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

Reference number
ISO 15472:2010(E)

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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.

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.

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
$E_{\text{meas}\,n}$	average of the measured binding energies for a peak, n, in Table 2, in eV
$E_{\text{meas}\,ni}$	one of a set of measurements of binding energy for peak n in Table 2, in eV
$E_{\text{ref}\,n}$	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
$U_{95}^{\text{c}}(E)$	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}
$\sigma_{\text{R}n}$	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.

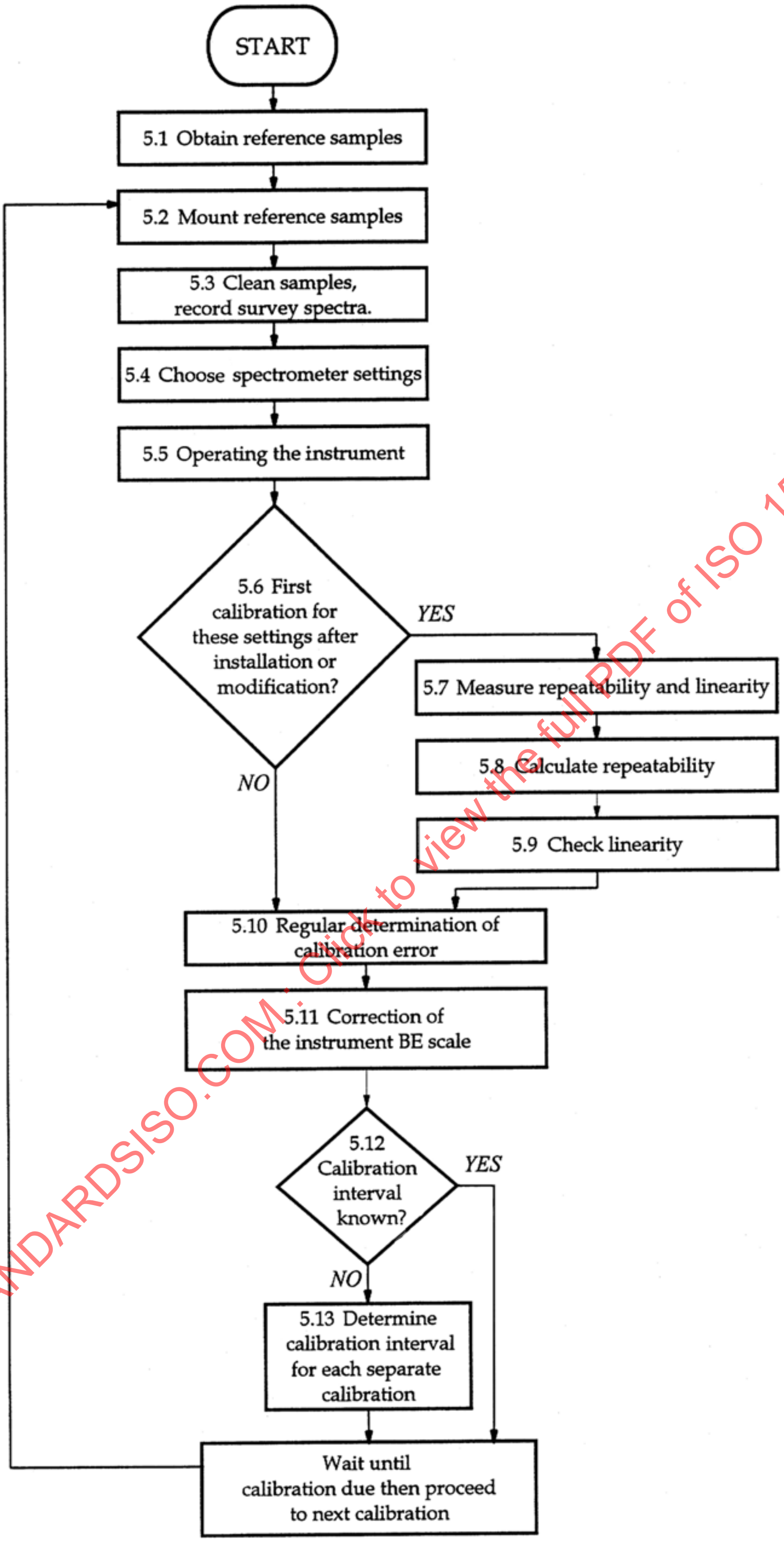


Figure 1 — Flowchart of the sequence of operations of the method
(subclause numbers are given with each item for cross-referencing with the body of the text)

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	$\pm$0,1		$\pm$0,2		*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}	$\pm$0,022	$\pm$0,043	$\pm$0,122	$\pm$0,143	*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.

5.6 Options for initial or subsequent calibration measurements

In order to maintain the binding-energy scale of an instrument in calibration, the binding-energy repeatability standard deviation, the scale linearity error and the calibration interval all need determination. If any of these have not been determined, proceed as below. If all of these have been determined for the relevant spectrometer settings through prior use of this International Standard and if the instrument has not been modified, undergone significant repair or been moved, proceed directly to 5.10, as shown in the flowchart of Figure 1.

5.7 Measurements for the peak binding-energy repeatability standard deviation and the scale linearity

5.7.1 The repeatability standard deviation of the peak binding energy, σ_R, is measured, as described from 5.7.4 to 5.7.7, using the Au $4f_{7/2}$, Ag $3d_{5/2}$ or Cu L_3VV, and Cu $2p_{3/2}$ peaks and need usually only be done for the first energy calibration for a given combination of settings. The value of σ_R is valid only for the selected set of conditions and involves a significant contribution from the sample-positioning procedure used for the analysis. For consistency, this sample-positioning procedure shall follow a documented protocol which takes account of the manufacturer's recommendations. This part shall be conducted for each choice of spectrometer operating settings requiring energy calibration as chosen at 5.4. It may also need to be repeated after any substantive modifications to the instrument.

NOTE The sample-positioning procedure will depend on the instrument design, the type of sample, the sample shape and the requirements for analysis. In many cases, the correct sample position is determined by maximizing the spectral intensity. Where optimization involves setting two or more interacting parameters, a consistent strategy of optimization is necessary. Where optimization involves a monochromator, changes in the sample position may lead to shifts in the recorded peak energy so that in the maximization of intensity it may be necessary to measure intensities in the energy range up to ±0,5 eV from the nominal peak binding energy. For these systems, the intensity optimization may be found to be more sensitive to the sample position at low, rather than at high, binding energies or, more rarely, *vice versa*. Optimization is usually most effective at the binding energy where the intensity is most sensitive to the sample position. It may be useful to conduct 5.7 several times in order to refine the sample-positioning procedure and obtain low values of the repeatability standard deviations.

5.7.2 The binding-energy scale linearity is determined, as described at 5.7.6, using the Cu L_3VV Auger electron peak for unmonochromated Al and Mg X-rays and the Ag $3d_{5/2}$ photoelectron peak for monochromated Al X-rays. It is conducted at the same time as the repeatability measurements, in order to reduce the effort and reduce the uncertainty.

5.7.3 The order of acquisition of the data is defined from 5.7.4 to 5.7.7 and, for unmonochromated Al or Mg X-rays, is

Au $4f_{7/2}$, Cu $2p_{3/2}$, Cu L_3VV, with this sequence repeated six further times

and, for monochromated Al X-rays, is

Au $4f_{7/2}$, Cu $2p_{3/2}$, Ag $3d_{5/2}$, with this sequence repeated six further times.

NOTE The Au $4f_{7/2}$ peak often is the weakest peak although, depending on the spectrometer, sometimes the Cu L_3VV peak may be weaker. Starting with the Au $4f_{7/2}$ peak facilitates a common set of conditions to be used for all peaks.

5.7.4 Set the gold sample at the analytical position with an angle of emission of the detected electrons in the range 0° to 56° from the sample normal. Use the documented sample-positioning procedure and record the Au $4f_{7/2}$ peak binding energy using the set of conditions chosen at 5.4 with appropriate X-ray power and channel dwell time to achieve more than 40 000 counts per channel at the peak. Scan with the channel energy interval set at approximately 0,05 eV or 0,1 eV depending on the way you wish to determine the peak binding energy as described later in 5.8.1. Scan from at least 1 eV below the peak energy to 1 eV above the peak energy. Ensure that the correct peak has been identified using the wide-energy (survey) scan. The reference binding energy of the Au $4f_{7/2}$ peak, peak 1, is given in Table 2.

Many spectrometer control units offer a wide range of energy scale scan rates. High scan rates can cause the measured peak binding energy to shift. Ensure that the scan rate used gives no significant peak shift.

NOTE The reference binding-energy values for the calibration peaks vary with the angle of emission, θ. The reference values in this International Standard are only valid for $0° \leqslant \theta \leqslant 56°$ and so the method has been restricted to this angular range [2]. For $\theta > 56°$, the larger shifts of the peaks lead to significant errors in the calibration.

Table 2 — The reference values for the peak positions on the binding-energy scale [11],[12], $E_{\text{ref } n}$

Peak number, n	Assignment	$E_{\text{ref } n}$ eV		
		Al Kα	Mg Kα	Monochromatic Al Kα
1	Au $4f_{7/2}$	83,95	83,95	83,96
2	Ag $3d_{5/2}$	(368,22)	(368,22)	368,21
3	Cu L_3VV	567,93	334,90	—
4	Cu $2p_{3/2}$	932,63	932,62	932,62
NOTE 1 Table 2 is a refinement of earlier tables [13],[14].				
NOTE 2 The Ag data included in parentheses are not normally used for calibrations.				

5.7.5 Remove the gold sample from the analysis position and replace it with the copper sample with the same angle of emission, using your sample-positioning procedure. Record the Cu $2p_{3/2}$ peak, maintaining the same chosen set of spectrometer settings as for the gold sample and allowing sufficient acquisition time to provide more than 40 000 counts per channel at the peak. Scan from at least 1 eV below the peak energy to 1 eV above the peak energy. Ensure that the correct peak has been identified using the wide-energy (survey) scan.

5.7.6 For the chosen combination of spectrometer settings of pass energy, retardation ratio, slits, lens settings, etc., next record the Cu L_3VV peak if you are using unmonochromated Al or Mg X-rays or replace the copper sample with the silver sample at the same angle of emission, position it with the positioning procedure and record the Ag $3d_{5/2}$ peak if you are using monochromated Al X-rays.

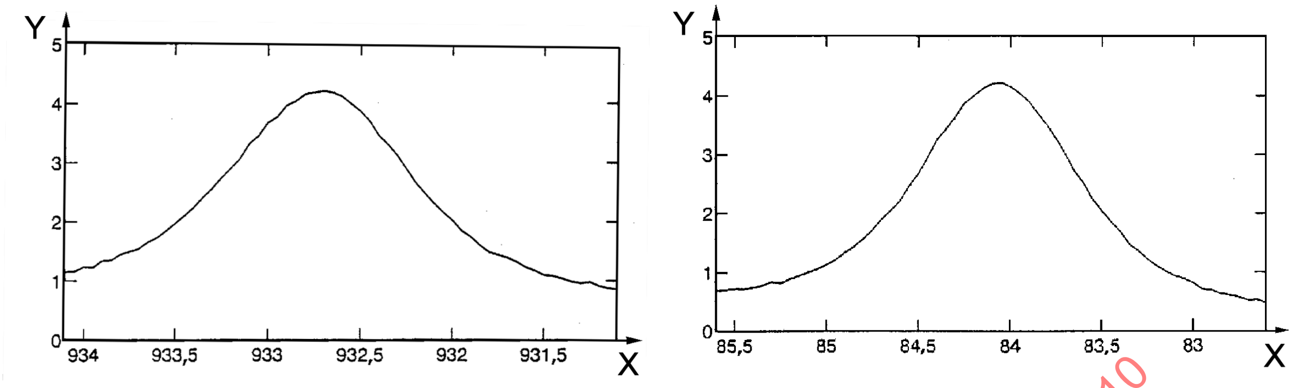
5.7.7 Repeat 5.7.4, 5.7.5 and 5.7.6, in order, a further six times to obtain seven independent records of each of the three peaks. To save time, the scan widths for these spectra may be reduced to the range ±0,5 eV from the peak unless a wider interval is made necessary by your choice of software for determining the peak binding energy in 5.8.1.3.

5.8 Calculating the peak binding-energy repeatability standard deviation

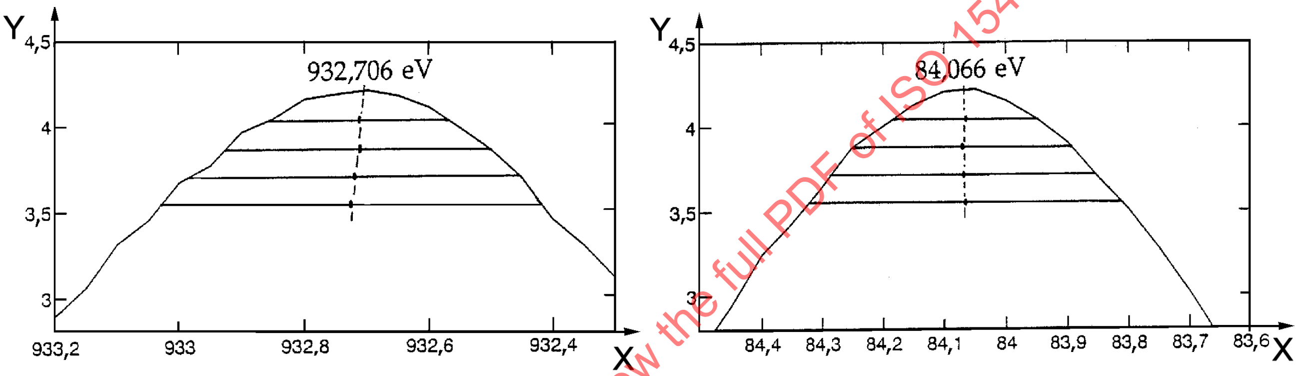
5.8.1 Determine the measured peak binding energies by one of the three methods described in 5.8.1.1, 5.8.1.2 and 5.8.1.3.

NOTE The first method is provided for analysts with instruments that only provide a graphical output. The second and third methods are recommended for those with digital data.

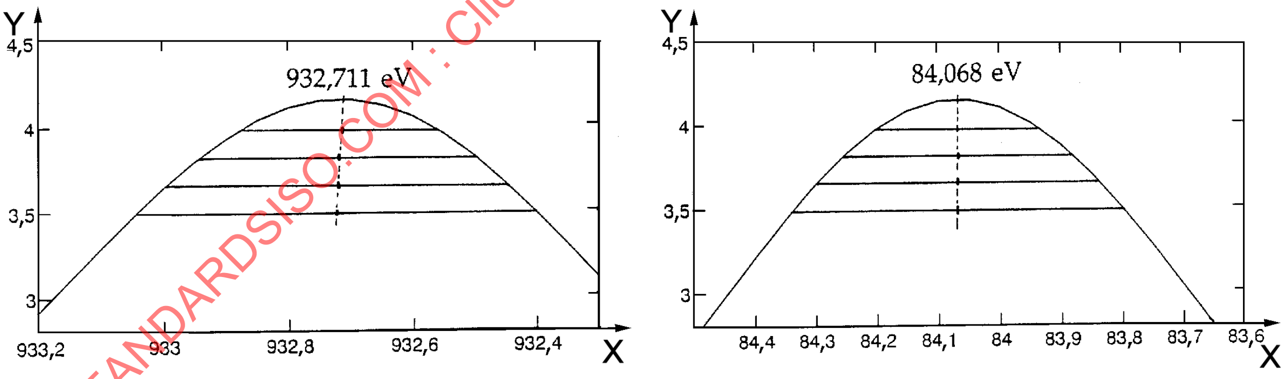
5.8.1.1 For the first method, determine the mid-point of the chords drawn horizontally across the peak at an intensity of 84 % of the peak height above zero counts, and at three or more further intensities approximately equally spaced in the range 84 % to 100 % of the peak intensity above zero, as shown in Figure 2. These mid-points are then projected to a value at the peak, giving the peak energy, as shown in Figure 2, either graphically or computationally using a best-fit line for the four or more mid-points.



a) Cu $2p_{3/2}$ b) Au $4f_{7/2}$



c) Cu $2p_{3/2}$ detail, unsmoothed d) Au $4f_{7/2}$ detail, unsmoothed



e) Cu $2p_{3/2}$ detail, smoothed f) Au $4f_{7/2}$ detail, smoothed

Key

X binding energy (eV)

Y counts × 10^4

Figure 2 — 5 eV scans around a) the Cu $2p_{3/2}$ and b) the Au $4f_{7/2}$ peaks using Mg Kα X-rays, a pass energy of 50 eV, and 0,05 eV energy steps, with details c) and d) unsmoothed and e) and f) smoothed by a 9-point Savitzky and Golay function [15]
[Figures 2 c) to 2 f) show the bisected-chord method of finding the peak binding energy]

NOTE The precision of this procedure may be improved if, prior to the procedure, the data are smoothed with a Savitzky and Golay cubic/quadratic routine [15] with a width equal to or less than half of the full width at half the maximum intensity (FWHM) of the peak above background, as shown by the 9-point smooth in Figures 2 e) and 2 f). For a peak with an FWHM of 1,0 eV and an energy interval of 0,1 eV, this smooth would be 5 points.

5.8.1.2 For the second method, use a least-squares fit of a parabola to the data around the top of the peak. The data points selected shall be approximately equal in number above and below the energy of the maximum intensity and shall start and finish at intensities in the range 85 % to 95 % of the peak intensity above zero intensity for unmonochromated Al X-ray sources, 80 % to 95 % of the peak intensity above zero intensity for unmonochromated Mg X-ray sources, and 75 % to 95 % of the peak intensity above zero intensity for monochromated Al X-ray sources. If this least-squares fitting is not available in your software, you may use the simple least-squares calculation procedure, given in Annex A, requiring six data points. If the intensity constraints need relaxation, use the highest part of the peak that contains six data points.

NOTE The energy intervals for use of the procedure in Annex A are given at A.2.

5.8.1.3 The third method is also a least-squares fit to the data points in the intensity interval defined in 5.8.1.2, but uses the software available in some data systems for peak fitting to define the peak binding energy. This shall only be used if the peak fitting can be and is restricted to the data points defined in 5.8.1.2. A constant background may be subtracted or added to aid the fitting, but no asymmetric background such as a sloping line, or a Shirley or Tougaard background, shall be subtracted or utilized as part of the fitting procedure. The fitting shall be made by using a single peak of a symmetrical function, such as a Gaussian, Lorentzian or Voigt, or a sum or product of such functions. Some software systems do not fully conform to these requirements and so, the first time that this method is used, one record of data for each peak shall be confirmed using one of the methods given in 5.8.1.1 or 5.8.1.2.

Some software systems generate asymmetric versions of the line shapes which are not simply Gaussian, Lorentzian or Voigt. Ensure that such asymmetries are set to zero in conducting the fit.

5.8.2 Tabulate the seven values of the measured binding energies for each of the three peaks.

5.8.3 Calculate the average binding energy, $E_{\text{meas }n}$, from the set of seven measurements, $E_{\text{meas }ni}$, for each peak, n. Next, calculate the repeatability standard deviation, σ_{R1}, of the seven Au 4f$_{7/2}$ peak energy measurements, $E_{\text{meas }1i}$, from 5.7 using the equation:

$$\sigma_{\text{R1}}^2 = \sum_{i=1}^{7} \frac{\left(E_{\text{meas }1i} - E_{\text{meas }1}\right)^2}{6} \tag{1}$$

where $E_{\text{meas }1}$ is the average value of the $E_{\text{meas }1i}$ values. The repeatability standard deviations, σ_{R2} or σ_{R3}, and σ_{R4}, for the Ag 3d$_{5/2}$ or Cu L$_3$VV, and the Cu 2p$_{3/2}$, peaks are calculated in a similar way. The overall repeatability standard deviation, σ_{R}, is taken as the greatest of σ_{R1}, σ_{R2} or σ_{R3}, and σ_{R4}.

NOTE It is helpful to record the value of σ_{R} in your version of Table 1.

5.8.4 Review the Cu 2p$_{3/2}$ and Au 4f$_{7/2}$ peak energies for any systematic changes with time through their order of acquisition. Such systematics may indicate an inadequate warm-up period or other source of drift. If this appears to be the case, take appropriate action (e.g. increase the warm-up period) and repeat 5.7.

5.8.5 The values of the repeatability standard deviation should be less than 0,05 eV for an instrument in good working condition. If σ_{R4} or σ_{R1} exceeds this value, check the stabilities of the voltage supplies to the instrument, the adequacy of the system ground and the sample-positioning procedure. If $\sigma_{\text{R}} > \delta/4$, it will be necessary to increase the proposed value of δ or find a way of reducing σ_{R}.

NOTE In an interlaboratory study [16] in which copper samples were repositioned each time after analysing a different sample, 87 % of the results gave $\sigma_{\text{R4}} \leqslant 0{,}030$ eV whereas repeated measurements without moving the samples reduced σ_{R4} such that $\sigma_{\text{R4}} \leqslant 0{,}021$ eV [3]. Values of σ_{R4} as low as 0,001 eV have been measured [3].

5.9 Checking the binding-energy scale linearity

5.9.1 Subtract the reference energies, $E_{\mathrm{ref}\ n}$, given in Table 2 from the corresponding values of the average measured binding energies, $E_{\mathrm{meas}\ n}$, determined at 5.8.3, to obtain the measured instrument offset energies, $\varDelta_n$, for each peak, n. Thus

$$\varDelta_n = E_{\mathrm{meas}\ n} - E_{\mathrm{ref}\ n} \tag{2}$$

5.9.2 To determine whether the binding-energy scale is sufficiently linear for the intended application, it is necessary to calculate the measured binding-energy scale linearity error, ε_2, at the Ag 3d$_{5/2}$ (monochromated Al X-rays) peak or ε_3 at the Cu L$_3$VV (unmonochromated Al or Mg X-rays) peak using Equation (4), (5) or (6), which will be described below. This error is the difference between the measured instrument offset energy, $\varDelta_2$ or $\varDelta_3$, and that deduced from the measured Cu 2p$_{3/2}$ and Au 4f$_{7/2}$ peak binding energies assuming the scale to be linear. For monochromated Al X-rays, ε_2 is given by:

$$\varepsilon_2 = \varDelta_2 - \left[\frac{\varDelta_1 (E_{\mathrm{ref}\ 4} - E_{\mathrm{ref}\ 2}) + \varDelta_4\ (E_{\mathrm{ref}\ 2} - E_{\mathrm{ref}\ 1})}{E_{\mathrm{ref}\ 4} - E_{\mathrm{ref}\ 1}} \right] \tag{3}$$

For unmonochromated X-rays, ε_3 is given by a similar equation with $\varDelta_2$ and $E_{\mathrm{ref}\ 2}$ replaced by $\varDelta_3$ and $E_{\mathrm{ref}\ 3}$, respectively. Numerically, these equations reduce to:

$$\varepsilon_2 = \varDelta_2 - 0{,}665\varDelta_1 - 0{,}335\varDelta_4 \qquad \text{(for monochromated Al X-rays)} \tag{4}$$

$$\varepsilon_3 = \varDelta_3 - 0{,}430\varDelta_1 - 0{,}570\varDelta_4 \qquad \text{(for unmonochromated Al X-rays)} \tag{5}$$

and

$$\varepsilon_3 = \varDelta_3 - 0{,}704\varDelta_1 - 0{,}296\varDelta_4 \qquad \text{(for unmonochromated Mg X-rays)} \tag{6}$$

Calculate the value of ε_2 or ε_3 from Equation (4), (5) or (6) for the relevant X-ray source.

NOTE It is helpful to record the value of ε_2 or ε_3 in your version of Table 1.

5.9.3 The uncertainties of ε_2 and ε_3, for a confidence level of 95 %, in eV, are less than U^{l}_{95}, where U^{l}_{95} is given by the following equation:

$$U^{\mathrm{l}}_{95} = \left[(1{,}2\sigma_{\mathrm{R}})^2 + (0{,}026)^2 \right]^{1/2} \tag{7}$$

Calculate U^{l}_{95}. The binding-energy scale may be considered to be linear, for practical purposes, if $|\varepsilon_2|$ or $|\varepsilon_3|$ is less than U^{l}_{95}. If the value of $|\varepsilon_2|$ or $|\varepsilon_3|$ is greater than U^{l}_{95}, the scale is non-linear. This non-linearity may be acceptable, however, if $|\varepsilon_2|$ or $|\varepsilon_3|$ is less than $\delta/4$; that is, the linearity error may be regarded as sufficiently small compared to the chosen tolerance limit, δ.

EXAMPLE If σ_{R} is 0,020 eV (the illustrative value in Table 1), the uncertainty U^{l}_{95} is 0,035 eV.

NOTE 1 The derivation of Equation (7) is given in B.1.

NOTE 2 In an interlaboratory study [17], 10 out of 12 instruments exhibited $|\varepsilon_3|$ values less than 0,05 eV and these may be considered linear for $\delta = 0{,}2$ eV. Seven of the 12 had $|\varepsilon_3|$ values less than 0,025 eV and may be considered linear for $\delta = 0{,}1$ eV.

5.9.4 If $|\varepsilon_2|$ or $|\varepsilon_3|$ is greater than $\delta/4$, it is recommended that corrective action be taken. This may require a revision of your operating procedures followed by a repeat of 5.7, contact with your instrument vendor or an upward revision of δ.

NOTE The above is not a full test of linearity. A full test would need extensive test equipment and is beyond the scope of this International Standard.

5.10 Procedure for the regular determination of the calibration error

5.10.1 The calibration error shall be determined at regular intervals for each combination of spectrometer operating settings for which energy calibration of the spectrometer is required, after σ_R and ε_2 or ε_3 have been determined for those settings. Each determination of the calibration error shall be made prior to expiration of the calibration interval established in a previous use of the calibration procedure, as described at 5.13.

5.10.2 For the regular calibration, only the Au 4f$_{7/2}$ and Cu 2p$_{3/2}$ peaks need be used. The order of measurement shall be Au 4f$_{7/2}$, Cu 2p$_{3/2}$, with this sequence repeated one further time unless previous calibrations using this procedure have shown that $\sigma_R < \delta/8$, when this repeat may be ignored. The number of repeat measurements for the regular calibration, m, is thus 1 or 2. For each measurement, the sample shall be set at the same angle of emission, with that angle in the range 0° to 56° from the surface normal. The sample-positioning procedure shall be used. Determine the peak binding energies as described at 5.8.1, and calculate the measured instrument offset energies, Δ_1 and Δ_4, from Equation (2).

NOTE For modified Auger parameter measurements with monochromated Al X-rays, the Cu L$_3$VV peak should be added following the Cu 2p$_{3/2}$ peak. Details are given in Annex D.

5.10.3 The corrected binding-energy value, E_{corr}, is assumed to be linearly related to the measured binding energy, E_{meas}, by:

$$E_{\text{corr}} = (1+a)E_{\text{meas}} + b \tag{8}$$

The energy scaling error, a, is given by:

$$a = \frac{\Delta_1 - \Delta_4}{E_{\text{ref 4}} - E_{\text{ref 1}}} \tag{9}$$

and the zero offset error, b, by:

$$b = \frac{\Delta_4\, E_{\text{ref 1}} - \Delta_1\, E_{\text{ref 4}}}{E_{\text{ref 4}} - E_{\text{ref 1}}} \tag{10}$$

where $E_{\text{ref 1}}$ and $E_{\text{ref 4}}$ are as given in Table 2.

NOTE The values of a and b are the slope and intercept for $-\Delta$ versus E, not Δ versus E.

5.10.4 The uncertainty, U_{95}, at a confidence level of 95 % for this calibration, is given by:

$$\left(U_{95}\right)^2 = \left(U_{95}^{\text{cl}}\right)^2 + \left(1{,}2\left|\varepsilon_2 \text{ or } \varepsilon_3\right|\right)^2 \tag{11}$$

where, for binding energies in the range 0 eV to 1 040 eV, U_{95}^{cl} is given by:

$$U_{95}^{\text{cl}} = 2{,}6\sigma_R \qquad \text{for two measurements } (m = 2) \tag{12}$$

or

$$U_{95}^{\text{cl}} = 3{,}7\sigma_R \qquad \text{for one measurement } (m = 1) \tag{13}$$

NOTE 1 It is helpful to record the values of U_{95}^{cl} and U_{95} in your version of Table 1 for your chosen value of m.

NOTE 2 The derivations of Equations (11) to (13) are given in Annex B.

5.11 Procedures for correction of the instrument binding-energy scale

5.11.1 Implementation of the calibration of the spectrometer now depends on the instrument, its software, the magnitudes of the instrument offset energies, $\varDelta_n$, the repeatability standard deviation, σ_R, and the tolerance limits, $\pm\delta$, to which you wish to work.

If the values of $\left(\left|\varDelta_n\right| + U_{95}\right)$ for peaks 1 and 4 are both less than $\delta/4$, it may not be necessary to recalibrate the instrument after the calibration check. It is, of course, better that the instrument be recalibrated after each calibration check, but whether to do so must be judged in terms of the effort and required uncertainty. The manufacturer's calibration instructions to the analyst should now be followed to implement the calibration. For many systems, these permit the analyst only to change the spectrometer work function, ϕ. Your strategy will depend on what facilities are available on your instrument, but three suggestions are provided below.

In these suggestions, the corrected value for the binding energy, E_{corr}, is given by:

$$E_{\text{corr}} = E_{\text{meas}} + \Delta E_{\text{corr}} \tag{14}$$

where ΔE_{corr} is a correction value which depends on the option used.

5.11.1.1 Option 1 is to leave the instrument unchanged and to add a post-acquisition correction, ΔE_{corr}, to the measured binding energy where, from Equation (8):

$$\Delta E_{\text{corr}} = aE_{\text{meas}} + b \tag{15}$$

and where a and b are given by Equations (9) and (10).

5.11.1.2 Option 2 minimizes the post-acquisition correction to be applied over the binding-energy range 0 eV to 1 040 eV. Here, an increase $\Delta\phi$ is added to the value of the spectrometer work function used in the instrument, where:

$$\Delta\phi = \tfrac{1}{2}(\varDelta_1 + \varDelta_4) \tag{16}$$

The post-acquisition correction for subsequently measured binding energies is given by:

$$\Delta E_{\text{corr}} = a\left(E_{\text{meas}} - \frac{E_{\text{ref 1}} + E_{\text{ref 4}}}{2}\right) \tag{17}$$

This option causes ΔE_{corr} to be zero at 508,3 eV binding energy so that the post-acquisition corrections to the measured binding energies are minimized over the binding-energy range 0 eV to 1 040 eV.

5.11.1.3 Option 3 reduces the post-acquisition correction to zero for a particular binding energy selected by the analyst (corresponding to the binding energy for a frequently measured element). Here an increase, $\Delta\phi$, is applied to the spectrometer work function, given by:

$$\Delta\phi = aE_{\text{elem}} + b \tag{18}$$

where E_{elem} is the binding energy for the frequently measured element. Now the post-acquisition correction for subsequently measured binding energies is given by:

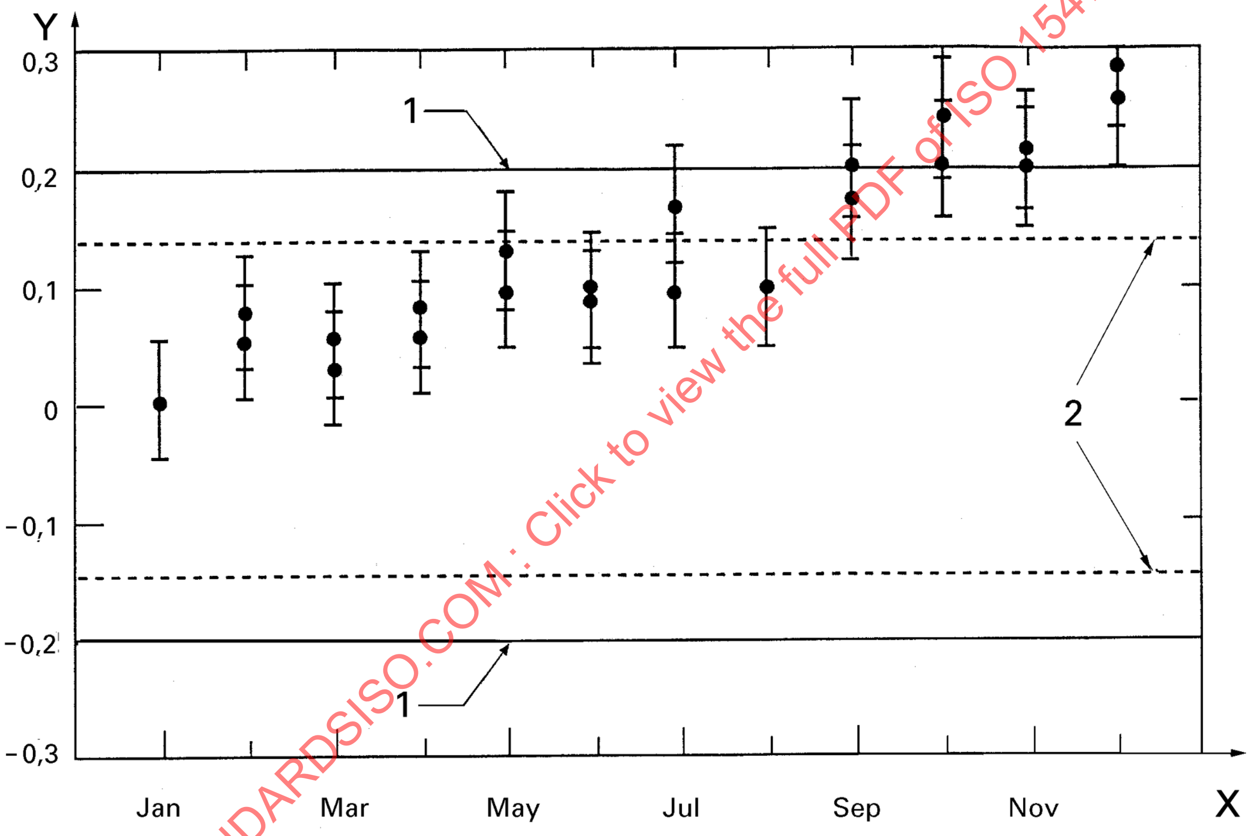
$$\Delta E_{\text{corr}} = a(E_{\text{meas}} - E_{\text{elem}}) \tag{19}$$

and ΔE_{corr} is zero at the binding energy of E_{elem}.

5.11.2 If, following 5.11.1, in the full, or a chosen restricted, range of binding energies required for analysis, the subsequent sum $\left|\Delta E_{\text{corr}}\right| + \left|U_{95}\right|$ remains below δ over the calibration interval, the post-acquisition correction, ΔE_{corr}, defined in 5.11.1.1, 5.11.1.2 or 5.11.1.3 may be ignored when analysing XPS data. The calibration, however, is now valid only for the range of binding energies selected here.

5.11.3 The corrective procedure chosen shall be documented together with the values of Δ_1, Δ_4, a, b, the valid kinetic energy range and $\Delta\phi$, if used. The corrective procedure shall be checked the first time the procedure is used by repeating the calibration to ensure that all actions have been correctly undertaken.

5.11.4 If this is the first calibration, prepare a control chart as in Figure 3. For all calibrations, add to the control chart the measured values of Δ_1 and Δ_4 if no post-acquisition correction to the binding-energy scale is applied, but include $\Delta_1 + \Delta E_{\text{corr}}$ (evaluated at $E_{\text{ref 1}}$) and $\Delta_4 + \Delta E_{\text{corr}}$ (evaluated at $E_{\text{ref 4}}$) if a post-acquisition correction is to be applied, as a function of the date of calibration. On this chart, also add the corresponding uncertainties, U_{95}, of these measurements and the tolerance limits, $\pm\delta$. The warning limits at $\pm 0{,}7\delta$ shall be shown to indicate when recalibration is necessary.



Key

X calibration date

Y Δ_1, Δ_4 (eV)

1 tolerance limit

2 warning limits

NOTE The plotted points represent the values for Δ_1 and Δ_4 which, here, are shown to illustrate an instrument that has not been recalibrated since the start in January and in which no post-acquisition correction to the binding-energy scale is applied. It is first out of calibration in July and should, since it has both passed the upper warning limit and reached the 4-month time limit, have been recalibrated in May. The uncertainties shown for each point (U_{95}) are for a confidence level of 95 % and include the scale linearity error and its uncertainty. This illustrates the example in Table 1 with $m = 2$ and $\delta = 0{,}2$ eV.

Figure 3 — Control chart [18],[19] to monitor the calibration status of an instrument

5.12 Next calibration

5.12.1 The next calibration is made before the sum of the calibration uncertainty, U_{95}, and the instrumental drift causes the total uncertainty in the calibration, at a confidence level of 95 %, to exceed $\pm\delta$. The calibration is therefore made at or before the calibration interval defined by the work in 5.13. If the interval is not known, proceed to 5.13, determine the interval and then proceed to 5.12.2 at that interval.

5.12.2 Repeat the procedure from 5.2 to 5.6 and 5.10 to 5.11 at the calibration interval defined in 5.13 unless the instrument has been modified or undergone significant change. Each time, note any change made to the calibration and the cumulative change since the calibrations started. Ensure that the cumulative change does not exceed any figure advised by the manufacturers. In all cases record the instrument settings for the calibration, including the pass energy or retardation ratio, slits or aperture settings, lens settings, and the X-ray source used.

5.13 Establishing the calibration interval

5.13.1 With the equipment running throughout the day, measure the Cu $2p_{3/2}$ and Au $4f_{7/2}$ binding energies at hourly intervals. Any drift shows that it may be necessary to leave some of the electronic units on for some specified minimum time (or perhaps to leave the units on continuously) to achieve adequate stability. Note the ambient temperature with each measurement and check for any correlation. Whatever procedure, in terms of warm-up times, etc., is used for the calibration shall also be used during analysis where conformance with this International Standard is required.

NOTE 1 For modified Auger parameter measurements with monochromated Al X-rays, the Cu L_3VV peak should be added following the Cu $2p_{3/2}$ peak. Details are given in Annex D.

NOTE 2 Drift is most likely to arise from temperature changes in either the voltage supplies for the spectrometer dispersing elements or the X-ray monochromator system. These drifts occur as a function of the time of operation and so may, for example, be repeated similarly each day. Thus, tests at 9.00 a.m. each day miss any diurnal drift. Drifts of the Cu $2p_{3/2}$ peak energy have been observed to be both larger and smaller than those of the Au $4f_{7/2}$ peak.

5.13.2 If the stability during the first day is adequate, measure the Cu $2p_{3/2}$ and Au $4f_{7/2}$ binding energies at progressively greater intervals of time such that U_{95} added to the greater of the changes in Δ_1 and Δ_4 between calibrations remains less than $\pm 0{,}7\delta$. The last interval becomes the maximum useful calibration interval until it is found that the drift rate data indicate that a shorter or longer period is appropriate. This interval shall not exceed 4 months.

NOTE For many instruments, a calibration interval of one or two months has been found adequate. A judgement of what is an adequate interval and what are appropriate tolerance limits depends on the analytical requirements and the instrument behaviour.

Annex A
(normative)

Least-squares determination of the peak binding energy by a simple computational method

A.1 Symbols

c_i count value in the ith channel

E_0 binding energy for the first data channel at lower binding energy than the channel for the absolute maximum intensity in the peak, in eV

E_p least-squares estimate of the peak binding energy, in eV

g channel separation, in eV

i channel number with its origin for the first data channel at lower binding energy than the channel for the absolute maximum intensity in the peak

p sum of the counts over six channels about the peak

q first moment of the distribution of counts over six channels about the peak divided by g

r second moment of the distribution of counts over the six channels about the peak divided by g^2

A.2 The least-squares method

A least-squares estimate of the energy of the peak may be conveniently determined by selecting the three data values on each side of the estimated peak binding energy. For unmonochromated Al or Mg X-ray sources, the data shall be obtained at channel separations of 0,1 eV or in the range 0,09 eV to 0,11 eV. For monochromated Al X-ray sources, where the full width at half maximum (FWHM) intensity of the peaks is less than 1,0 eV, these channel separations shall be 0,05 eV or in the range 0,045 eV to 0,055 eV but, where the FWHMs are equal to or greater than 1,0 eV, the condition for the unmonochromated sources shall apply.

The least-squares estimation of the peak binding energy, E_p, is given by [20]:

$$E_\mathrm{p} = E_0 + \frac{g}{2}\left(\frac{r - \frac{47}{15}q - \frac{8}{5}p}{r - q - \frac{8}{3}p} \right) \tag{A.1}$$

where

E_0 is the binding energy of the first data channel at lower binding energy than that for the maximum count, in eV;

g is the channel separation, in eV.

The parameters p, q and r are defined by:

$$p = \sum_{i=-2}^{3} c_i \tag{A.2}$$

$$q = \sum_{i=-2}^{3} i c_i \tag{A.3}$$

$$r = \sum_{i=-2}^{3} i^2 c_i \tag{A.4}$$

where

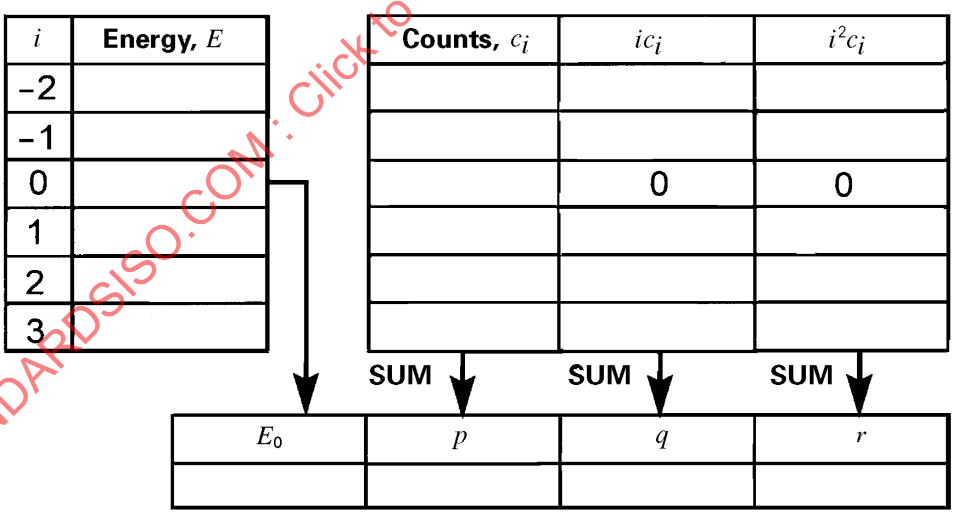
i is the channel number with value zero for the first data channel at lower binding energy than that for the maximum counts;

c_i is the count value for that channel.

Table A.1 may assist the computation. Table A.2 illustrates a completed version of this table for the Au 4f$_{7/2}$ peak.

In Reference [20], equations are provided to show the uncertainty in the value of E_p arising from the uncertainty associated with the statistics of Poissonian counts in the peak. The standard uncertainty is approximately 5 meV for the defined conditions.

Table A.1 — Table for entering values to compute E_p



i	**Energy, E**
−2	
−1	
0	
1	
2	
3	

Counts, c_i	ic_i	i^2c_i
	0	0

SUM SUM SUM

E_0	p	q	r

$$E_p = E_0 + \frac{g}{2}\left(\frac{r - \frac{47}{15}q - \frac{8}{5}p}{r - q - \frac{8}{3}p}\right)$$

Table A.2 — Table A.1 showing an example evaluation of E_p for the Au 4f$_{7/2}$ peak

i	**Energy**, E	**Counts**, c_i	ic_i	i^2c_i
-2	83,76	43 804	-87 608	175 216
-1	83,86	49 259	-49 259	49 259
0	83,96	52 958	0	0
1	84,06	53 889	53 889	53 889
2	84,16	51 903	103 806	207 612
3	84,26	47 812	143 436	430 308

SUM **SUM** **SUM**

E_0	p	q	r
83,96	299 625	164 264	916 284

$$E_\mathrm{p} = E_0 + \frac{g}{2}\left(\frac{r - \frac{47}{15}q - \frac{8}{5}p}{r - q - \frac{8}{3}p}\right)$$

$$= 83{,}96 \text{ eV} + (0{,}1 \times 0{,}83) \text{ eV}$$

$$= 84{,}043 \text{ eV}$$

Annex B
(informative)

Derivation of uncertainties

B.1 Computation of the uncertainty for the energy scale linearity error

For defining the repeatability standard deviations, σ_{R1} and σ_{R4}, for the Au 4f$_{7/2}$ and Cu 2p$_{3/2}$ peaks, k measurements are made. In this International Standard, k is chosen as 7. The uncertainties with which instrument offset energies Δ_1 and Δ_4 at $E_{\mathrm{ref\,1}}$ and $E_{\mathrm{ref\,4}}$ are then determined are given by $\pm U^{\mathrm{c}}_{95}\,(E_{\mathrm{ref\,1}})$ and $\pm U^{\mathrm{c}}_{95}\,(E_{\mathrm{ref\,4}})$ for a confidence level of 95 %, where

$$U^{\mathrm{c}}_{95}(E_{\mathrm{ref\,1}}) = t_{k-1}\sigma_{\mathrm{R1}}/k^{1/2} \tag{B.1}$$

and

$$U^{\mathrm{c}}_{95}(E_{\mathrm{ref\,4}}) = t_{k-1}\sigma_{\mathrm{R4}}/k^{1/2} \tag{B.2}$$

and where t_{k-1} is Student's t-factor for a two-sided distribution for k–1 degrees of freedom. In this annex, all uncertainties are for a confidence level of 95 %.

The uncertainty for the offset energy at a measured energy, E_{meas}, predicted from a straight line passing through the offset energies Δ_1 and Δ_4 at $E_{\mathrm{ref\,1}}$ and $E_{\mathrm{ref\,4}}$, is given by [2]:

$$U^{\mathrm{c}}_{95}(E_{\mathrm{meas}}) = t_{k-1}\left[\left(\frac{E_{\mathrm{meas}} - E_{\mathrm{ref\,1}}}{E_{\mathrm{ref\,4}} - E_{\mathrm{ref\,1}}}\right)^2 \times \frac{\sigma^2_{\mathrm{R4}}}{k} + \left(\frac{E_{\mathrm{ref\,4}} - E_{\mathrm{meas}}}{E_{\mathrm{ref\,4}} - E_{\mathrm{ref\,1}}}\right)^2 \times \frac{\sigma^2_{\mathrm{R1}}}{k}\right]^{\frac{1}{2}} \tag{B.3}$$

If, at this point, σ_{R} is equated with the greater of σ_{R4} and σ_{R1}, the uncertainty of the calibration at the energy of the linearity test, $E_{\mathrm{ref\,2}}$ or $E_{\mathrm{ref\,3}}$, is equal to or less than $U^{\mathrm{c}}_{95}\,(E_{\mathrm{ref\,2}})$, where

$$U^{\mathrm{c}}_{95}\,(E_{\mathrm{ref\,2}}) = t_{k-1}\frac{\sigma_{\mathrm{R}}}{k^{1/2}}\left[\left(\frac{E_{\mathrm{ref\,2}} - E_{\mathrm{ref\,1}}}{E_{\mathrm{ref\,4}} - E_{\mathrm{ref\,1}}}\right)^2 + \left(\frac{E_{\mathrm{ref\,4}} - E_{\mathrm{ref\,2}}}{E_{\mathrm{ref\,4}} - E_{\mathrm{ref\,1}}}\right)^2\right]^{\frac{1}{2}} \tag{B.4}$$

$$= 0{,}76\,t_{k-1}\frac{\sigma_{\mathrm{R}}}{k^{1/2}} \tag{B.5}$$

The coefficient 0,76 is calculated for unmonochromated Mg X-rays. For unmonochromated and for monochromated Al X-rays, this coefficient is lower, at 0,71 and 0,74, respectively. Equation (B.5) thus covers all three X-rays. The uncertainty of the measurement of the linearity test peak energy is given by $t_{k-1}\sigma_{\mathrm{R2}}/k^{½}$ or $t_{k-1}\sigma_{\mathrm{R3}}/k^{½}$. The uncertainty of the measured binding-energy scale linearity errors, ε_2 or ε_3, is given by the quadrature sum of one of these two terms and two further terms. The first such term is $U^{\mathrm{c}}_{95}\,(E_{\mathrm{ref\,2}})$ from Equation (B.5) and the second is the uncertainty of the linearity test peak's binding energy with respect to the Au 4f$_{7/2}$ and Cu 2p$_{3/2}$ peak binding energies. The value of the latter is 0,026 eV [2]. Thus, if σ_{R} is now equated with the greatest of σ_{R1}, σ_{R2} or σ_{R3}, and σ_{R4}, then:

$$\left(U_{95}^{\mathrm{l}}\right)^2 = \left(1{,}26\frac{t_{k-1}\sigma_{\mathrm{R}}}{k^{1/2}}\right)^2 + \left(0{,}026\right)^2 \mathrm{eV} \qquad \text{(B.6)}$$

Taking k as 7, $t_{k-1} = 2{,}447$, and from Equation (B.6):

$$U_{95}^{\mathrm{l}} \leqslant \left[(1{,}2\sigma_{\mathrm{R}})^2 + (0{,}026)^2\right]^{1/2} \mathrm{eV} \qquad \text{(B.7)}$$

as shown in Equation (7) in 5.9.3.

B.2 Computation of uncertainties for the regular calibration

The errors in the binding-energy scales of most instruments will be approximately linear with the binding energy, E. Even if ε_2 or ε_3 have been shown to be less than U_{95}^{l} so that the scale may be taken to be linear, this is only known at the energy $E_{\mathrm{ref\,2}}$ or $E_{\mathrm{ref\,3}}$ to the uncertainty U_{95}^{l}. Analysis of this situation, where σ_{R} is equal to the greatest of σ_{R1}, σ_{R2} or σ_{R3}, and σ_{R4}, gives the overall uncertainty U_{95}^{cl} for the binding-energy range 0 eV to 1 040 eV, where [2]

$$U_{95}^{\mathrm{cl}} \leqslant \frac{1{,}5 t_6 \sigma_{\mathrm{R}}}{m^{1/2}} \qquad \text{(B.8)}$$

and where m is the number of repeats in the routine calibration.

This gives:

$$U_{95}^{\mathrm{cl}} \leqslant 2{,}6\sigma_{\mathrm{R}} \qquad \text{for } m = 2 \qquad \text{(B.9)}$$

$$\leqslant 3{,}7\sigma_{\mathrm{R}} \qquad \text{for } m = 1 \qquad \text{(B.10)}$$

as shown in Equations (12) and (13) in 5.10.4. If $|\varepsilon_2|$ or $|\varepsilon_3|$ is greater than U_{95}^{l} but less than $\delta/4$, calibrations are still valid. The value of ε_2 or ε_3 must now be included in the uncertainty of the calibration. If the energy scale error is assumed to have a second-order dependence on E, the non-linearity contribution would maximize at $1{,}15\varepsilon_2$ or $1{,}15\varepsilon_3$ and minimize at $-1{,}15\varepsilon_2$ or $-1{,}15\varepsilon_3$ in the binding-energy range 0 eV to 1 100 eV. Again, a third-order energy scale error is contained within $\pm 1{,}2\varepsilon_2$ or $\pm 1{,}2\varepsilon_3$. The total energy scale uncertainty, U_{95}, is thus usefully given by:

$$U_{95} = \left[\left(U_{95}^{\mathrm{cl}}\right)^2 + \left(1{,}2|\varepsilon_2 \text{ or } \varepsilon_3|\right)^2\right]^{1/2} \qquad \text{(B.11)}$$

as shown in Equation (11) in 5.10.4.

Annex C
(informative)

Citation of the uncertainties of measured binding energies

C.1 General

This International Standard specifies a method for determining the calibration uncertainty for the binding-energy scale of an X-ray photoelectron spectrometer. Analysts may then wish to cite the uncertainty with which they may determine further (i.e. new) peak energies. For the purposes of this International Standard, this will be called the analytical uncertainty. There are three common situations to consider, as outlined below. All three involve the repeatability standard deviation of the new peak, σ_{Rnew}.

C.2 Energy difference between photoelectron peaks measured for two chemical states in one spectrum in which the surface potential is constant throughout the sample analysed

In this case, since spectrometers rarely have scale errors greater than 0,1 % and the energy differences of chemical states are less than 10 eV, many of the uncertainties of the present calibration may be ignored. The repeatability measurements at 5.7 have a significant contribution from the effects of sample position and, since this aspect is common to both of the relevant peaks, it is ignored. If the peak profiles do not overlap and there are more than 40 000 counts at the peak, the uncertainty of the separation will approach 0,02 eV. For weaker peaks, this uncertainty deteriorates [20]. If the peaks overlap, the maxima of the spectral intensity will not occur at the same energies as for the constituent peaks. It is customary then to use peak synthesis software which provides the binding energies for each constituent peak. The analytical uncertainties, for valid software, are then dominated by the statistics of the peak fitting [21],[22], rather than any of the items discussed in the present calibration, and may exceed 0,1 eV.

C.3 Energy difference between photoelectron peaks measured for a chemical state in two samples analysed sequentially

As in C.2, most of the calibration uncertainties may be ignored and the analytical uncertainty depends on the repeatability standard deviations for the two peaks. If the repeatability standard deviation, σ_{Rnew}, for a new peak being measured is equal to the value of σ_{R} determined in the calibration, the analytical uncertainty at a confidence level of 95 % for the energy difference, for conductors, is given by:

$$\text{Analytical uncertainty} = t_{k-1} 2^{1/2} \sigma_{\mathrm{R}} \tag{C.1}$$

If $k = 7$, then

$$\text{Analytical uncertainty} = 3{,}5\sigma_{\mathrm{R}} \tag{C.2}$$

For insulators, the uncertainty of the charge referencing needs inclusion. This uncertainty may dominate the other terms. Where adventitious carbon referencing is used and where the repeatability standard deviation for the carbon peaks is also σ_{R}, the analytical uncertainty will be no smaller than $2^{1/2}$ times the values given in Equations (C.1) and (C.2).

It should be noted that, for many peaks of interest, σ_{Rnew} will be greater than σ_{R} since the peaks will often be broader and less intense than the relevant metal peaks and may have been determined as a result of a peak-fitting analysis [21]. Derivation of σ_{Rnew} for these cases may be found in the literature [22].