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Surface chemical analysis — Auger electron spectroscopy and X-ray photoelectron spectroscopy — Methods used to determine peak intensities and information required when reporting results

Analyse chimique des surfaces — Spectroscopie des électrons Auger et spectroscopie de photoélectrons par rayons X — Méthodes utilisées pour la détermination de l'intensité des pics et informations requises pour l'expression des résultats

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Foreword

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This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

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This third edition cancels and replaces the second edition (ISO 20903:2011), which has been technically revised. The main changes compared to the previous edition are as follows:

— subclause 6.3 has been replaced to include modern methods for dealing with co-existing chemical states;

— minor editorial changes have been introduced for clarity.

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.

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Introduction

An important feature of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) is the ability to obtain a quantitative analysis of the surface region (≈1 nm to 10 nm) of a solid sample. Such an analysis requires the determination of the intensities of spectral components.

There are several methods of peak-intensity measurement that are applicable to AES and XPS. In practice, the choice of method will depend upon the type of sample being analysed, the capabilities of the instrumentation used, and the methods of data acquisition and treatment available.

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Surface chemical analysis — Auger electron spectroscopy and X-ray photoelectron spectroscopy — Methods used to determine peak intensities and information required when reporting results

1 Scope

This document specifies the necessary information required in a report of analytical results based on measurements of the intensities of peaks in Auger electron and X-ray photoelectron spectra. Information on methods for the measurement of peak intensities and on uncertainties of derived peak areas is also provided.

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*

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3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115-1 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Symbols and abbreviated terms

A peak area

AES Auger electron spectroscopy

b number of channels over which intensities are averaged to obtain a baseline

eV electron volts

n number of channels in a spectrum

XPS X-ray photoelectron spectroscopy

y_i number of counts in the ith channel of a spectrum

ΔE channel width (in electron volts)

Δt dwell time per channel (in seconds)

$\sigma(A)$ standard deviation of calculated peak area

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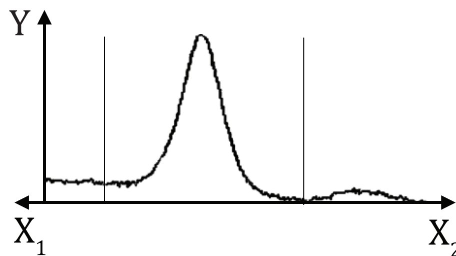
5 Methods for peak-intensity determination — direct spectrum

5.1 General

Figure 1 a) shows a portion of an X-ray photoelectron spectrum in which intensity is plotted as a function of kinetic energy increasing to the right or of binding energy increasing to the left. The intensity is plotted usually in units of counts or sometimes in units of counts per second. Intensities may also be plotted as a digitized voltage; this procedure is often used when the intensity of an Auger differential spectrum is obtained from an analogue detection system. Energies are commonly expressed in electron volts.



a) XPS peak whose intensity is to be measured, the vertical lines indicate suitable limits for the construction of a Shirley background

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b) XPS peak shown in a) following the subtraction of the inelastic background (the shaded area indicates the peak area to be measured)

Key

X_1 binding energy (eV)

X_2 kinetic energy (eV)

Y intensity

Figure 1 — Illustration of procedure involved in the determination of the intensity of a single peak in an X-ray photoelectron spectrum (as described in **5.2** and **5.3**).

The intensity of a single peak in an X-ray photoelectron spectrum can be measured by using the procedure described in 5.2 and 5.3 or by using computer software as described in 5.4. The measurement of peak intensities for a spectrum containing overlapping peaks is described in 5.5. Information on the uncertainty of a measured peak area for a single peak is given in 5.6.

The intensity of a single peak in a direct Auger-electron spectrum can be measured by following the procedure described in 5.2 and 5.3, although it may be necessary first to subtract a secondary-electron background[1][2]. Alternatively, computer software can be used to measure the peak intensity as described in 5.4.

In some cases, the peak of interest may be superimposed on a sloping background. This background could arise from multiple inelastic scattering of Auger electrons or photoelectrons of initially high energy, from multiple inelastic scattering of primary electrons (in AES), or from photoemission by bremsstrahlung radiation (for XPS with an unmonochromated X-ray source). It may be necessary (e.g. with use of the Tougaard inelastic background described in 5.2) or desirable to subtract this background from the spectrum in the vicinity of the peak before proceeding with the peak-intensity measurements described in 5.2 to 5.5. This subtraction can usually be performed by fitting a straight line to the sloping

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background at energies between about 10 eV and 30 eV above the peak of interest, extrapolating this line to lower energies, and subtracting the spectral intensities from this linear background. If a linear function is judged to be invalid for describing the sloping background over the spectral range of interest (e.g. for modelling the background of scattered primary electrons in AES), an exponential function can be utilized[3].

5.2 Selection and subtraction of an inelastic background

An appropriate inelastic background shall be selected and subtracted from the measured spectrum. Three types of inelastic background are in common use:

a) linear background;

b) integral or Shirley background[4];

c) Tougaard background[5][6][7] and Werner background[8][9], based on physical models describing inelastic electron scattering in solids.

Information on procedures and software for determining the Shirley, Tougaard and Werner backgrounds is given in the scientific literature[4]-[13] and ISO/TR 18392[14].

From a practical viewpoint, the selection of a particular background will depend on (a) whether the relevant software is conveniently available and (b) the type of sample analysed. For insulators, the linear background is often satisfactory, while the Shirley background is often employed for metals. While these two backgrounds are simple and convenient to apply, the limits of these two backgrounds (the starting and ending points on the energy scale) should be chosen carefully so that the background is as nearly continuous as possible with the spectrum in the region of overlap.

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Tougaard's approach, in particular, for background determination and subtraction[5][6][7] has found favour over the Shirley background because it describes the physics of the inelastic-scattering process more accurately[15][16]. The Tougaard and the Werner approaches have a further advantage in that they are insensitive to the precise positions of the starting and ending energy points providing they are clearly in the spectral region well away from the main peak of interest (typically starting at an energy at least 10 eV higher than that of the peak of interest and ending at an energy at least 50 eV lower). This requirement is a disadvantage in that spectra have to be recorded over a larger energy range than if the linear or Shirley background is used.

As an example, Figure 1 a) shows an XPS peak whose intensity is to be measured. Vertical lines have been drawn to indicate suitable limits for use of the Shirley background. The spectrum after subtraction of this background is shown on an expanded energy scale in Figure 1 b). For clarity of display, the zero of the intensity scale in Figure 1 b) has been placed at 2 % of the ordinate axis. The end points in Figure 1 b) are at the same positions as those in Figure 1 a).

Averaging over neighbouring channels may be helpful in defining the signal level at the selected end points, thus improving the precision of peak-height or peak-area measurement. The sets of points to be averaged may be located inside or outside of the chosen end points or may be symmetrically placed about the end points. The end points shall be chosen to be sufficiently far from the peak so that the averaging process does not include significant peak intensity. Harrison and Hazell[17] have derived an expression for the estimated uncertainty in a peak-area measurement (see 5.6) and have shown that a large contribution to this uncertainty comes from uncertainties arising from the choice of end points and the intensities at these end points.

Smoothing of a spectrum, using a Savitzky-Golay[18] convolution with a width less than 50 % of the full width at half-maximum intensity of the peak, may improve the precision of a peak-height determination. However, smoothing should be avoided for peak-area determination since it cannot improve the precision and, if over-done, will distort the spectrum.

Annex B gives information on the choice of suitable energy limits for the determination of peak intensities or areas in XPS spectra.

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5.3 Measurement of peak intensity

5.3.1 Measurement of peak height

A peak height is determined (i) by direct measurement from a chart output using a ruler, (ii) by using computer software to obtain the intensity difference from the baseline to the peak maximum or (iii) by using computer software to fit an appropriate analytical peak shape (Gaussian, Lorentzian or a mixture of the two[10][11][12]) to the experimental spectrum (that is, the group of data points defining the peak of interest). The length of the vertical line with arrows in Figure 1 b) is a measure of the peak height in units defined by the intensity scale (either counts or counts per second).

The use of peak heights in subsequent data processing has advantages arising from the speed of processing and the ease with which this method can be applied with many instruments. However, using peak height as a measurement of intensity has several disadvantages: (i) it is insensitive to peak-shape changes arising from the complex chemistry of an element, (ii) it ignores spectral intensity from secondary features in the spectrum (such as satellite peaks) and (iii) the measured height is very dependent on the choice of inelastic background.

Instruments should be operated with settings chosen to avoid significant nonlinearities in the intensity scales[19]; alternatively, corrections should be made for counting losses due to the finite dead time of the counting electronics[19]. Spectra should be corrected for the intensity-energy response function of the instrument before peak heights are measured[20]. Further information is provided in Annex A.

5.3.2 Measurement of peak area

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All modern AES and XPS instruments have computer software that can be used to determine the peak area (e.g. by summing the counts above the inelastic background or by numerical integration). Alternatively, the peak area can be calculated from the parameters obtained after fitting the peak with an appropriate analytical function[10][11][12]. The shaded area in Figure 1 b) illustrates the peak area obtained from integration of the peak defined by the end points and subtraction of the inelastic background in Figure 1 a).

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The measured intensity in each channel of an AES or XPS spectrum depends on a number of instrumental parameters and settings[20]. For specified instrumental conditions, the measured intensity for each channel can be simply expressed as a number of counts (or counts/second) per eV; Annex A provides further information. A peak area (or peak intensity) is then expressed as the total number of counts (or counts/second) for a specified energy region of summation or integration.

Instruments should be operated with settings chosen to avoid significant nonlinearities in the intensity scales[19]; alternatively, corrections should be made for counting losses due to the finite dead time of the counting electronics[19]. Spectra should be corrected for the intensity-energy response function of the instrument before peak areas are measured[20]. Further information is provided in Annex A.

In practical AES and XPS, an analyst generally wishes to compare intensities of peaks that were measured with identical instrumental settings [e.g. analyser mode, pass energy (for the constant-analyser-energy mode) and retarding ratio (for the constant-retarding-ratio mode)] but differences in certain other settings (e.g. different energy channel widths or different dwell times). The analyst often will not know certain parameters that affect the absolute intensities of measured peaks (see Annex A) since only relative intensities are needed for practical analyses. In such cases, peak intensities can be determined from simple summations or integrations of measured spectra for the particular conditions, and these intensities are often expressed in units of counts·eV or counts·eV/second. Corrections of peak areas can then be made as needed for different channel widths and dwell times. Annex A provides further information.

The use of peak intensities derived from measurements of peak areas has some clear advantages over the use of measurements of peak heights. First, account can be taken in the measurement of peak areas of any chemical changes that result in reduced peak height and increased peak width (compared to the corresponding values for the elemental solid). Second, any satellite intensity can be easily included in the measurement of peak area. However, the uncertainty of a peak-area measurement may increase for

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complex specimen materials with many elemental components that could have overlapping spectral features (as described in 5.5). In such cases, the value of the derived peak area may depend on the choice and placement of the inelastic background function in 5.2.

5.4 Measurement of a peak intensity with computer software

Computer software can be used to fit a selected analytical function describing the shape of a peak and another function describing the inelastic background to a measured spectrum[10][11][12]. This process essentially combines the steps described in 5.2 and 5.3 into a single procedure. Prior removal of X-ray satellites from XPS spectra recorded using unmonochromated radiation may be necessary if they contribute intensity in the region of the spectrum defined by the integration limits (see 5.2).

Peak shapes in AES may be more complex than those in XPS, and analytical functions used to fit XPS spectra may then be unsatisfactory for similar fits of AES spectra. In such cases, peak intensities can be derived using spectral addition/subtraction, least-squares analysis with suitable reference spectra, or principal-component analysis[21].

5.5 Measurement of peak intensities for a spectrum with overlapping peaks

In many practical cases, a spectrum in the region of interest may consist of two or more overlapping peaks because of the presence of chemically shifted peaks from the same element, the presence of peaks from multiple elements or the presence of peaks arising from X-ray satellites. As an example, Figure 2 shows an X-ray photoelectron spectrum for an oxidized vanadium foil that was measured with an unmonochromated Al Kα X-ray source. In this spectrum, the more intense peaks arise from vanadium 2p and oxygen 1s photoelectrons; there is also a weaker peak due to oxygen 1s photoelectrons excited by the Al $K\alpha_{3,4}$ satellite line that overlaps the vanadium 2p peaks. Correct identification of chemical state requires calibration of the instrumental binding-energy scale[22] and, for non-conductive specimens, use of charge-control or charge-correction procedures[23].

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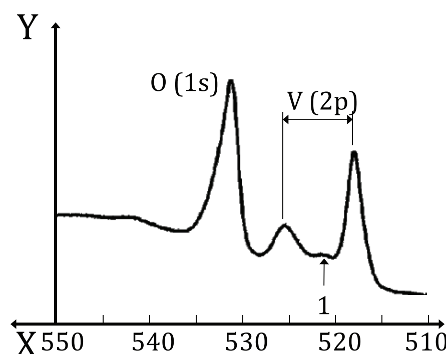
For a spectrum with overlapping peaks, intensities shall be measured from fits of analytical functions to a selected spectral region[10][11][12]. Peak heights and peak areas can be determined from values of the parameters found for each peak.



Key

X binding energy (eV)

Y intensity

1 O(1s) X-ray satellites

Figure 2 — X-ray photoelectron spectrum measured with unmonochromated Al Kα X-rays for an oxidized vanadium foil

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