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Standard Approaches to XPS and AES Quantification—A Summary of ISO 18118:2024 on the Use of Relative Sensitivity Factors

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ABSTRACT

Quantitative analysis of electron spectroscopy data from techniques such as Auger electron spectroscopy (AES) and X-ray photo-electron spectroscopy (XPS) typically requires the use of relative sensitivity factors (RSFs). Virtually, all routine XPS experiments attempt to turn peak intensities into elemental or chemical compositions using RSFs. The comparability and reproducibility of surface chemical analysis by electron spectroscopies therefore require the standardisation of RSFs and their use. RSFs may be determined either from theoretical calculations based on photo-ionisation cross-sections or empirically through direct measurement of homogeneous reference samples of known composition. The accurate use of sensitivity factors, even empirically determined RSFs, requires accounting for the effect of material differences on relative intensities, the so-called 'matrix effects'. ISO 18118:2024 is the most recently revised version of the ISO standard for the use and determination of empirical RSFs for quantitative analysis of homogeneous materials by AES and XPS. This article provides a summary of the new, updated standard and the methods described therein, noting in particular the revisions made since the previous edition, ISO 18118:2015.

1 | Introduction

Relative sensitivity factors (RSFs) are widely used to obtain quantitative information from electron spectroscopy data. When an electron spectroscopy measurement is performed, there are a number of factors that influence the detected photoelectron intensity. Some of these are instrumental, for example, the energy-dependent spectrometer response function (SRF) (commonly referred to as a transmission function), or the placement of the detector with respect to the sample position, incident beam direction and polarisation—that is, the instrument geometry [1]. Other contributing factors are sample dependent, such as the photoemission cross-section [2, 3], sample density, shake-up features and scattering behaviour of electrons in the material (both elastic and inelastic)

[4]. Combined, these factors lead to significant differences in the detected intensity of photoemission peaks from elements at otherwise equivalent atomic concentrations [5]. Thus, to deduce the concentration of materials from electron spectroscopy data, the analysis procedure must account for these differences. In general, some or all of the sample dependent factors, as well as the angular emission dependence from the instrument geometry, are accounted for through the use of RSFs.

RSFs can be determined theoretically by combining modelled or calculated values for each of these parameters, or empirically based on direct measurements of reference samples, and are usually normalised to the value for a specific photoemission line from a particular element—typically one for

which many compounds can be formed, such as fluorine or carbon—which is referred to as the 'key element' [6]. Once an appropriate library of RSF values for a given instrument has been obtained, and any energy dependence of the SRF has been corrected for [7–10], these can then be used to determine the homogeneous-equivalent atomic concentration of the different components of a sample.

2 | Scope

Both the updated version of the International Organization for Standardization (ISO) standard ISO 18118 published in 2024 [11] and the previous editions of the standard [12] provide methods and guidance for the use and calculation of experimentally determined RSFs in Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) and follow the same broad scope. These RSFs are separated into three broad types:

i. elemental relative sensitivity factors (ERSFs) determined either from measurements of pure elements or of compounds;

ii. atomic relative sensitivity factors (ARSFs) that incorporate partial correction for matrix effects; and

iii. average matrix relative sensitivity factors (AMRSFs) that incorporate a nearly complete correction for matrix effects.

The standard comprises three main sections: the main body of the standard that covers the appropriate measurement conditions, analysis procedures and determination of composition from electron spectroscopy data using RSFs; Annex A that provides sources and formulae for determining the different types of empirical RSF from the relevant parameters; and Annex B that provides information on causes of uncertainty.

The standard is explicitly for use in the analysis of the chemical composition of homogeneous materials; however, it should be noted that the methodology described is appropriate for the standard practice of reporting homogeneous-equivalent atomic concentrations from measurements of heterogeneous samples. Additionally, the standard does not address peculiarities that can arise in the analysis of single-crystal samples, and so, it is recommended only for use with polycrystalline or amorphous samples.

Following periodic review by the members of ISO Technical Committee 201—Surface Chemical Analysis, Sub Committee 7—Electron Spectroscopies, a revision of ISO standard 18118 was initiated, with the aim of significantly simplifying the standard for better accessibility and removing or replacing any outdated formulae or referenced work.

3 | Revisions

Through the periodic review process, several required revisions to ISO 18118 were identified by international experts and changes implemented. These changes are focussed on the simplification and restructuring of Annex A that describes how ERSFs, ARSFs

and AMRSFs can be determined. Previously, this annex detailed the use of formulae from the scientific literature for determining parameters such as the inelastic mean free path, elastic scattering correction factor and backscattering correction factor; several of these formulae had since been superseded by more accurate work or were only valid in fairly narrow regimes—for example, formulae that were only accurate for a small range of electron kinetic energies and were thus inapplicable for Hard X-ray Photoelectron Spectroscopy (HAXPES [13]) sources. While the literature references for the previously employed equations are still made available, this section has now been reworked to have a clearer, easier to follow structure and to recommend the use of modern, freely available databases as the primary source of necessary parameters.

4 | Content Summary

4.1 | Determination of Composition Using Sensitivity Factors

Once a set of sensitivity factors has been determined, they may be applied to determine the relative atomic composition of a homogeneous sample (or the homogeneous-equivalent atomic composition of a heterogeneous sample) using Formula (1):

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

where $X_{i,\text{unk}}$ is the atomic fraction of element i in the unknown sample, $I_{i,\text{unk}}$ is the measured intensity of element i in the unknown sample and $S_{i,\text{RSF}}$ is the RSF for element i. The denominator $\sum_{j=1}^{n}\left(\frac{I_{j,\text{unk}}}{S_{j,\text{RSF}}}\right)$ is likewise the sum of the intensities of all other present elements $j=1$ to n, divided by their corresponding RSFs. The sensitivity factors used in Formula (1) should either be ARSFs or AMRSFs, to partially or almost fully account for matrix effects. If only ERSFs are used then additional terms specifically to account for matrix effects must be included; these factors may vary between 0.1 to 8 for AES and 0.3 to 3 for XPS. For non-homogeneous samples, $X_{i,\text{unk}}$ can still be determined but then represents the *homogeneous-equivalent* atomic fraction. For many electron spectroscopy experiments, this is the value that is reported and may be used in further calculations to elucidate structure.

4.2 | Measurement and Analysis

When using experimentally derived RSFs, it is important that the instrument conditions and settings used for the measurement of an unknown sample are the same as those used in the reference measurements. The following requirements are made by ISO 18118:2024, in order to make use of a set of RSFs:

• The excitation source energy (incident electron energy in AES or X-ray energy in XPS) used for measurements should be the same as that used to measure the RSFs.

• The energy resolution (as determined by choice of apertures, pass energies or retardation ratios) used for measurements should be the same as that used to measure the RSF's.

- The energy step and scan-rate should be selected such that negligible distortion (e.g., broadening of peaks due to large step size) is observed in the acquired data.

- The incident beam current (for either electrons in AES or X-rays in XPS) should be adjusted along with the detector voltage to ensure that the measured signal is within the linear range of the detector, as described by ISO 21270 [14].

- For AES, the gain of the detector system should be adjusted to ensure that all relevant peaks are within the range for linear detector response, and the time constant should be sufficiently short to ensure no distortion of spectral features [15].

- For AES, when utilising the differential spectrum, the modulation energy used for measurements should be the same as that used to measure the RSFs [15].

Additionally, the data processing used in the analysis of measurements should be consistent with that used for the measurement of the RSFs—for example, choice of background for XPS peaks, or the numerical procedure for calculating the differential spectrum in AES. It is also recommended to perform regular calibrations (e.g., every 6 months) of the SRF and monitor the constancy of the intensity scale, as per ISO 24237 [16] as variations or drift will affect the accuracy of results.

4.3 | Annex A—Formulae for RSFs

Annex A contains the basic principles and formulae for the calculation of sensitivity factors from measured reference data. The annex also provides formulae for conversion between ERSFs, ARSFs and AMRSFs, as well as sources for the parameters required. In this revision of the standard, considerable simplifications have been made to this section, and the recommended sources for many parameters have been updated; typically, most parameters are now recommended to be obtained from freely available databases (detailed below), although methods for their direct calculation are also referenced.

In an electron spectroscopy measurement, quantitative analysis of an unknown, homogeneous sample can be achieved by comparison of peak intensities measured from that sample to the corresponding peak intensities measured from a reference sample with known composition. This intensity ratio is given by Formula (2):

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

where X_i is the atomic fraction of element i, N is the atomic density, Q_i is the correction for elastic electron scattering, R_i is the backscattering correction factors for AES (this term is unity for XPS), λ_i is the electron inelastic mean free path and the subscripts unk and ref denote the values for unknown and reference samples, respectively.

Formula (2) can be simplified by combining the material parameters into a matrix factor term, F. Upon rearranging,

the atomic fraction of an element, i, in an unknown sample consisting of n elements can then be determined using Formula (3):

$$X_{i,\text{unk}} = \frac{X_{i,\text{ref}} \left(\frac{I_{i,\text{unk}}}{I_{i,\text{ref}}} \right) F_i}{\sum_{j=1}^{n} X_{j,\text{ref}} \left(\frac{I_{j,\text{unk}}}{I_{j,\text{ref}}} \right) F_j}. \tag{3}$$

In practice, values for I_{ref} are typically normalised to the intensity of a selected peak from a selected 'key' element, I_{key}, and the composition of the reference material. These normalised values are what are referred to as RSFs and may also incorporate some level of correction for matrix factors, resulting in Formula (1).

4.3.1 | ERSFs

ERSFs are the simplest form of sensitivity factor, with no accounting for matrix factors. These are calculated using measured I_{ref} values from either pure materials (pure-element RSFs or PERSFs) or compounds normalised to the chosen I_{key}, as per Formula (4):

$$S_{i,E} = \frac{X_{\text{key}} I_{i,\text{ref}}}{X_{i,\text{ref}} I_{\text{key}}} \tag{4}$$

where $S_{i,E}$ is the ERSF and X_{key} is the atomic fraction of the key element in the key material.

As these sensitivity factors make no correction for matrix factors, their use in Formula (1) would introduce significant errors if matrix effects are not separately accounted for.

4.3.2 | ARSFs

ARSFs partially account for the matrix factors—the most significant contributor to the matrix factors is typically the atomic densities. ARSFs are thus defined to include ratios of atomic densities. These can be obtained using ERSFs using Formula (5):

$$S_{i,\text{At}} = \left(\frac{N_{\text{key}}}{N_i} \right) S_{i,E} \tag{5}$$

where $S_{i,\text{At}}$ is the ARSF, N_{key} is the atomic density of the key element and N_i is the atomic density of element i. Atomic densities can be determined from the bulk density of the solid material.

4.3.3 | AMRSFs

AMRSFs provide a nearly complete correction for matrix effects, by consideration of all the contributing parameters. This is done by selecting a nominal average matrix material that must then be used consistently—the specific choice itself is otherwise relatively unimportant. The parameters of this nominal average material are determined or obtained from an appropriate database and used in Formula (6):

$$S_{i,\text{av}} = \left(\frac{N_{\text{av}} Q_{\text{av}} R_{\text{av}} \lambda_{\text{av}}}{N_i Q_i R_i \lambda_i} \right) S_{i,E} \tag{6}$$

where $S_{i,\text{av}}$ denotes the AMRSF and the subscript 'av' denotes parameters for the chosen average matrix material.

The recommended sources for the parameters in Formula (6) have changed significantly since the previous edition of this standard for several reasons, including: improved sources becoming available; the complexity of the methods previously described; and that some of the previous parameterisations could not be used for HAXPES systems. Several of these parameters can be sourced most easily and accurately from publicly available databases, such as the elastic scattering corrections, Q [17–21], the backscattering corrections for AES, R [22], and the inelastic mean free paths, λ [23–30].

4.4 | Annex B—Information on Uncertainty of the Analytical Results

Annex B discusses the sources of uncertainty for typical AES and XPS measurements. A brief discussion on the effect of the analysis volume on comparability between measurements has been added, primarily due to the proliferation of HAXPES, leading to more potential variation in x-ray energy between different measurements.

The uncertainty sources highlighted in this section are:

- Matrix effects, for which the correction factor may vary between 0.1 to 8 for AES and 0.3 to 3 for XPS [5, 31]

- Sample morphology, including both lateral and depth variations in composition

- Surface topography, because relative intensities of emitted electrons can change with roughness, particle size and so forth

- Radiation damage, which can be very significant in some AES experiments and can also be observed in XPS of some materials

- Ion-sputtering effects—this may cause surface roughening, and when compounds are analysed, sputtering may preferentially remove the different components of the sample at different rates, changing the composition

- Surface contamination, which may differentially attenuate the signal from electrons of different kinetic energies

- Analysis volume, because a sample may vary in composition both laterally and with depth, which will depend on the experimental geometry and excitation source used.

5 | Conclusion

Sensitivity factors are crucial to be able to obtain quantitative electron spectroscopy measurements—for these measurements to also be comparable, it is necessary to have a standardised method for the generation of sensitivity factor libraries. It is also important that the types of sensitivity factors used for various measurements are understood and that the differences between sensitivity factor libraries, such as to what extent they account for matrix factors, are clearly defined. The revised standard ISO 18118:2024 has been updated to address recent developments both in theory and instrumentation within the field of electron spectroscopies, as well as being simplified to make the generation and use of appropriate sensitivity factors more accessible to the increasing audience of electron spectroscopy users. This standard is available online from the ISO website (https://www.iso.org/) or through national standards bodies. The use of sensitivity factors in both AES and XPS is a routine requirement to obtain useful, quantitative analyses, and standards such as this one should continue to provide clear, unambiguous direction on the practicalities associated with electron spectroscopy experiments.

Data Availability Statement

Data sharing is not applicable as no new data were generated.

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