INTERNATIONAL STANDARD

ISO
15472

Second edition
2010-05-01

Surface chemical analysis — X-ray photoelectron spectrometers — Calibration of energy scales

Analyse chimique des surfaces — Spectromètres de photoélectrons X — Étalonnage en énergie

iTeh STANDARD PREVIEW
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ISO 15472:2010
https://standards.iteh.ai/catalog/standards/sist/ac0216e1-da6c-4b1c-a8cc-
0156f169e156/iso-15472-2010

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15472 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *X-ray photoelectron spectroscopy*.

This second edition cancels and replaces the first edition (ISO 15472:2001), of which it constitutes a minor revision affecting only Subclause 5.8.1.2. As a result of use of ISO 15472:2001, it became clear that the constraint in 5.8.1.2 limiting users to start and finish at intensities in the range 87 % to 95 % of the peak intensity above zero intensity was over-cautious. For a narrow peak, such as that for gold, it is necessary to include more of the peak to include the required number of data points. This can be done as indicated in the new text of 5.8.1.2 without compromising the accuracy.

Introduction

X-ray photoelectron spectroscopy (XPS) is used extensively for the surface analysis of materials. Elements in the sample (with the exception of hydrogen and helium) are identified from comparisons of the binding energies of their core levels, determined from the measured photoelectron spectra, with tabulations of those energies for the different elements. Information on the chemical state of such elements can be derived from the chemical shifts of measured photoelectron and Auger electron features with respect to those for reference states. Identification of chemical states is based on measurements of chemical shifts with accuracies in the range down to 0,1 eV; individual measurements should therefore be made and reference sources need to be available with appropriate accuracies. Calibrations of the binding-energy scales of XPS instruments are therefore required, often with an uncertainty of 0,2 eV or less.

This method for calibrating instrumental binding-energy scales uses metallic samples of pure copper (Cu), silver (Ag) and gold (Au) and is applicable to X-ray photoelectron spectrometers with unmonochromated aluminium (Al) or magnesium (Mg) X-rays or monochromated Al X-rays. It is valid for the binding-energy range 0 eV to 1 040 eV.

XPS instruments calibrated for providing analyses within the scope of ISO/IEC 17025[1] and for other purposes may need a statement of the estimated calibration uncertainty. These instruments are in calibration for binding-energy measurements within certain defined tolerance limits, $\pm\delta$. The value of δ is not defined in this International Standard since it will depend on the application and design of the XPS instrument. The value of δ is selected by the user of this International Standard, based on experience in the use of the standard, the calibration stability of the instrument, the uncertainty required for binding-energy measurements in the intended applications of the instrument and the effort incurred in conducting the calibration. This International Standard provides information by which a suitable value of δ may be chosen. Typically, δ is equal to or greater than 0,1 eV and greater than about 4 times the repeatability standard deviation, σ_R. To be in calibration, the divergence from the reference binding-energy values plus the expanded calibration uncertainty for a 95 % confidence level, when added to the instrumental drift with time, must not exceed the chosen tolerance limits. Before the instrument is likely to be out of calibration, it will have to be re-calibrated to remain in calibration. An instrument is re-calibrated when a calibration measurement is made and action is taken to reduce the difference between the measured and reference values. This difference may not necessarily be reduced to zero but will normally be reduced to a small fraction of the tolerance limits required for the analytical work.

This International Standard does not address all of the possible defects of instruments, since the required tests would be very time-consuming and need both specialist knowledge and equipment. This International Standard is, however, designed to address the basic common problems in the calibration of the binding-energy scales of XPS instruments.

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Surface chemical analysis — X-ray photoelectron spectrometers — Calibration of energy scales

1 Scope

This International Standard specifies a method for calibrating the binding-energy scales of X-ray photoelectron spectrometers, for general analytical purposes, using unmonochromated Al or Mg X-rays or monochromated Al X-rays. It is only applicable to instruments which incorporate an ion gun for sputter cleaning. This International Standard further specifies a method to establish a calibration schedule, to test for the binding-energy scale linearity at one intermediate energy, to confirm the uncertainty of the scale calibration at one low and one high binding-energy value, to correct for small drifts of that scale and to define the expanded uncertainty of the calibration of the binding-energy scale for a confidence level of 95 %. This uncertainty includes contributions for behaviours observed in interlaboratory studies but does not cover all of the defects that could occur. This International Standard is not applicable to instruments with binding-energy scale errors that are significantly non-linear with energy, to instruments operated in the constant retardation ratio mode at retardation ratios less than 10, to instruments with a spectrometer resolution worse than 1,5 eV, or to instruments requiring tolerance limits of ±0,03 eV or less. This International Standard does not provide a full calibration check, which would confirm the energy measured at each addressable point on the energy scale and which would have to be performed in accordance with the manufacturer's recommended procedures.

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

3 Symbols and abbreviated terms

a measured energy-scaling error

b measured zero-offset error, in eV

E_{corr} corrected result for the binding energy corresponding to a given E_{meas}, in eV

E_{elem} binding energy of a frequently measured element at which the indicated binding-energy scale is set, after calibration, to read correctly, in eV

E_{meas} a measured binding energy, in eV

$E_{meas\,n}$ average of the measured binding energies for a peak, n, in Table 2, in eV

$E_{meas\,ni}$ one of a set of measurements of binding energy for peak n in Table 2, in eV

$E_{ref\,n}$ reference values for the position on the binding-energy scale of peak n in Table 2, in eV

FWHM   full width at half maximum peak intensity above the background, in eV

j number of repeat measurements for a new peak

k number of repeat measurements for the Au $4f_{7/2}$, Cu $2p_{3/2}$ and Ag $3d_{5/2}$ or Cu L_3VV peaks in the repeatability standard deviation and linearity determinations

m number of repeat measurements for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks in the regular calibrations

n designation of the peak identifier in Table 2

t_x Student's t-value for x degrees of freedom of a two-sided distribution for a confidence level of 95 %

U_{95} total uncertainty of the calibrated energy scale at a confidence level of 95 %, in eV

$U_{95}^c(E)$ uncertainty at a confidence level of 95 % arising from the calibration using the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks at binding energy E, assuming perfect scale linearity, in eV

U_{95}^l uncertainty of ε_2 or ε_3 at a confidence level of 95 % from Equation (7), in eV

U_{95}^{cl} uncertainty of the calibration at a confidence level of 95 % in the absence of a linearity error, from Equations (12) and (13)

XPS   X-ray photoelectron spectroscopy

Δ_n offset energy, given by the average measured binding energy for a calibration peak minus the reference energy, in eV, for $n = 1, 2, 3, 4$ in Table 2, for a given X-ray source

ΔE_{corr} correction to be added to E_{meas}, after calibration, to provide the corrected result for the binding energy

$\Delta \phi$ the average of Δ_1 and Δ_4 from Equation (16)

δ value of the tolerance limit of energy calibration at a confidence level of 95 % (set by the analyst), in eV

ε_2 measured scale linearity error at the Ag $3d_{5/2}$ peak from Equation (4), in eV

ε_3 measured scale linearity error at the Cu L_3VV peak from Equation (5) or (6), in eV

σ_R maximum of σ_{R1}, σ_{R2} or σ_{R3}, and σ_{R4}

σ_{Rn} repeatability standard deviation for the seven measurements of the binding energy of peak n in Table 2, in eV

σ_{Rnew} repeatability standard deviation for a new peak, in eV

A list of additional symbols used in Annexes A and D will be found in those annexes.

4 Outline of method

Here, the method is outlined so that the detailed procedure, given in Clause 5, may be understood in context. To calibrate an X-ray photoelectron spectrometer using this International Standard, it will be necessary to obtain and prepare copper and gold reference foils in order to measure the binding energies of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ photoelectron peaks with the appropriate instrumental settings. These peaks are chosen as they are near the high and low binding-energy limits used in practical analysis. For binding-energy scale linearity tests with instruments using monochromated Al Kα X-rays, a silver reference sample is also needed and, for

this test, the Ag $3d_{5/2}$ peak is used. For equivalent tests using unmonochromated X-rays, this same peak or, more conveniently, the Cu L_3VV Auger electron peak is used. These peaks are well-established for this purpose and relevant reference data exist for emission angles in the range 0° to 56° from the sample normal. These initial steps are described from 5.1 to 5.5 and shown in the flowchart of Figure 1 with the relevant subclause headings paraphrased.

For the first calibration, it is assumed that there has been no characterization of the spectrometer behaviour. Thus, at 5.7, measurements are made of the binding energies of the Cu $2p_{3/2}$, Ag $3d_{5/2}$ or Cu L_3VV, and Au $4f_{7/2}$ peaks in a sequence repeated seven times. These data give the repeatability standard deviations σ_{R1}, σ_{R2} or σ_{R3}, and σ_{R4} for the three peaks used. These standard deviations have contributions from the stability of the spectrometer electronic supplies, from the sensitivity of the measured peak energy to the sample position and from the statistical noise at the peak. In the procedure, conditions are defined to ensure that the statistical noise is relatively small. The other two contributions may vary with the measured binding energy and so σ_R is defined as the greatest of the values obtained for the three peaks used. The value of σ_R may depend on the sample-positioning procedure. At 5.7.1, the use of a consistent sample-positioning procedure is required and the final calibration is only valid for samples positioned using this positioning procedure.

Studies of spectrometers show that, in general, any measured error in the peak energies varies approximately linearly with the peak binding energy. The equations presented in this International Standard are valid only for this most common situation and are based on the principle that the difference between the measured binding energies and the reference binding energies are both small and are linearly, or close to linearly, dependent on the binding energy. This linearity may fail if the instrument is defective and so a test is provided at 5.7 and 5.9 to confirm the closeness to linearity at an intermediate energy. For convenience, this test involves the copper Auger electron peak for both Al and Mg unmonochromated X-ray sources. However, for monochromated Al X-rays, the effective X-ray energy for different instruments may vary by up to 0,2 eV, depending on the precise settings of the monochromator, and so the relative energies of the photoelectron and Auger electron peaks may also vary [2] by up to 0,2 eV. The linearity test for monochromated Al X-rays is therefore made with a photoelectron peak and, for this purpose, the Ag $3d_{5/2}$ peak is chosen [3]. In conducting the measurements for this International Standard, this change from the Cu L_3VV peak to the Ag $3d_{5/2}$ peak, and the consequent need to add the Ag sample, are the only changes in procedure contingent on the use of monochromated Al X-rays in place of unmonochromated X-rays.

If the linearity test is adequate, a binding-energy scale correction may be derived using a simple regular calibration procedure defined at 5.10. Exactly how the binding-energy scale is corrected depends on practical details of the instrument being calibrated, and so a number of strategies are given at 5.11. The analyst also needs to consider the uncertainty with which the peak binding energies need to be measured. Table 1 shows values of some of the typical parameters, defined in this International Standard, which lead to illustrative tolerance limits of ±0,1 eV and ±0,2 eV at a confidence level of 95 %. Note, in Table 1, the importance of the allowable drift between calibrations. Thus, following the flowchart in Figure 1, the calibration interval is determined from measurements of the instrument drift as described at 5.13. The regular calibration is then made at the appropriate calibration interval to maintain the instrumental binding-energy scale within the required tolerance limits.

In this International Standard, measurements are described to establish the uncertainty of the calibration at a confidence level of 95 %, directly after the calibration. The error of the binding-energy scale will generally increase with time and, during the interval between calibrations, must not exceed the tolerance limits of $\pm\delta$ chosen by the analyst to define the quality of their measurements. Completing a table such as the example in Table 1 will assist the user in defining a suitable value for δ. If you have no idea of the capability of your instrument, if the manufacturer's data give no assistance and if you have no clear idea of your requirements, start with Table 1 with δ set at 0,1 eV. Go through the procedure described in this International Standard, filling in the rows, and finally check if this value of δ is feasible for your instrument. If not, review your operating procedures and either reduce one or more of the terms contributing to U_{95} or increase the value of δ that you can accept.

It is important to note that δ is the tolerance limit for the accuracy of the calibration of the instrumental binding-energy scale. Subsequent binding-energy measurements may have uncertainties greater than δ as a result of peak breadth, poor counting statistics, peak synthesis or charging effects. Guidance on reporting the uncertainty of subsequent measurements is given in Annex C. Above, it is noted that the effective X-ray energies for monochromated Al X-rays may vary from instrument to instrument and so, in Annex D, a method is given to measure this energy.
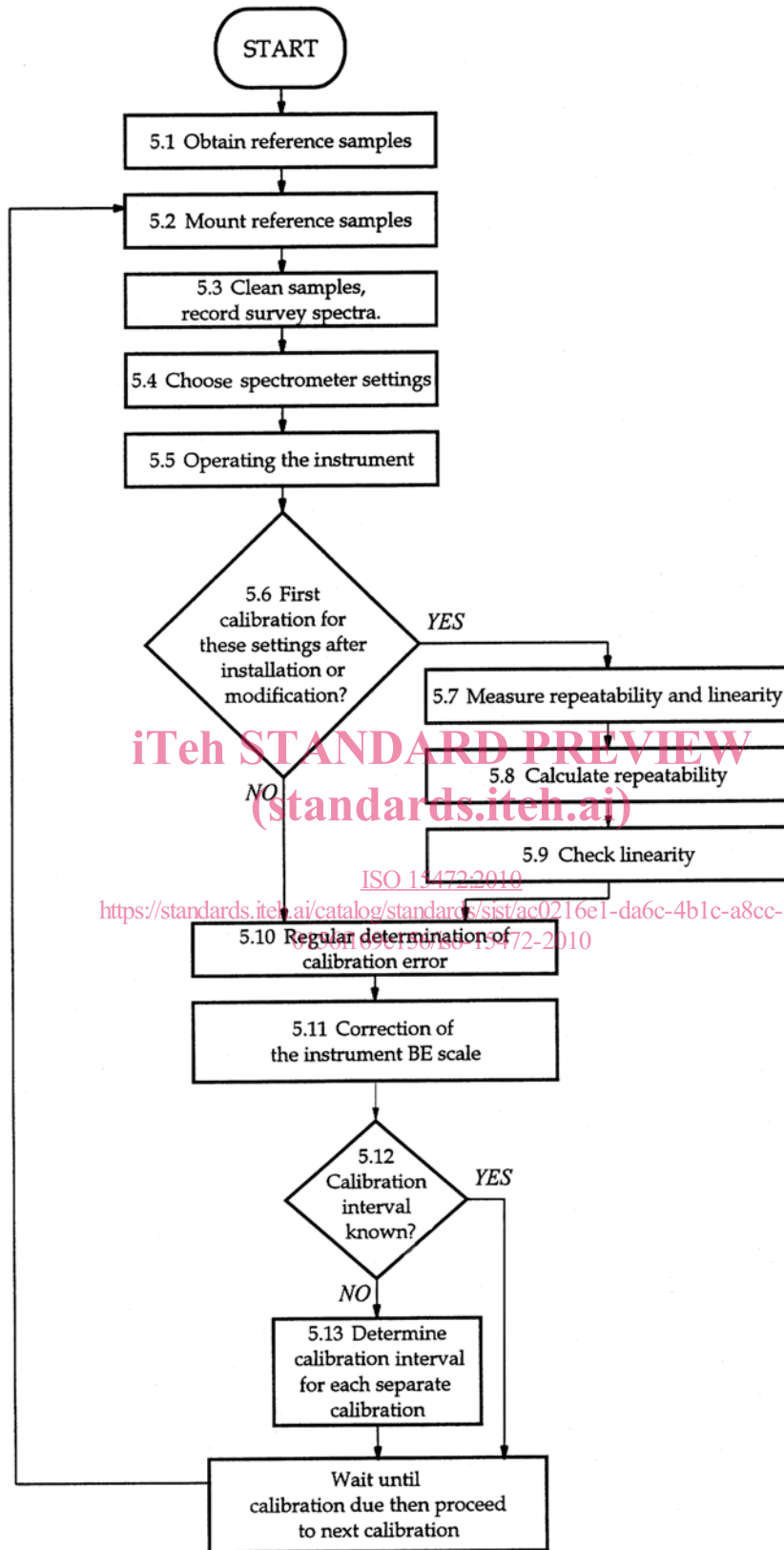
Figure 1 — Flowchart of the sequence of operations of the method
(subclause numbers are given with each item for cross-referencing with the body of the text)

Table 1 — Contributions to an error budget for binding-energy scale calibration
(The uncertainties are for a confidence level of 95 %. The examples illustrate the effect of your choices on the uncertainty of calibration and the required interval between recalibrations.)

Item	Symbol	Calculated from	Examples				
			If you require a high accuracy		If you require a lower accuracy		
Tolerance limits, eV	$\pm\delta$	You choose	$\pm0,1$		$\pm0,2$		*Your choice is dictated by the accuracy you require and the number of spectra you have time to acquire in regular calibrations.*
Repeatability standard deviation, eV	σ_R	Eq (1)	0,020		0,020		*Characteristic of your spectrometer measured at first calibration (see 5.7).*
Number of times each pair of spectra is acquired	m	You choose $m = 1$ or 2	$m = 1$	$m = 2$	$m = 1$	$m = 2$	
Uncertainty of calibration measurements, eV	U_{95}^{cl}	Eq (12) or (13)	0,074	0,052	0,074	0,052	
Measure of scale non-linearity, eV	ε_2 or ε_3	Eq (4), (5) or (6)	0,020	0,020	0,020	0,020	*Characteristic of your spectrometer measured at first calibration (see 5.7).*
Uncertainty of energy scale after calibration, eV	U_{95}	Eq (11)	0,078	0,057	0,078	0,057	
Maximum allowable drift between calibrations, eV	$\pm(\delta-U_{95})$	δ and U_{95}	$\pm0,022$	$\pm0,043$	$\pm0,122$	$\pm0,143$	*Define the drift allowable before you are in danger of exceeding your chosen limits $\pm\delta$ eV.*
Maximum calibration interval (for a steady drift rate of 0,025 eV per month), months	—	Subclause 5.13	0,9	1,7	4,9	5,7	*Choose a convenient interval below this maximum, and less than 4 months, with safety margin for any erratic behaviour.*
Your choice of calibration interval, months	—	You choose based on observed drift behaviour	Option not practical	1	3	4	

5 Procedure for calibrating the energy scale

5.1 Obtaining the reference samples

For the calibration of X-ray photoelectron spectrometers with unmonochromated Al or Mg X-ray sources, use samples of Cu and of Au. For instruments with a monochromated Al X-ray source, add Ag. The samples shall be polycrystalline and of at least 99,8 % purity metals which, for convenience, are usually in the form of foils typically of an area 10 mm by 10 mm, and 0,1 mm to 0,2 mm thick.

NOTE   If the samples appear to need cleaning, a short dip in 1 % nitric acid may be used for Cu and Ag with subsequent rinsing in distilled water. If the Cu sample has been stored in the air for more than a few days, the dip in nitric acid will make the sample cleaning, required later in 5.3.1, much easier.

5.2 Mounting the samples

Mount the samples of Cu, Au and, if appropriate, Ag on the sample holder or on separate sample holders, as appropriate, using fixing screws, or other metallic means, to ensure electrical contact: do not use double-sided adhesive tape.

5.3 Cleaning the samples

5.3.1 Achieve ultra-high vacuum and clean the samples by ion sputtering to reduce the contamination until the heights of the oxygen and carbon 1s signals are each less than 2 % of the height of the most intense metal peak in each survey spectrum. Record a survey (widescan) spectrum for each of the samples to ensure that the only significant peaks are those of the required pure elements. The quality of vacuum necessary here is such that the oxygen and carbon 1s peak heights shall not exceed 3 % of the heights of the most intense metal peaks by the time you have reached completion of 5.10 or at the end of the working day (whichever is the earlier).

NOTE 1   Inert-gas ion-sputtering conditions that have been found suitable for cleaning are 1 min of a 30 µA beam of 5 keV argon ions covering 1 cm^2 of the sample.

NOTE 2   Example XPS spectra may be found in References [4] to [8] of the Bibliography.

5.3.2 Try to conduct all relevant parts of this International Standard in one working day. If more than one day is required, confirm the cleanness of the samples at the start of each day's work.

5.4 Choosing the spectrometer settings for which energy calibration is required

Choose the spectrometer operating settings for which the energy calibration is required. The calibration procedure from 5.4 to 5.13 shall be repeated for each X-ray source and combination of spectrometer settings of pass energy, retardation ratio, slits, lens settings, etc., for which a calibration is required. Record the values of these settings in the spectrometer calibration log.

NOTE   The designs of spectrometers and their circuits vary, and a spectrometer calibration made for one combination of lens settings, slits and pass energy will not necessarily be valid for any other setting of the lens, slits and pass energy. Many spectroscopists make accurate measurements under one optimum set of conditions and then only that set of analyser conditions needs calibration. Any calibration made is only valid for the combination of settings used.

5.5 Operating the instrument

Operate the instrument in accordance with the manufacturer's documented instructions. The instrument shall have fully cooled following any bakeout. Ensure that the operation is within the manufacturer's recommended ranges for X-ray power, counting rates, spectrometer scan rate and any other parameter specified by the manufacturer. Check that the detector multiplier settings are correctly adjusted. For multidetector systems, ensure that any necessary optimizations or checks described by the manufacturer are conducted prior to this calibration.

NOTE 1   Many manufacturers recommend that the control and high-voltage electronics are switched on for at least 4 h before conducting any work where accurate energy referencing is important. It may also be necessary to have operated the X-ray anode for a period, for example 1 h, before making accurate measurements.

NOTE 2   Monochromators may need a warm-up time, and the X-ray energies transmitted may depend on the ambient temperature or the temperature around the monochromator. Records of these temperatures may help diagnose any problems observed of peak energy drift.

NOTE 3   High counting rates [9] or incorrect detector voltages [9],[10] can cause peak distortions which lead to erroneous peak energy assignments.