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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

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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

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PREFACE

This Standard was prepared by the Standards Australia Committee CH-016, Spectroscopy. This Standard is identical with, and has been reproduced from, ISO 18118:2004, *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*.

The objective of this Standard is to provide 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.

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Reference to International Standard		*Australian Standard*	
ISO		AS ISO	
18115	Surface chemical analysis—Vocabulary	18115	Surface chemical analysis—Vocabulary

The other ISO document listed as a normative reference in Clause 2 has not been adopted as Australian Standard.

The terms 'normative' and 'informative' have been used in this Standard to define the application of the annex to which they apply. A 'normative' annex is an integral part of a Standard, whereas an 'informative' annex is only for information and guidance.

CONTENTS

Page

1 Scope ... 1
2 Normative references ... 1
3 Terms and definitions ... 1
4 Symbols and abbreviated terms ... 2
5 General information ... 3
6 Measurement conditions ... 4
6.1 General ... 4
6.2 Excitation source ... 4
6.3 Energy resolution ... 4
6.4 Energy step and scan rate ... 4
6.5 Signal intensity ... 4
6.6 Gain and time constant (for AES instruments with analogue detection systems) ... 4
6.7 Modulation to generate a derivative spectrum ... 4
7 Data-analysis procedures ... 5
8 Intensity-energy response function ... 5
9 Determination of chemical composition using relative sensitivity factors ... 5
9.1 Calculation of chemical composition ... 5
9.2 Uncertainties in calculated compositions ... 6
Annex A (normative) **Equations for relative sensitivity factors** ... 7
A.1 Symbols and abbreviated terms ... 7
A.2 Principles ... 9
A.3 Relative sensitivity factors ... 10
Annex B (informative) **Information on uncertainty of the analytical results** ... 17
B.1 Symbols and abbreviated terms ... 17
B.2 Introduction ... 17
B.3 Matrix effects ... 17
B.4 Sample morphology ... 18
B.5 Surface topography ... 18
B.6 Radiation damage ... 18
B.7 Ion-sputtering effects ... 18
B.8 Surface contamination ... 19
Bibliography ... 20

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 may 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 International Standard provides guidance on the measurement and use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials by AES and XPS.

AUSTRALIAN STANDARD

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 International Standard 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.

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 18115, *Surface chemical analysis — Vocabulary*

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 apply. The definitions of absolute elemental sensitivity factor and relative elemental sensitivity factor from ISO 18115 are given for convenience in 3.1 and 3.2. Definitions of average matrix relative sensitivity factor and pure-element relative sensitivity factor from a future amendment to ISO 18115 are given in 3.3 and 3.4.

3.1
absolute elemental sensitivity factor
coefficient for an element with 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 The choice of use of atomic concentration or atomic fraction should be made clear.

NOTE 2 The type of sensitivity factor used should be appropriate for the equations used in the quantification process and for the type of sample analysed, for example, of homogeneous samples or segregated layers.

NOTE 3 The source of the sensitivity factors should be given in order that the correct matrix factors or other parameters have been used.

NOTE 4 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.

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3.2
relative elemental sensitivity factor
coefficient proportional to the absolute elemental sensitivity factor, where the constant of proportionality is chosen such that the value for a selected element and transition is unity

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

NOTE 2 The type of sensitivity factor used should be appropriate for the analysis, for example, of homogeneous samples or segregated layers.

NOTE 3 The source of the sensitivity factors should be given in order that the correct matrix factors or other parameters have been used.

NOTE 4 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.

3.3
average matrix relative sensitivity factor
coefficient proportional to the intensity calculated for a pure element in an average matrix with 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 The choice of use of atomic concentration or atomic fraction should be made clear.

NOTE 2 The type of sensitivity factor used should be appropriate for the equations used in the quantification process and for the type of sample analysed, for example, of homogeneous samples or segregated layers.

NOTE 3 The source of the sensitivity factors should be given. Matrix factors are taken to be unity for average matrix relative sensitivity factors.

NOTE 4 Sensitivity factors depend on parameters of the excitation source, the spectrometer and the orientation of the sample to these parts of the instrument.

3.4
pure-element relative sensitivity factor
coefficient proportional to the intensity measured for a pure sample of an element with 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 The choice of use of atomic concentration or atomic fraction should be made clear.

NOTE 2 The type of sensitivity factor used should be appropriate for the equations used in the quantification process and for the type of sample analysed, for example, of homogeneous samples or segregated layers.

NOTE 3 The source of the sensitivity factors should be given in order that the correct matrix factors or other parameters have been used. Matrix factors are significant and should be used with pure-element relative sensitivity factors.

NOTE 4 Sensitivity factors depend on parameters of the excitation source, the spectrometer and the orientation of the sample to these parts of the instrument.

4 Symbols and abbreviated terms

AES	Auger electron spectroscopy
AMRSF	average matrix relative sensitivity factor
ARSF	atomic relative sensitivity factor
ERSF	elemental relative sensitivity factor

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IERF	intensity-energy response function
S_i^{At}	atomic relative sensitivity factor for element i
S_i^{Av}	average matrix relative sensitivity factor for element i
S_i^{E}	elemental relative sensitivity factor for element i
RSF	relative sensitivity factor
XPS	X-ray photoelectron spectroscopy

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). Equations defining these three types of RSF are given in A.3 of Annex A, and the principles on which these equations are based are given in A.2 of Annex A.

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.3). The matrix correction factors for AES can vary between 0,1 and 8 [1] while for XPS they can vary between 0,3 and 3 [2]. 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 may 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. It is therefore 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

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correct. In addition, the intensity-energy response function (IERF) of the instrument may change with time as described in Clause 8. Such changes can be detected and corrective actions taken using calibration software available from the UK National Physical Laboratory [4]. Alternatively, an analyst can check for possible changes in IERF 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

In AES, the incident-electron energy and in XPS the X-ray source 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 [5].

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 [6] 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.

NOTE Procedures to check for linear detector response in pulse-counting systems are described in ISO 21270. The first method described there may 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 energy to the analyser [7,8] or by numerical processing of a measured direct spectrum [9,10]. 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.

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NOTE The details of the peak attenuation in numerical differentiation and of the Savitzky and Golay differentiation method in AES can be obtained from References [9] and [10].

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 ASTM E 995 [11]). The backgrounds most commonly used for this purpose [12] are a linear background, a Shirley background [13] or a Tougaard background [14].

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 [11,15]. See also 6.7.

NOTE 1 Details of background-subtraction procedures are given in ASTM E 995 [11].

NOTE 2 Details of peak attenuation in numerical differentiation and of the Savitzky and Golay differentiation method in AES can be obtained from References [9] and [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 Intensity-energy response function

The intensity-energy response function (IERF) 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 [1,17,18]. In general, the IERF 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) may have different IERFs 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 calibration software available from the UK National Physical Laboratory [4] 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.

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 may be determined using Equations (A.5) and (A.6) or one of the other equations given in Annex A. Equation (A.6) is commonly used but ignores matrix terms. For some types of relative sensitivity factor, these matrix terms are effectively unity, and may be ignored but, when other types of sensitivity factor are used, the matrix factors may 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.

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NOTE 1 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.

NOTE 2 In some applications, it may 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 and reference samples, and the composition is calculated from Equation (A.4) of Annex A. If the two materials are close in composition, matrix correction factors can be ignored and Equation (A.4) 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 International Standard. Scraping, fracturing or cleaving of the reference sample, where feasible, may 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 Equation (A.6) using ERSFs, S_i^{E}, supplied by the instrument manufacturer or as measured by the analyst.

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 Equation (A.6) using ARSFs, S_i^{At}, or AMRSFs, S_i^{Av}.

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

NOTE 2 The AMRSFs can be obtained from Equation (A.10) together with Equations (A.11) to (A.34).

9.2 Uncertainties in calculated compositions

Many factors can contribute to the uncertainty of a chemical composition determined from RSFs [19]. Information on possible uncertainties in such measurements is given in Annex B.

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Annex A
(normative)

Equations for relative sensitivity factors

A.1 Symbols and abbreviated terms

AES	Auger electron spectroscopy
A_i	atomic mass of element i
C_i	number of atoms of element i in the molecular formula of the compound
$E_{\mathrm{b},i}$	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_i^{unk}	measured intensity of element i in the unknown sample
I_j^{unk}	measured intensity of element j in the unknown sample
I_i^{ref}	measured intensity of element i in the reference sample
I_j^{ref}	measured intensity of element j in the reference sample
I_{key}	measured intensity of the key material
M_i	molecular mass of the compound containing element i
N_{A}	Avogadro constant
N_{av}	atomic density for the average matrix sample
N_i	atomic density of element i
N_{v}	number of valence electrons per atom or molecule
N^{key}	atomic density of the key element
N^{ref}	atomic density of the reference sample
N^{unk}	atomic density of the unknown sample

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n	number of identified elements in the unknown sample
Q_{av}	elastic-scattering correction factor for the average matrix sample
Q_i	elastic-scattering correction factor for element i
$Q_i(0)$	elastic-scattering correction factor for element i at emission angle $\alpha = 0$ with respect to the surface normal
Q_i^{ref}	elastic-scattering correction factor for element i in the reference sample
Q_i^{unk}	elastic-scattering correction factor for element i in the unknown sample
r_i^{ref}	backscattering factor for element i in the reference sample
r_i^{unk}	backscattering factor for element i in the unknown sample
r_{av}	backscattering factor for the average matrix sample
r_i	backscattering factor for element i
RSF	relative sensitivity factor
S_i^{E}	elemental relative sensitivity factor for element i
S_i^{At}	atomic relative sensitivity factor for element i
S_i^{Av}	average matrix relative sensitivity factor for element i
S_i^{RSF}	relative sensitivity factor for element i
S_j^{RSF}	relative sensitivity factor for element j
S_i^{Ep}	pure-element relative sensitivity factor for element i
S_i^{Ec}	elemental relative sensitivity factor for element i in a specified compound
U_0	over-voltage ratio, given by the ratio of the primary energy to the binding energy of the electrons in a particular shell or subshell
X_i^{unk}	atomic fraction of element i in the unknown sample
X_i^{ref}	atomic fraction of element i in the reference sample
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
ζ_i	ratio of the transport mean free path to the inelastic mean free path for element i
ρ	density of the solid ($\mathrm{kg \cdot m^{-3}}$)
ω_i	single-scattering albedo for element i
θ	angle of incidence of electron beam

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$\Gamma_{i,0}$	a coefficient for determining ζ_i for element i
$\Gamma_{i,1}$	a coefficient for determining ζ_i for element i
$\Gamma_{i,2}$	a coefficient for determining ζ_i for element i
$\Gamma_{i,3}$	a coefficient for determining ζ_i for element i
λ_{av}	electron inelastic mean free path for the average matrix sample
λ_i	electron inelastic mean free path for element i
λ_i^{ref}	electron inelastic mean free path for element i in the reference sample
λ_i^{unk}	electron inelastic mean free path for element i in the unknown sample

A.2 Principles

Quantitative analysis of a homogeneous sample can be accomplished through comparison of an Auger-electron or photoelectron peak intensity, I_i^{unk}, from an unknown sample (the sample material whose surface composition is to be determined) with the corresponding peak intensity, I_i^{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 ratio is given by [1,20,21,22,23,24]:

$$\frac{I_i^{\mathrm{unk}}}{I_i^{\mathrm{ref}}} = \frac{X_i^{\mathrm{unk}} N^{\mathrm{unk}} Q_i^{\mathrm{unk}} (1 + r_i^{\mathrm{unk}}) \lambda_i^{\mathrm{unk}}}{X_i^{\mathrm{ref}} N^{\mathrm{ref}} Q_i^{\mathrm{ref}} (1 + r_i^{\mathrm{ref}}) \lambda_i^{\mathrm{ref}}} \tag{A.1}$$

where X_i^{unk} and X_i^{ref} are the atomic fractions of the element i in the unknown and reference samples, respectively, N^{unk} and N^{ref} are the corresponding atomic densities, Q_i^{unk} and Q_i^{ref} are the corresponding corrections for elastic-electron scattering [25], r_i^{unk} and r_i^{ref} are the corresponding backscattering factors for AES (these terms are zero for XPS), and λ_i^{unk} and λ_i^{ref} are the corresponding electron inelastic mean free paths. It should be understood that the elastic-scattering correction terms and the inelastic mean free paths in Equation (A.1) are determined at the electron energy E_i for the particular Auger-electron or photoelectron peak of interest. The backscattering factor terms are determined at the electron energy E_i for the binding energy $E_{\mathrm{b},i}$ corresponding to the initial ionization that was responsible for the Auger peak of element i being measured.

From Equation (A.1), X_i^{unk} can be obtained as follows:

$$X_i^{\mathrm{unk}} = \left(\frac{I_i^{\mathrm{unk}}}{I_i^{\mathrm{ref}}}\right) \frac{X_i^{\mathrm{ref}} N^{\mathrm{ref}} Q_i^{\mathrm{ref}} (1 + r_i^{\mathrm{ref}}) \lambda_i^{\mathrm{ref}}}{N^{\mathrm{unk}} Q_i^{\mathrm{unk}} (1 + r_i^{\mathrm{unk}}) \lambda_i^{\mathrm{unk}}} = X_i^{\mathrm{ref}} \left(\frac{I_i^{\mathrm{unk}}}{I_i^{\mathrm{ref}}}\right) F_i \tag{A.2}$$

where F_i is a matrix correction factor for element i in the comparison of measurements made with a particular unknown sample and a particular reference sample. For AES, if the reference intensities are for pure elements with X_i^{ref} values of unity, the F_i are in the range 0,1 to 8 [1] with one-third of the values outside the range 0,5 to 1,5. For XPS, the F_i are closer to unity and range from 0,3 to 3 [2].

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The atomic fraction of the element i in an unknown sample with n identified elements is then given by [1,24]:

$$X_i^{\text{unk}} = \frac{\left(\dfrac{I_i^{\text{unk}}}{I_i^{\text{ref}}}\right) F_i}{\sum_{j=1}^{n} \left(\dfrac{I_j^{\text{unk}}}{I_j^{\text{ref}}}\right) F_j} \tag{A.3}$$

This equation must be solved iteratively since the matrix factors depend on the composition of the material. This composition is, of course, unknown until Equation (A.3) is solved. If, for simplicity, it is assumed that the atomic densities, backscattering factors and inelastic mean free paths are the same for the two samples considered in Equation (A.2), the matrix correction factors $F_i = 1$ and the reference atomic fractions $X_i^{\text{ref}} = 1$. For these assumptions, if the unknown sample consists of n elements, the atomic fractions X_i of these elements can be obtained from [24]:

$$X_i^{\text{unk}} = \frac{\left(\dfrac{I_i^{\text{unk}}}{I_i^{\text{ref}}}\right)}{\sum_{j=1}^{n} \left(\dfrac{I_j^{\text{unk}}}{I_j^{\text{ref}}}\right)} \tag{A.4}$$

While Equation (A.4) 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 for X_i^{unk} for pure elements) in AES are between 0,1 and 8 (with one-third of the values outside the range 0,5 to 1,5) [1] while for XPS the F_i values range from 0,3 to 3 [2].

Values of I_i^{ref} are needed for a quantitative analysis to obtain the fractional compositions X_i^{unk} from measured values of I_i^{unk} for an unknown sample using Equation (A.3) or (A.4). The I_i^{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^{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 Equation (A.3) and the additional matrix effects discussed in B.2], values of I_i^{ref} for the same element i from different compounds may be different [26,27].

It is generally convenient in practice to make use of I_i^{ref} values that have been normalized to unity for a particular peak from a selected key element [1,7,28,29,30,31,32,33]. In XPS, the 1s photoelectron line of fluorine in lithium fluoride has been generally used for this purpose while the silver $M_{4,5}VV$ Auger-electron line has been commonly used in AES.

A.3 Relative sensitivity factors

A.3.1 Introduction

Defining equations are given here for three different types of relative sensitivity factor (RSF) that can be obtained from I_i^{ref} values. The RSFs, S_i^{RSF}, for an element i in an unknown material containing n elements, can be used to evaluate the atomic fraction, X_i^{unk}, of the element i from the following equation:

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$$X_i^{\text{unk}} = \frac{\left(\dfrac{I_i^{\text{unk}} F_i}{S_i^{\text{RSF}}}\right)}{\sum_{j=1}^{n}\left(\dfrac{I_j^{\text{unk}} F_j}{S_j^{\text{RSF}}}\right)} \tag{A.5}$$

Equation (A.5) can be obtained from Equation (A.3) by equating S_i^{RSF} with normalized values of I_i^{ref}. If, for simplicity, the matrix correction factors are neglected, Equation (A.5) becomes:

$$X_i^{\text{unk}} = \frac{\left(\dfrac{I_i^{\text{unk}}}{S_i^{\text{RSF}}}\right)}{\sum_{j=1}^{n}\left(\dfrac{I_j^{\text{unk}}}{S_j^{\text{RSF}}}\right)} \tag{A.6}$$

The three types of RSF defined below (elemental RSFs, atomic RSFs and average matrix RSFs that are designated S_i^{E}, S_i^{At}, and S_i^{Av}, respectively) give analytical results of increasing accuracy. These RSFs can be used for surface analyses in place of S_i^{RSF} in Equation (A.6).

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^{E}, S_i^{At} or S_i^{Av}) shall be used in an analysis.

A.3.2 Elemental relative sensitivity factors (with no correction for matrix effects)

A.3.2.1 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.3.2.2 and A.3.2.3, respectively.

A.3.2.2 Pure-element relative sensitivity factors

The pure-element relative sensitivity factor (PERSF), S_i^{Ep}, can be obtained from measurements of S_i^{ref} for the selected element and a measurement of the peak intensity for the selected key material, I_{key}:

$$S_i^{\text{Ep}} = \frac{I_i^{\text{ref}}}{I_{\text{key}}} \tag{A.7}$$

The use of these sensitivity factors in Equation (A.5) requires that the matrix factors F_i given in Equation (A.2) are evaluated for pure elements (i.e. $X_i^{\text{ref}} = 1$). The use of these sensitivity factors in Equation (A.6) leads to errors in AES between 0,1 and 8 in AES [1] and 0,3 and 3 in XPS [2].

A.3.2.3 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^{ref} for the selected element in that compound and of I_{key} for the particular key material:

$$S_i^{\text{Ec}} = \frac{I_i^{\text{ref}}}{X_i^{\text{ref}} I_{\text{key}}} \tag{A.8}$$

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where X_i^{ref} is the atomic fraction of element i in the compound. As noted in A.2, values of S_i^{Ec} for the same element i in different compounds may be different due in part to uncorrected matrix factors and in part to limitations of the experimental measurements (such as different attenuations of peaks of different energies due to surface contamination on un-cleaned samples or to preferential sputtering effects if the sample surfaces were cleaned by ion bombardment. It was hoped in early measurements that, by measuring many compounds, the effects of surface contamination could be averaged out. For example, ratios of RSFs obtained for two elements from measurements with different compounds containing those elements showed a standard deviation of typically 14 % [34]. In addition, evaluations of the RSFs from different data sets indicated a poor correlation with theoretical predictions [26,35].

The use of these sensitivity factors in Equation (A.5) requires that the F_i matrix factors given in Equation (A.2) are evaluated for compounds where, in each matrix factor, the X_i^{ref} values may differ. These matrix factor values may differ from those for pure elements. The use of these sensitivity factors in Equation (A.6) leads to errors likely to be slightly lower than those given above for pure elements.

A.3.2.4 Sets of elemental relative sensitivity factors

Measurements of S_i^{Ep} and S_i^{Ec} for a particular instrument and for particular experimental conditions have often been combined to yield a set of elemental RSFs, S_i^{E}.

NOTE Instrument suppliers may provide a set of elemental RSFs.

A.3.3 Atomic relative sensitivity factors (with partial correction of matrix effects)

The ratio of atomic densities in Equation (A.2) is generally the most important contribution to the matrix correction factor F_i. Atomic relative sensitivity factors (ARSFs) can be defined [20,31] that include ratios of atomic densities to provide in this way a partial correction of matrix effects. The ARSFs, S_i^{At}, can be obtained from the elemental relative sensitivity factors obtained from pure elements and from compounds, S_i^{E}, using the following equation:

$$S_i^{\text{At}} = \left(\frac{N^{\text{key}}}{N_i} \right) S_i^{\text{E}} \tag{A.9}$$

where N^{key} and N_i are the atomic densities for the key element and for element i, respectively.

These sensitivity factors are used with Equation (A.6) with errors significantly lower than those for pure-element relative sensitivity factors.

A.3.4 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 Equation (A.1). The average matrix relative sensitivity factors (AMRSFs), S_i^{Av}, are obtained from elemental RSFs, S_i^{E}, with the following equation [1,2,36]:

$$S_i^{\text{Av}} = \left(\frac{N_{\text{av}} Q_{\text{av}} (1 + r_{\text{av}}) \lambda_{\text{av}}}{N_i Q_i (1 + r_i) \lambda_i} \right) S_i^{\text{E}} \tag{A.10}$$

where the terms N_{av}, Q_{av}, r_{av} and λ_{av} are the atomic density, the elastic-scattering correction, the backscattering factor and the inelastic mean free path for a hypothetical average matrix, respectively. The corresponding terms in the denominator of Equation (A.10) are for element i in either a pure elemental solid or a compound of known composition. This removes most of the effects of the matrix factors in Equation (A.5) so that only Equation (A.6) need be considered. In using Equation (A.6), the standard uncertainty associated with residual matrix effects in the use of Equation (A.10) for AES has been shown to be less than 3 % for electron energies greater than 175 eV and less than 1,2 % for electron energies greater than 500 eV [1,36]. These

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standard uncertainties are less than those for the parameters in the denominator of Equation (A.10). Equation (A.6) may thus be used with AMRSFs to the same accuracy as Equation (A.5) when that equation is used with PERSFs and full calculations of the matrix factors. A further advantage of the AMRSF approach is that there is no need for an iterative calculation.

Values for the parameters in the denominator of Equation (A.10) for an Auger electron or photoelectron of energy E_i can be obtained as follows [1,2,36].

The atomic density N_i for a pure elemental solid can be calculated from:

$$N_i = 1000 \rho N_A / A_i \tag{A.11}$$

where A_i is the atomic mass of element i, N_A is the Avogadro constant ($6{,}022 \times 10^{23}$ mol^{-1}) and ρ is the density of the elemental solid (kg·m^{-3}). For a compound, N_i can be calculated from:

$$N_i = 1000 \rho C_i N_A / M_i \tag{A.12}$$

where M_i is the molecular mass of the compound containing element i, C_i is the number of atoms of element i in the molecular formula of the compound and ρ (kg·m^{-3}) is the density of the compound. Values of atomic masses and densities (kg·m^{-3}) can be obtained from handbooks [37,38].

The parameter Q_i is a function of the atomic number and the electron emission angle with respect to the surface normal. Values of this parameter can be obtained from published information [25] or, more simply, from a database [39]. If desired, the value of Q_i can be calculated from the following equations [25]:

$$Q_i = (1-\omega_i)^{0,5} H(\cos\alpha, \omega_i) \tag{A.13}$$

$$\omega_i = \frac{1}{1+\zeta_i} \tag{A.14}$$

$$H(\cos\alpha, \omega_i) = \frac{1+1{,}907\,8\cos\alpha}{1+1{,}907\,8\cos\alpha(1-\omega_i)^{0,5}} \tag{A.15}$$

$$\zeta_i = \exp\left(\Gamma_{i,3}\ln^3 E_i + \Gamma_{i,2}\ln^2 E_i + \Gamma_{i,1}\ln E_i + \Gamma_{i,0}\right) \tag{A.16}$$

where α is the emission angle with respect to the surface normal, ζ_i is the ratio of the transport mean free path to the inelastic mean free path for element i, and the values of $\Gamma_{i,3}$, $\Gamma_{i,2}$, $\Gamma_{i,1}$ and $\Gamma_{i,0}$ for element i can be obtained from Table A.1 [25].

The value of Q_i can be also calculated easily from the following equation [40]:

$$Q_i = Q_i(0) \times \left(0{,}863 + 0{,}308\cos\alpha - 0{,}171\cos^2\alpha\right) \tag{A.17}$$

where $Q_i(0)$ is the elastic-scattering correction for element i when $\alpha = 0$. The value of $Q_i(0)$ can be obtained from the following expressions [40]:

$$Q_i(0) = (1-\omega_i)^{0,5}\left[0{,}091 + 0{,}092\,3\left(\frac{2{,}908}{1+1{,}908(1-\omega_i)^{0,5}}\right)\right] \quad \text{when } \omega_i \geqslant 0{,}245 \tag{A.18}$$

and

$$Q_i(0) = (1-\omega_i)^{0,5}(1+0{,}412\omega_i) \quad \text{when } \omega_i < 0{,}245 \tag{A.19}$$

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The backscattering factor r_i is a function of the atomic number Z, the incident electron energy and the angle of incidence of the electron beam, θ. Values of r_i can be obtained from the following equations [41,42] or from a database [43]:

For $\theta = 0°$, $$r_i = (2{,}34 - 2{,}10Z^{0{,}14})U_0^{-0{,}35} + 2{,}58Z^{0{,}14} - 2{,}98 \quad \text{(A.20)}$$

For $\theta = 30°$, $$r_i = (0{,}462 - 0{,}777Z^{0{,}20})U_0^{-0{,}32} + 1{,}15Z^{0{,}20} - 1{,}05 \quad \text{(A.21)}$$

For $\theta = 45°$, $$r_i = (1{,}21 - 1{,}39Z^{0{,}13})U_0^{-0{,}33} + 1{,}94Z^{0{,}13} - 1{,}88 \quad \text{(A.22)}$$

where U_0 is the ratio of the incident electron energy E_{pr} to the binding energy $E_{\text{b},i}$ of the core level for the element i being ionized by backscattered electrons (to give the Auger peak being measured). Equations (A.20) to (A.22) can be used for incident electron energies between 3 keV and 10 keV.

The inelastic mean free path λ_i (nm) is a function of the sample material and the electron energy. Values of this parameter can be obtained from published equations [44] or, more simply, from databases [43,45]. If desired, the values can be calculated from the following equations [44]:

$$\lambda_i = \frac{0{,}1E_i}{E_{\text{p}}^2[\beta \ln(\gamma E_i) - (C/E_i) + (D/E_i^2)]} \text{ nanometres} \quad \text{(A.23)}$$

$$\beta = -0{,}10 + 0{,}944(E_{\text{p}}^2 + E_{\text{g}}^2)^{-0{,}5} + 0{,}069(\rho/1\,000)^{0{,}1} \quad \text{(A.24)}$$

$$\gamma = 0{,}191(\rho/1\,000)^{-0{,}5} \quad \text{(A.25)}$$

$$C = 1{,}97 - 0{,}91U \quad \text{(A.26)}$$

$$D = 53{,}4 - 20{,}8U \quad \text{(A.27)}$$

$$U = N_{\text{v}}\rho/1\,000M_i \quad \text{(A.28)}$$

$$E_{\text{p}} = 28{,}8(N_{\text{v}}\rho/1\,000M_i)^{0{,}5} \quad \text{(A.29)}$$

where E_i is the electron energy (eV), ρ is the density of the sample (kg·m^{-3}), N_{v} is the number of valence electrons per atom or molecule, E_{g} is the band-gap energy (eV) and M_i is the atomic or molecular mass.

Values of N_{av} (atoms·m^{-3}) and Q_{av} for the average matrix in Equation (A.10) are [1,2,36]:

$$N_{\text{av}} = 5{,}20 \times 10^{28} \text{ atoms} \cdot \text{m}^{-3} \quad \text{(A.30)}$$

$$Q_{\text{av}} = 0{,}951 - \left(\frac{E_i - 2\,310}{10\,300}\right)^2 \quad \text{(A.31)}$$

Using the physical constants for the hypothetical average matrix [1] ($Z = 40{,}57$, $N_{\text{v}} = 4{,}684$, $\rho = 6\,767$ kg·m^{-3}, $M_i = 137{,}51$, $E_{\text{g}} = 0$ eV), the values of r_{av} and λ_{av} in Equation (A.10) can be calculated from the following equations:

$$r_{\text{av}} = 1{,}353 - 1{,}187U_0^{-0{,}35} \quad \text{for } \theta = 0° \quad \text{(A.32)}$$

$$r_{\text{av}} = 1{,}362 - 1{,}168U_0^{-0{,}32} \quad \text{for } \theta = 30° \quad \text{(A.33)}$$

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$$r_{\text{av}} = 1{,}260 - 1{,}039 U_0^{-0{,}33} \qquad \text{for } \theta = 45° \tag{A.34}$$

$$\lambda_{\text{av}} = \frac{0{,}000\,523 E_i^3}{48{,}6 - 1{,}76 E_i + 0{,}051\,8 E_i^2 (-2{,}61 + \ln E_i)} \quad \text{nanometres} \tag{A.35}$$

where U_0 is the ratio of the incident electron energy to the binding energy of the core level for the element i being ionized by backscattered electrons and E_i is the Auger or photoelectron kinetic energy (eV) of element i.

Table A.1 — Coefficients $\Gamma_{i,3}$, $\Gamma_{i,2}$, $\Gamma_{i,1}$ and $\Gamma_{i,0}$ of element i for determining ζ_i [25]

Atomic number	$\Gamma_{i,3}$	$\Gamma_{i,2}$	$\Gamma_{i,1}$	$\Gamma_{i,0}$
3	–0,009 449 05	0,187 260	–0,307 224	0,283 110
4	0,003 600 07	–0,052 317 7	1,152 71	–3,504 85
5	0,003 843 92	–0,064 491 0	1,269 89	–4,491 31
6	0,017 955 4	–0,304 704	2,532 51	–6,435 59
7[a]	0,009 621 54	–0,143 247	1,460 61	–4,002 01
8[a]	0,001 287 68	0,018 210 4	0,388 702	–1,568 44
9[a]	–0,007 046 18	0,179 668	–0,683 202	0,865 138
10[a]	–0,015 380 0	0,341 125	–1,755 11	3,298 71
11	–0,023 713 9	0,502 582	–2,827 01	5,732 29
12	–0,027 257 2	0,562 785	–3,149 76	6,043 67
13	–0,029 221 1	0,608 573	–3,504 76	6,787 97
14	–0,031 546 4	0,659 172	–3,884 56	7,626 46
15	–0,031 282 0	0,648 236	–3,789 85	7,396 24
16	–0,031 273 6	0,657 242	–3,933 17	8,059 03
17[a]	–0,024 321 1	0,540 729	–3,344 89	7,267 15
18[a]	–0,017 368 5	0,424 216	–2,756 61	6,475 28
19	–0,010 416 0	0,307 703	–2,168 33	5,683 40
20	–0,009 861 32	0,296 051	–2,076 64	5,260 26
21	0,003 532 95	0,035 553 8	–0,392 266	1,326 55
22	0,022 482 5	–0,318 054	1,763 35	–3,243 57
23	0,022 312 8	–0,319 174	1,798 19	–3,579 67
24	0,036 387 6	–0,594 219	3,581 14	–7,367 29
25	0,025 767 4	–0,398 297	2,396 56	–5,049 57
26	0,016 165 3	–0,214 086	1,214 43	–2,572 78
27	–0,000 105 87	0,096 669 0	–0,752 442	1,495 58
28	–0,001 240 25	0,109 994	–0,770 173	1,347 56
29	–0,021 855 4	0,507 199	–3,306 77	6,659 82
30	–0,039 883 8	0,870 509	–5,780 48	12,353 6
31	–0,048 804 4	1,046 91	–6,951 92	15,171 1
32	–0,047 081 7	1,030 86	–6,977 48	15,860 1
33	–0,049 699 6	1,093 52	–7,484 95	16,961 5
34	–0,040 643 5	0,939 953	–6,672 34	15,848 7
35[a]	–0,024 121 5	0,650 474	–5,060 20	13,093 6
36[a]	–0,007 599 47	0,360 996	–3,448 07	10,338 4
37	0,008 922 55	0,071 517 4	–1,835 93	7,583 29
38	0,034 378 7	–0,409 408	1,161 74	1,360 45
39	0,072 220 6	–1,134 84	5,763 59	–8,351 11
40	0,087 928 5	–1,432 74	7,613 60	–12,345 9

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Table A.1 (*continued*)

Atomic number	$\Gamma_{i,3}$	$\Gamma_{i,2}$	$\Gamma_{i,1}$	$\Gamma_{i,0}$
41	0,109 828	–1,859 20	10,374 6	–18,661 2
42	0,121 609	–2,094 83	11,922 4	–21,843 7
43[a]	0,130 667	–2,279 15	13,153 2	–24,584 2
44	0,139 724	–2,463 47	14,383 9	–27,324 7
45	0,138 944	–2,467 47	14,539 0	–27,871 1
46	0,124 196	–2,188 73	12,786 0	–24,405 4
47	0,138 696	–2,509 84	15,144 7	–29,771 9
48	0,110 743	–1,964 48	11,584 6	–22,150 6
49	0,104 637	–1,861 27	11,015 3	–20,942 9
50	0,100 837	–1,802 77	10,738 0	–20,496 2
51	0,092 914 9	–1,656 82	9,839 03	–18,655 7
52	0,089 548 0	–1,602 30	9,554 24	–18,061 5
53[a]	0,084 998 3	–1,512 27	8,939 28	–16,589 8
54[a]	0,080 448 5	–1,422 23	8,324 33	–15,118 2
55	0,075 898 8	–1,332 20	7,709 37	–13,646 5
56	0,086 199 2	–1,533 03	9,013 95	–16,565 7
57	0,102 827	–1,851 84	11,044 0	–21,063 0
58[a]	0,116 179	–2,085 63	12,356 5	–23,364 6
59[a]	0,129 531	–2,319 41	13,669 0	–25,666 2
60[a]	0,142 883	–2,553 20	14,981 5	–27,967 8
61[a]	0,156 236	–2,786 98	16,294 0	–30,269 5
62[a]	0,169 588	–3,020 77	17,606 5	–32,571 1
63[a]	0,182 940	–3,254 55	18,919 0	–34,872 7
64	0,196 292	–3,488 34	20,231 5	–37,174 3
65[a]	0,196 258	–3,478 91	20,101 8	–36,689 0
66	0,196 223	–3,469 47	19,972 1	–36,203 6
67[a]	0,199 287	–3,525 51	20,299 5	–36,902 5
68[a]	0,202 350	–3,581 56	20,626 9	–37,601 4
69[a]	0,205 414	–3,637 60	20,954 4	–38,300 3
70[a]	0,208 477	–3,693 64	21,281 8	–38,999 2
71[a]	0,211 541	–3,749 69	21,609 2	–39,698 1
72	0,214 604	–3,805 73	21,936 6	–40,397 0
73	0,224 201	–4,016 85	23,457 1	–43,795 6
74	0,236 340	–4,259 54	25,056 9	–47,299 7
75	0,241 096	–4,383 34	26,071 4	–49,840 0
76	0,226 617	–4,126 42	24,585 1	–47,266 6
77	0,216 236	–3,944 91	23,546 6	–45,375 2
78	0,206 050	–3,778 52	22,687 4	–43,906 5
79	0,209 509	–3,886 39	23,668 5	–46,545 1
80[a]	0,188 563	–3,494 45	21,232 2	–41,463 5
81	0,167 617	–3,102 50	18,795 8	–36,381 9
82	0,158 079	–2,941 25	17,924 8	–34,810 0
83	0,132 015	–2,471 95	15,161 8	–29,404 9

[a] Interpolated values.

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Annex B
(informative)

Information on uncertainty of the analytical results

B.1 Symbols and abbreviated terms

AES	Auger electron spectroscopy
F_i	matrix correction factor
RSF	relative sensitivity factor
XPS	X-ray photoelectron spectroscopy

B.2 Introduction

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) [19]. 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 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 equations 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.

B.3 Matrix effects

B.3.1 General

Matrix effects are an important contribution to the intensity in both AES and XPS. If, in quantitative analysis, matrix effects are ignored, results may 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.3.2 Matrix effects on RSFs

As indicated by Equation (A.2) in Annex A, the matrix correction factor F_i depends on ratios of four terms (atomic density, elastic-scattering correction factor, backscattering 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 [46]. Almost complete correction of matrix effects can be obtained through the use of average matrix RSFs. For XPS, the standard uncertainty associated with the use of average matrix RSFs is less than 2 % [2]. For AES, for electron energies greater than 175 eV, this standard uncertainty is less than 3 % [1].

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B.3.3 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.

B.4 Sample morphology

The composition of a practical sample may 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 [47] or from analyses of the intensity due to inelastic scattering in the vicinity of Auger-electron or photoelectron peaks [48].

B.5 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 [6,49,50].

B.6 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 [51,52,53]. 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 [51,53], damage by X-rays and photoelectrons in XPS can also be observed in some types of material (e.g. polymers and some inorganic compounds)[51,52]. 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.7 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 may occur [55,56,57]. This phenomenon is called preferential sputtering [33]. 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 [56]. The effects of surface roughening can be minimized by rotation of the sample during ion sputtering [56].

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B.8 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.

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