
**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

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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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 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.

This International Standard is expected to have two main areas of application. First, it provides a description of methods that may be used in the determination of the intensity of a peak for an element in a given spectrum. Information is given on the origin of uncertainties in the processes involved, and on how these uncertainties may be reduced. Second, this International Standard specifies reporting requirements for the methods used for peak-intensity measurements so that other analysts may use published results with confidence.

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 International Standard 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 referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115, *Surface chemical analysis — Vocabulary*

3 Terms and definitions

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

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 i th channel of a spectrum

ΔE channel width (in electron volts)

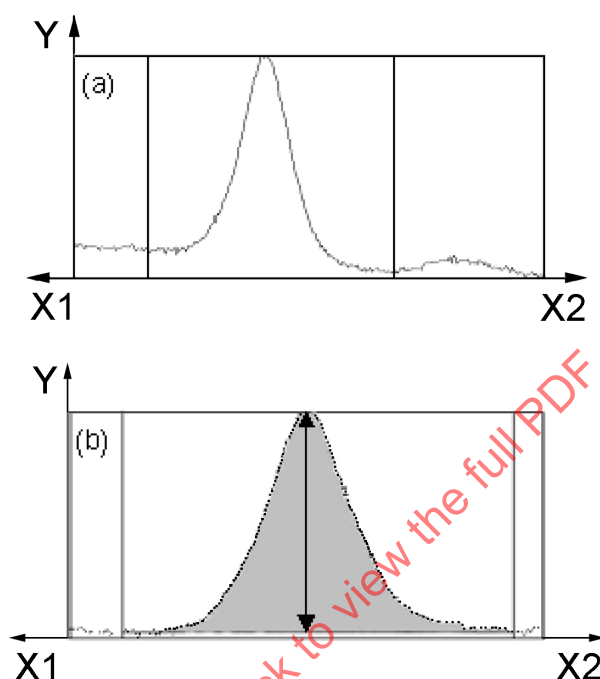
Δt dwell time per channel (in seconds)

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

5 Methods for peak-intensity determination — Direct spectrum

5.1 General

Figure 1a) 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 (e.g. for measurements of the intensity of an Auger differential spectrum from an analogue detection system). Energies are commonly expressed in electron volts.



Key

X1 binding energy (eV)
 X2 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 the following two subclauses (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 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

It is necessary to select an appropriate inelastic background and then to subtract this background 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 [5-7] 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.

Tougaard's approach, in particular, for background determination and subtraction [5-7] 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. It is important that the end points are 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 overdone, will distort the spectrum.

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 ^[10-12]) 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.

NOTE 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

Methods used in the past to determine the peak area have included: (i) tracing the peak shape onto paper, cutting the paper into the shape of the peak and weighing the paper, (ii) plotting the peak onto paper printed with a square grid pattern and counting the grid squares and (iii) using a planimeter, a mechanical device for making area measurements. However, most 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 ^[10-12]. 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).

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.

NOTE 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 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

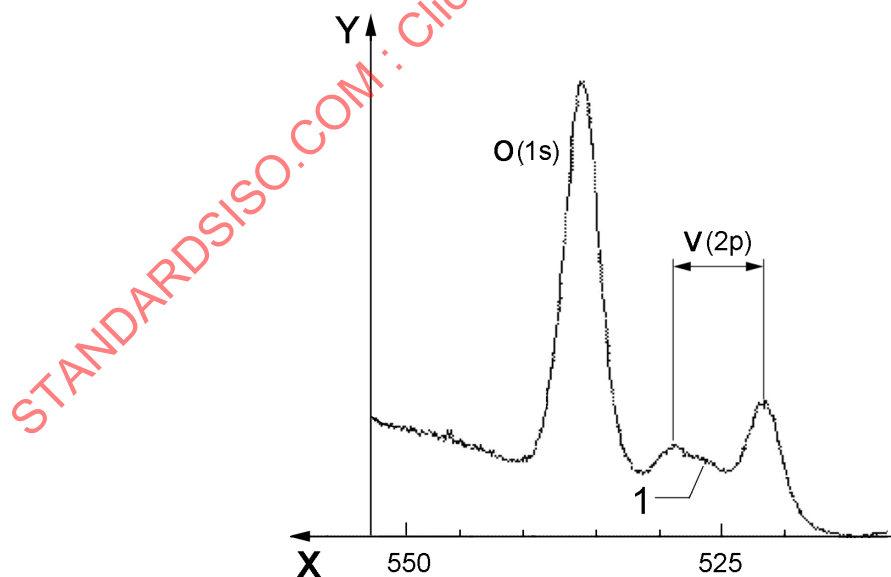
Computer software can be used to fit a selected analytical function describing the shape of a peak and another function describing the inelastic background to a measured spectrum [10-12]. This process essentially combines the steps described in 5.2 and 5.3 into a single procedure. Prior removal of X-ray 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 vanadium phosphate that was measured with an unmonochromated Al $K\alpha$ 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.

For a spectrum with overlapping peaks, it is necessary to measure intensities from fits of analytical functions to a selected spectral region [10-12]. 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 $K\alpha$ X-rays for vanadium phosphate

5.6 Uncertainty in measurement of peak area

The uncertainty in the result of a measurement (such as peak area) generally consists of several components that may be grouped into two categories according to the method used to estimate their numerical values [22]:

type A: those which are evaluated by statistical methods;

type B: those which are evaluated by other means.

The type A uncertainty indicates the component of uncertainty arising from a random effect while the type B uncertainty indicates the component of uncertainty arising from a systematic effect [22]. For measurements of peak areas, type A uncertainties can arise from counting statistics in the measurement of a spectrum and the fitting of an inelastic background to the spectrum (5.2). Type B uncertainties typically arise from the choice of the inelastic background function (5.2), the selection of end points (5.2), the choice of a function to describe a measured peak shape (5.3 and 5.4), the choice of computer software used for peak fitting [23] and the choice of initial parameter values in a non-linear least-squares fitting algorithm. The total uncertainty of a measurement can be obtained from the standard deviation (for the type A uncertainties) and an evaluation of the type B uncertainties [22].

The standard deviation, $\sigma(A)$, of the measured peak area, A , of a single peak measured in counts-eV/second is given by the following expression [17]:

$$\sigma(A) = \left(\frac{\Delta E}{\Delta t} \right) \left[\left(\sum_{i=2}^{n-1} y_i \right) + \frac{(n-2)^2(y_1 + y_n)}{4} \right]^{0,5} \quad (1)$$

where ΔE is the channel width (or energy step) in the spectrum (in eV), Δt is the dwell time per channel (in seconds), n is the number of channels in the spectrum and y_i is the number of counts in the i th channel. If the peak area is measured in counts-eV, $\sigma(A)$ from Equation (1) should be multiplied by Δt .

Equation (1) includes contributions from statistical noise in the experimental spectrum and from the uncertainty arising from placement of the baseline [the final term in Equation (1)], the latter being particularly significant for noisy spectra. The latter uncertainty can be reduced as explained in 5.2, in which case $\sigma(A)$ becomes:

$$\sigma(A) = \left(\frac{\Delta E}{\Delta t} \right) \left[\left(\sum_{i=2}^{n-1} y_i \right) + \frac{(n-2)^2(y_1 + y_n)}{4b} \right]^{0,5} \quad (2)$$

where b is the number of channels adjacent to the end points for which intensities are averaged to obtain the baseline. The final term in Equation (2) will usually be larger than the previous term, in which case $\sigma(A)$ will be reduced by approximately $b^{0,5}$ over the value obtained from Equation (1) [17].

The determination of uncertainties in peak areas for a spectrum with overlapping peaks is more complex than for the case of a single peak. The type B uncertainties may be larger than the type A uncertainties, particularly if there is a high degree of peak overlap and if assumptions have to be made concerning the inelastic background function and the function describing the peak shape. Information on type A and type B uncertainties can be found in the scientific literature [17, 24-28].

6 Methods for peak intensity determination — Auger-electron differential spectrum

6.1 General

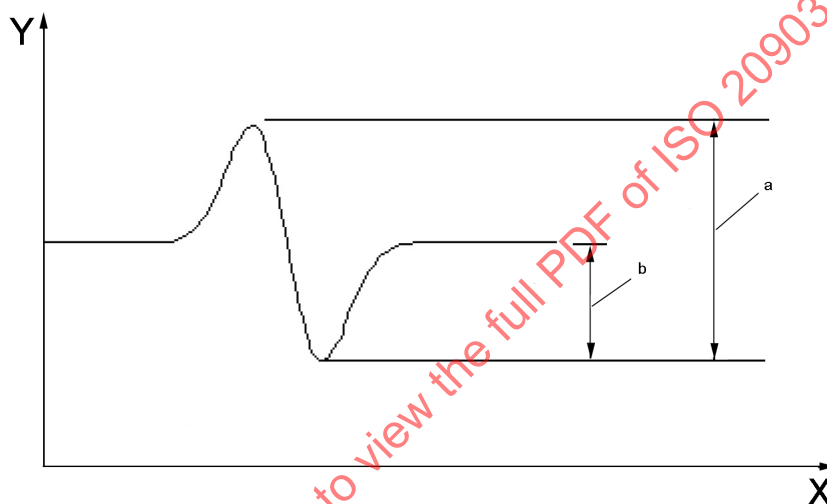
In Auger electron spectroscopy, spectra are often displayed in the differential mode in which the first derivative of the direct spectrum is plotted as a function of kinetic energy. If the direct spectrum is recorded as intensity in counts versus energy in electron volts, the intensity in the differential spectrum will be in units of counts per electron volt.

6.2 Measurement of Auger-electron differential intensity

Two methods, illustrated in Figure 3, are commonly used to measure peak intensity of an Auger-electron differential spectrum:

- peak-to-peak intensity (measured from the positive to the negative excursions in a differential spectrum);
- peak-to-background intensity (measured from the negative excursion to the background on the high-kinetic-energy side of the spectral feature).

Measurements of these intensities were generally made electronically in early commercial AES instruments but numerical methods for differentiation are now also employed [18]. The measurements of peak-to-peak or peak-to-background intensities can be made rapidly, and are therefore useful in, for example, depth-profiling studies.



Key

X kinetic energy (eV)

Y intensity

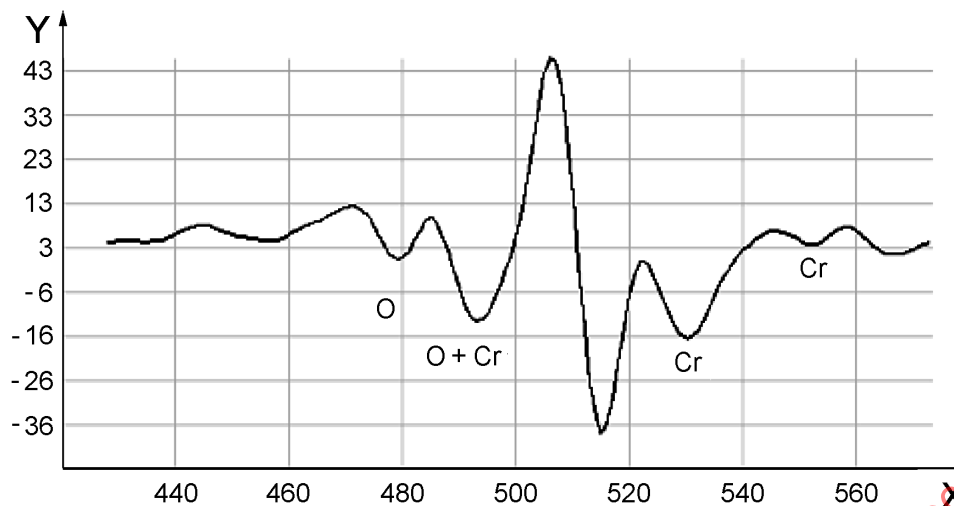
a Peak-to-peak.

b Peak-to-background.

Figure 3 — Schematic diagram of an Auger-electron differential spectrum indicating measurements of peak-to-peak and peak-to-background intensities

6.3 Uncertainties in measurement of Auger-electron differential intensity

Auger-electron lineshapes in direct spectra are generally more complex than XPS lineshapes, and these lineshapes may change appreciably with change of chemical state [29]. As a result, peak-to-peak and peak-to-background intensities in AES differential spectra can change significantly with chemical state. Compositions derived from AES differential spectra may therefore have larger uncertainties than the compositions obtained from direct spectra in XPS. Additional complications can arise from energy shifts of Auger peaks (e.g. in the vicinity of an interface due to different chemical states or to different amounts of surface charge) and with overlapping peaks from different elements. Figure 4 is an example of an AES differential spectrum with overlapping features due to chromium and oxygen. In such cases, elemental intensities may be derived from spectral addition/subtraction, least-squares analysis with elemental or compound spectra, factor analysis or principal-component analysis [21]. Seah *et al.* have reviewed problems involved in the analysis of AES differential spectra and, for quantitative analysis using the differential spectrum, recommend numerical broadening to reduce the effects of peak-shape changes [30].

**Key**

X kinetic energy (eV)
Y intensity

Figure 4 — Auger-electron differential spectrum of oxidized chromium showing overlapping peaks due to chromium and oxygen

7 Reporting of methods used to measure peak intensities

7.1 General requirements

The analyst shall report the algorithms used for any processing of a spectrum (e.g. smoothing) prior to the intensity measurement as well as those used for the intensity measurement in a report of the analysis. If a sloping background was subtracted from a spectrum prior to further processing (as described in 5.1), the functional form of the background and how it was determined shall be reported. The analyst shall report the channel width for the spectrum.

7.2 Methods used to determine peak intensities in direct spectra

7.2.1 Intensity measurement for a single peak, as described in 5.2 and 5.3

The analyst shall report the type of inelastic background utilized (5.2). If a linear or Shirley background was used, information shall be provided on the selected limits and whether intensities were averaged in some manner at these end points. If intensities were averaged, the analyst shall identify the number of data channels that were averaged and their location with respect to the end points. If a straight line was fitted to the intensities of two groups of data channels, the energy ranges of the two groups of channels shall be specified.

If the Tougaard or Werner background was used, the energy range of the spectrum that was analysed shall be specified. The morphological model and values of all parameters used in the analysis shall also be reported.

The analyst shall specify whether a peak height or a peak area was determined, and how the value was determined (5.3).

7.2.2 Intensity measurements from peak fitting, as described in 5.4 and 5.5

The analyst shall report the analytical functions used to describe peak shapes (e.g. Gaussian, Lorentzian and various combination functions [10-12, 23]), as well as the inelastic background, the energy interval over which a fit was made, the extent to which derived peak parameters depended on initial estimates of these values, and any constraints on peak parameters. The analyst shall report values of the peak parameters. The reported intensities may be peak areas or peak heights. The analyst shall report derived uncertainties or estimates of uncertainties of peak areas or peak heights [25].

7.3 Methods used to obtain and determine peak intensities in Auger-electron differential spectra

7.3.1 Method used to obtain differential spectra

The analyst shall report the method used to obtain the differential spectrum. If the differential spectrum was acquired by the phase-sensitive-detection method, the analyst shall specify the frequency of the modulation, the waveform of the modulation (e.g. sinusoidal or square-wave), the peak-to-peak amplitude of the modulation (as the corresponding electron energy in eV) and whether the modulation was applied to the sample or the analyser. If the differential spectrum was acquired by a numerical method, the analyst shall report the numerical algorithm and the parameters of that algorithm.

7.3.2 Method used to determine peak intensities, as described in 6.2

The analyst shall report whether peak-to-peak or peak-to-background intensities were measured. Information shall be provided on whether intensities were determined by an electronic system of the instrument or by a numerical method. The analyst shall report the numerical algorithm, if used, and the source of any reference spectra.

Annex A (informative)

Instrumental effects on measured intensities

Two types of instrumental effect are described that affect measured Auger-electron and X-ray photoelectron spectra. First, it is desirable (for simplicity) that instrumental settings be chosen so that observed intensities for the spectral regions of interest are linearly dependent on the incident beam current (for AES) or the incident X-ray flux (for XPS) on the sample. Otherwise, the intensity measurements should be corrected for the dead-time counting losses in the electronics ^[19].

The second type of instrumental effect is the varying intensity response of the electron spectrometer (consisting generally of the analyser, lens system, apertures and detector) for electrons of different energies from the sample ^[31]. In general, the intensity-energy response of the spectrometer will be different depending on its various settings (e.g. analyser operated in the constant-analyser-energy or constant-retarding-ratio mode, lens voltages and aperture sizes), possible local effects (imperfect alignment of the sample, stray fields and unwanted electrons from other sources), ageing of the detector (with resulting reductions in detector efficiency and possible variations in efficiency as a function of electron energy) and possible instrumental misalignments resulting from additions or modifications of components, bakeouts, etc. The intensity-energy response may thus vary with time. In order to ensure that meaningful comparisons can be made of intensities measured at different times or of intensities measured on different instruments, the instrumental intensity scale should be calibrated ^[20, 32]. Such calibrations will also minimize the need to re-determine relative sensitivity factors ^[33] as a result of any instrumental changes. A simpler procedure can be utilized, however, to evaluate the repeatability and constancy of the intensity scale with time ^[34, 35].

If the intensity scale of an electron spectrometer has been calibrated, it is then possible to express measured AES or XPS intensities in absolute units [i.e. the number of electrons per unit solid angle per eV per incident electron per unit time (in AES) or the number of electrons per unit solid angle per eV per incident photon per unit time (in XPS)] ^[20]. Thus, integrations over the whole energy spectrum and the whole solid angle of emission give, for a calibrated spectrometer, the total number of electrons emitted per incident electron (in AES) or per incident photon (in XPS). For AES, this ratio is the total electron yield (the sum of the conventionally defined secondary-electron and backscattered-electron yields), and is dimensionless (i.e. a number).

In practical XPS, the incident flux of X-rays on the sample area viewed by the analyser is generally unknown. For many AES and XPS applications, the analyst will not generally know or need to know the solid angle of acceptance of the spectrometer, the range of electron energies passed by the analyser for a given channel for the chosen settings, or the absolute detection efficiency. It is then convenient to express spectral intensities more simply as the number of counts (or counts per second) recorded in each channel for an instrument with digital signal electronics for specified instrumental operating conditions and measurement time or, equivalently, the measured current for an instrument with analogue signal electronics, again for specified instrumental operating conditions. It is often desirable, however, to determine the intensity at the maximum of a specified AES or XPS peak (for a specified primary-beam current in AES or for a specified operating power of the X-ray source in XPS) for specified spectrometer settings in order to assess the performance of an AES or XPS instrument ^[36, 37].