, N_i can be calculated from Formula (A.11):

$$N_i = 1\,000 \rho N_{\mathrm{A}} / A_i \tag{A.11}$$

where

A_i is the atomic mass of element i;

N_{A} is the Avogadro constant ($6{,}022 \times 10^{23}$ mol^{-1});

ρ is the density of the elemental solid (kg·m^{-3}).

For a compound, atomic density can be calculated using Formula (A.12):

$$N_i = 1\,000 \rho C_i N_{\mathrm{A}} / M_i \tag{A.12}$$

where

M_i is the molecular mass of the compound;

C_i is the number of atoms of a chosen element in the molecular formula of the compound;

ρ is the density of the solid (kg·m^{-3}).

Values of atomic masses and densities (kg·m^{-3}) can be obtained from handbooks[39][40].

A.2.4.2 Obtaining elastic scattering correction

The parameter Q_i and Q_{Av} are a function of the atomic number, kinetic energy of the electron, and the electron emission angle with respect to the surface normal. Values for these parameters can be obtained from published information[25] or from a database[27],[39],[42],[53].

A.2.4.3 Obtaining the backscattering correction factor for AES

The backscattering correction factors, R_i and R_{Av}, are a function of the atomic number Z, the incident electron energy, and the angle of incidence of the electron beam, θ. For AES, R_i and R_{Av} values of can be obtained from the NIST Backscattering-Correction-Factor Database for Auger Electron Spectroscopy[45]. The database values can be obtained from a simplified model, which does not account for any changes to the primary beam within the Auger-electron emission depth, or a more reliable, but slower advanced model. In cases where the primary energy is close to the core-level ionization energy for the relevant Auger transition, or for high angles of incidence of the primary electrons, the advanced model should be used[43][45].

A.2.4.4 Acquiring values for the inelastic mean free path

Values for the inelastic mean free path, λ_i and λ_{Av}, are a function of the sample/matrix material and the electron energy. In the case of electron energy, the electron energy considered should be the kinetic energy attributed to the element/line for $I_{i,\text{ref}}$ for both λ_i and λ_{Av}. Values of this parameter can be obtained from published formulae[47] or from databases[45][48],[49],[50],[51].

Annex B
(informative)

Information on uncertainty of the analytical results

B.1 General

Besides the uncertainty on the determination of peak intensities,[65],[66] many factors contribute to the uncertainty in a determination of surface composition from AES or XPS measurements with the use of relative sensitivity factors (RSFs).[21] It is not generally possible to determine or estimate standard uncertainties for many of these factors, partly because definitive experiments have not yet been conducted to establish uncertainties for some matrix-effect parameters (for example, values of electron inelastic mean free paths, elastic-scattering correction factors, and backscattering correction factors). In addition, practical samples often are not chemically homogenous over the analytical volume and their surfaces are not atomically flat, as assumed in the development of formulae for RSFs in Annex A; the analytical uncertainty will thus depend on the extent to which a particular sample deviates from the idealized structure. Finally, other simplifying assumptions (for example, the neglect of matrix effects on spectral-line shapes in some types of intensity measurement or the neglect of radiation damage, ion-sputtering effects, and surface contamination) lead to uncertainties whose magnitudes again depend on the particular sample. Brief information on these sources of uncertainty is given in this Annex.

NOTE Useful information on the accuracy of quantitative XPS analyses can be obtained from the works of Brundle *et al*[66],[67]. They describe important issues in measurements of peak intensities including selection of an appropriate background and the effects of chemical state on satellite intensities.

B.2 Matrix effects

B.2.1 General

Matrix effects are an important contribution to the intensity in both AES and XPS. If, in quantitative analysis, matrix effects are ignored, results can be biased by up to a factor of 8 in AES[1] and 3 in XPS.[2] Different approaches include these effects in different ways, some more conveniently than others.

B.2.2 Matrix effects on RSFs

As indicated by Formula (A.3), the matrix correction factor F_i depends on ratios of four terms (atomic density, elastic-scattering correction factor, backscattering correction factor, and electron inelastic mean free path) for the unknown sample and a selected reference material. Values of F_i can range from 0,1 to 8 for AES[1] and from 0,3 to 3 for XPS.[2] Analyses based on elemental RSFs (with no correction for matrix effects) will have uncertainties of the order of F_i.

Atomic RSFs will be more accurate than elemental RSFs because a correction is made for different atomic densities in the unknown and reference samples, generally the largest matrix effect.[54] Almost complete correction of matrix effects can be obtained through the use of average matrix RSFs. The standard uncertainty associated with residual matrix effects in the use of Formula (A.10) for AES and XPS have been shown to be less than 3 % for electron energies greater than 175 V and less than 1,2 % for AES for electron energies greater than 500 eV and 1,1 % for XPS with Al Ka in the electron energies between 200 and 1 506 eV and 1,4 % for XPS with Mg ka in the electron energies between 200 and 1 273 eV[1],[2],[38].

B.2.3 Matrix effects on intensity measurements

Changes in local chemical environment can drastically affect the shapes and average energies of core-valence-valence Auger spectra, can modify the spectral shape associated with intrinsic (e.g. shake-up) excitations, and can modify the spectral shape associated with extrinsic excitations (i.e. inelastic-scattering processes associated with the transport of signal electrons in the sample and in the vicinity of the sample-vacuum interface). The magnitudes of these effects are not well documented although they are expected to be larger in intensity measurements from differential spectra than from direct spectra; they are also expected to be larger in intensity measurements from peak heights in direct spectra than from peak areas in direct spectra. It is therefore recommended that signal intensities be determined from peak areas in direct spectra whenever this approach is feasible (that is, for samples for which there are negligible overlaps in the spectral components due to different elements).

Reference [16] shows how differentiation should be performed when measurements are made with different chemical states of an element in order to obtain consistent results. This reference also gives similar information on the determination of peak areas.

NOTE The methods cannot be adapted to the measurement of single-crystal materials, where Auger electrons and photoelectrons experience significant scattering and diffraction, and the measured intensities can change by 30 % to 50 %.

B.3 Sample morphology

The composition of a practical sample can vary with position. Possible variations of composition in the plane of the sample can be determined from instruments equipped with focused electron or X-ray beams or with imaging electron optics if the composition changes occur over distances larger than the lateral resolution. Possible variations of composition with depth from the sample surface can be determined from analyses of spectra obtained at two or more emission angles[55] or from analyses of the intensity due to inelastic scattering in the vicinity of Auger-electron or photoelectron peaks[56].

B.4 Surface topography

The reference samples and, if possible, the unknown samples should have similar surface topographies since the relative intensities of electrons with different energies can change with surface roughness, angle of electron-beam incidence in AES, and particle size[8][57][58].

B.5 Radiation damage

The chemical composition of some materials will change following irradiation with electrons or X-rays during analysis by AES and XPS, and great care should be taken in these cases to minimize sample damage during measurements.[59][60][61] Both the total incident radiation dose and the radiation flux can be important parameters. While electron-beam-induced damage and heating effects in AES can be significant,[59][61] damage by X-rays and photoelectrons in XPS can also be observed in some types of material (e.g. polymers and some inorganic compounds).[59][60] Materials that are susceptible to radiation damage should not be used as reference materials. Radiation damage can be minimized by reducing the incident current density (in AES) or X-ray flux (in XPS), by aligning the sample on one region of the surface and acquiring spectral data on another, and by reducing the measurement time.

B.6 Ion-sputtering effects

When sputtering a multi-component sample with ions, as in composition-depth profiling, a change in the equilibrium surface composition of the sample can occur.[63][64] This phenomenon is called preferential sputtering.[35] RSFs obtained from measurements of the sputtered surface of a multi-component reference sample will have errors if significant preferential sputtering occurs, and preferential sputtering will similarly affect determinations of surface composition for an unknown sample. If, however, the unknown and reference samples have similar preferential-sputtering effects, then this source of uncertainty in measurement of the composition of the unknown sample will be minimized.

Ion bombardment is also expected to lead to surface roughening, atomic mixing, and structural changes.[64] The effects of surface roughening can be minimized by rotation of the sample during ion sputtering[64].

B.7 Surface contamination

Surface contamination should be removed before measurements to determine RSFs and, if possible, before analysis of the unknown sample since the Auger electrons and photoelectrons of interest will be attenuated by a contamination layer.

B.8 Analysis volume

Electrons of different kinetic energies will be detected from differing volumes within the sample. In situations where different excitation energies are available, e.g. for XPS with multiple x-ray sources present on one instrument, or a tuneable x-ray source such as at a synchrotron, this can be used to compare data between different analysis volumes. In this scenario, any set of RSFs are valid only for the instrument setup for which they are acquired, and comparisons between quantifications using different excitation energies are valid only where the assumption of sample homogeneity holds across the largest analysis volume measured.