ISO/~~DIS~~PRF 5861~~:2023(E)~~

ISO/TC 201/SC 7~~/WG 2~~

Secretariat: BSI

Date: ~~2023-07-06~~2024-04-03

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

PROOF

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: + 41 22 749 01 11
~~Email~~E-mail: copyright@iso.org
Website: ~~www.iso.org~~www.iso.org

Published in Switzerland

Contents

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.

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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at ~~www.iso.org/patents.~~www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

Field Code Changed

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at ~~www.iso.org/members.html~~www.iso.org/members.html.

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 Kα 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.

Surface chemical analysis~~–~~ — X-ray photoelectron spectroscopy — Method of intensity calibration for quartz-crystal monochromated Al Kα 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 Kα 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 ~~terminological~~terminology databases for use in standardization at the following addresses:

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

— ~~—~~IEC Electropedia: available at ~~https://www.electropedia.org/~~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.

LDPE	low density poly(ethene), or low density polyethylene, CAS No. 9002-88-4
XPS	X-ray photoelectron spectroscopy

For the purposes of this document the following symbols apply.

A	XPS peak area	$\mathrm{eV\ s^{-1}}$
a	an exponent	
b	an exponent	
β	detection angle between incoming X-rays and outgoing electrons	
C	count rate from reference material	$\mathrm{s^{-1}}$
D	noise rate	$\mathrm{s^{-1}}$
E	analyser kinetic energy	eV
F	correction for angular emission	
g	instrument geometry factor	
h	magnitude of the slope of the survey spectra intensity ratio	$\mathrm{keV^{-1}}$
I	angle-averaged reference intensity	$\mathrm{I_A}$
K	reference kinetic energy, equal to $E + q$	eV
M	number of independent parameters in a functional description of T	
Q	relative throughput: ratio of signal rate, S, to the reference intensity, R	$\mathrm{I_A^{-1}\ s^{-1}}$
q	electric potential energy of reference material relative to spectrometer	eV
R	reference intensity for the XPS instrument	$\mathrm{s^{-1}}$
S	signal rate ($\mathrm{s^{-1}}$): the difference between count rate, C, and noise rate, D	
s	average matrix relative sensitivity factor	
σ_C	standard uncertainty of count rate	$\mathrm{s^{-1}}$
σ_Q	standard uncertainty of relative throughput Q	$\mathrm{I_A^{-1}\ s^{-1}}$
σ_q	mean standard uncertainty of relative throughput Q	$\mathrm{I_A^{-1}\ s^{-1}}$
σ_S	standard uncertainty of signal rate S	$\mathrm{s^{-1}}$
σ_T	standard uncertainty of relative response T	$\mathrm{I_A^{-1}\ s^{-1}}$
T	relative response of a spectrometer	$\mathrm{I_A^{-1}\ s^{-1}}$
W	X-ray anode power	W
W_r	X-ray anode power used during LDPE reference material analysis	W
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~~A.1 shows a flow chart ~~(Figure A.1)~~(Figure A.1) for instrument set-up and the acquisition of data and summarises the steps to be taken in ~~clause 5.~~Clause 5.

5.2 X-ray photoelectron spectrometer

5.2.1 Operating requirements

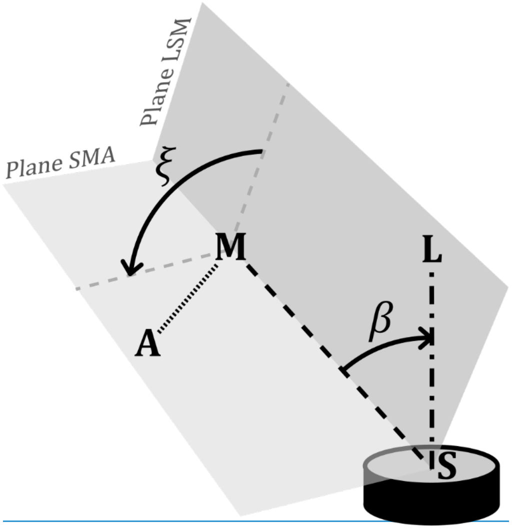
The XPS instrument requires a monochromated Al Kα X-ray source and a charge compensation system such as a low energy electron flood source or low energy ion source. The XPS spectrometer shall be operated in a pulse-counting mode. Count rates that are used for calibration following the procedures in this 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.

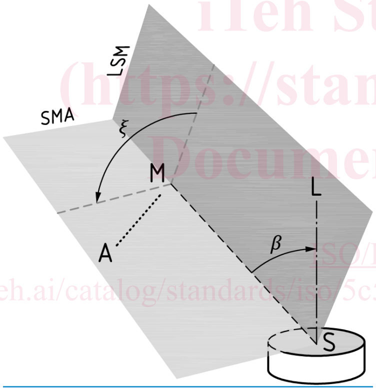
NOTE Linearity of the intensity scale can be confirmed using methods described in other documents~~[1,2]~~,[1,2].

Scattering in electron spectrometers can be diagnosed and minimised~~[3,4]~~,[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~~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)~~ Formula (1).

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

$$g=[(2{,}990-0{,}765\cos\beta)(0{,}500-0{,}042\cos 2\xi)\sin^2\beta]-0{,}995 \qquad (1)$$