INTERNATIONAL STANDARD

ISO 19668

First edition
2017-08

Surface chemical analysis — X-ray photoelectron spectroscopy — Estimating and reporting detection limits for elements in homogeneous materials

Analyse chimique des surfaces — Spectroscopie de photoélectrons par rayons X — Estimation et production de rapports sur les limites de détection des éléments contenus dans les matériaux homogènes

Reference number
ISO 19668:2017(E)

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Foreword

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

Introduction

X-ray photoelectron spectroscopy (XPS) is a technique widely employed to measure the chemical composition of material surfaces. In many applications, it is used to either confirm or deny the presence of an elemental species at a surface. In either case, it is important to understand the minimal concentration of the element that can be detected by XPS under the measurement conditions either to provide an assessment of confidence in a result or to understand how the measurement conditions should be changed to achieve the required detection limit.

This document provides a straightforward approach to calculating detection limits in X-ray photoelectron spectroscopy from experimental data in common analytical situations. It also provides informative annexes which allow the uncertainty in the calculated detection limit to be determined (see Annex A) and describe how the XPS detection limit is defined (see Annex B). Example data and calculations are provided in Annex C. Annex D contains useful conversions and references which describe how detection limits may be estimated for an X-ray photoelectron spectrometer in the absence of any data except that from a reference material such as clean silver.

These calculations are of critical importance because the technique is routinely used to measure the concentration of elements, which are present in low concentrations at a material surface, and knowledge of the limit of detection provides a statement of confidence when no element can be detected. Furthermore, if a particular detection limit is required, it permits the analyst to calculate the acquisition time required to achieve the specified limit of detection.

Surface chemical analysis — X-ray photoelectron spectroscopy — Estimating and reporting detection limits for elements in homogeneous materials

1 Scope

This document specifies a procedure by which elemental detection limits in X-ray photoelectron spectroscopy (XPS) can be estimated from data for a particular sample in common analytical situations and reported. This document is applicable to homogeneous materials and is not applicable if the depth distribution of elements is inhomogeneous within the information depth of the technique.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

ISO 18115-2, *Surface chemical analysis — Vocabulary — Part 2: Terms used in scanning-probe microscopy*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115-1 and ISO 18115-2 and the following apply.

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

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

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

3.1
reference element
chemical element present in the sample for which a peak area and relative composition can be measured

3.2
specified element
chemical element for which the detection limit calculation is being undertaken

4 Symbols and abbreviated terms

A_i	summed intensity of the photoelectron line of element *i*, counts or cps
A_C	critical level of detection for a peak in summed intensity, counts or cps
A_D	minimal detectable summed intensity for a peak at the required level of confidence
AMRSF	average matrix relative sensitivity factor
a_m	coefficients of order *m* in a polynomial equation

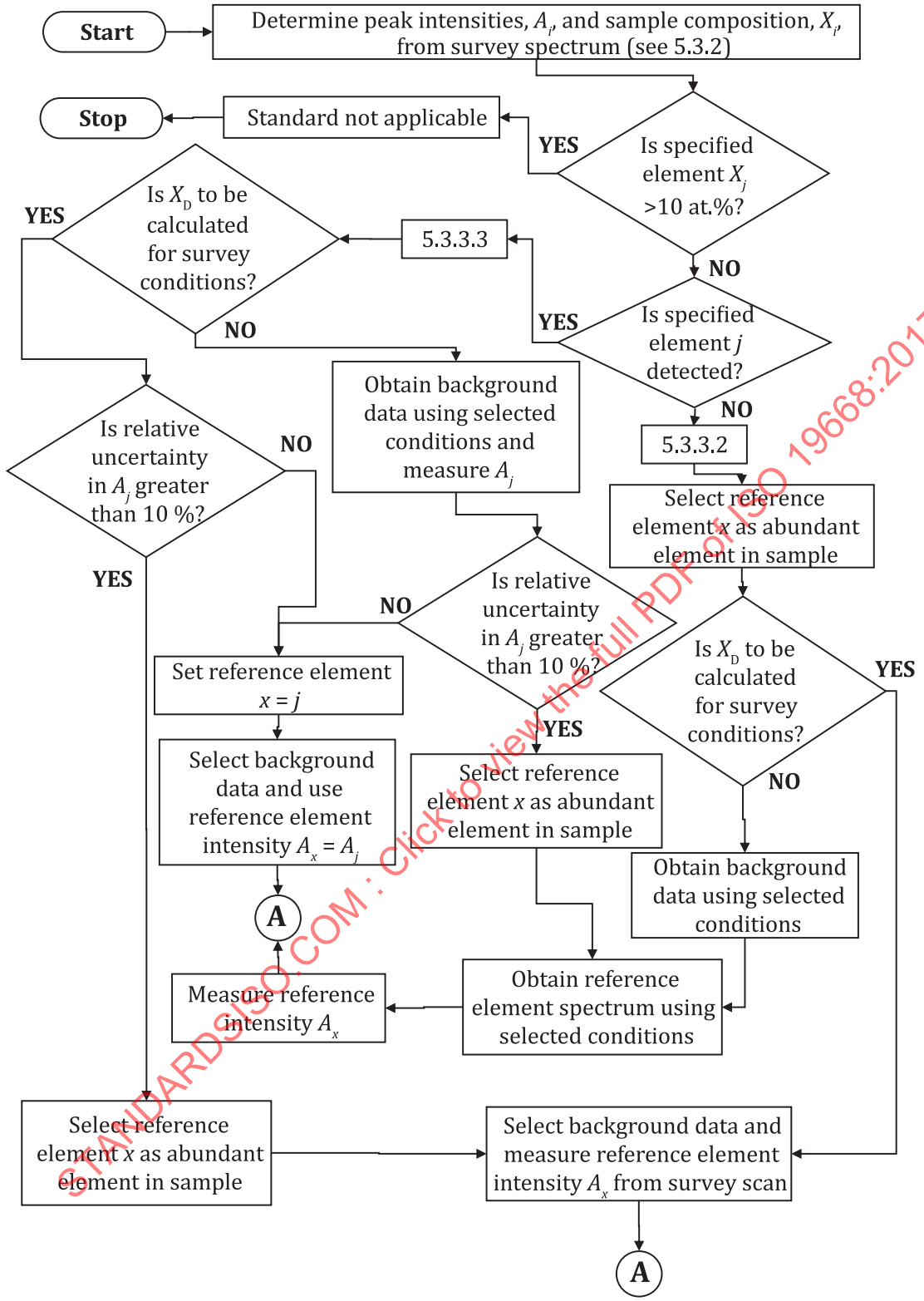
at.%	atomic percent concentration
α	average emission angle of electrons relative to the surface normal of the sample
$B(E)$	function of E describing background, counts or cps
BE	binding energy
b	number of data points that define the background under a peak
c	number of data points from b that are used in a summed intensity measurement
cps	counts per second
d	diameter of the atoms of the specified element
$\delta_{A(x)}$	relative uncertainty of peak intensity, A_x
δ_S	relative uncertainty of the detection limit, S
$\delta_{\sigma(B)}$	relative uncertainty of the standard deviation of the background σ_B
$\delta_{X(D)}$	relative uncertainty of the detection limit, X_D
E	numerical value of either BE or KE, eV
E_j	numerical value of either BE or KE of the photoelectron peak used to detect element j, eV
eV	electron volts
ε	step size in spectrum, eV
F	factor by which the acquisition time should be changed to achieve target detection limit
FWHM	full width at half maximum
G	goodness of fit
G_{min}	minimized value of G
Γ_D	XPS detection limit of a thin overlayer of the specified element expressed as areic density
$I(E)$	function of E describing intensity in a spectrum
i	element within the sample
j	element for which the detection limit is to be estimated
k	coverage factor
λ	inelastic mean free path of electrons with kinetic energy E_j in the sample
KE	kinetic energy
M	number of terms, excluding the constant term, in a polynomial description of B
m	index in a general polynomial equation with integer values 0 to M
N	number of data points in background spectrum
n	data point indicator with integer values 1 to N

q	factor to account for data smoothing introduced by electron detectors
θ_D	XPS detection limit of a thin overlayer of the specified element expressed in monolayers
$R(E)$	function of E describing the difference between I and B, counts or cps
RSF	elemental relative sensitivity factor
S_i	RSF of the photoelectron line used to measure the concentration of element i
σ_A	standard deviation of a summed intensity measurement
σ_B	standard deviation of I in background region
$T(E)$	factor that transforms $I(E)$ to have units of counts
t_D	XPS detection limit of a thin overlayer of the specified element expressed as a thickness
W_i	FWHM in eV of the photoelectron line used to detect element i
x	element used as a photoelectron intensity reference
X_i	atomic fraction of element i expressed in units of at.%
X_D	minimal detectable concentration of an element expressed in units of at.%
X_T	target XPS detection limit
XPS	X-ray photoelectron spectroscopy
y	number of data points from b that solely describe the peak

5 Calculating and reporting detection limits from XPS data

5.1 General

This clause provides a step-by-step procedure for the calculation of a detection limit for a specified element from XPS data. The data should cover the binding energy (BE) region in which a photoelectron peak is expected from the specified element for which the detection limit is to be calculated. The element may be below detectable levels or present at low concentrations; slightly different procedures will be used in each case. These procedures are described in 5.3.3.2 and 5.3.3.3, respectively. Various simplifying approximations are used in this document to enable the calculations to be performed in a practical manner. The typical uncertainty in the calculated XPS detection limits using this procedure is between 10 % and 25 %, which is sufficient for practical XPS analysis. A flow chart describing the steps required for the collection of data is provided in Figure 1, and a flow chart describing the steps required to calculate XPS detection limits is provided in Figure 2.



NOTE Point "A" connects to the flow chart in Figure 2.

Figure 1 — Flow chart describing steps in data collection for estimating XPS detection limits

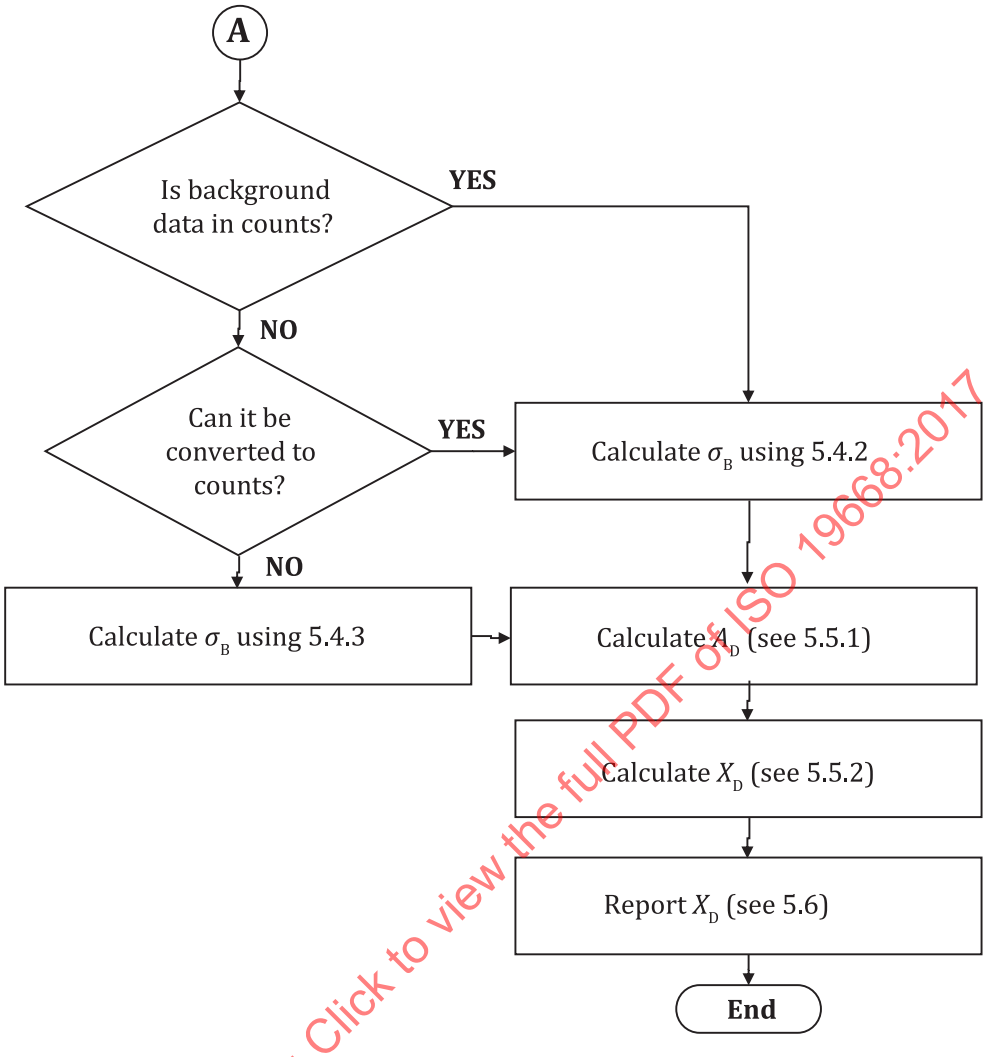


Figure 2 — Flow chart describing the steps in estimating XPS detection limits

5.2 Required data

The procedure requires knowledge of the relative sensitivity factors (RSFs), S_i, for photoelectron peaks of all elements, i, detected in the sample and the RSF, S_j, for the relevant photoelectron peak of the specified element, j. The BE or kinetic energy (KE) for the relevant photoelectron peak of the specified element, E_j, shall also be known to within 10 eV.

5.3 XPS measurements

5.3.1 General

The procedure requires knowledge of the chemical composition of the sample, as determined by XPS, as well as a spectrum which spans the BE of the photoelectron peak of the element for which the detection limit is to be calculated. If no peak for the specified element is observed, then an additional spectrum of an element that is present may be required.

5.3.2 Composition of the sample

Acquire a survey scan and identify all detectable elements. The summed intensities, A_i, of these elements shall be measured either from the survey scan or from individual, narrow spectra of all detectable elements identified. The summed intensities shall be converted into a composition using the

experimentally determined RSFs for those elements or through the use of an appropriate transmission function correction and average matrix relative sensitivity factors (AMRSFs) to obtain X_i. If the element, j, for which the detection limit is to be calculated is observed in the sample, it shall have a concentration, X_j, less than 10 at.%, and preferably less than 1 at.%.

NOTE 1 Guidance for XPS analysis, peak intensity determination and the use of RSFs can be found in References [1], [3] and [4].

NOTE 2 If no transmission function correction is used, then the RSFs for the specific operating mode of the instrument used for measuring the composition is applied here.

5.3.3 Spectra for detection limit calculation

5.3.3.1 General

The spectrum used for the detection limit calculation shall be at, or close to, the expected BE position of the photoelectron line for the specified element j. At least 20 data points in the background region of the spectrum are required and shall be selected from the spectral data as specified in 5.3.3.2 and 5.3.3.3. These selected data are termed "the background data" in the following. The background data should contain no sharp spectral features from any elements in the sample. In some situations, it is also necessary to have a reference spectrum of an element that is present in the sample. If the specified element is not detected in the survey scan, proceed to 5.3.3.2, otherwise proceed to 5.3.3.3.

5.3.3.2 Specified element is not detected in the sample

If the detection limits are to be calculated for the experimental conditions used for the survey scan (see 5.3.2), a reference element, x, present in the survey scan shall be selected. The reference element shall have an intense photoelectron peak that is as close as possible in BE to the peak position of the specified element, j. Determine the summed intensity, A_x, of the photoelectron peak of reference element x from the survey scan. The background data shall be selected from the survey scan and extend evenly above and below the expected position for the peak of element j.

If the detection limits are to be calculated from data acquired under different experimental conditions to those used for the survey scan (see 5.3.2), acquire a spectrum using these conditions and extending evenly above and below the expected position for the peak of element j. This shall be the background data. Select a reference element, x, present in the survey scan. The reference element shall have an intense photoelectron peak that is as close as possible in BE to the peak position of the specified element, j. Acquire a spectrum of this peak using identical experimental conditions to the background data. Determine the summed intensity, A_x, of the photoelectron peak of reference element x from this spectrum.

NOTE 1 Element x is normally the most abundant element in the sample.

NOTE 2 C.1 provides two examples of this case.

5.3.3.3 Specified element is detected in the sample

If the detection limits are to be calculated for the experimental conditions used for the survey scan (see 5.3.2), select the background data from a region of the spectrum at lower BE (higher KE) than the peak. Determine the summed intensity, A_j. If the peak for element j is sufficiently intense, such that the relative uncertainty in A_j, its summed intensity measurement, is less than 10 %, it shall be used as the reference element x and A_x shall be equal to A_j. If the uncertainty is greater than 10 %, then a reference element x shall be selected. The reference element shall have an intense photoelectron peak that is as close as possible in BE to the peak position of the specified element, j. Determine the summed intensity, A_x, of the photoelectron peak of reference element x.

If the detection limits are to be calculated from data acquired under different experimental conditions to those used for the survey scan, a spectrum using these conditions shall be acquired extending evenly above and below the position for the peak of element j. The energy range shall be wide enough that

more than 20 data points can be selected as the background data from a region of the spectrum at lower BE (higher KE) than the peak. Determine the summed intensity, A_j. If the peak for element j is sufficiently intense, such that the relative uncertainty in A_j, its summed intensity measurement, is less than 10 %, it shall be used as the reference element x and A_x shall be equal to A_j. If the uncertainty is greater than 10 %, then a reference element x shall be selected. The reference element shall have an intense photoelectron peak that is as close as possible in BE to the peak position of the specified element, j. Acquire a spectrum of this peak using identical experimental conditions to the background data. Determine the summed intensity, A_x, of the photoelectron peak of reference element x from this spectrum.

NOTE 1 A.2 provides a method for estimating the uncertainty in summed intensity measurement.

NOTE 2 C.2 provides an example of this case.

5.4 Calculation of background noise

5.4.1 General

This subclause describes a method to estimate the background noise in the spectrum from the background data selected in 5.3.3. If the data are in counts or can be converted into counts by a known factor or function, proceed to 5.4.2. The method described in 5.4.3 may be used in all cases.

NOTE The method in 5.4.3 requires significantly more effort and time than the method in 5.4.2.

5.4.2 Standard deviation of intensity from counts

When the data are in counts, or can be converted into counts through a known factor or function, the standard deviation of the background intensity may be calculated by assuming Poisson statistics as the square root of the average intensity in counts following Formula (1):

$$\sigma_B = \sqrt{\frac{\sum_{n=1}^{N}\left[T(E_n)I(E_n)\right]}{\sum_{n=1}^{N}\left[T(E_n)\right]^2}} \quad (1)$$

where

σ_B is the average standard deviation of I in background region;

$I(E_n)$ is the intensity at E_n;

$T(E_n)$ is the factor or function to change $I(E_n)$ to have units of counts;

E_n is the energy for point n in the background region;

N is the number of data points in background spectrum;

n is the data point indicator with integer values 1 to N.

NOTE 1 If the data are in counts, then $T(E_n) = 1$ for all E_n.

NOTE 2 If the data are in counts per second (cps), then $T(E_n)$ is the product of dwell time per point and number of scans for all E_n.

NOTE 3 If the data $I(E_n)$ have been transformed by a transmission function, then $T(E_n)$ is the scaled transmission function which will return the data into units of counts. Transmission functions will normally convert data into cps, so for this purpose $T(E_n)$ will normally be the product of the transmission function, the dwell time per point and the number of scans.

5.4.3 Standard deviation of intensity from background fit

The background data shall be fitted with a polynomial, *B(E)*. The functional form of *B(E)* is provided in Formula (2):

$$B(E)=\sum_{m=0}^{M} a_m (E-E_j)^m \tag{2}$$

where

a_m are the coefficients of order m in a polynomial equation;

E is the numerical value of either BE or KE, eV;

E_j is the expected position of the peak for element j;

m is the index in a general polynomial equation with integer values 0 to M;

M is the degree of the polynomial description of *B(E)*.

The value of M should initially be set to 1 and should not exceed 4.

Initial trial values of a_m should be used to calculate the residual of the fit, *R(E)*, using Formula (3) and the goodness of the fit, *G*, using Formula (4):

$$R(E)=I(E)-B(E) \tag{3}$$

where

I(E) is the intensity in the spectrum at a given energy, *E*.

$$G=\sqrt{\frac{1}{(N-M-1)}\sum_{n=1}^{N}\left[R(E_n)\right]^2} \tag{4}$$

where

N is the number of data points in background spectrum;

n is the data point indicator with integer values 1 to N;

E_n is the numerical value of either BE or KE, eV, at data point n.

The initial trial values of a_m shall be changed iteratively to minimize *G*. Once the fit is minimized, the residuals, *R(E)*, shall be plotted against *E* and inspected visually to ensure that there are no significant systematic deviations with energy between *I(E)* and *B(E)*. If there are systematic variations, either

a) the value of M shall be increased by one and the fitting procedure repeated. The value of M shall not be greater than 4, or

b) the value of N should be decreased to N = 20, or

c) a different photoelectron peak from the specified element j shall be used.

Once a fit to the background has been found, the minimized value of *G*, $G_{\min}$, shall be used to estimate the standard deviation of the background, σ_B, using Formula (5):

$$\sigma_B = qG_{\min} \tag{5}$$

where

q is equal to 1 for single channel detectors and equal to 1,15 for multi-channel detectors.

NOTE The factor 1,15 for multi-channel detectors arises from the manner in which the detector channel outputs are placed into energy bins. See A.1.1 and Reference [4].

5.5 Calculation of the elemental detection limit

5.5.1 Calculation of the minimal detectable summed intensity

Calculate the minimal detectable summed intensity, A_D, using Formula (6):

$$A_D = 4,9k\sigma_B\sqrt{\frac{W_j}{\varepsilon}} \tag{6}$$

where

k is the coverage factor to achieve the desired level of confidence. k = 2,33 is recommended;

W_j is the FWHM in eV of the photoelectron line used to detect specified element j;

ε is the step size in spectrum, eV.

Typical values of k are 1,645, 2, 2,33 or 3. k = 2,33 is recommended here; see B.2.

NOTE 1 Formula (6) is only valid for linear background subtraction.

NOTE 2 The form of Formula (6) is adapted from Reference [6] and a justification is provided in Annex B.

If no peak for element j is observed in the spectrum, the value of W_j may not be known. In the absence of other information, the value W_x of the reference element x shall be used.

5.5.2 Calculation of the XPS detection limit

The method used to calculate the XPS detection limit from A_D is referenced to a summed intensity from a reference element, A_x, described in 5.3.3. It is important that this reference summed intensity is expressed in the same units as A_D, i.e. either counts or cps. If the reference peak area is expressed in counts.eV or cps.eV then it will be converted to summed intensity in counts or cps by dividing the value by the step size in spectrum, ε.

The detection limit, X_D, of specified element j shall be calculated using Formula (7):

$$X_D = \frac{A_D X_x S_x}{A_x S_j} \tag{7}$$

where

S_x is the RSF of the photoelectron line used to measure the concentration of element x;

S_j is the RSF of the photoelectron line used to measure the concentration of element j;

X_x is the atomic fraction of element x expressed in units of at.%.

If no transmission function has been applied, the RSFs for the specific operating mode of the instrument used to acquire spectra in 5.3.3 shall be applied here.

5.6 Reporting the elemental detection limit

The detection limits calculated from the procedure described in this document shall be reported to one or two significant figures, depending upon the uncertainty associated with the calculation. These uncertainties are described in Annex A.

The following information shall be reported:

a) the specified element and photoelectron peak for which the detection limit was calculated;

b) the elemental composition of the sample for which the detection limit was calculated;

c) the coverage factor, *k*, used for the calculation;

d) the instrument and operating conditions for which the detection limit was calculated;

e) the means of calculating the background noise, either

   1) from the square root of the intensity, or

   2) from the standard deviation of the background;

f) the element and photoelectron peak used as the reference intensity.

Annex A
(informative)

Uncertainties associated with XPS detection limits

A.1 Uncertainty in the measurement of background noise

A.1.1 Uncertainty associated with the method in 5.4.2 and 5.4.3

The uncertainty associated with the measurement of σ_B using experimental XPS data is described in detail in Reference [5]. The major uncertainties are associated with:

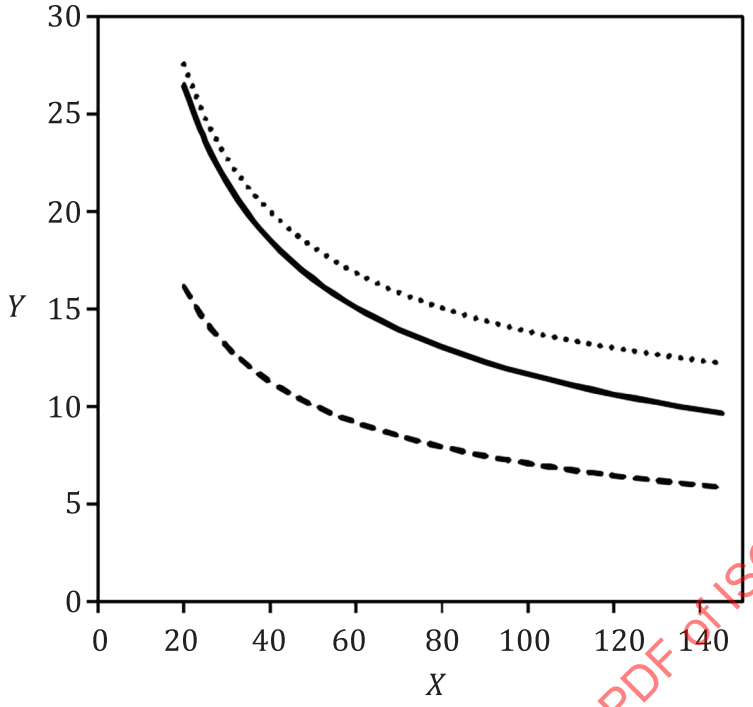
a) the statistical uncertainty arising from a finite N;

b) the detector saturation at high count rates and other nonlinear responses;

c) the smoothing effect of energy binning in multi-channel detector systems.

In the following, it is assumed that uncertainties due to b) are small. The effect of c) introduces a bias in the measured noise, the magnitude of which depends upon the level of mismatch in the spacing between instrument detector channels and energy channels in the spectrum. To correct this bias, the measured noise should be multiplied by a factor of between 1 and 1,25 for a five-channel system[5] with a probable value of ~1,15. This result is general and is used in 5.4.2 to correct the bias with an additional relative uncertainty contribution to σ_B of ~8 %.

For the method described in 5.4.3, the most significant uncertainty arises from a). To achieve better than 10 % uncertainty in σ_B at the 90 % confidence level (i.e. G_{min} is within 10 % of the true σ_B in 90 % of measurements), it is necessary to have $N > 135$. The dependence of the relative uncertainty in σ_B on the number of points in the background data and the number of fitting parameters is provided in Figure A.1.



Key

————	90 % confidence level
.....	relative uncertainty of a multi-channel detector after the correction for bias
— — — —	relative standard uncertainty (68,3 % confidence level)
X	$(N–M)$
Y	uncertainty in σ_B (%)

Figure A.1 — Relative uncertainty in the use of G_{min} to calculate σ_B at the 90 % confidence level for a single channel detector as a function of $N–M$

If the value of σ_B has been determined from the average intensity of the counts (see 5.4.2), then the associated uncertainty is generally smaller than the approach given in 5.4.3. If Poisson statistics for XPS data is assumed, the uncertainty in the measurement of σ_B is related to the uncertainty in determining the mean intensity. The relative uncertainty in σ_B is directly related to the product of the mean intensity, $< IT >$, and the number of data points, N. At the 90 % confidence level, the relative uncertainty in the determination of $< IT >$ is $1{,}645(< IT > N)^{-0{,}5}$ and the relative uncertainty in σ_B is consequently $\sim 0{,}82(< IT > N)^{-0{,}5}$. This rises above 5 % only when the product $< IT > N$ is less than 300 counts and the relative uncertainty for σ_B is typically much lower than 1 % if the detector provides a linear response.

The limiting factor with the method in 5.4.2 is the assumption of linearity in the detector. Typical uncertainties from nonlinearity in detectors used in XPS are in the regime of a few per cent, but can be much larger[7]. Therefore, unless the product $< IT > N$ is less than 300 counts, and in the absence of other information regarding the spectrometer performance, a relative uncertainty of 5 % in σ_B should be assumed as a precautionary value.

A.2 Uncertainty in summed intensity measurement

The uncertainty associated with the measurement of A depends upon both the intensity of the peak and the number of points on either side of the peak used to define the background under the peak.

Formula (A.1) describes the variance in the summed intensity[6] determined by linear background subtraction when A is expressed in counts and the noise follows Poisson statistics:

$$\sigma_A^2 = A + \sigma_B^2 (y+c)\left[1 + \frac{(y-c)}{b}\right] \tag{A.1}$$

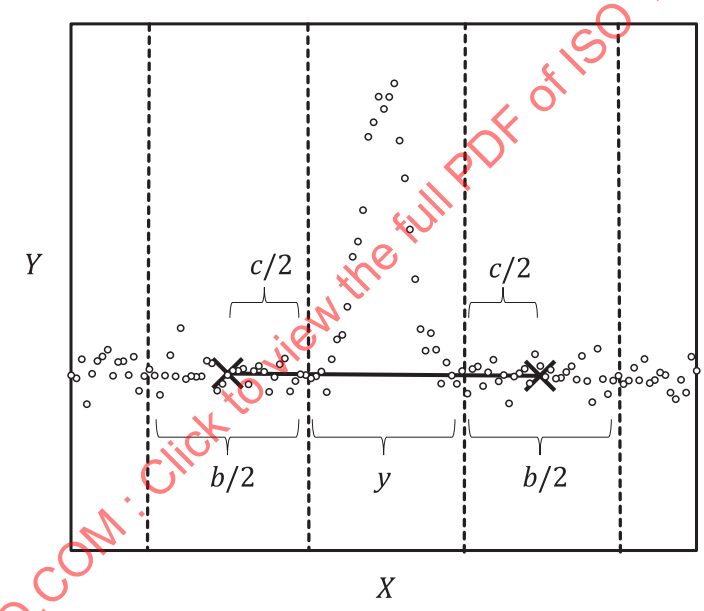
where

b is the number of data points that define the background under the peak;

c is the number of data points from b that are used in a summed intensity measurement;

σ_A is the standard deviation of the summed intensity measurement;

y is the number of data points solely describing the peak.



Key

X kinetic energy

Y intensity

Figure A.2 — Simulated data demonstrating the definitions of y, b and c

Figure A.2 illustrates a typical method used to measure summed intensities using a linear background. The linear background is defined by the line joining the two points (marked as crosses in Figure A.2) determined to be the mean value of energy and intensity for each region. The background is subtracted from the data and the resulting intensities are summed across the energy range selected for the peak-area measurement. The term y in Formula (A.1) is the number of points between the two background regions which comprise only points defining the peak with no background points. The term b in Formula (A.1) is the total number of points in the two background regions. (In Figure A.2, half of these are above the peak and half below.) The term c defines the number of points in the background regions that are also used for the summed intensity measurement itself. In commonly used strategies for peak-area measurement, half of the background points are included in the peak-area measurement. In this case, $c = b/2$ and Formula (A.1) is minimized when $b = 2y$. Note, however, that for any value of b, the uncertainty is always lower for the case $c = 0$. For $b = 2y$, the uncertainty for the $c = 0$ case is 75 % of the $c = b/2$ case. For $b > 2y$, the uncertainty *increases* with b for the $c = b/2$ case and *decreases* with b for the $c = 0$ case.

A.3 Uncertainty in the calculated detection limit

The relative uncertainty associated with the detection limit X_D calculated from Formula (7) may be estimated using Formula (A.2). It is assumed that both RSFs S_x and S_j have the same uncertainty. Typically, the relative uncertainty in RSFs is less than 5 %. The relative uncertainty in A_D is the same as that of σ_B and the uncertainty of X_x is a combination of the uncertainties in A_x and S_x. Hence,

$$\delta^2_{X(D)} = \delta^2_{\sigma(B)} + 2\delta^2_{A(x)} + 3\delta^2_S \tag{A.2}$$

where

$\delta_{X(D)}$ is the relative uncertainty of the detection limit, X_D;

$\delta_{\sigma(B)}$ is the relative uncertainty of σ_B;

$\delta_{A(x)}$ is the relative uncertainty of A_x;

δ_S is the relative uncertainty of S_x and S_j.

Annex B
(informative)

Definition of XPS detection limits

B.1 Definition of the critical level for peak detection

An error of the first kind, i.e. deciding an element is present when it is not, may be made if the critical level for detection, A_C, is set too low. From Formula (A.1) with A set to zero, Formula (B.1) describes the relevant relationship[8] in terms of the coverage factor, k, the standard deviation in the background, σ_B, the number of points used to measure the summed intensity comprising the peak, y, the number of points used to define the linear background, b, and the number of background points that were also used in the peak-area measurement, c.

$$A_C = k\sigma_B\sqrt{(y+c)\left[1+\frac{(y-c)}{b}\right]} \tag{B.1}$$

It is reasonable to assume that the extent of the elemental peak spans, $y = 3W_j/\varepsilon$, and the background region can be selected to include two equally sized areas on either side of the peak, thus $b = 6W_j/\varepsilon$. The value of c is assumed to be half of this, therefore $y = c$. This leads to Formula (B.2), which is valid if the position of the peak is precisely known.

$$A_C = 2{,}45k\sigma_B\sqrt{\frac{W_j}{\varepsilon}} \tag{B.2}$$

An error of the first kind will occur with a probability of 5 % when k = 1,645. However, the precise position of the elemental peak is often not known for several reasons, such as chemical shifts or charging effects. The probability of an error of the first kind is thus somewhat higher. For example, if the position of the peak is uncertain such that it may appear in three uncorrelated positions (over a range of approximately 6 W_j), then with k = 1,645, the probability of an error of the first kind rises to 14 %. It is therefore safer to set k = 2,33, which, if the position is well known, corresponds to a probability of an error of the first kind occurring 1 % of the time and remains below 5 % for practical situations in which the precise position of the elemental peak is uncertain.

B.2 Definition of the XPS detection limit

The summed intensity detection limit, A_D, is set as the minimal detectable value[8]. This is the level at which an error of the second kind, i.e. deciding an element is absent (measured area < A_C) when it is actually present (with true area A_D), occurs with a probability equal to that of an error of the first kind.

Accurate calculation of A_D is not trivial and relies upon knowledge of the standard deviation of the signal for a peak at the detection limit, therefore an iterative method is required. For a rigorous statistical treatment of the concept of detection limits, ISO 11843-6 should be consulted[2]. Here, for simplicity, it is assumed that A_D is equal to twice the critical level for detection, A_C[8]. This leads directly to Formula (6). Formula (6) is an underestimate of a more rigorous calculation of A_D[2] and typically in error by <1 %. However, if both the background counts are very low (less than 1 000 counts) and the data step size is large ($W_j < 3\varepsilon$), the error can be greater than 5 %.

Note that with k = 2,33 an error of the second kind occurs with a probability of 1 %, regardless of prior knowledge of the position of the peak and also that the presence of an element may still be inferred with more than 95 % confidence provided that the observed X_j is greater than half the XPS detection limit, X_D.

Annex C
(informative)

Examples

C.1 XPS detection limit when no peak is detected

C.1.1 General

Here, the detection limit for titanium in two samples is used as an example. The first sample is polystyrene and the second silver. This example illustrates the background fitting process and calculations. The required information for estimating the detection limit is provided in Table C.1. In this clause, the detection limits are calculated for the survey spectrum and this serves to provide both the composition and the reference summed intensities used in the calculation. The data were acquired on a Kratos AXIS Ultra[1)] operating in the constant analyser transmission mode with 160 eV pass energy and using monochromatic AlKα radiation with an anode power of 75W and a multi-channel detector. Data acquisition was performed with 1 eV step size, 200 ms dwell time per point and two sweeps.

Table C.1 — Physical parameters for detection limit calculation

Elemental peak	BE (eV)	KE (eV)	S
Ti $2p_{3/2}$	~455	~1 030	4,64
C 1s	285,0	1 201,6	1
Ag 3d[a]	368,3	1118,3	15,5

[a] Ag $3d_{5/2}$ and Ag $3d_{3/2}$ combined.

NOTE The S and KE values provided here are specific to the XPS instrument used.

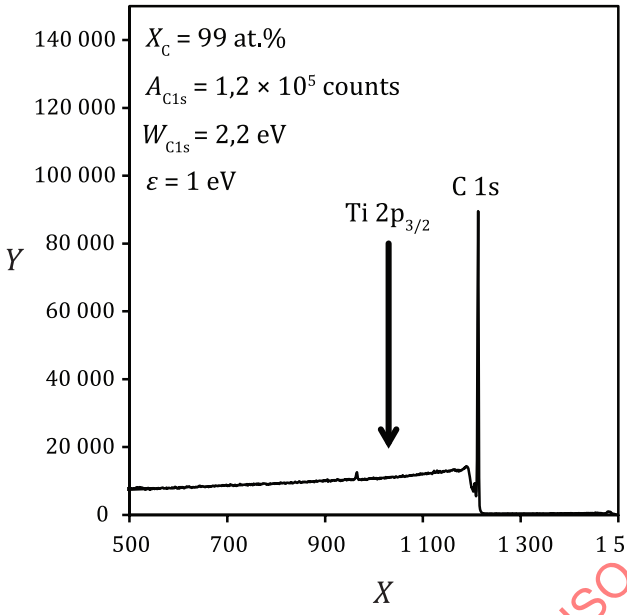
C.1.2 XPS detection limit for titanium in polystyrene

The survey scan for polystyrene is shown in Figure C.1 a) along with values for the reference summed intensity and width, A_{C1s} and W_{C1s}, respectively. Since titanium is not present, $W_{Ti2p3/2}$ cannot be measured, therefore it is set equal to W_{C1s}; see 5.5.1. A small amount of oxygen was detected and the concentration of carbon was determined to be X_C = 99 at.%. Figure C.1 b) displays the data selected as the background in the Ti $2p_{3/2}$ region along with a linear (M = 1) fit to provide B. The residuals, R, shown in Figure C.1 c) show no systematic bias and therefore the reduced value of G may be used to estimate σ_B. In Table C.2, the results of Formulae (6) and (7) are provided using σ_B estimated as described in both 5.4.2, square root of the intensity, and 5.4.3, standard deviation of the background.

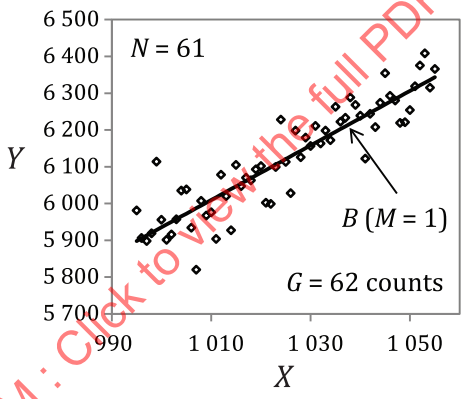
Table C.2 — Calculated detection limits for titanium in polystyrene

Parameter	5.4.2	5.4.3
σ_B	78 counts	72 counts
A_D (k = 2,33)	1 320 counts	1 220 counts
X_D (k = 2,33)	0,23 at.%	0,21 at.%

1) Kratos AXIS Ultra is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.



a) XPS survey spectrum of polystyrene, indicating the expected position of Ti $2p_{3/2}$



b) Background data extracted from a) with linear fit, B, and goodness of fit, G

c) Residuals, R, of the fit shown in b)

Key

X kinetic energy (eV)

Y counts

R residuals

NOTE For Figure C.1 a), values extracted from the spectrum are listed.

Figure C.1 — XPS detection limit of titanium in polystyrene

C.1.3 XPS detection limit for titanium in silver

The survey scan for silver is shown in Figure C.2 a) along with values for the reference summed intensity and width, A_{Ag3d} and $W_{Ag3d5/2}$, respectively. Since titanium is not present, $W_{Ti2p3/2}$ cannot be measured, therefore it is set equal to $W_{Ag3d5/2}$; see 5.5.1. No other elements were detected and the

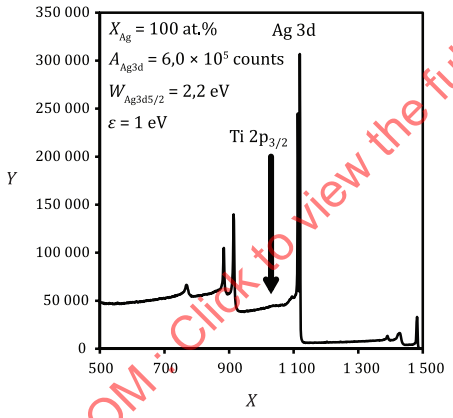
concentration of silver was taken to be X_{Ag} = 100 at.%. Figure C.2 b) displays the data selected as the background in the Ti $2p_{3/2}$ region along with a quadratic (M = 2) fit to provide B. The residuals, R, in Figure C.2 c) show systematic bias, therefore a cubic fit (M = 3) was performed as shown in Figure C.2 d) and e). The reduced value of G from the cubic fit may be used to estimate σ_B, since no systematic bias is evident. Increasing M to 4 does not significantly alter the reduced value of G. This also indicates that M = 3 is sufficient.

In Table C.3, the results of Formulae (6) and (7) are provided using σ_B estimated as described in both 5.4.2, square root of the intensity, and 5.4.3, standard deviation of the background.

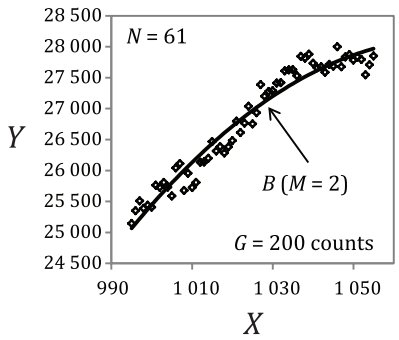
NOTE If a quadratic (M = 2) fit to B had been used, the detection limit would be estimated to be 2,2 at.%. A linear fit (M = 1) would provide 4,7 at.%.

Table C.3 — Calculated detection limits for titanium in silver

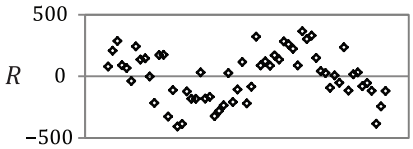
Parameter	5.4.2	5.4.3
σ_B	164 counts	169 counts
A_D (k = 2,33)	2 780 counts	2 860 counts
X_D (k = 2,33)	1,5 at.%	1,6 at.%



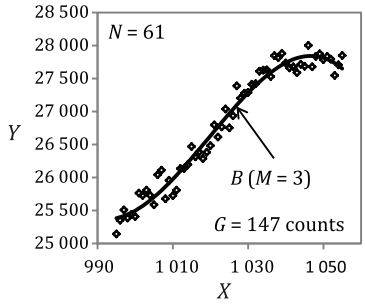
a) XPS survey spectrum of silver, indicating the expected position of Ti $2p_{3/2}$



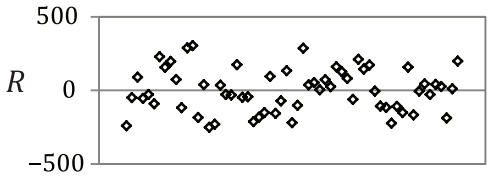
b) Background data extracted from a) with quadratic fit, B, and goodness of fit, G



c) Residuals, R, of the fit shown in b)



d) Background data extracted from a) with cubic fit, B, and goodness of fit, G



e) Residuals, R, of the fit shown in d)

Key

X kinetic energy (eV)

Y counts

R residuals

NOTE For Figure C.2 a), values extracted from the spectrum are listed.

Figure C.2 — XPS detection limit of titanium in silver

C.2 XPS detection limit when a peak is present

C.2.1 XPS detection limit for iodine in a polymer

The detection limit for iodine in a polymer is calculated. The composition of the polymer from an XPS survey scan is 71,2 at.% carbon, 26,8 at.% oxygen, 1,9 at.% nitrogen and 0,1 at.% iodine. A detailed spectrum of the I $3d_{5/2}$ peak is shown in Figure C.3 a). The data were acquired on a Kratos AXIS Ultra[2)] operating in the constant analyser transmission mode with 80 eV pass energy and using monochromatic AlKα radiation with an anode power of 75W. Data acquisition was performed with 0,1 eV step size, 500 ms dwell time per point and one sweep. The relative uncertainty in the area of the I $3d_{5/2}$ peak was calculated to be 8 % using Formula (A.1); this was deemed an acceptable uncertainty to use the I $3d_{5/2}$ peak itself as the reference peak x. In this way, Formula (7) simplifies to Formula (C.1), and the associated relative uncertainty in X_D is ~20 % at the 90 % confidence level.

$$X_D = \frac{A_D X_j}{A_j} \tag{C.1}$$

Figure C.3 a) indicates the region at higher KE (lower BE) selected for background analysis. These data are treated as in example C.1.2 in Figures C.3 b) and c) to obtain an estimate of σ_B. In Table C.4, the results of Formulae (6) and (7) are provided using σ_B calculated as described in both 5.4.2, square root of the intensity, and 5.4.3, standard deviation of the background.

2) Kratos AXIS Ultra is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.