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

National foreword

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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*.

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

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

— 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.

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

[SOURCE: ISO 18115-1, 4.50]

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

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
PE	pass energy
XPS	X-ray photoelectron spectroscopy

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

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:

- 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;
- 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.

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.

4.6 Element identity

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

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.

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.

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.

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”.

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.

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.

5.11 Peak asymmetry parameters

Most software packages are able to calculate a peak asymmetry factor for each of the fitted peaks. Alternatively, the analyst can choose that the software does not apply such a factor or can force the software to use the same factor for some or all of the peaks within the envelope being fitted. The asymmetry factor shall be reported along with any constraints or links applied by the analyst.

5.12 The peak-fitting process

Peak fitting is an iterative process. There are many mathematical methods which can be used to accomplish peak fitting. Each method has its own set of advantages and disadvantages (involving, for example, speed of convergence, likelihood of reporting results from a false minimum, outcome depends upon starting conditions, etc.). Examples of fitting algorithms include Powell, Levenberg-Marquardt, and simplex. The method used shall be reported, if known or selectable from the software. The software used in the peak fitting-process shall be reported.

5.13 Residual spectrum

The residual spectrum shall be reported along with the spectrum as acquired and the fitted spectrum. The residual spectrum is the difference between the background-subtracted spectrum and the sum of all of the fitted peaks (the overall fitted envelope). The residual spectrum gives some indication of the quality of the fit. Some features in the residual spectrum, such as an oscillation which is greater in amplitude than the general noise in the residual spectrum, can indicate that an additional peak should be included in the fitted spectrum.

6 Multi-spectrum peak fitting

6.1 General

Some types of analysis require that the same region of the XPS spectrum be acquired many times and that peak fitting be applied to each instance of that region of the spectrum. Examples of the type of acquisition where this might be required include the following:

- depth profiles;
- line scans;
- images;
- angle-resolved measurements;
- temperature-programmed measurements.

In measurements of this type, peak-fitting parameters and background parameters shall be applied to each spectrum in the set. In the unlikely event that each spectrum in the set is fitted individually, then the parameters for each spectrum shall be reported. If, as is more usual in these circumstances, the parameters for a single or reference spectrum are derived and these are propagated through the data set, then the parameters for the reference spectrum shall be reported along with any constraints or linkages that are applied to the fitting of the remaining spectra. The analyst shall report the information specified in the following subclauses.

6.2 Peak fitting methods for multi-spectrum data sets

When data from measurements such as these are being processed, peak fitting will have to be applied to each spectrum in the series. If the analyst fits each peak in the set, then the parameters, as described in Clause 5, shall be reported for at least one of the spectra. Any differences in the chosen or calculated parameters or constraints applied during the fitting process used when fitting the other spectra shall also be reported.

More commonly, the analyst will fit one spectrum (the "reference spectrum") of the set and the remaining peaks will be fitted using an appropriate computational method. For the reference spectrum, those parameters described in Clause 5 shall be reported. If the parameters or constraints are not identical for each spectrum in the set, then the method used to propagate the constraints prior to fitting each spectrum shall be reported.

6.3 Propagation of constraints

In fitting peaks throughout the data set, each parameter may be treated in one of the following number of ways relative to the one spectrum that has been fitted.

a) Each spectrum may be fitted individually with a set of constraints selected by the analyst. While possible, this method is unlikely to be adopted.

b) Each of the spectra is fitted using parameters having the same constraints as those defined for the reference spectrum.

c) Different reference spectra may be used for different sections of the data set. The spectra in each section of the data set will have constraints which are determined by the appropriate reference spectrum.

d) The value of each parameter calculated when fitting the reference spectrum is used throughout. For example, the position of the peak may have been allowed some tolerance when fitting the reference spectrum but, in the fitting of subsequent spectra, the position of that peak is forced to be in the position calculated for the reference spectrum.

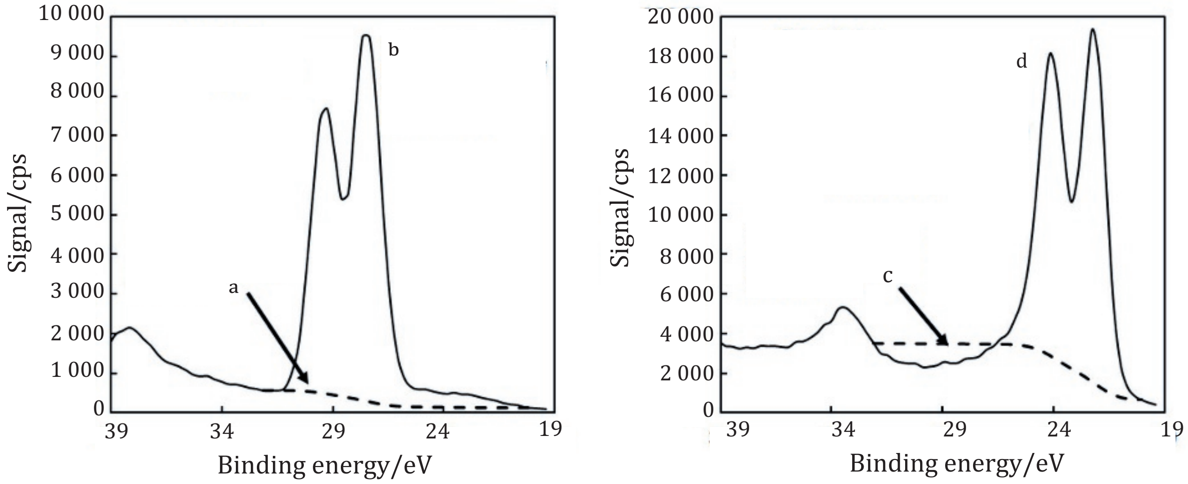
e) The value of each parameter calculated when fitting the reference spectrum is used throughout but a tolerance is applied to the subsequent spectra. For example, the position of a peak may have been allowed to have a value of $w \pm x$ eV when fitting the reference spectrum, a value of y eV was then calculated as the position of that peak. It may be that the analyst chooses to constrain the position of the peaks in the subsequent calculations to fall within a range of $y \pm z$ eV.

It may be that more than one of the above may be used in propagating constraints through a given set of spectra. The chosen method(s) of propagation of each of the constraints shall be reported.

An example of how the fitting of multi-spectrum data sets shall be reported is provided in Annex B.

6.4 Background propagation

It may be inappropriate to use the same parameters for the calculation of the background for each spectrum in a set of spectra. Figure 1 shows an example of such a data set. In this example, a Shirley background has been applied to each spectrum using the same spectral range and other parameters. At the beginning of the profile, the peaks are at a binding energy characteristic of tantalum oxide and at the end of the profile the peaks can be found at a binding energy appropriate to elemental tantalum. The fact that the peaks have shifted means that the background is in the wrong place for the spectra derived from elemental tantalum. This will have an obvious effect upon the quantification of data which include these spectra.



Key

— spectrum

– – background

a Fitted background is appropriate for this level.

b Ta 4f from oxide layer (first level of the set of depth profile data).

c Fitted background is not appropriate for this level.

d Ta 4f from metal substrate (last level of the set of depth profile data).

NOTE In each case, a Shirley background has been applied to the spectrum.

Figure 1 — Ta 4f spectra from the first and last levels of a sputter depth profile of tantalum oxide on tantalum

It is clear that some means of adjusting or calculating the background parameters for each spectrum in the set should be used to avoid the type of problem illustrated here. The means used shall be reported.

7 Satellite subtraction

Satellite subtraction is only required if an X-ray source is used without a monochromator. The X-ray spectrum from such a source will consist of peaks at a number of different energies. Photons at each of these energies will produce peaks in the XPS spectrum. As the spectra from the sources commonly used in XPS are well known, it is often possible to calculate and subtract the contribution made by the less intense components of the X-ray spectrum to the XPS spectrum. Such a subtraction can be helpful to the analyst prior to calculating a peak fit. If this operation is applied to the data, it shall be reported. In addition, as the details of the X-ray spectrum from a given anode depend upon the kinetic energy of the electrons as they strike the anode, this parameter shall also be reported.

8 Doublet subtraction

When the peak being fitted is due to various chemical states of an element and the transition giving rise to these peaks is a doublet, it is possible to mathematically subtract the contribution of the less intense component of the doublet from the overall peak envelope. This can have the effect of simplifying the spectrum and can make the presence of weak peaks in the envelope more obvious to the analyst. If this procedure is used prior to peak fitting, the parameters used shall be reported. As a minimum, the following parameters shall be reported:

- Background type and value of any adjustable parameters required to define the background. It is likely that the definition of the background will be identical to those reported in accordance with 5.2, 5.3, and 5.4. If this is the case, it is unnecessary to report these parameters again.
- Peak area ratio which is assumed in the calculation.
- Peak separation assumed in the calculation.
- If the peaks are assumed to have differing widths, this shall be reported.

9 Spectrum deconvolution

Mathematical procedures exist that allow better energy resolution spectra to be calculated from data acquired at a lower resolution. This is achieved by deconvolving the contributions of the spectrometer to the measured spectrum. This can have the advantage of increasing acquisition speed to result in data having high resolution accompanied by a satisfactory signal to noise ratio. If this procedure is used prior to peak fitting, the deconvolution method and the relevant parameters shall be reported.

10 Fit quality and uncertainties

10.1 General

Sufficient information shall be reported to allow an analyst to assess the quality of the fitted spectrum and the magnitude of the errors that might be present in the derived parameters, peak position and peak area, for example. Uncertainties shall be reported from the peak-fitting software, if available, otherwise they shall be calculated. The methods described in Annex D may be used if they are appropriate to the instrument from which the data were collected.

10.2 Fit quality

The residual spectrum (see 5.13) provides a good indication of the quality of the fitted spectrum and shall be reported if available but the statistical methods provide a more quantitative indication of the quality. Different software systems provide different measures of the goodness of fit. Whatever is provided shall be clearly stated.

The reduced chi square is a very useful parameter for judging the quality of a fitted spectrum and shall be reported. The definition of this quantity is given in D.1.2.

10.3 Uncertainty in the reported binding energies

The estimate of the uncertainty in the calculated peak positions shall be reported. If such an estimate is not provided with the software being used, a method for calculating the uncertainty, provided in D.1.4, may be used. An alternative method may be used to calculate the uncertainties, if preferred.

10.4 Uncertainty in the peak areas

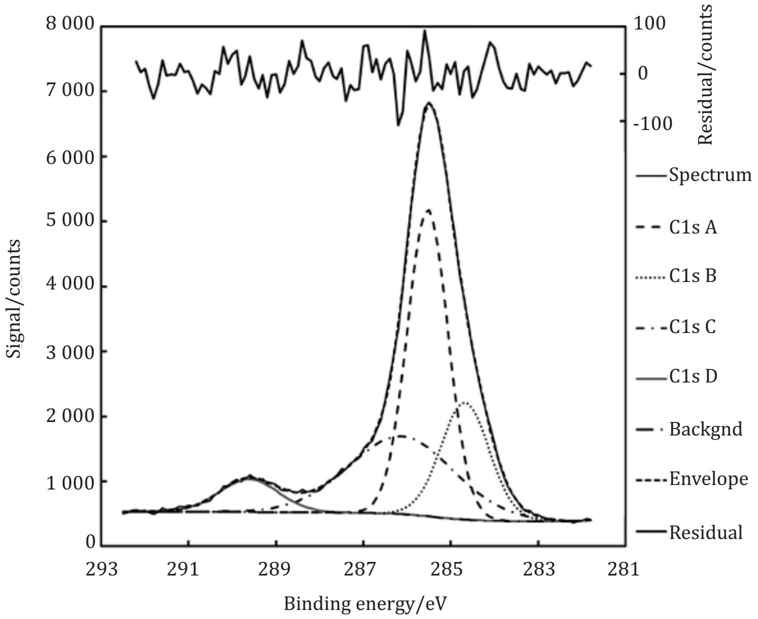
The uncertainty in the calculated peak areas shall be reported. If such an estimate is not provided with the software being used, a method for calculating the uncertainty is provided in D.1.5 and may be used.

Annex A
(informative)

Example of reporting peak fitting

Figure A.1 shows the C 1s region of an XPS spectrum from a sample of Al_2O_3 having a thin layer of carbonaceous contamination at its surface. It shows the acquired spectrum along with the fitted peaks from carbon in four chemical states. The Shirley background is also shown along with the residual spectrum.

It should be noted that the parameters reported for the fitting of this spectrum have been chosen to illustrate the requirements of this International Standard. They do not imply a recommended method for fitting the spectrum.



NOTE The peaks used in the fitting process are shown along with the calculated background and the residual. Data provided by Thermo Fisher Scientific.

Figure A.1 — A C 1s spectrum from a sample of Al_2O_3 having a thin layer of carbonaceous contamination at its surface

Table A.1 and Table A.2 report all of the parameters described in this International Standard. Table A.1 lists the parameters that relate to the whole spectrum while Table A.2 shows the parameters and peak-fitting constraints applied to individual peaks within the spectrum. These tables were taken from the output of the Thermo Scientific Avantage data system. The format was modified and abbreviated to suit this International Standard. The format of these tables represents a satisfactory method for reporting peak-fitting parameters but any format that reports the parameters clearly and unambiguously may be used.

The data reported in Table A.1 are required when a single spectral region in an analysis is fitted. It is often the case that fitting is required for more than one spectral region in a given analysis. Many of the parameters in Table A.1 will apply to all spectral regions and it is necessary to report these only once. Only those parameters that are different for each spectral region need to be reported for each region.

These are likely to be the parameters under the subheadings “spectrum” and “background” and the value of chi square.

Table A.1 — Experimental conditions and parameters applied prior to peak fitting the spectrum shown in Figure A.1

Item	Clause	Reported value
Spectrometer		
Model	4.2	Thermo Scientific ESCALAB 250Xi
Spectrum type	4.2	Scanned
Adjustable slit/slit widths	4.3	No adjustable slits
Pass energy	4.3	20 eV
Detector type	4.4	six Channel electron multipliers
X-ray source		
Type	4.5	Al Kα
Monochromator used	4.5	Yes
X-ray spot size	4.5	500 µm
Spectrum		
Element identity	4.6	C 1s
Binding energy range	4.7	281,8 to 292,5 eV
Step size	4.8	0,1 eV
Maximum intensity	4.4	6,839 counts, 27 400 counts/s
Charge compensation		
Used	4.9	No
Spectrum shift	4.9	Not required
Background		
Type	5.5	Shirley iterated
Lower BE	5.2	281,8 eV
Higher BE	5.2	292,8 eV
Range for end point average	5.3	0,5 eV (at both high and low BE)
Application of fitted background	5.5	Calculated during fitting process
Fitting method		
Software used	5.12	Thermo Scientific Avantage version 5,926
Type	5.12	Powell
Peak shape model	5.10	Gauss-Lorentz
Reduced $\Delta\chi_1^2$ (See D.1.5 for definition)	10.2	0,75
Spectrum pre-processing		
Satellite subtraction	Clause 7	Not required
Doublet subtraction	Clause 8	Not applied
Spectrum deconvolution	Clause 9	Not applied

NOTE For convenience, a blank template is provided in Annex C for recording these parameters. This does not imply that the format shown is mandatory.

Table A.2 — Example of a peak table for the spectrum shown in Figure A.1 with the parameters calculated in the fitting process and the constraints applied during the fitting

Peak reference	Peak label[a]	Peak BE /eV	Standard deviation of the BE/eV[b]	Peak height /counts	Area (cps.eV)	Standard deviation of the area/%[b]	FWHM /eV	L/G Mix (%) product	Tail mix (%)	Tail height (%)	Tail exponent
A	C1s A	285,53	0,008	4,720	22,248	10	1,13	18	100	0	0
Constraints for peak A		[c]					0,5 to 3,5		fixed[d]	fixed[d]	fixed[d]
B	C1s B	284,67	0,03	1,804	10,104	6	1,34	18	100	0	0
Constraints for peak B								A*1[e]	fixed[d]	fixed[d]	fixed[d]
C	C1s C	286,12	0,03	1,198	14,548	5	2,91	18	100	0	0
Constraints for peak C								A*1[e]	fixed[d]	fixed[d]	fixed[d]
D	C1s D	289,62	0,02	506	3,451	3	1,63	18	100	0	0
Constraints for peak D								A*1[e]	fixed[d]	fixed[d]	fixed[d]

NOTE No template is provided for this table because the format used may be that which is available in the software used.

[a] It may be preferred that a chemical state may be included in the peak label, for example the peak labelled C 1s D might have a label such as C 1s (O = C-O).

[b] The standard deviation of these parameters was calculated using the methods described in Annex D.

[c] If a cell in a constraint row is blank, this means that the parameter can take any value calculated by the fitting process.

[d] If the word “fixed” appears in a constraint cell, it means that the parameter was chosen by the analyst and was not changed during the fitting process. The “Tail” components in this table are used when peak asymmetry is to be included in the fitting process. In this example, if the tail mix is 100 %, then the fitted peak is forced to be symmetrical.

[e] The L/G Mix (%) of the C 1s B, C 1s C, and C 1s D peaks were forced to take a value equal to that of the L/G Mix (%) of the C 1s A peak.

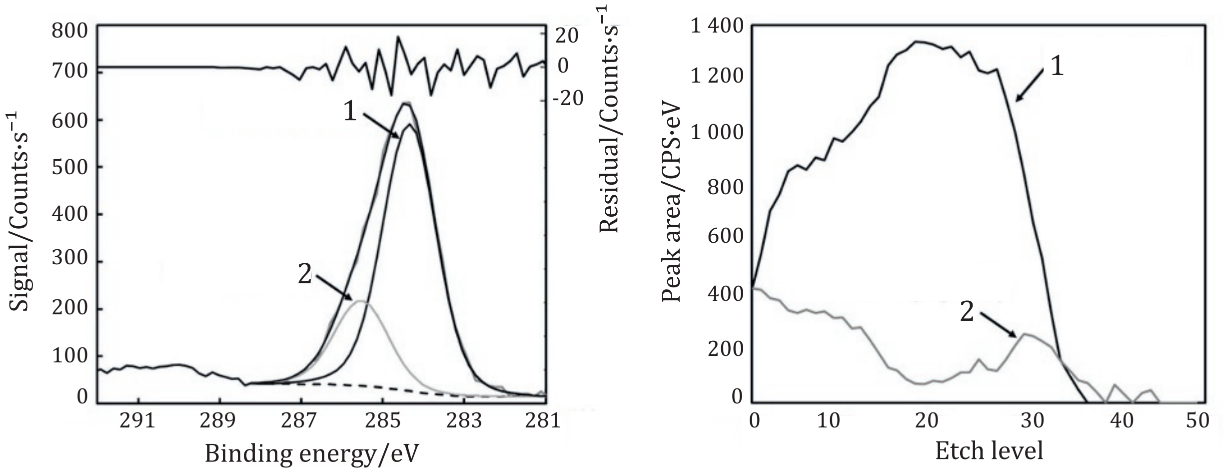
Annex B
(informative)

Reporting peak fitting for multi-level data sets

Many types of measurement with XPS require that a spectrum of a given element or elements be collected several times. An example of such a measurement is the acquisition of depth profile data. In many cases, it will be necessary to fit all of the peaks acquired in such an experiment or all peaks from a given element or elements. This Annex provides an example of how the peak fitting shall be reported under such circumstances. The format for this example was chosen for convenience. Other formats can be used if they are more easily produced from the software which is used to fit the peaks. The purpose of this Annex is to illustrate the way in which the peak-fitting procedure shall be reported it does not provide instructions or recommendations for the peak-fitting procedure. Other aspects of the experimental procedure may have to be reported which, for a depth profile, include the nature of the ion beam, beam current beam energy, rastered area, etch time per level, etc. Requirements for reporting these aspects of the experimental method do not fall within the scope of this International Standard.

The example used in this Annex is from a depth profile of a carbon-containing material on a substrate of silicon dioxide. For convenience, only the profile of carbon will be considered here. As is normally the case when acquiring a depth profile, a spectrum was measured from each of the relevant elements, the sample is then etched using an energetic beam of ions and the spectrum acquisition is repeated. The cycle is then repeated until the required depth is reached, spectra are then available from each of a number of levels in the sample. In order to extract the required information from the data, it is often necessary to fit the peaks for some or all of the elements at every level in the data set.

Figure B.1 shows a fitted C 1s spectrum from level 9 of a 50-level depth profile. This was used as a reference spectrum for fitting all of the C 1s spectra in the profile. The spectra were fitted with two peaks, labelled “C 1s (Low BE)” and “C 1s (High BE)”’. The areas of these peaks were then plotted as a depth profile against “Etch Level” in the same figure. The horizontal axis could be expressed in other units, such as “etch time” or “depth”; the units may be selected by the analyst.



Key

1	C 1s (low BE)
2	C 1s (high BE)

NOTE 1 Spectra were collected at each of the 50 levels (or depths) within the sample. The fitted C 1s spectrum is from level 9 which, for peak-fitting purposes, was treated as a reference spectrum. The peak-area profile was constructed from the fitted spectra from all 50 levels.

NOTE 2 Data provided by Thermo Fisher Scientific.

Figure B.1 — Example of a depth profile of a carbon-containing layer

In this case, the spectrum shown was fitted and used as a reference. The fitting for this spectrum shall be reported in the manner described in Clause 6 and illustrated in Annex D. This will not be repeated here.

If the values of the peak-fitting parameters are fixed or constrained when applied to the other peaks in the data set, then these shall be reported. A method for reporting this is illustrated in Table B.1.

Table B.1 — Example of a table which can be used to report the way in which constraints have been imposed upon the peak-fitting parameters in the construction of a depth profile

Number of levels in the data set	50	
Levels fitted	All	
Reference level	9	
Peak labels	**C 1s (Low BE)**	**C 1s (High BE)**
Peak binding energy in fitted reference level[a]	284,3 eV	285,5 eV
Constraint applied in other levels	284,3 eV Fixed	Constrained to be in the range 285,5 to 286,7 eV
Full width at half maximum intensity in the reference spectrum[a]	1,57 eV	1,57 eV
Full width at half maximum intensity in the reference spectrum	Constrained to be within the range 1,0 to 1,8 eV	Equal to the value for C 1s (Low BE)
L/G Mix/% in reference spectrum[a]	18,6	18,6

[a] These rows are optional if the equivalent of Table A.2 is reported.

Table B.1 *(continued)*

L/G Mix/% in other levels	18,6 Fixed to be equal to the value in the reference spectrum	18,6 Fixed to be equal to the value in the reference spectrum
[a] These rows are optional if the equivalent of Table A.2 is reported.		

Table B.1 lists those parameters that might change or have the potential to change according to the level being fitted. In this example, the peaks have been assumed to be symmetrical but if asymmetric peaks are fitted, the appropriate parameters shall be included in the report.

If the peaks from more than one element are fitted as part of the profile, a table such as Table B.1 shall be provided for each element whose peaks are fitted.

If a number of reference spectra from the same element is used for fitting different ranges within the experimental data, then a table such as Table B.1 shall be reported for each range within the profile.

In this example, a reference spectrum was taken from within the data set being analysed. The reporting requirements remain the same if a reference spectrum is chosen from a different data set.

Annex C
(informative)

Template for reporting peak fitting parameters

Item	**Reported value**
Spectrometer	
Model	
Spectrum type	
Adjustable slit/slit widths	
Pass Energy	
Detector type	
X-ray Source	
Type	
Monochromator used	
X-ray spot size	
Spectrum	
Element identity	
Binding energy range	
Step size	
Maximum Intensity	
Charge compensation	
Used	
Spectrum shift	
Background	
Type	
Lower BE	
Higher BE	

Item	**Reported value**
Range for end point average	
Application of fitted background	
Fitting method	
Software used	
Type	
Peak Shape Model	
Reduced $\Delta\chi_1^2$	
Spectrum pre-processing	
Satellite subtraction	
Doublet subtraction	
Spectrum deconvolution	

Annex D
(informative)

Statistical methods

D.1 Definitions and formulae

This Annex provides some of the definitions and formulae that may be helpful in applying a statistical analysis to a fitted spectrum. For a detailed description of these statistical techniques, Reference [5] may be consulted. These methods may only be applied if the measurement statistics follow a Poissonian distribution.

Other methods are available and may be used.

D.1.1 Chi square

Chi square is calculated as given in Formula (D.1):

$$\chi^2 = \sum_{i=1}^{N} \left[\frac{r_i^2}{c_i} \right] \tag{D.1}$$

where

N is the number of channels in the spectrum (i.e. the number of data points);

i is the channel number;

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

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

When fitting has been correctly completed, the value of chi square has been minimized and its value becomes $\chi^2_{\min}$.

D.1.2 Reduced chi square

Reduced chi square is calculated as given in Formula (D.2):

$$\text{Reduced } \chi^2 = \frac{\chi^2}{(N - M)} \tag{D.2}$$

where

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

M is the number of independently adjustable parameters used in the fitting process.

The term $N - M$ is known as the number of degrees of freedom.

D.1.3 Fit acceptability

If the fit is acceptable, then the value of reduced chi square will be close to unity. A large deviation from unity means that $\chi^2_{\min}$ is either too large or too small to be accounted for by random statistics. The deviation from unity which would indicate that factors other than random counting statistics are affecting the fit will depend upon the number of degrees of freedom. For example, if $N - M$ is 30 and the reduced chi square is outside the range 0,5 to 1,8, then it is extremely likely that factors other than counting statistics are affecting the quality of the peak fit. If $N - M$ is 200, then the range becomes 0,7 to 1,3. These values are meant to serve as a guide and are not rigorously derived. A more rigorous method is given in Reference [5].

If the reduced chi square is outside of the acceptable range, it may be because of the following:

a) model spectrum is incorrect or inappropriate; for example, a Gaussian peak shape might have been assumed when, in reality, it is asymmetric;

b) peak may have been omitted from the model spectrum;

c) there may be a “spike” in the measured spectrum;

d) it may be that the optimum fit has not been achieved.

D.1.4 Estimating the uncertainty in peak positions

Having obtained a minimum value for χ^2, as described above, the position of one of the fitted peaks in the spectrum shall be changed from the value that produced the minimum value of χ^2 by a small amount (Δa eV) and fixed in that position before running the peak-fitting routine again. This will result in a new value of χ^2 which differs from the original value by an amount $\Delta\chi^2$. The standard deviation for the binding energy of that peak in the same way is then given by Formula (D.3):

$$\sigma_a = \frac{\Delta a}{\sqrt{\Delta\chi^2}} \tag{D.3}$$

This procedure can be followed for each of the peaks in the given spectrum.

D.1.5 Estimating the uncertainty in peak areas

Peak areas are not generally used as fitting parameters since they are calculated from two parameters (peak height and peak width) both of which are used to fit the peak. Estimating the uncertainty in the peak areas is therefore more complex than estimating uncertainties in the peak positions. It can be accomplished as follows.

a) Having obtained a value for $\chi^2_{\min}$, as described above, the height of one of the fitted peaks in the spectrum shall be changed from the value that produced $\chi^2_{\min}$ (h_0) by a small amount (Δh counts, where Δh is about 2 % of the original peak height), fixed at that value and the width of the peak fixed at w_0 before running the peak-fitting routine again. This will produce a new value of χ^2, χ^2_1. The value of $\chi^2_1 - \chi^2_{\min}$ is now expressed as $\Delta\chi^2_1$.

b) Similarly, the width of one of the fitted peaks in the spectrum shall be changed from the value that produced $\chi^2_{\min}$ (w_0) by a small amount (Δw counts, where Δw is about 2 % of the original peak width), fixed at that value and the height of the peak fixed at h_0 before running the peak-fitting routine again. This will produce a new value of χ^2, χ^2_2. The value of $\chi^2_2 - \chi^2_{\min}$ is now expressed as $\Delta\chi^2_2$.

c) Both the height and the width are changed (by Δh and Δw, respectively), fixed at these values and the fitting routine run again. This produces a new value of χ^2, χ^2_3 from which $\Delta\chi^2_3$ shall be derived.

d) Repeat the above procedure for each of the fitted peaks. The relative standard deviation in peak area can be calculated for each peak using the following Formula (D.4):

$$\frac{\sigma_A}{A} = \frac{pw_0 + qh_0}{w_0 h_0 \left(aq^2 + bpq + cp^2\right)^{1/2}} \quad \text{(D.4)}$$

where

$$a = \frac{\Delta\chi_1^2}{\left(\Delta w\right)^2} \quad \text{(D.5)}$$

$$b = \frac{\Delta\chi_3^2 - \left(\Delta\chi_1^2 + \Delta\chi_2^2\right)}{\Delta w \Delta h} \quad \text{(D.6)}$$

$$c = \frac{\Delta\chi_2^2}{\left(\Delta h\right)^2} \quad \text{(D.7)}$$

$$p = 2aw_0 - bh_0 \quad \text{(D.8)}$$

$$q = 2ch_0 - bw_0 \quad \text{(D.9)}$$

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