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Standard**

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**Surface chemical analysis — X-ray
photoelectron spectroscopy —
Method of intensity calibration for
quartz-crystal monochromated Al
K α XPS instruments**

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

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Introduction

X-ray photoelectron spectroscopy is routinely used to measure the elemental composition of surfaces and the depth distribution of those elements. The translation of peak intensities into elemental compositions and depth distributions in the absence of reference materials relies upon comparison of the relative peak intensities to external reference data. The kinetic energies of the peaks being compared are different and therefore it is important to know the relative transmission and detection efficiency of electrons at different kinetic energies to achieve a meaningful comparison to the external reference data. International interlaboratory studies demonstrate that XPS instruments display markedly different transmission characteristics. Consistent intensity scale calibration enables the direct comparison of XPS results and enables international trade through trust in measurements throughout the supply chain and in the comparability of data from analytical service providers.

This document provides a method to determine the relative response of X-ray photoelectron spectrometers which utilise quartz-crystal-monochromated Al K α radiation as the excitation source. Clean low-density poly(ethylene) is employed as a reference material. Measured intensities from clean low-density poly(ethylene) are compared to reference intensities at specific electron kinetic energies to determine the relative response of electrons to the detector. The resulting relative response function is traceable to accurate reference spectra for copper, silver and gold held by the National Physical Laboratory, UK.

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Surface chemical analysis — X-ray photoelectron spectroscopy — Method of intensity calibration for quartz-crystal monochromated Al K α XPS instruments

1 Scope

This document specifies a procedure by which the intensity scale of an X-ray photoelectron spectrometer that employs a concentric hemispherical analyser can be calibrated using low-density poly(ethylene). This document is applicable to instruments using quartz-crystal-monochromated Al K α X-rays and is suitable for all instrument geometries. The intensity calibration is only valid for the specific settings of the instrument (pass energy or retardation ratio, lens mode, slit and aperture settings) used during the calibration procedure. The intensity calibration is applicable at kinetic energies higher than 180 eV. The intensity calibration is suitable for instruments that do not have an ion gun for the purpose of cleaning metal specimens in-situ (i.e. Au, Ag, Cu), or exhibit detector saturation when these specimens are measured using standard instrument parameters.

This document is not applicable to XPS instruments which do not have a system of charge compensation, or instruments that have a non-linear intensity response. This document is not applicable to instruments and operating modes which generate significant intensity from electrons scattered internally in the spectrometer (i.e. >1 % contribution of scattering intensity to the total spectral intensity).

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*

3 Terms and definitions

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

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1 relative throughput

ratio of measured signal rate to the known intensity from a reference sample as a function of electron kinetic energy

Note 1 to entry: Relative throughput is related to the spectrometer response function and is distinguished in this document as the experimentally determined response.

4 Symbols and abbreviated terms

For the purposes of this document the following abbreviations apply.

ISO 5861:2024(en)

LDPE low density poly(ethylene), or low density polyethylene, CAS RN^{®1)}
9002-88-4

XPS X-ray photoelectron spectroscopy

For the purposes of this document the following symbols apply.

<i>A</i>	XPS peak area	eV s ⁻¹
<i>a</i>	an exponent	
<i>b</i>	an exponent	
β	detection angle between incoming X-rays and outgoing electrons	
<i>C</i>	count rate from reference material	s ⁻¹
<i>D</i>	noise rate	s ⁻¹
<i>E</i>	analyser kinetic energy	eV
<i>F</i>	correction for angular emission	
<i>g</i>	instrument geometry factor	
<i>h</i>	magnitude of the slope of the survey spectra intensity ratio	keV ⁻¹
<i>I</i>	angle-averaged reference intensity	I _A
<i>K</i>	reference kinetic energy, equal to $E + q$	eV
<i>M</i>	number of independent parameters in a functional description of T	
<i>Q</i>	relative throughput: ratio of signal rate, S , to the reference intensity, R	I _A ⁻¹ s ⁻¹
<i>q</i>	electric potential energy of reference material relative to spectrometer	eV
<i>R</i>	reference intensity for the XPS instrument	s ⁻¹
<i>S</i>	signal rate: the difference between count rate, C , and noise rate, D	s ⁻¹
<i>s</i>	average matrix relative sensitivity factor	
σ_C	standard uncertainty of count rate	s ⁻¹
σ_Q	standard uncertainty of relative throughput Q	I _A ⁻¹ s ⁻¹
σ_q	mean standard uncertainty of relative throughput Q	I _A ⁻¹ s ⁻¹
σ_S	standard uncertainty of signal rate S	s ⁻¹
σ_T	standard uncertainty of relative response T	I _A ⁻¹ s ⁻¹
<i>T</i>	relative response of a spectrometer	I _A ⁻¹ s ⁻¹
<i>W</i>	X-ray anode power	W
<i>W_r</i>	X-ray anode power used during LDPE reference material analysis	W

1) CAS Registry Number[®] is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

X	root mean square error of a functional description of T relative to Q	
x	relative atomic concentration	at. %
ξ	dihedral angle between X-ray anode-monochromator-sample plane and monochromator-sample-electron analyser plane	
Y	XPS signal rate from a sample	s^{-1}
Z	calibrated XPS intensity from a sample	I_A

5 Requirements

5.1 General

Annex A.1 shows a flow chart (Figure A.1) for instrument set-up and the acquisition of data and summarises the steps to be taken in Clause 5.

5.2 X-ray photoelectron spectrometer

5.2.1 Operating requirements

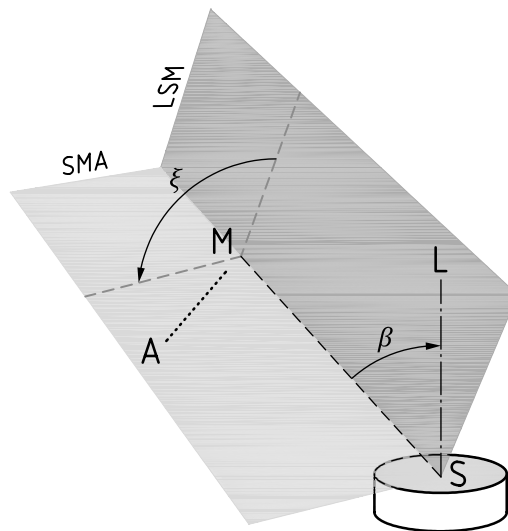
The XPS instrument requires a monochromated Al $K\alpha$ X-ray source and a charge compensation system such as a low energy electron flood source or low energy ion source. The XPS spectrometer shall be operated in a pulse-counting mode. Count rates that are used for calibration following the procedures in this document shall be within the linear operating regime of the detector. The pass energy and slit widths of the spectrometer shall be set to minimise the contribution of electrons scattered within the analyser to the recorded count rate. In the case that analyser internal scattering can be measured, the contribution shall comprise less than 1 % of the count rate.

NOTE Linearity of the intensity scale can be confirmed using methods described in other documents^[1,2].

Scattering in electron spectrometers can be diagnosed and minimised^[3,4], but significant scattering intensity shall be reported to the instrument manufacturer for corrective action. For concentric hemispherical analysers, higher pass energies and smaller entrance slit widths reduce the effect of scattering. A pass energy of 50 eV or higher is usually sufficient to ensure that the major scattering contributions are significantly less than 1 %.

5.2.2 Instrument geometry

The geometry of the XPS spectrometer shall be known. The geometry is characterised by two angles: the detection angle β which is the angle between the incoming X-rays from the monochromator and the outgoing electrons directly toward the electrostatic lens column; and ξ , the dihedral angle between the plane defined by the centres of the X-ray anode, the monochromator, and the sample (which is assumed to be in the focal point of the X-ray spot and analyser defined analysis spot) and the plane defined by the centres of the monochromator, sample and electrostatic lens column. Figure 1 provides a schematic of the XPS instrument geometry used in this document to help identify the angles β and ξ . The instrument manufacturer will know the exact angles of β and ξ from chamber design schematics.

**Key**

A	centre of X-ray anode	M	centre of quartz-crystal monochromator
S	analysis point on sample	L	centre of analyser lens
β	angle between lines MS and SL	ξ	dihedral angle between planes LSM and SMA

Figure 1 — Schematic of XPS instrument geometry showing the angles β and ξ

From these two angles, the geometry factor of the instrument shall be calculated using [Formula \(1\)](#).

$$g = \left[(2,990 - 0,765 \cos \beta)(0,500 - 0,042 \cos 2\xi) \sin^2 \beta \right] - 0,995 \quad (1)$$

where

g is the instrument geometry factor;

β is the detection angle;

ξ is the dihedral angle.

NOTE 1 [Formula \(1\)](#) contains numerical values that arise from the nearly identical angular emission distributions of C 1s and C 2s electrons and the X-ray polarisation induced by the monochromator^[5].

NOTE 2 Most commercial spectrometers have a coplanar dihedral angle, $\xi = 180^\circ$, and a detection angle, β , between 45° and 60° . Useful numerical values of g are: $-0,434\ 2$ for $\beta = 45^\circ$; $-0,217\ 7$ for $\beta = 54,7^\circ$; $-0,099\ 3$ for $\beta = 60^\circ$ and; $+0,374\ 4$ for $\beta = 90^\circ$.

NOTE 3 Exact angles of β and ξ can be obtained from the instrument manufacturer.

5.3 Reference material

The reference material shall be LDPE sheet of approximately 1 mm thickness free from obvious polymer damage or discolouration. Cut the LDPE sheet to a size suitable for analysis using clean metal scissors and affix to a sample holder. Use a brand-new disposable scalpel, or a scalpel cleaned with an isopropanol alcohol-soaked tissue, to uniformly scrape the surface immediately prior to inserting it into the XPS instrument. A visual inspection of the XPS survey scans should exhibit no peaks other than those due to carbon. If this condition is met, then the LDPE sheet is suitable as a reference material for use with this document. At the conclusion of this protocol, the reference LDPE should be stored in the dark, avoiding exposure to humidity and high temperatures or proximity to volatile solvents or fumes, until required.

If peaks due to elements apart from carbon are observable in the LDPE X-ray photoelectron spectrum, the sample shall be removed and cleaned again by additional scraping using a different clean metal scalpel. If

repeated cleaning does not remove the non-carbon elemental peaks, then an alternative source of LDPE shall be sought.

In subsequent uses of this document, stored and previously used LDPE reference samples shall be scraped before use.

NOTE 1 Contamination can also arise from the XPS instrument and sample holder. Failure to obtain clean LDPE can also indicate that the XPS instrument requires baking or sample holders require cleaning.

NOTE 2 Clean, uncoated razor blades without a lubricant coating such as PTFE can be used in place of a scalpel.

5.4 Frequency of intensity scale calibration

Intensity calibration shall be performed at a maximum interval of one year, or more frequently if changes in intensity response are identified and occur over a shorter period. Intensity calibration is also required after maintenance, alteration of instrument configuration, or a bake-out.

NOTE ISO 24237, repeatability and constancy of intensity scale, ISO 16129, procedures for assessing the day-to-day performance of an X-ray photoelectron spectrometer and other documents provide methods for identifying changes in instrument response^[6-8].

6 Data acquisition

6.1 General

Annex A.1 shows a flow chart (Figure A.1) for instrument set-up and the acquisition of data that summarises the steps to be taken in Clause 6. Additionally, A.2 shows a flow chart (Figure A.2) for the inspection of data and determining $Q(E)$ that summarises the steps to be taken in Clause 6.

6.2 Preparation

6.2.1 XPS Instrument

Operate the instrument in accordance with the manufacturer's instructions. Turn on the XPS instrument control and high voltage power supplies at least three hours before proceeding. Set the instrument to the required operating mode, pass energy or retardation ratio, slit widths and aperture settings for which the intensity calibration is required.

6.2.2 LDPE reference sample

Prepare the LDPE reference sample by mounting on a sample holder and scraping with a scalpel described in 5.3. Immediately place the reference sample in the instrument load lock, evacuate the load lock chamber and transfer it to the analysis chamber as soon as possible. Position the reference sample away from the analysis position so that it will not be exposed to X-rays during X-ray source warm up, see 6.2.3.

6.2.3 X-ray source and electron flood source

Turn on the X-ray source at a normal operating power. Turn on the electron flood source and set it to typical operating parameters. Wait for at least 30 min for the X-ray source and electron flood source to equilibrate before proceeding. The X-ray power used for acquiring the reference spectra, W_r , shall be recorded.

Similar to instrument parameters described in 6.2.1, the resulting intensity calibration obtained from this procedure is also a function of the X-ray source energy, optics, and spot size. Multiple calibrations shall be obtained for different X-ray source parameters except for W_r .