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# 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*

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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.

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# 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 |
|------|------------------------------|
| $\alpha$ | 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, $A_x$ |
| $\delta_S$ | relative uncertainty of the detection limit, $S$ |
| $\delta_{\sigma(B)}$ | relative uncertainty of the standard deviation of the background $\sigma_B$ |
| $\delta_{X(D)}$ | 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 |
| $\varepsilon$ | 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 $G$ |
| $\Gamma_D$ | 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 |
| $\lambda$ | 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 |
|---|---|
| $\theta_D$ | 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 $i$ |
| $\sigma_A$ | standard deviation of a summed intensity measurement |
| $\sigma_B$ | 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.
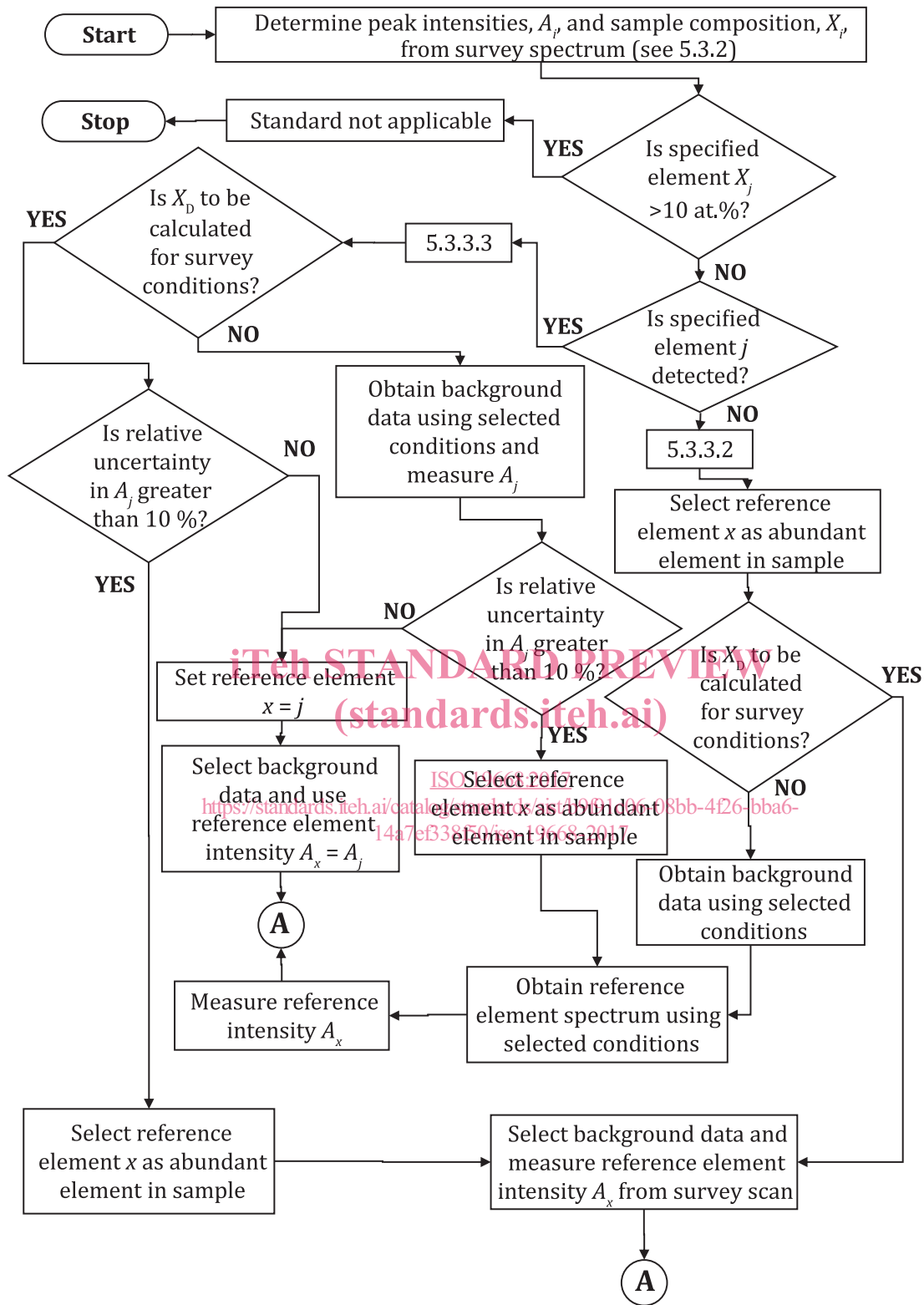
NOTE    Point "A" connects to the flow chart in Figure 2.

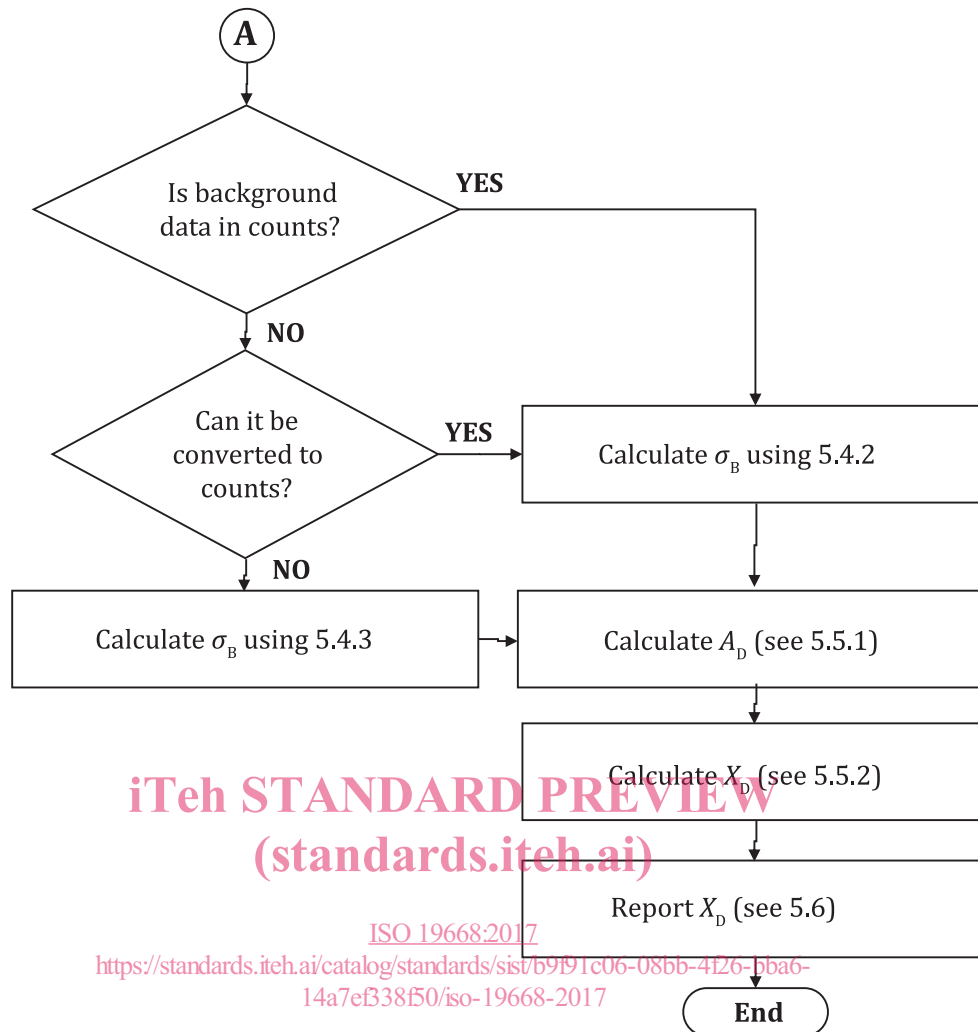**Figure 1 — Flow chart describing steps in data collection for estimating XPS detection limits**

A

Is background
data in counts? —**YES**→

**NO**

Can it be
converted to
counts? —**YES**→ Calculate $\sigma_B$ using 5.4.2

**NO**

Calculate $\sigma_B$ using 5.4.3 → Calculate $A_D$ (see 5.5.1)

Calculate $X_D$ (see 5.5.2)

Report $X_D$ (see 5.6)

End

**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