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Surface chemical analysis — Electron spectroscopies — Minimum reporting requirements for peak fitting in X-ray photoelectron spectroscopy

Analyse chimique des surfaces — Spectroscopie d'électrons — Exigences minimales pour le rapport d'ajustement de pic en spectroscopie de photoélectrons X

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

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Introduction

X-ray photoelectron spectra produced from the surfaces of many materials are complex and frequently consist of overlapping or unresolved peaks. The lack of resolution can be due to instrumental parameters, the X-ray line width, the natural line width of the transition, or a contribution from all of these. It is frequently necessary, therefore, to use a mathematical procedure to fit some or all of the peaks in XPS spectra in order to establish the position and intensity of each of the component peaks contained within each peak envelope. This is often the first step in the identification of the chemical states which give rise to the overall peak envelope and the quantification of each chemical state present. The analyst must therefore have confidence in both the position (to establish the chemical state) and the peak area (to allow accurate quantification) of each peak reported following peak fitting.

The mathematical procedure applies model peak and background shapes, the defining parameters of which are varied in order to obtain the optimum fit to the experimental data. Most commonly, the model peak shapes are some combination of Gaussian and Lorentzian functions.

Many of the parameters that should be reported following peak fitting are those that define these curves. Other factors are those which are selected by the analyst to ensure that the peak-fitting process results in a chemically meaningful description of the peak envelope or to minimize the time taken for the fitting process. These include parameters that the analyst

— chooses to fix at a constant value during the fitting process,

— defines as a range of values over which the parameter can vary during the fitting process, and

— mathematically links the value of a parameter to that of another parameter

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Peak fitting is a purely mathematical process from which quantitative and qualitative results are obtained which may be related to the chemistry of the surface being analysed. The results will depend upon the analyst's choice of parameters and constraints and this choice will influence the interpretive conclusions that the analyst reaches from the peak-fitting results. For that reason, it is important that these parameters and constraints are reported. This will allow another analyst to

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— assess the reliability and validity of the conclusions drawn from the peak fitting exercise,

— repeat the peak-fitting process on the same data set and obtain the same results, and

— repeat the peak-fitting process on data which has been obtained from a similar sample and be in a position to make a valid comparison of the data sets.

Most software packages which have been designed for use with XPS data contain a peak-fitting routine. These routines allow the operator to select appropriate parameters and apply the desired constraints to the fitting process. It is highly likely that the software will provide an output which reports these and usually includes the facility to copy them for use with another spectrum. Such an output will make reporting the appropriate parameters particularly convenient.

This International Standard is not intended to provide instructions for either fitting XPS peaks or for linking the outcome of a peak-fitting routine to the chemistry of the surface being analysed. Indeed, in the examples shown in this International Standard, it is not claimed that the fitting shown is the only way fitting can be done or even that the examples show the optimum peak fitting method. The examples serve to illustrate the purpose of this International Standard.

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Surface chemical analysis — Electron spectroscopies — Minimum reporting requirements for peak fitting in X-ray photoelectron spectroscopy

1 Scope

The purpose of this International Standard is to define how peak fitting and the results of peak fitting in X-ray photoelectron spectroscopy shall be reported. It is applicable to the fitting of a single spectrum or to a set of related spectra, as might be acquired, for example, during a depth profile measurement. This International Standard provides a list of those parameters which shall be reported if either reproducible peak fitting is to be achieved or a number of spectra are to be fitted and the fitted spectra compared. This International Standard does not provide instructions for peak fitting nor the procedures which should be adopted.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
background, inelastic
intensity distribution in the spectrum for particles originally at one energy but which are emitted at lower energies due to one or more inelastic scattering processes

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[SOURCE: ISO 18115-1, 4.50]

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2.2
background, Shirley
background calculated to fit the measured spectrum at points at higher and lower kinetic energy than the peak or peaks of interest such that the background contribution at a given kinetic energy is in a fixed proportion to the total peak area above that background for higher kinetic energies.

[SOURCE: ISO 18115-1:2010, 4.54]

2.3
background, Tougaard
intensity distribution obtained from a model for the differential inelastic scattering cross section with respect to energy loss and the three-dimensional distribution of the emitting atoms in the surface region

[SOURCE: ISO 18115-1:2010, 4.57]

2.4
pass energy
mean kinetic energy of the detected particles in the energy dispersive portion of the energy analyser

[SOURCE: ISO 18115-1:2010, 4.325]

2.5
peak fitting
procedure whereby a spectrum, generated by peak synthesis, is adjusted to match a measured spectrum

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2.6
peak synthesis
procedure whereby a synthetic spectrum is generated using either model or experimental peak shapes in which the number of peaks, peak shapes, peak widths, peak positions, peak intensities, and background shape and intensity are adjusted for peak fitting

[SOURCE: ISO 18115-1:2010, 4.329]

2.7
residual spectrum
difference between the experimentally acquired spectrum and the synthesized spectrum

3 Symbols and abbreviated terms

3.1 Abbreviated terms

BE binding energy

eV electron volt

FWHM full width at half maximum

L/G ratio of the intensity of the Lorentzian component to the Gaussian component of a pseudo Voigt peak consisting of the sum of a Gaussian and a Lorentzian function

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PE pass energy

XPS X-ray photoelectron spectroscopy

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3.2 Symbols

χ^2_{min} value of χ^2 after the minimization process has been completed

χ^2 chi square

σ_a standard deviation for the binding energy of a peak

c_i total number of counts in channel i prior to background subtraction

i channel number in a spectrum

M number of independently adjustable parameters used in the fitting process

N number of energy channels in the part of the spectrum being fitted

r_i spectrum residual in channel i (obtained from the total number of counts, not counts per second)

Δa energy by which a peak position is changed (from the position which results in the minimum chi square value) during the process of estimating the uncertainty in the peak position

Δh amount by which a peak height is changed (from the value which results in the minimum chi square value) during the process of estimating the uncertainty in the peak intensity

Δw amount by which a peak width is changed (from the value which results in the minimum chi square value) during the process of estimating the uncertainty in the peak width

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4 Reporting of relevant data acquisition parameters

4.1 General

This Clause applies to the instrumental parameters that can affect the shape of a peak, peak envelope, or background in a spectrum. Such parameters will therefore affect the parameters that define the fitted spectrum and so they shall be reported.

4.2 Spectrometer

There are instrumental and acquisition parameters that influence the shape of the peaks in an XPS spectrum. These parameters can also affect the results of any peak fitting activity and shall be reported.

In addition, the relationship between instrumental parameters and the results obtained from peak fitting may depend upon the precise design of instrument used. An example of this is the relationship between the pass energy used to acquire the data and the resolution of the peaks in the spectrum. It is therefore necessary to report the manufacturer and the model of the instrumentation used. This can either be the model name (including a version identifier, if appropriate) of the complete spectrometer or the model names of the key components.

4.3 Instrument resolution

The parameters that can affect the results of a subsequent peak fitting shall be reported. These include any of the following factors which can affect the resolution of the spectrometer:

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— chosen pass energy;

— if the spectrometer has adjustable slits which control instrument resolution at the entrance and/or exit of the analyser, the settings for those slits;

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— if the spectrometer has a transfer lens having an adjustable angular acceptance and/or an adjustable field of view aperture, the settings of each of these can affect the resulting resolution and shall therefore be reported.

Clearly, the above parameters do not form part of the peak-fitting process and the relationship between the values reported and the shape of the spectrum may be dependent upon the spectrometer used. The value of each of these parameters shall be reported so that a meaningful comparison can be made between peak-fitted data obtained from different spectrometers can be made.

4.4 Detector

The type of detector employed in the spectrometer can have an effect upon the shape of the acquired spectrum. Common types of detector include multiple channel electron multipliers and channel plate detectors. The type of detector employed shall be reported. Instruments with channel plates or a large number of channel electron multipliers may be operated in either the “scanned mode” or the “snapshot mode” depending upon whether the median energy of the analyser changes during the spectrum acquisition (scanned) or whether it is constant (snapshot). The type of spectrum acquired shall be reported.

If the quality and reliability of the fitted spectrum is to be fully assessed, then there shall be some indication of the amplitude of the noise in the spectrum. The majority of XPS spectrometers use an electron multiplier connected to some form of pulse counting equipment. This means that the dominant form of noise in the spectrum is due to Poissonian statistics. Since this form of noise is purely statistical, it is only related to the number of counts in each of the channels of the spectrum. For the purposes of reporting peak fitting results, it is only necessary to report the number of counts in the channel that contains the maximum number of counts. It should be noted that if the data are transformed in some way (for example, by correcting for the transmission function of the instrument), then the data may not conform to Poissonian statistics.

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If the instrument used to acquire the spectra has multiple detectors, it is likely that the data have been unavoidably smoothed; this reduces the noise amplitude from that expected from Poisson statistics. The extent to which the noise amplitude is reduced depends upon the design of the spectrometer and the conditions chosen by the analyst to acquire the spectrum (for example, the energy difference between successive data points in relation to the energy difference between adjacent detectors). This will reduce the relative noise amplitude in the spectrum but reporting the number of counts in the peak maximum will provide an indication of the likely influence of noise upon the peak fitting process.

NOTE 1 It is the number of counts that is important here not the number of counts per second.

At high count rates, the output from electron multipliers will become nonlinear. This will affect the peak shape and influence the quality of the fitted spectrum. For the purposes of reporting peak-fitting results, it is only necessary to report the count rate in the channel that contains the maximum number of counts. A method for checking the linearity of a detector may be found in ISO 21270.

NOTE 2 It is the number of counts per second that is important here not the number of counts.

4.5 X-ray source

The type of X-ray source used to obtain the spectra shall be reported. This includes the nature of the anode (aluminium, magnesium, etc.) or X-ray energy and whether an X-ray monochromator was used. The type of X-ray source used will affect not only the shapes of the peaks being fitted but also the nature of any satellite peaks which might be present in the spectrum and which might need to be taken into account during the fitting process. Some monochromators have the ability to focus the X-ray beam in order to control the spot size and therefore, the analysis area. If such a monochromator is used, then the selected spot size shall be recorded because this might have an effect upon the resolution of the peaks.

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4.6 Element identity

The identity of the element (or elements) contributing to the peak envelope being fitted shall be reported.

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Often, doublet peaks are included within a single envelope and are part of a single peak-fitting process. In this case, it is not necessary to list the component doublet (e.g. reporting Si 2p would be sufficient). In some cases when the components of a doublet are widely separated, a fit may be applied to a single component. If this is the case, the identity of the fitted transition shall be reported.

4.7 Energy range in the spectrum

The energy window in the spectrum used for peak fitting shall be recorded.

4.8 Energy step size in spectrum

The number of data points present in the spectrum will affect the quality and reliability of the fitted spectrum. For this reason, the energy difference between adjacent energy channels shall be reported. This applies to both scanned and “snapshot” spectra.

4.9 Charge compensation

For the analysis of insulating samples, some form of charge compensation or static charge correction is usually required if a reliable spectrum is to be obtained. For example, this may be accomplished using a low-energy beam of electrons or a combination of electrons and low-energy ions. The type of charge compensation shall be reported along with some indication of the approach used for setting the conditions (for example, the identity of the spectral peak used and whether the settings were adjusted to optimize peak position, peak shape, or peak width). If the charge compensation causes a shift in the peak positions, the size of the shift shall be reported. If the spectrum has been corrected for this charge, shift the size and direction of the shift shall be reported. The identity of any peak used as a reference for charge compensation shall be reported along with its energy.

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5 Reporting of single-spectrum peak-fitting parameters

5.1 General

This Clause applies to the type of measurement that leads to the acquisition of individual spectra. A later Clause will apply to measurements that lead to multiple spectra, examples of which are depth profiles, line scans, and the type of images which have a spectrum at each pixel.

The Clause describes parameters which shall be reported together with any fitting constraints or linkages.

5.2 Background range

When peak-fitting is carried out on a spectrum, it is necessary to consider the background. The chosen background should extend beyond the peak envelope at both higher and lower binding energies. There are circumstances under which the choice of background range can severely affect the values calculated for the peak areas (for example, when there is an energy loss feature in the spectrum close to the peak being fitted). For this reason, the energy of each extreme of the fitted background shall be reported along with the type of averaging algorithm used (arithmetic average, polynomial fit, etc.) if this is known.

5.3 Background integration range

If the background contains significant noise, it might be necessary to take an average intensity over a range of energies at each end of the chosen background range. This defines more accurately the start and end positions of the background on the intensity axis. If background averaging has been used, then that shall be reported along with the energy range or number of data points from which the average has been calculated.

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A detailed explanation of how and why peak intensities depend upon the chosen limits for the background is given in Reference [3] and Reference [4]. Some of the factors involved here include the presence of energy-loss features and shake-up peaks and how the relative intensity of these features can depend upon the chemical state of the element.

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5.4 Background type

There are several types of background that may be used in XPS. It is beyond the scope of this International Standard to indicate when each type should be used under any given circumstance, but the one used by the analyst shall be reported. Examples of background types include linear, Shirley, Tougaard, etc. Other types of background exist including ones developed by instrument manufacturers or software designers. A Shirley background may be calculated using either an iterative or non-iterative method. The type of calculation shall be reported.

The choice of background type can have a major effect upon the quantification of the spectrum and even upon the relative quantification of the peaks within a given peak envelope. The background type chosen shall therefore be reported along with any adjustable parameters which have been used to define the background.

5.5 Application of a fitted background

A background may be fitted prior to the peak-fitting procedure and subtracted from the peak envelope; this will be termed the static approach. Alternatively, background fitting may be an iterative process which is applied during the peak fitting process; this will be termed the active approach. As this choice can affect the quantification of the spectrum, it shall be reported as either “static background fitting” or “active background fitting”.

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5.6 Setting the peak parameters

Each parameter of the peaks reported following the peak fitting procedure can be a result of the following:

- peak-fitting procedure alone when the parameter is left to vary freely during the optimization process;
- values fixed by the analyst;
- peak-fitting procedure constrained by the analyst such that each parameter can only fall within a range defined by the analyst;
- imposed correlation between parameters;
- initial values chosen by the analyst prior to the fitting procedure.

For the fitting of a given peak envelope, it may be that more than one or even all of the above may be used. The method used to arrive at the value of each of the parameters associated to each of the peaks employed shall be reported.

The particular set of parameters depends on the choice of the line shape employed. The parameters mentioned in the following subclauses are common to most of them.

5.7 Peak area and peak height

Peak fitting is often applied in order to obtain peak areas for the purpose of quantification. The area of each fitted peak shall be reported. The peak height is often the parameter that is optimized during the peak-fitting procedure. However, some software directly optimizes the value of the area. The particular choice shall be reported.

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5.8 Peak area and peak height ratios

When fitting a peak envelope which contains doublet peaks of known relative intensity and known separation, it can aid the peak-fitting process to constrain the peak fitting such that the correct relative intensity and peak separation are maintained. If such constraints have been applied, these shall be reported.

The correct relative intensity may be achieved by constraining either the peak-area ratio or the peak-height ratio during the fitting procedure. If either of these parameters are constrained, the constraint shall be reported.

5.9 Full width at half maximum

A constraint may be applied which forces the peak width of components of the fitted peak envelope to be equal. An example where this may be appropriate is in the fitting of a doublet peak. Alternatively, it may aid the fitting process if the peak width is constrained such that it can only take a value between two defined extremes. If either of these constraints has been applied, it shall be reported.

5.10 Peak shape

Most software packages calculate a Lorentz/Gauss (L/G) product, sum, convolution, or ratio for each of the fitted peaks when fitting peaks. Alternatively, the analyst can apply a fixed ratio or can force the software to use the same ratio for some or all of the peaks within the envelope being fitted (e.g. when fitting doublets). The Lorentz/Gauss ratio shall be reported along with any constraints or links applied by the analyst.

If some other method is used to describe the peak shape, the method and the values of any adjustable parameters shall be reported.

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