



# Standard Practice for Calibration of the Electron Binding-Energy Scale of an X-Ray Photoelectron Spectrometer<sup>1</sup>

This standard is issued under the fixed designation E2108; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice describes a procedure for calibrating the electron binding-energy (BE) scale of an X-ray photoelectron spectrometer that is to be used for performing spectroscopic analysis of photoelectrons excited by unmonochromated aluminum or magnesium  $K\alpha$  X-rays or by monochromated aluminum  $K\alpha$  X-rays.

1.2 The calibration of the BE scale is recommended after the instrument is installed or modified in any substantive way. Additional checks and, if necessary, recalibrations are recommended at intervals chosen to ensure that BE measurements are statistically unlikely to be made with an uncertainty greater than a tolerance limit, specified by the analyst, based on the instrumental stability and the analyst's needs. Information is provided by which the analyst can select an appropriate tolerance limit for the BE measurements and the frequency of calibration checks.

1.3 This practice is based on the assumption that the BE scale of the spectrometer is sufficiently close to linear to allow for calibration by measurements of reference photoelectron lines having BEs near the extremes of the working BE scale. In most commercial instruments, X-ray sources with aluminum or magnesium anodes are employed and BEs are typically measured at least over the 0–1200 eV range. This practice can be used for the BE range from 0 eV to 1040 eV.

1.4 The assumption that the BE scale is linear is checked by a measurement made with a reference photoelectron line or Auger-electron line that appears at an intermediate position. A single check is a necessary but not sufficient condition for establishing linearity of the BE scale. Additional checks can be

made with specified reference lines on instruments equipped with magnesium or unmonochromated aluminum X-ray sources, with secondary BE standards, or by following the procedures of the instrument manufacturer. Deviations from BE-scale linearity can occur because of mechanical misalignments, excessive magnetic fields in the region of the analyzer, or imperfections or malfunctions in the power supplies. This practice does not check for, nor identify, problems of this type but simply verifies the linearity of the BE scale.

1.5 After an initial check of the BE-scale linearity and measurements of the repeatability standard deviation for the main calibration lines for a particular instrument, a simplified procedure is given for routine checks of the calibration at subsequent times.

1.6 This practice is recommended for use with X-ray photoelectron spectrometers operated in the constant-pass-energy or fixed-analyzer-transmission mode and for which the pass energy is less than 200 eV; otherwise, depending on the configuration of the instrument, a relativistic equation could be needed for the calibration. The practice should not be used for instruments operated in the constant-retardation-ratio mode at retardation ratios less than 10, for instruments with an energy resolution above 1.5 eV, or in applications for which BE measurements are desired with tolerance limits of  $\pm 0.03$  eV or less.

1.7 On instruments equipped with a monochromated aluminum  $K\alpha$  X-ray source, a measurement of the position of a specified Auger-electron line can be used, if desired, to determine the average energy of the X-rays incident on the specimen. This information is needed for the determination of modified Auger parameters.

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee E42 on Surface Analysis and is the direct responsibility of Subcommittee E42.03 on Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy.

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responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>2</sup>

E456 Terminology Relating to Quality and Statistics

E673 Terminology Relating to Surface Analysis (Withdrawn 2012)<sup>3</sup>

E902 Practice for Checking the Operating Characteristics of X-Ray Photoelectron Spectrometers (Withdrawn 2011)<sup>3</sup>

E1016 Guide for Literature Describing Properties of Electrostatic Electron Spectrometers

E1078 Guide for Specimen Preparation and Mounting in Surface Analysis

E1523 Guide to Charge Control and Charge Referencing Techniques in X-Ray Photoelectron Spectroscopy

2.2 *ISO Standards*:<sup>4</sup>

ISO 9001:2015 Quality management systems—Requirements

ISO 15472:2010 Surface chemical analysis—X-ray photoelectron spectrometers—Calibration of energy scales

ISO 18115-1:2013 Surface chemical analysis—Vocabulary—Part 1: General terms and terms used in spectroscopy

## 3. Terminology

3.1 *Definitions*—Since Terminology E673 was withdrawn in 2012, definitions of terms used in Auger and X-ray photoelectron spectroscopy are now based on ISO 18115-1:2013.<sup>5</sup> For definitions of terms used in statistics, see Terminology E456.

3.2 *Symbols and Abbreviations*—Table 1 shows definitions of the symbols and abbreviations used in this practice.

## 4. Summary of Practice

4.1 A procedure is given for calibrating the BE scale of an X-ray photoelectron spectrometer equipped with one or more of the following sources of characteristic K $\alpha$  X-rays: magnesium (Mg) source; unmonochromated aluminum (Al) source; or monochromated Al source. This procedure is based on ISO 15472:2010. In a first calibration for particular operating conditions of the instrument, or after the instrument has been modified, measurements are made of the BEs of specified core levels of copper and gold, and these values are then compared with corresponding reference energies (1).<sup>6</sup> The linearity of the BE scale is checked at a single point on the scale using a measurement of the position of either a specified core level of silver (monochromated Al source) or a specified Auger-

electron transition of copper (Mg source or unmonochromated Al source) (1, 2); additional checks can be made, if desired, with secondary standards. Procedures are given for determining the components of an uncertainty budget in BE measurements and for determining the uncertainties of BE measurements (at the 95 % confidence level) at various times following a calibration. The analyst can thus establish tolerance limits, for example, at the same level of confidence, based on the instrument stability and the analyst's needs so that BE measurements statistically are likely to be made within these limits during specified time intervals following a calibration. The instrument is then adjusted by following the procedures of the instrument manufacturer or subsequent BE measurements are corrected by following the procedure outlined in this practice. For a routine check of the instrumental calibration, either one or two measurements are made for each of the same core levels of copper and gold. Fig. 1 is a flow chart that summarizes the steps of the calibration procedure; references are given to relevant sections of this practice. An optional procedure is provided for determining the average energy of the X-rays from a monochromated Al X-ray source, using a measured position of a copper Auger peak.

## 5. Significance and Use

5.1 X-ray photoelectron spectroscopy is used extensively for the surface analysis of materials. Elements (with the exception of hydrogen and helium) are identified from comparisons of the binding energies determined from photoelectron spectra with tabulated values. Information on chemical state can be derived from the chemical shifts of measured photoelectron and Auger-electron features with respect to those measured for elemental solids.

5.2 Calibrations of the BE scales of XPS instruments are required for four principal reasons. First, meaningful comparison of BE measurements from two or more XPS instruments requires that the BE scales be calibrated, often with an uncertainty of about 0.1 eV to 0.2 eV. Second, identification of chemical state is based on measurement of chemical shifts of photoelectron and Auger-electron features, again with an uncertainty of typically about 0.1 eV to 0.2 eV; individual measurements, therefore, should be made and literature sources need to be available with comparable or better accuracies. Third, the availability of databases (3) of measured BEs for reliable identification of elements and determination of chemical states by computer software requires that published data and local measurements be made with uncertainties of about 0.1 eV to 0.2 eV. Finally, the growing adoption of quality management systems, such as, ISO 9001:2015, in many analytical laboratories has led to requirements that the measuring and test equipment be calibrated and that the relevant measurement uncertainties be known.

5.3 The actual uncertainty of a BE measurement depends on instrument properties and stability, measurement conditions, and the method of data analysis. This practice makes use of tolerance limits  $\pm\delta$  (chosen, for example, at the 95 % confidence level) that represent the maximum likely uncertainty of a BE measurement, associated with the instrument in a specified time interval following a calibration (ISO

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>4</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

<sup>5</sup> <https://www.iso.org/obp/ui/#iso:std:iso:18115:-1:ed-2:v1:en>.

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

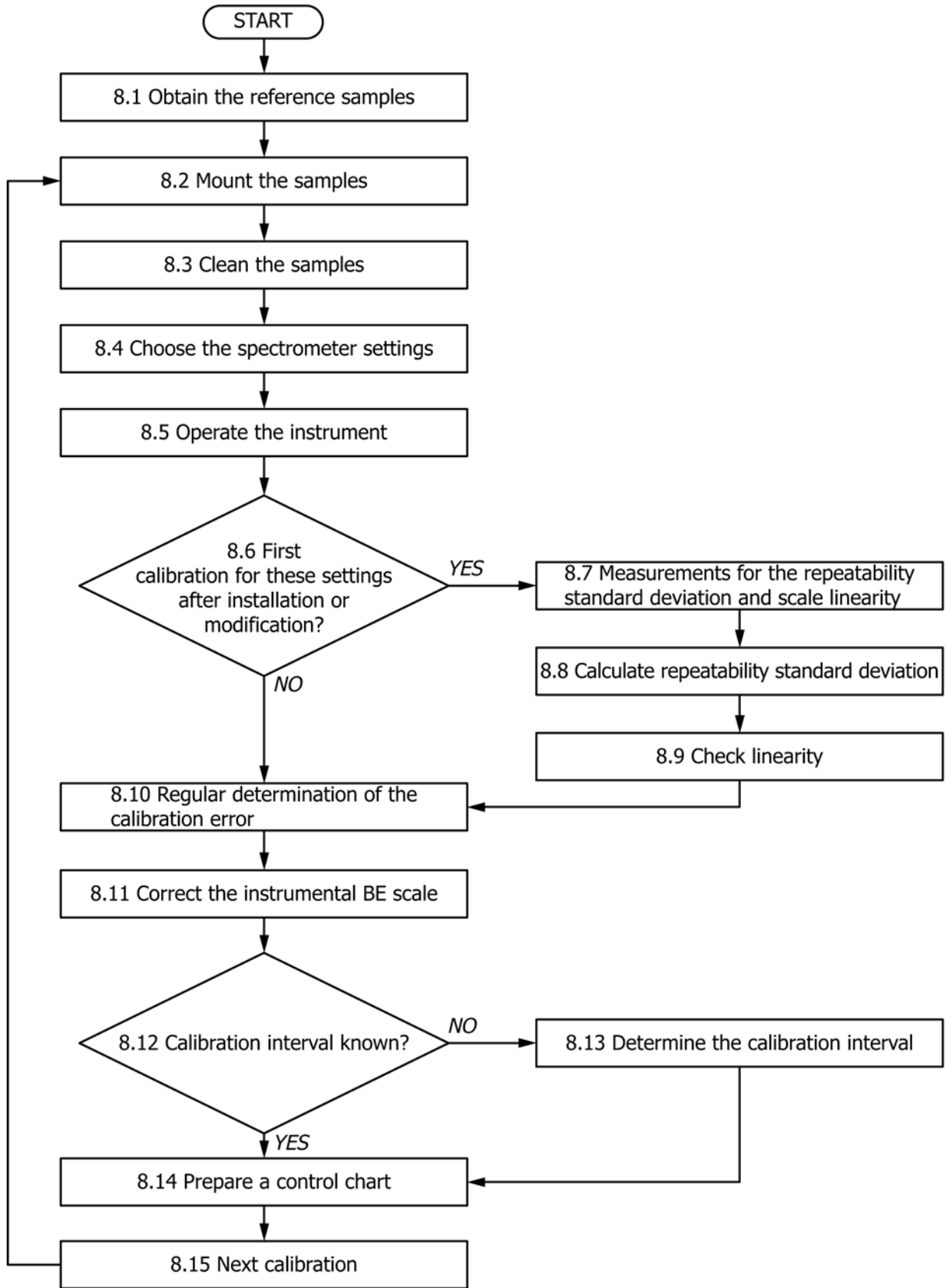
**TABLE 1 Definitions of Symbols and Abbreviations**

$a$	measured energy scaling error
$BE$	binding energy, in eV
$b$	measured zero offset error, in eV
$c_i$	number of counts in the $i$ -th channel
$eV$	electron volts
$E_{corr}$	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
$E_K$	kinetic energy of a peak, with reference to the Fermi level, in eV
$E_{meas}$	a measured binding energy, in eV
$E_{meas\ n}$	average of the measured binding energies for the peak, $n$ , in <a href="#">Table 3</a> , in eV
$E_{meas\ ni}$	one of a set of measurements of binding energy for the peak, $n$ , in <a href="#">Table 3</a> , in eV
$E_{ref\ n}$	reference values for the position of peak, $n$ , in <a href="#">Table 3</a> , on the binding energy scale, in eV
$E_p$	peak binding energy, in eV
$E_0$	binding energy for first data channel at lower binding energy than the channel with the maximum number of counts, for a peak, in eV
FWHM	full width at half maximum peak intensity above the background, in eV
$g$	channel energy separation, in eV
$h\nu_{Al}$	effective X-ray energy from an unmonochromated Al X-ray source, in eV
$h\nu_{Al}^{mon}$	effective X-ray energy from a monochromated Al X-ray source, in eV
$h\nu_{Mg}$	effective X-ray energy from an unmonochromated Mg X-ray source, in eV
$i$	index to represent channel number, where $i = 0$ represents the first channel at lower binding energy than the channel with the maximum number of counts, for a peak, in eV
$j$	number of repeat measurements for a new peak
$k$	number of repeat measurements for the Au 4f <sub>7/2</sub> , Cu 2p <sub>3/2</sub> and Ag 3d <sub>5/2</sub> or Cu L <sub>3</sub> VV peaks in the repeatability standard deviation and linearity determinations
$m$	number of repeat measurements for the Au 4f <sub>7/2</sub> and Cu 2p <sub>3/2</sub> peaks in the regular calibrations
$n$	designation of the peak identifier in <a href="#">Table 3</a>
$p$	parameter in <a href="#">Eq A1.1</a> , defined in <a href="#">Eq A1.2</a> and <a href="#">Section A1.2</a>
$q$	parameter in <a href="#">Eq A1.1</a> , defined in <a href="#">Eq A1.3</a> and <a href="#">Section A1.2</a>
$r$	parameter in <a href="#">Eq A1.1</a> , defined in <a href="#">Eq A1.4</a> and <a href="#">Section A1.2</a>
$t_x$	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 <sub>7/2</sub> and Cu 2p <sub>3/2</sub> peaks at binding energy $E$ , assuming perfect scale linearity, in eV
$U_{95}^{\varepsilon_2}$	uncertainty of $\varepsilon_2$ or $\varepsilon_3$ at a confidence level of 95 % from <a href="#">Eq 7</a> and <a href="#">Section 8.9.3</a> , in eV
$U_{95}^{\varepsilon_3}$	uncertainty of the calibration at a confidence level of 95 % in the absence of a linearity error, from <a href="#">Eq 12</a> or <a href="#">Eq 13</a> and <a href="#">Section 8.10.4</a> , in eV
XPS	X-ray photoelectron spectroscopy
$\alpha$	Auger parameter, in eV
$\alpha'$	modified Auger parameter, in eV
$\Delta_n$	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 <a href="#">Table 3</a> , for a given X-ray source
$\Delta E_{corr}$	correction to be added to $E_{meas}$ , after calibration, to provide the corrected result for the binding energy, in eV
$\Delta E_{corr\ n}$	value of $\Delta E_{corr}$ for peaks 1 and 4 in <a href="#">Table 3</a> , in eV
$\Delta E_n$	drift of the binding-energy scale following a calibration for peaks 1 and 4 in <a href="#">Table 3</a> , in eV
$\Delta\phi$	the average of $\Delta_1$ and $\Delta_4$ from <a href="#">Eq 16</a> and <a href="#">Section 8.11.1.2</a> , in eV
$\Delta h\nu$	difference between $h\nu_{Al}^{mon}$ and $h\nu_{Al}$ , in eV
$\delta$	value for the tolerance limit of energy calibration at a confidence level of 95 % (set by the analyst), in eV
$\varepsilon_2$	measured scale linearity error at the Ag 3d <sub>5/2</sub> peak from <a href="#">Eq 4</a> and <a href="#">Section 8.9.2</a> , in eV
$\varepsilon_3$	measured scale linearity error at the Cu L <sub>3</sub> VV peak from <a href="#">Eq 5</a> or <a href="#">Eq 6</a> and <a href="#">Section 8.9.2</a> , in eV
$\sigma_R$	maximum of $\sigma_{R1}$ , $\sigma_{R2}$ or $\sigma_{R3}$ , and $\sigma_{R4}$ , in eV
$\sigma_{Rn}$	repeatability standard deviation for the seven measurements of the binding energy of peak, $n$ , in <a href="#">Table 3</a> , in eV
$\sigma_{Rnew}$	repeatability standard deviation for a new peak, in eV

15472:2010). A user should select a value of  $\delta$  based on the needs of the analytical work to be undertaken, the likely measurement and data-analysis conditions, the stability of the instrument, and the cost of calibrations. This practice gives information on the various sources of uncertainty in BE measurements and on measurements of instrumental stability. The analyst should initially choose some desired value for  $\delta$  and then make tests, as described in [8.14](#) to determine from subsequent checks of the calibration whether BE measurements are made within the limits  $\pm\delta$ . Information is given in [Appendix X1](#) on how to evaluate for a material of interest the uncertainty of a BE measurement that is associated with the

uncertainty of the calibration procedure. This information is provided for four common analytical situations. It is important to note that some BE measurements may have uncertainties larger than  $\delta$  as a result of poor counting statistics, large peak widths, uncertainties associated with peak fitting, and effects of surface charging.

5.4 Instrument settings typically selected for analysis should be used with this practice. Separate calibrations should be made if key operating conditions, such as choices of analyzer pass energy, aperture sizes, or X-ray source, are varied. Settings not specified in this practice are at the discretion of the



NOTE 1—The number associated with each step indicates the section in which the operation is described.

FIG. 1 Flowchart Indicating Sequence of Operations for the Calibration.

user, but those same settings should be recorded and consistently used whenever this practice is repeated in order that the current results will be directly comparable to the previous results.

5.5 All of the operations described in Section 8 should be performed the first time that the BE scale is calibrated or after any substantial modification of the instrument. For later checks of the calibration, to be performed on a regular schedule, only the operations in 8.2 – 8.5, 8.10, 8.11, and 8.14 need to be performed. While the measurements described in 8.7 – 8.9 for the first calibration require moderate time and effort, they are essential for ensuring that realistic tolerance limits  $\pm\delta$  have been chosen. The control chart, described in 8.14, is a simple and effective means of demonstrating and documenting that the BE scale of the instrument is in calibration, that is, within the tolerance limits, for a certain period of time.

5.6 The average energy of the X-rays incident on the specimen for instruments equipped with a monochromated Al X-ray source will generally be slightly higher, by up to about 0.2 eV, than the average X-ray energy for instruments equipped with an unmonochromated Al X-ray source (4). The actual energy difference depends on the alignment and thermal stability of the X-ray monochromator. An optional procedure is given in Appendix X2 to determine this energy difference from measurements of the Cu  $L_3VV$  Auger-electron peak. This information is needed for the determination of modified Auger parameters and Auger-electron kinetic energies on instruments with the monochromated Al X-ray source.

## 6. Apparatus

6.1 *X-ray Photoelectron Spectrometer*—The X-ray photoelectron spectrometer is the instrument to be calibrated. The essential components of the spectrometer are an X-ray source (preferably with an X-ray tube containing one or more anodes of aluminum, or magnesium, or both), an ion gun for sample sputtering, a specimen holder that can hold three or more specimens, and an electron energy analyzer with which photoelectron intensities are measured as a function of photoelectron binding energy (the analyzer collecting photoelectrons under a given angular range as specified in 6.4). Some instruments with an Al X-ray source are equipped with an X-ray monochromator, and also a charge compensation device. XPS instruments also measure the intensities of Auger electrons that are emitted at characteristic energies. See Practice E902 for procedures to check the operating characteristics of an X-ray photoelectron spectrometer and Guide E1016 for information on the properties of electrostatic electron spectrometers.

6.2 *Reference Specimens*—The reference specimens, with which the spectrometer is calibrated, are polycrystalline foils of high-purity (at least 99.8 % pure) copper and gold. For instruments with a monochromated Al X-ray source, a polycrystalline silver film of similar purity is also required as a reference specimen. If desired, other high-purity metals can be used to check the linearity of the BE scale throughout its range. See Guide E1078 for guidance on specimen preparation and mounting. The foil dimensions should be chosen to be com-

patible with the specimen holder of the X-ray photoelectron spectrometer, and typically are 10 by 10 mm with a thickness of 0.2 mm.

6.3 *Ion Gun*—This practice requires use of an ion gun on the X-ray photoelectron spectrometer for sputter cleaning of the reference specimens used for the calibration measurements.

6.4 *Electron Emission Angle*—The electron emission angle should be between  $0^\circ$  and  $56^\circ$  with respect to the surface normal (5). The reference energies used in this practice are only valid for this range of emission angles.

## 7. Principle of the Calibration Method

7.1 For calibration of the XPS instrument with chosen instrumental settings, for example, X-ray source, analyzer pass energy, energy step size, and apertures, measurements are made of the binding energies of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  photoelectron peaks. These peaks are chosen because they are near the low and high BE limits for many practical analyses, Au and Cu foils of sufficient purity are readily available, the foil surfaces can be cleaned readily by ion sputtering, and the reference energies needed for the calibration have been validated for a range of operating conditions (5). In an initial calibration of the instrument (or a calibration made after any substantive instrumental modifications), a check of the BE-scale linearity is made with either the Ag  $3d_{5/2}$  photoelectron peak (with a monochromated Al X-ray source) or with the Cu  $L_3VV$  Auger-electron peak (with an unmonochromated Al or Mg X-ray source). In this first calibration, a series of seven independent measurements are made for each of the Au  $4f_{7/2}$ , Cu  $2p_{3/2}$  and either Ag  $3d_{5/2}$  or Cu  $L_3VV$  peaks (see 8.7). These measurements are made to determine the repeatability standard deviations for measurements of the three peaks. These standard deviations have contributions from changes in outputs of the spectrometer power supplies, from the sensitivity of the measured BE to sample position, and from counting statistics in the recorded spectra (although the latter uncertainty is relatively small for the conditions specified in this practice). The magnitudes of the other two contributions may vary with BE, and so an overall repeatability standard deviation  $\sigma_r$  is defined as the largest of the repeatability standard deviations for the three peaks. The calibration will be valid only if the sample-positioning procedure used for regular analyses is the same as the procedure used in the calibration.

7.2 It has been found in interlaboratory comparisons of XPS measurements that any measured error in measured BEs varies approximately linearly with BE. This practice is based on the assumption that the differences between measured BEs and reference BEs for the designated peaks are both small and linearly, or close to linearly, dependent on BE. A test of the validity of this assumption is provided (see 8.7 and 8.9) by a measurement at an intermediate point on the BE scale using the Ag  $3d_{5/2}$  photoelectron peak (monochromated Al X-ray source) or the Cu  $L_3VV$  Auger peak (unmonochromated X-ray sources). The Ag  $3d_{5/2}$  measurement is needed for monochromated Al X-ray sources because the average X-ray energy from this source may be larger, by up to 0.2 eV, than for an unmonochromated Al X-ray source and, as a result, the relative

energies of photoelectron and Auger-electron peaks may vary by up to 0.2 eV (4). The Ag 3d<sub>5/2</sub> peak could be used for the linearity check with unmonochromated X-ray sources, if desired, but it will generally be simpler to make this check with the Cu L<sub>3</sub>VV Auger peak because the copper foil is already required for measurement of the Cu 2p<sub>3/2</sub> peak. Additional checks of BE-scale linearity can be made, if desired, using appropriate elemental metals and the corresponding recommended BEs as secondary standards (6).

7.3 If the BE scale is judged to be sufficiently linear (see 8.9), subsequent checks of the calibration can be performed with the number *m* of measurements for each of the Au 4f<sub>7/2</sub> and Cu 2p<sub>3/2</sub> photoelectron peaks chosen to be 1 or 2, as described in 8.10. An expression is given in this section for calculating the uncertainty *U*<sub>95</sub> of the BE-scale calibration at the 95 % confidence level (at the time of the calibration).

7.4 The means by which the BE scale is corrected following a calibration or a calibration check depends on practical details of the instrument. Some methods for making this correction are described in 8.11.

7.5 The tolerance limit  $\delta$  for the calibration at the 95 % confidence limit is an important parameter to be chosen by the analyst. This parameter also is the tolerance limit, that is, the maximum allowed inaccuracy, again at the 95 % confidence limit, for measured BEs for some defined time following a calibration. The chosen value of  $\delta$  depends in part on the analytical requirements and in part on the stability of the instrumental BE scale. Table 2 shows illustrative values for the various uncertainties that contribute to *U*<sub>95</sub> for values of  $\delta$  of 0.1 eV and 0.2 eV and for values of *m* of 1 or 2. The difference between  $\delta$  and *U*<sub>95</sub> is the maximum drift of the instrumental BE scale that should be allowed between calibration checks.

**TABLE 2 Contributions to an Error Budget for Calibration of the BE scale (from ISO 15472:2010)**

NOTE 1—The uncertainties are for a 95 % confidence level. The numerical values shown are illustrations to indicate the effects of different choices (in the values of  $\delta$  and *m*) on the uncertainty of the calibration *U*<sub>95</sub> and the required interval between calibrations for assumed values of  $\sigma_1$ ,  $\epsilon_2$ , or  $\epsilon_3$ , and the average drift rate of the BE scale.

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	$\sigma_R$	Eq 1 and Section 8.8.3	0.020		0.020		(Characteristic of your spectrometer measured at first calibration (see 8.7)).
Number of times each pair of spectra is acquired	<i>m</i>	You choose <i>m</i> = 1 or 2	<i>m</i> = 1	<i>m</i> = 2	<i>m</i> = 1	<i>m</i> = 2	
Uncertainty of calibration measurements, eV	<i>U</i> <sub>95</sub> <sup>cl</sup>	Eq 12 or Eq 13 and Section 8.10.4	0.074	0.052	0.074	0.052	
Measure of scale non-linearity, eV	$\epsilon_2$ or $\epsilon_3$	Eq 4 and Section 8.9.2, Eq 5 or Eq 6 and Section 8.9.2	0.020	0.020	0.020	0.020	(Characteristic of your spectrometer measured at first calibration (see 8.7)).
Uncertainty of energy scale after calibration, eV	<i>U</i> <sub>95</sub>	Eq 11 and Section 8.10.4	0.078	0.057	0.078	0.057	
Maximum allowable drift between calibrations, eV	$\pm (\delta - U_{95})$	$\delta$ and <i>U</i> <sub>95</sub>	$\pm 0.022$	$\pm 0.043$	$\pm 0.122$	$\pm 0.143$	(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	-	Section 8.13	0.9	1.7	4.9	5.7	(Choose a convenient interval below this maximum, and less than four months, with safety margin for any erratic behavior.)
Your choice of calibration interval, months	-	You choose based on observed drift behavior	Option not practical	1	3	4	(No more than 70 % of the maximum interval in the preceding row to allow a safety margin.)

Information on how to determine the maximum interval between calibration checks is given in 8.13. It is strongly recommended that analysts prepare their own version of Table 2 using numerical values from their measurements and the indicated equations and steps.

7.6 An analyst unfamiliar with this practice will have to make an initial choice for  $\delta$ , and it is suggested that a value of 0.1 eV be chosen. To decide whether the selected value of  $\delta$  is realistic, this practice should be followed and a version of Table 2 should be completed. In general, the value of  $\delta$  should be based on the accuracy needs of the planned analytical work, the expected measurement and data-analysis conditions, the linearity of the BE scale, the stability of the instrument, and a judgment based on the needs and benefits of calibration with the chosen value of  $\delta$  versus the cost in instrument and staff time in performing calibrations. For example, if  $\delta$  is chosen to be too small, calibration checks may have to be made too frequently to account for possible drift of the BE scale in the interval between calibration checks. Other options in such a situation are to review the operating procedures, for example, the sample-alignment procedure, or the calibration procedure, for example, the choice of  $m$ ), to determine if one or more of the terms contributing to  $U_{95}$  can be reduced. Otherwise,  $\delta$  may need to be increased to an acceptable value.

## 8. Calibration Procedure

8.1 *Obtain the Reference Samples*—Use gold and copper reference samples for XPS instruments with unmonochromated X-ray sources. For instruments with a monochromated Al X-ray source, also use a silver sample on the first occasion that the instrument is calibrated for the settings chosen in 8.4; for later determinations of the calibration error, as described in 8.10, use of the silver sample is not necessary. The samples shall be polycrystalline and with a purity of at least 99.8 %. The samples can be foils of typical dimensions 10 by 10 mm and with thicknesses between 0.1 and 0.2 mm.

NOTE 1—If the Cu and Ag samples appear discolored, a short dip in 1 % nitric acid may be used to clean the surfaces with subsequent rinsing in distilled water. If the Cu sample has been stored in air for more than a few days, the cleaning with nitric acid will reduce the time needed for later sputter cleaning (see 8.3.1).

8.2 *Mount the Samples*—Mount the Au and Cu samples and, if required, the Ag sample on the sample holder of the instrument or on separate sample holders, as appropriate, using fixing screws or other metallic means to ensure electrical contact. Double-sided adhesive tape should not be used when performing energy scale calibration work.

### 8.3 Clean the Samples:

8.3.1 Achieve ultra-high vacuum in the analytical chamber and clean the samples by ion sputtering until the heights of the carbon and oxygen signals are each less than 2 % of the height of the most intense metal peak in a survey spectrum for each metal (if the silver sample is heavily contaminated it can also be pre-cleaned using a pencil eraser or metal polish). Record a survey (widescan) spectrum for each sample to ensure that the only significant peaks are those expected for the particular metal. The pressure of active gases in the analytical chamber

should be low enough so that the heights of the carbon and oxygen 1 s peaks shall not exceed 3 % of the height of the most intense metal peak by the time the measurements are completed (see 8.10) or at the end of the working day, whichever is earlier.

NOTE 2—Suitable sputtering conditions with an inert gas are 1 min of a 30  $\mu$ A beam of argon ions covering 1 cm<sup>2</sup> of the surface.

NOTE 3—Illustrative survey spectra for Au, Ag, and Cu may be found in Refs (7-11).

8.3.2 It is desirable to complete the measurements in one working day. If a longer time is needed, additional surface cleaning of the samples probably will be needed (see 8.3.1).

8.4 *Choose the spectrometer settings for which energy calibration is required*—Choose the operating settings of the spectrometer for which energy calibration is required. The calibration procedure (see 8.4 – 8.13) shall be repeated for each X-ray source and selected combination of pass energy, retardation ratio, apertures, lens settings, etc. for which a calibration is needed. A calibration is only valid for the particular X-ray source and operating conditions. Record the chosen operating settings.

NOTE 4—The designs of XPS instruments and their electronic controls vary considerably. As a result, a calibration made for a particular X-ray source and a particular combination of pass energy, apertures, and lens settings will not necessarily be valid for another X-ray source or another combination of spectrometer settings (4). Many analysts make all or most of their BE measurements for only one set of conditions; as a result, the instrument may only need calibration for these conditions.

8.5 *Operate the Instrument*—Operate the instrument according to the manufacturer's documented instructions. The instrument shall have fully cooled following any bakeout. Ensure that the X-ray source power, counting rates, spectral scan rate, and other parameters are within the recommended ranges specified by the manufacturer. Check that the settings for the multiplier detector have been adjusted correctly. For multidetector systems, ensure that any optimizations or checks recommended by the manufacturer have been performed.

NOTE 5—Many manufacturers recommend that control and high-voltage electronics be switched on at least four hours before performing accurate BE measurements. Also, it may be necessary to operate the X-ray source for some minimum period, for example, 1 h, before making such measurements. XPS instruments with an X-ray monochromator may also need a warm-up time since the average X-ray energy at the sample may depend on the ambient temperature or the temperature in the vicinity of the monochromator; records of these temperatures could help to identify any problems associated with drifts of measured peak positions.

NOTE 6—If the counting rates are too high (12) or the detector voltages are set incorrectly (12, 13), spectral peaks can be distorted and the resulting peak positions may be incorrect.

8.6 *Options for Initial or Subsequent Calibration Measurements*—For the first time that the instrument has been calibrated for a particular combination of spectrometer settings (see 8.4), it is necessary to determine the repeatability standard deviation for BE measurements, the BE-scale linearity error, and the calibration interval. If any of these have not been determined, follow 8.7 – 8.9; otherwise, proceed to 8.10. If the instrument has been modified, undergone significant repair, or been moved, the steps in 8.7 – 8.9 should be followed.

8.7 Measurements for the Repeatability Standard Deviation and Scale Linearity:

8.7.1 The repeatability standard deviation for the peak BE,  $\sigma_R$ , is determined from repeated measurements of the Au 4f<sub>7/2</sub>, Ag 3d<sub>5/2</sub> or Cu L<sub>3</sub>VV, and Cu 2p<sub>3/2</sub> peaks as described in this section and in 8.8. The value of  $\sigma_R$  is valid only for the selected conditions (see 8.4), and involves a significant contribution from the sample-positioning procedure (4, 5). A consistent sample-positioning procedure, following a documented protocol, for example, from the manufacturer’s recommendations, should be followed both for the calibration measurements and for regular analytical work.

NOTE 7—The sample-positioning procedure will depend on the instrument design, the type and shape of the samples, and the analytical requirements. In many cases, the correct sample position is determined by maximizing the spectral intensity. When optimization involves adjustment of two or more interacting parameters, a consistent optimization strategy is necessary. If the optimization involves an X-ray monochromator, changes in the sample position may lead to shifts in the energy of the recorded peak; thus, it may be necessary to measure peak intensities in an energy range of up to ±0.5 eV from the nominal peak BE. In this case, intensity optimization may be more sensitive to sample position at low, rather than high, binding energies or, more rarely, vice versa. Optimization is usually most effective at the BE where the intensity is most sensitive to sample position. It may be useful to perform the operations in 8.7 several times to refine the sample-positioning procedure and to obtain a lower value of  $\sigma_R$ .

8.7.2 The BE-scale linearity error,  $\epsilon_2$  or  $\epsilon_3$ , is determined from measurements of the Cu L<sub>3</sub>VV Auger-electron peak for unmonochromated Mg or Al X-ray sources and from measurements of the Ag 3d<sub>5/2</sub> photoelectron peak for a monochromated Al X-ray source. These measurements are performed at the same time as the repeatability measurements to reduce the overall effort and to reduce the measurement uncertainty.

8.7.3 The order of data acquisition for the measurements described in 8.7.4 – 8.7.7 should be as follows:

8.7.3.1 *Unmonochromated Mg or Al X-rays:* Au 4f<sub>7/2</sub>, Cu 2p<sub>3/2</sub>, Cu L<sub>3</sub>VV, with this sequence repeated six additional times.

8.7.3.2 *Monochromated Al X-rays:* Au 4f<sub>7/2</sub>, Cu 2p<sub>3/2</sub>, Ag 3d<sub>5/2</sub>, with this sequence repeated six additional times.

NOTE 8—The Au 4f<sub>7/2</sub> peak is often the weakest peak although, depending on the spectrometer, sometimes the Cu L<sub>3</sub>VV peak may be weaker. Initial measurements with the Au 4f<sub>7/2</sub> peak should facilitate the use of a common set of measurement conditions for all peaks.

8.7.4 Set the gold sample at the analytical position with the angle of emission for the detected electrons with respect to the surface normal between 0° and 56°. Position the sample using the documented procedure and record the Au 4f<sub>7/2</sub> peak with appropriate X-ray power and channel dwell time so that more than 40 000 counts per channel are acquired in the vicinity of the peak. Scan the peak with the channel energy interval set at approximately 0.05 eV or 0.1 eV depending on the method planned for determination of the peak BE (see 8.8.1). Scan from at least 1 eV below the peak energy to at least 1 eV above the peak energy. Ensure that the correct peak has been measured from the wide-scan (survey) spectrum (see 8.3.1). The reference BE for the Au 4f<sub>7/2</sub> peak, peak 1, is given in Table 3.

NOTE 9—The reference BE values for the calibration peaks vary with

TABLE 3 Reference Binding Energies,  $E_{ref, n}$  for the Peaks Used in the Calibration Procedure for the Indicated X-Ray Sources (1, 2)

NOTE 1—The Ag data included in parentheses are not normally used in the calibration.

Peak Number, <i>n</i>	Assignment	$E_{ref, n}$ (eV)		Monochromatic Al K $\alpha$
		Al K $\alpha$	Mg K $\alpha$	
1	Au 4f <sub>7/2</sub>	83.95	83.95	83.96
2	Ag 3d <sub>5/2</sub>	(368.22)	(368.22)	368.21
3	Cu L <sub>3</sub> VV	567.93	334.90	-
4	Cu 2p <sub>3/2</sub>	932.63	932.62	932.62

angle of electron emission (5). The reference BE values in Table 3 are only valid for emission angles between 0° and 56° (5). If larger emission angles are used, significant errors will be introduced into the calibration.

NOTE 10—A wide range of spectral scan rates are available on commercial XPS instruments. If the scan rate is too high, the measured peak BE will be shifted. The scan rate should be chosen so that there is no significant peak shift.

8.7.5 Set the copper sample at the analytical position with the same emission angle as in 8.7.4. Position the sample with the documented procedure and record the Cu 2p<sub>3/2</sub> peak, with the same spectrometer settings as those used in 8.7.4, so that more than 40 000 counts per channel are acquired in the vicinity of the peak. Scan from at least 1 eV below the peak energy to at least 1 eV above the peak energy. Ensure that the correct peak has been measured from the wide-scan (survey) spectrum (see 8.3.1). The reference BE for the Cu 2p<sub>3/2</sub> peak, peak 4, is given in Table 3.

8.7.6 If an unmonochromated Al or Mg X-ray source is being used, the Cu L<sub>3</sub>VV peak will be measured next. If a monochromated Al X-ray source is being used, set the silver sample at the analytical position with the same emission angle as in 8.7.4 and position the sample with the documented procedure. Record the Cu L<sub>3</sub>VV peak or the Ag 3d<sub>5/2</sub> peak, depending on X-ray source, with the same spectrometer settings as those used in 8.7.4, so that more than 40 000 counts per channel are acquired in the vicinity of the peak. Scan from at least 1 eV below the peak energy to at least 1 eV above the peak energy. Ensure that the correct peak has been measured from the wide-scan (survey) spectrum (see 8.3.1). The reference BEs for the Ag 3d<sub>5/2</sub> peak, peak 2, and the Cu L<sub>3</sub>VV peak, peak 3, are given in Table 3.

8.7.7 Repeat the steps in 8.7.4 – 8.7.6 an additional six times in order to obtain seven independent measurements for each of the three peaks. To save time, the energy-scan widths may be reduced to the range ±0.5 eV about the peak unless a wider range is needed if instrumental software is to be used for peak location (see 8.8.1.2).

8.8 Calculate the Repeatability Standard Deviation for the Peak Binding Energies:

8.8.1 Determine the peak binding energies from the spectra recorded in 8.7 using one of the three methods described in 8.8.1.1, 8.8.1.2, or 8.8.1.3 (specify in the documentation which of the three methods is utilized).

NOTE 11—The first two methods are useful for instruments that supply digital data, the third method for instruments that supply only graphical output.



8.8.1.1 Make a least-squares fit of a parabola to six data points around the top of the peak. There should be approximately the same number of data points above and below the energy for the maximum intensity, and the intensities for the first and last data points should be between 85 % and 95 % of the maximum intensity. Obtain the energy for the peak maximum from this fit. If software for this purpose is not conveniently available, the simple numerical procedure given in **Annex A1** can be used.

NOTE 12—If the procedure in **Annex A1** is utilized, a channel energy separation of 0.1 eV (or in the range 0.09 eV to 0.11 eV) should be selected for XPS with an unmonochromated X-ray source. For XPS with a monochromated Al X-ray source, the channel separation should be 0.05 eV (or in the range of 0.045 eV to 0.055 eV) if the FWHM of the peaks is less than 1.0 eV; otherwise, a channel width between 0.9 eV and 0.11 eV can be used.

NOTE 13—If the procedure in **Annex A1** is utilized, the intensities for the first and last data points could, if necessary, be between 80 % and 95 % of the maximum intensity. There would then be a slight increase (up to 6 meV) in the uncertainty of the derived peak binding energy.

8.8.1.2 Make a least-squares fit to the data points obtained in 8.8.1.1 with a suitable lineshape function available with software on the XPS instrument or on another computer. A Gaussian function, a Lorentzian function, a Voigt function, or a sum or product of such functions may be suitable functions for this purpose. A constant background can be used to aid the fitting, if desired, but no asymmetric background, such as a sloping line, a Shirley background, or a Tougaard background shall be subtracted from the measured intensities or utilized in the fitting procedure. Obtain the energy for the peak maximum from the fit.

NOTE 14—Photoelectron peaks in XPS generally are asymmetrical (14). The effects of any asymmetry in measured peaks on the determination of the energy for the peak maximum will be insignificant for this practice if fits are only made to groups of data points that are selected as specified in 8.8.1.1. While fits can be made to a larger number of data points comprising the peak, it will often be necessary to include an asymmetry parameter in the fitting function (14). In such cases, comparisons should be made of the resulting energy for the peak maximum and its uncertainty with the energy and uncertainty for the peak maximum obtained from an alternative method, such as those described in 8.8.1.1 and 8.8.1.3. These comparisons should be made for each measured peak and for each selected set of operating conditions (see 8.4).

8.8.1.3 Draw chords horizontally across the peak at an intensity of 84 % of the maximum peak height (above zero counts) and at three or more further intensities approximately equally spaced in the range 84 to 100 % of the maximum peak height (above zero counts). Locate the midpoints of the chords. Draw a line through these midpoints; alternatively, a linear least-squares fit can be made to the positions of the chord midpoints. Obtain the energy for the peak maximum from the intersection of the line with a linear segment drawn to connect two data points in the vicinity of the peak maximum.

NOTE 15—The precision of this method of peak location may be improved by smoothing the data prior to its use. It is recommended that the data be smoothed with a Savitzky and Golay cubic/quadratic function having a width of equal to or less than half of the FWHM of the peak. For a peak with a FWHM of 1.0 eV measured with a channel energy separation of 0.1 eV, a five-point smooth would be performed.

8.8.2 Tabulate the seven values of the binding energies measured in 8.8.1 for each of the three peaks.

8.8.3 Calculate the average binding energy,  $E_{\text{meas } n}$ , from the set of seven measurements,  $E_{\text{meas } ni}$ , for each peak,  $n$ . Calculate the repeatability standard deviation,  $\sigma_{R1}$ , of the seven measurements of the Au 4f<sub>7/2</sub> peak energy,  $E_{\text{meas } li}$ , from the equation:

$$\sigma_{R1}^2 = \sum_{i=1}^7 \frac{(E_{\text{meas } li} - E_{\text{meas } l})^2}{6} \quad (1)$$

where  $E_{\text{meas } l}$  is the average value of the  $E_{\text{meas } li}$ . Calculate the repeatability standard deviations,  $\sigma_{R2}$  or  $\sigma_{R3}$ , and  $\sigma_{R4}$ , for the measured positions of the Ag 3d<sub>5/2</sub> or Cu L<sub>3</sub>VV and Cu 2p<sub>3/2</sub> peaks, respectively, in a similar way. The overall repeatability standard deviation,  $\sigma_R$ , is taken as the largest of  $\sigma_{R1}$ ,  $\sigma_{R2}$ , or  $\sigma_{R3}$ , and  $\sigma_{R4}$ .

NOTE 16—Record the value of  $\sigma_R$  in your version of **Table 2**.

8.8.4 Review the measured Au 4f<sub>7/2</sub> and Cu 2p<sub>3/2</sub> peak energies (from 8.8.2) for any systematic changes with time through their order of acquisition. Any such systematic change may indicate an inadequate warm-up period or some other form of drift. In this situation, take appropriate action, for example, increase the warm-up period, and repeat 8.7.

8.8.5 The values of the repeatability standard deviation for each peak should be less than 0.05 eV for an instrument in good working condition. If  $\sigma_{R1}$  or  $\sigma_{R4}$  exceeds this value, check the stabilities of the voltages applied to the instrument, the adequacy of the system ground, and the sample-positioning procedure. If  $\sigma_R$  is greater than  $\delta/4$ , it will be necessary either to find a way to reduce  $\sigma_R$  or increase the value of  $\delta$ .

NOTE 17—In an interlaboratory comparison in which copper samples were repositioned following analysis of another sample, 87 % of the results showed values of  $\sigma_{R4}$  that were equal to or less than 0.030 eV (15). In another interlaboratory study, values of  $\sigma_{R4}$  equal to or less than 0.021 eV were found from repeated measurements made without repositioning of the samples (4). Values of  $\sigma_{R4}$  as low as 0.001 eV have been reported (4).

## 8.9 Check the Linearity of the Binding-Energy Scale:

8.9.1 Subtract the reference energies,  $E_{\text{ref } n}$ , given in **Table 3** from the corresponding values of the average measured binding energies,  $E_{\text{meas } n}$ , determined in 8.8.3 to obtain the measured offset energies,  $\Delta_n$ , for each peak  $n$ . Thus,

$$\Delta_n = E_{\text{meas } n} - E_{\text{ref } n} \quad (2)$$

8.9.2 Calculate the scale linearity error  $\varepsilon_2$  for the Ag 3d<sub>5/2</sub> peak or  $\varepsilon_3$  for the Cu L<sub>3</sub>VV peak from **Eq 4**, **Eq 5**, or **Eq 6** below. This scale linearity error is the difference between the measured offset energy,  $\Delta_2$  or  $\Delta_3$ , and that deduced from the measured Au 4f<sub>7/2</sub> and Cu 2p<sub>3/2</sub> binding energies, the corresponding reference energies in **Table 3**, and the assumption that the scale is linear. For the Ag 3d<sub>5/2</sub> peak (measured with a monochromatic Al X-ray source),  $\varepsilon_2$  is given by:

$$\varepsilon_2 = \Delta_2 - \left[ \frac{\Delta_1 (E_{\text{ref } 4} - E_{\text{ref } 2}) + \Delta_4 (E_{\text{ref } 2} - E_{\text{ref } 1})}{E_{\text{ref } 4} - E_{\text{ref } 1}} \right] \quad (3)$$

For the Cu L<sub>3</sub>VV peak (measured with unmonochromated Al or Mg X-ray sources),  $\varepsilon_3$  is given by a similar equation with  $\Delta_2$  and  $E_{\text{ref } 2}$  replaced by  $\Delta_3$  and  $E_{\text{ref } 3}$ , respectively. Numerically, these equations reduce to:

$$\varepsilon_2 = \Delta_2 - 0.665 \Delta_1 - 0.335 \Delta_4 \quad (\text{for monochromated Al X rays}) \quad (4)$$

$$\varepsilon_3 = \Delta_3 - 0.430 \Delta_1 - 0.570 \Delta_4 \quad (\text{for unmonochromated Al X rays}) \quad (5)$$

and

$$\varepsilon_3 = \Delta_3 - 0.704 \Delta_1 - 0.296 \Delta_4 \quad (\text{for unmonochromated Mg X rays}) \quad (6)$$

NOTE 18—Record the value of  $\varepsilon_2$  or  $\varepsilon_3$  in your version of Table 2.

8.9.3 The uncertainties of  $\varepsilon_2$  and  $\varepsilon_3$  (at the 95 % confidence level) are less than  $U'_{95}$  where  $U'_{95}$  is given by the following equation:

$$U'_{95} = [(1.2 \sigma_R)^2 + (0.026)^2]^{1/2} \quad (7)$$

8.9.3.1 Calculate  $U'_{95}$  from Eq 7. For practical purposes, the BE scale may be considered to be linear if  $|\varepsilon_2|$  or  $|\varepsilon_3|$  is less than or equal to  $U'_{95}$ . If the value of  $|\varepsilon_2|$  or  $|\varepsilon_3|$  is greater than  $U'_{95}$ , the scale is nonlinear. This nonlinearity may nevertheless be acceptable if  $|\varepsilon_2|$  or  $|\varepsilon_3|$  is less than or equal to  $\delta/4$ ; that is, the linearity error may be regarded as sufficiently small compared to the chosen tolerance limit  $\delta$ .

NOTE 19—In an interlaboratory study, 10 out of 12 instruments exhibited values of  $|\varepsilon_3|$  less than 0.05 eV, and BE scales of these instruments may be considered linear for  $\delta = 0.2$  eV (16). Seven of the 12 instruments had  $|\varepsilon_3|$  values less than 0.025 eV, and the BE scales of these instruments can be considered linear for  $\delta = 0.1$  eV.

NOTE 20—The derivation of Eq 7 is given in ISO 15472:2010.

8.9.4 If  $|\varepsilon_2|$  or  $|\varepsilon_3|$  is greater than  $\delta/4$ , corrective action should be taken. Possible actions include revision of procedures for operating the instrument, an increase in the tolerance limit  $\delta$ , or review of the results with the instrument manufacturer.

NOTE 21—The analyst should recognize that the initial value chosen for the tolerance limit  $\delta$  (see 7.6) may not be achievable with a particular instrument.

NOTE 22—The procedure given in 8.9 is not a full test of the linearity of the BE scale. A full test would need extensive test equipment and is beyond the scope of this practice. Additional tests of BE-scale linearity can be made, however, at other points on the scale by using the recommended BE values of elemental metals (6) as secondary standards and following the methodology of this practice.

## 8.10 Regular Determination of the Calibration Error:

8.10.1 The calibration error shall be determined at regular intervals for each combination of spectrometer operating settings for which calibration of the BE scale is required. Each such determination of the calibration error shall be made prior to the expiration of the calibration interval established in a previous use of the calibration procedure, as described in 8.13.

NOTE 23—Before proceeding with 8.10, check that values of  $\sigma_R$  and of  $|\varepsilon_2|$  or  $|\varepsilon_3|$  have been determined (from 8.8 and 8.9) for the chosen combination of spectrometer settings.

8.10.2 Make the following measurements of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  peaks, as described in 8.7.4 and 8.7.5, respectively, depending on the value of  $\sigma_R$  relative to  $\delta/8$ .

8.10.2.1 If  $\sigma_R$  is less than or equal to  $\delta/8$ , make a single measurement of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  peaks (for which  $m$ , the number of repeat measurements of each peak, is 1).

8.10.2.2 If  $\sigma_R$  is greater than  $\delta/8$ , make two measurements each of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  peaks (for which  $m = 2$ ). These measurements should be made in the following sequence: Au  $4f_{7/2}$ , Cu  $2p_{3/2}$ , Au  $4f_{7/2}$ , and Cu  $2p_{3/2}$ .

For each of these measurements, ensure that the angle of electron emission is between  $0^\circ$  and  $56^\circ$  and that the sample is positioned using the previously used procedure. Determine the peak binding energies as described in 8.8.1, and calculate the offset energies  $\Delta_1$  and  $\Delta_4$  from Eq 2 (or the average offset energies if  $m = 2$ ).

NOTE 24—If measurements are desired of the effective X-ray energy on instruments equipped with monochromated Al X-ray source to determine modified Auger parameters, as described in Appendix X2, also measure the Cu  $L_{3VV}$  peak following the Cu  $2p_{3/2}$  peak, as described in 8.7.6.

8.10.3 This practice is based on the assumption that the corrected binding energy,  $E_{\text{corr}}$ , following the calibration is related linearly to the measured binding energy,  $E_{\text{meas}}$ , by:

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

where the energy scaling error,  $a$ , is given by:

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

and the zero offset error,  $b$ , by

$$b = \frac{\Delta_4 E_{\text{ref } 1} - \Delta_1 E_{\text{ref } 4}}{E_{\text{ref } 4} - E_{\text{ref } 1}} \quad (10)$$

where values of  $E_{\text{ref } 1}$  and  $E_{\text{ref } 4}$  are given in Table 3. Calculate values of  $a$  and  $b$  from Eq 9 and 10 using the values of  $\Delta_1$  and  $\Delta_4$  from 8.10.2.

8.10.4 The uncertainty of the calibration,  $U_{95}$ , at the 95 % confidence level is given by

$$(U_{95})^2 = (U_{95}^{\text{cl}})^2 + (1.2 |\varepsilon_2 \text{ or } \varepsilon_3|)^2 \quad (11)$$

where  $U_{95}^{\text{cl}}$ , the uncertainty of the calibration at the 95 % confidence level in the absence of a linearity error, is given by:

$$U_{95}^{\text{cl}} = 2.6 \sigma_R \text{ for } m = 2 \text{ measurements} \quad (12)$$

or

$$U_{95}^{\text{cl}} = 3.7 \sigma_R \text{ for } m = 1 \text{ measurement} \quad (13)$$

for binding energies in the range from 0 eV to 1040 eV. Calculate  $U_{95}^{\text{cl}}$  from Eq 12 or Eq 13, depending on your choice of  $m$  from 8.10.2, and calculate  $U_{95}$  from Eq 11 using the value of  $|\varepsilon_2|$  or  $|\varepsilon_3|$  from Eq 4, Eq 5, or Eq 6.

NOTE 25—Record the values of  $U_{95}^{\text{cl}}$  and  $U_{95}$  in your version of Table 2.

NOTE 26—The derivation of Eq 11-13 is given in ISO 15472:2010.

## 8.11 Correct the Instrumental Binding-Energy Scale:

8.11.1 The particular means by which the instrumental BE scale is corrected depends on the hardware and software of the instrument. Follow the manufacturer's instructions to implement the correction. For many commercial instruments, it is only possible for the analyst to adjust the spectrometer work function. Three possible correction strategies are described herein. The analyst should choose a strategy based on what is feasible with the instrument and on the needs of the analytical work. For each correction strategy, the corrected value for the binding energy,  $E_{\text{corr}}$ , corresponding to a measured binding energy,  $E_{\text{meas}}$ , is given by:

$$E_{\text{corr}} = E_{\text{meas}} + \Delta E_{\text{corr}} \quad (14)$$

where  $\Delta E_{\text{corr}}$  is a correction value appropriate to the strategy.

NOTE 27—If the values of  $(|\Delta_n| + U_{95})$  for the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  peaks determined in 8.10 are both less than  $\delta/4$ , it may not be necessary to make a new correction to the instrumental BE scale after the calibration check. While it is generally desirable for the instrument to be corrected after each calibration check, this step may be omitted if the costs of the time and effort involved are judged to be too large in comparison with the expected benefit of reduced uncertainty of the BE measurements.

8.11.1.1 For the first correction strategy, no change is made to the instrument. Instead, a post-acquisition correction,  $\Delta E_{\text{corr}}$ , is added to each measured binding energy. From Eq 8,

$$\Delta E_{\text{corr}} = aE_{\text{meas}} + b \quad (15)$$

where  $a$  and  $b$  are given by Eq 9 and 10.

8.11.1.2 For the second correction strategy, an increase  $\Delta\phi$  is added to the value of the spectrometer work function to minimize the post-acquisition correction  $\Delta E_{\text{corr}}$  to be applied over the BE range from 0 eV to 1040 eV. This work function increase is given by

$$\Delta\phi = 0.5(\Delta_1 + \Delta_4) \quad (16)$$

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

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

NOTE 28—With this strategy,  $\Delta E_{\text{corr}}$  is zero at a binding energy of 508.3 eV.

8.11.1.3 For the third correction strategy, an increase  $\Delta\phi$  is added to the value of the spectrometer work function to make the post-acquisition correction  $\Delta E_{\text{corr}}$  equal to zero at a particular point on the BE scale corresponding to the BE for a frequently measured element. This work function increase is given by:

$$\Delta\phi = aE_{\text{elem}} + b \quad (18)$$

where  $E_{\text{elem}}$  is the BE for the frequently measured element. The post-acquisition correction for subsequently measured binding energies is given by:

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

8.11.2 If the value of  $(|\Delta E_{\text{corr}}| + |U_{95}|)$  is expected to be less than  $\delta$  over the calibration interval for some specified useful range of binding energies, the post-acquisition correction  $\Delta E_{\text{corr}}$  from Eq 15, Eq 17, or Eq 19 need not be applied. The calibration, however, is then only valid for the specified BE range.

8.11.3 The correction procedure shall be documented carefully. For the first time that the correction procedure is applied, it is recommended that the calibration check be repeated to ensure that no mistakes have been made.

8.12 *Options for Next Calibration Check*—The next calibration check should be made before the sum of the calibration uncertainty,  $U_{95}$ , and the instrumental drift is likely to exceed  $\pm\delta$ . If the interval between calibration checks is not known, proceed to 8.13; otherwise, proceed to 8.14.

8.13 *Determine the Calibration Interval*:

8.13.1 With the instrument running throughout a working day, make single measurements of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  binding energies at hourly intervals, for example, as described in 8.7.4 and 8.7.5. Any drift in the measured binding energies

shows that it may be necessary to leave the electronics on for some specified minimum time, or perhaps, to leave the electronics on continuously to achieve adequate stability. Record the ambient temperature for each measurement and check for any correlation.

NOTE 29—The instrument should be left on for the same minimum time before regular BE measurements are made as found necessary here to ensure adequate stability of the BE scale if the BE measurements are required to be made within the tolerance limits  $\pm\delta$ .

NOTE 30—Drift of the BE scale is most likely to be due to temperature changes in either the voltage supplies for the spectrometer dispersing elements or the X-ray monochromator system, if used. These drifts occur as a function of elapsed time after switching on, and so may occur at a similar rate each day if the instrument is restarted each day at approximately the same time; thus, any check of the stability of the BE scale that is made at the same time each day would miss any diurnal drift. Drifts of the Cu  $2p_{3/2}$  peak have been observed to be both larger and smaller than those for the Au  $4f_{7/2}$  peak.

8.13.2 If the stability during the first day is adequate, make similar measurements of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  binding energies at progressively greater intervals of time and determine values of the drifts in the BE scale following a calibration,  $\Delta E_1$  and  $\Delta E_4$ , where  $\Delta E_1$  refers to the drift obtained from the Au  $4f_{7/2}$  peak and  $\Delta E_4$  refers to the drift obtained from the Cu  $2p_{3/2}$  peak. Values of  $\Delta E_1$  and  $\Delta E_4$  are given by:

$$\Delta E_n = E_{\text{meas } n} + \Delta E_{\text{corr } n} - E_{\text{ref } n} \quad (20)$$

where  $E_{\text{meas } n}$  is the measured BE for peaks 1 (Au  $4f_{7/2}$ ) and 4 (Cu  $2p_{3/2}$ ),  $E_{\text{corr } n}$  is obtained from Eq 15, Eq 17, or Eq 19 for each peak, depending on the correction strategy employed (see 8.11.1), and values of the reference energies,  $E_{\text{ref } n}$ , are given in Table 3. The measurements of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  binding energies should be made at time intervals such that  $U_{95}$  added to the greater of changes in  $\Delta E_1$  and  $\Delta E_4$  since the previous calibration remains less than  $0.7\delta$ . This last time interval is the maximum useful calibration interval until subsequent measurements (see 8.14) indicate that it should be revised. This interval shall not exceed four months.

NOTE 31—For many instruments, a calibration interval of between one and two months has been found to be satisfactory. The frequency of calibration, however, depends on the analytical requirements (choice of  $\delta$ ), the repeatability standard deviation, the BE-scale linearity error, and the stability of the instrument, as indicated in Table 2 and described in Section 7.

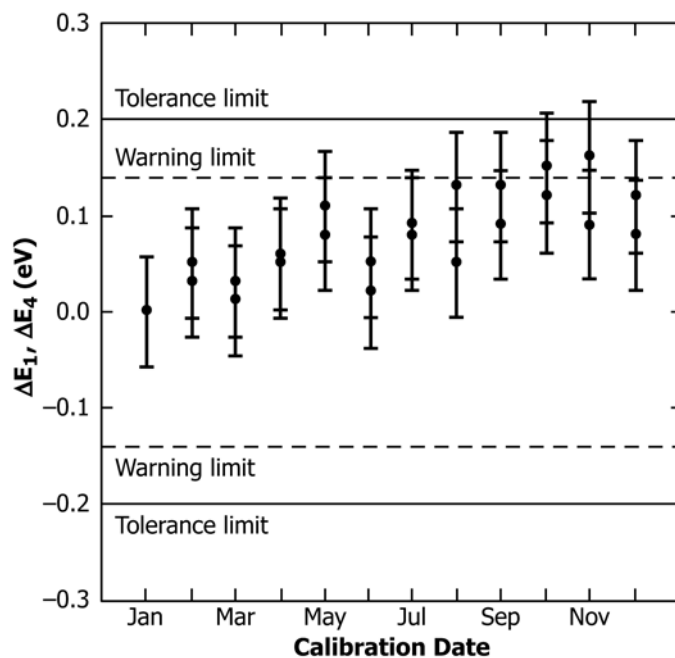
NOTE 32—To determine the drift in the effective X-ray energy on instruments with a monochromated Al X-ray source, include measurements of the Cu  $L_3VV$  peak in the sequence of measurements described in 8.13.1 and 8.13.2. Analyze these measurements as described in X2.5.5.

8.14 *Prepare a Control Chart*:

8.14.1 Calculate values of the drifts in the BE scale following previous calibration,  $\Delta E_1$  and  $\Delta E_4$ , from Eq 20 and measurements of the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  binding energies from 8.10.2. Calculate the calibration uncertainty,  $U_{95}$ , from Eq 11.

NOTE 33—Values of  $\Delta E_1$ ,  $\Delta E_4$ , and  $U_{95}$  should be recorded in a suitable log book together with the combination of instrumental settings selected in 8.4

8.14.2 Prepare a control chart, as shown in Fig. 2, in which values of  $\Delta E_1$  and  $\Delta E_4$  from 8.13.2 and 8.14.1 are plotted as a



NOTE 1—Values of the drifts in the BE scale for the Au 4f<sub>7/2</sub> and Cu 2p<sub>3/2</sub> peaks obtained from Eq 20,  $\Delta E_1$  and  $\Delta E_4$ , are plotted as a function of time (calibration date) since the initial calibration. The error bars indicate the calibration uncertainties,  $U_{95}$ , determined from Eq 11 for the example of Table 2 with  $m = 2$ . The solid lines indicate the tolerance limits,  $\pm\delta$ , to be selected by the analyst but here chosen to be  $\pm 0.2$  eV, and the dashed lines show the warning limits,  $\pm 0.7 \delta$ . The points shown here are illustrative values to indicate possible drifts in the values of  $\Delta E_1$  and  $\Delta E_4$ . In this example, the sum of the drift and  $U_{95}$  has first exceeded the tolerance limit of  $+0.2$  eV in October. This sum has exceeded the warning limit in May, and the instrument should have been recalibrated at that time.

FIG. 2 Example of a Control Chart to Monitor the Calibration Status of an XPS instrument (see 8.14.2)

function of time (calendar date). The range of the time axis should be about one year. Include values of the calibration uncertainty,  $U_{95}$ , as error bars on the plotted points. Draw solid lines to indicate the tolerance limits  $\pm\delta$  and dashed lines at  $\pm 0.7 \delta$ . The latter lines are warning limits to indicate when recalibration of the BE scale is necessary.

NOTE 34—Control charts should be prepared for each combination (section 8.4) of analyzer pass energy, retardation ratio, apertures, and lens settings for which the BE scale is calibrated.

8.14.3 Review the control chart of 8.14.2. The instrumental BE scale should be recalibrated (see 8.11) when  $|\Delta E_n| + U_{95} \geq 0.7 \delta$  where  $\Delta E_n$  here is the larger of  $\Delta E_1$  and  $\Delta E_4$  in the latest measurements. Examine any trends in the values of  $\Delta E_1$  and  $\Delta E_4$  that might signify average drifts of the BE scale different from those determined in 8.13.2 (due, perhaps, to seasonal changes) or more erratic behavior (due, perhaps, to an instrumental malfunction or to an operator mistake.) If the changes

in the values of  $\Delta E_1$  and  $\Delta E_4$  since the previous calibration are appreciably greater or less than expected from the measurements of 8.13.2, the interval to the next calibration should be proportionately decreased or increased, respectively.

NOTE 35—A control chart is a simple and effective means of demonstrating that the instrumental BE scale remains “in calibration” within the specified tolerance limits  $\pm\delta$  over an indicated period of time. Information on the citation of uncertainties of measured binding energies for several analytical situations is given in Appendix X1.

8.15 Next Calibration—The next calibration should be performed so that the calibration interval specified in 8.13.2 or 8.14.3 is not exceeded. The procedures given in 8.2 – 8.5, 8.10, 8.11, and 8.14 should be followed.

## 9. Keywords

9.1 binding energy; calibration; spectrometer; surface analysis; X-ray photoelectron spectroscopy (XPS)

(Mandatory Information)

**A1. LEAST-SQUARES DETERMINATION OF A PEAK BINDING ENERGY BY A SIMPLE COMPUTATIONAL PROCEDURE**

A1.1 The computational procedure described here can be used to determine the binding energy of a calibration peak from a least-squares fit of a parabola to six data points around the top of the peak as described in 8.8.1.1. Arrange the data values in order of increasing binding energy as illustrated in Table A1.1 where the index  $i$  is the channel number (with  $i = 0$  for the first data channel at lower binding energy than that for maximum counts) and  $c_i$  is the number of counts in the  $i$ -th channel. For the data set shown in Table A1.1, the maximum number of counts occurs for  $i = 1$  and a binding energy of 84.06 eV, but inspection of the data set indicates that the position of the peak maximum (the desired peak binding energy) should occur at a binding energy between 83.96 eV and 84.06 eV.

A1.2 The least-squares estimate of the peak binding energy,  $E_p$ , is given by (17):

$$E_p = E_0 + \frac{g}{2} \left( \frac{r - \frac{47}{15}q - \frac{8}{5}p}{r - q - \frac{8}{3}p} \right) \quad (\text{A1.1})$$

where  $E_0$  is the binding energy (in eV) of the first data channel at lower binding energy than that for the maximum count,  $g$  is the channel energy separation (in eV), and

$$p = \sum_{i=-2}^3 c_i \quad (\text{A1.2})$$

$$q = \sum_{i=-2}^3 ic_i \quad (\text{A1.3})$$

$$r = \sum_{i=-2}^3 i^2c_i \quad (\text{A1.4})$$

Eq A1.1-A1.4 can be easily evaluated with spreadsheet software available on many computers. An example showing steps in the evaluation of Eq A1.2-A1.4 is given in Table A1.1.

A1.3 The standard uncertainty in the peak binding energy obtained from Eq A1.1 is approximately 5 meV for the peak-measurement conditions described in 8.7 (17).

**TABLE A1.1 Example of Entries in a Spreadsheet to Determine the Energy of the Au 4f<sub>7/2</sub> Peak Using Eq A1.1**

NOTE 1—For this example,  $E_0 = 83.96$  eV,  $g = 0.1$  eV, and  $E_p = 84.043$  eV.

$i$	Binding Energy, (eV)	$c_i$	$ic_i$	$i^2c_i$
-2	83.76	43804	-87608	175216
-1	83.86	49259	-49259	49259
0	83.96	52958	0	0
1	84.06	53889	53889	53889
2	84.16	51903	103806	207612
3	84.26	47812	143436	430308
Summations:		$p = 299625$	$q = 164264$	$r = 916284$

APPENDIXES

(Nonmandatory Information)

**X1. CITATION OF THE UNCERTAINTIES OF MEASURED BINDING ENERGIES**

X1.1 This appendix provides information on how to evaluate, for a material of interest, the uncertainty of a binding energy that is associated with calibration uncertainty. This uncertainty will be referred to here as the analytical uncertainty, and can be cited in an analytical report. Information is given to determine the analytical uncertainty for four common analytical situations.

X1.2 It is customary to use peak fitting software to fit measured spectra and to determine peak binding energies from these fits. In such cases, the total analytical uncertainty will be given by the quadrature sum of the analytical uncertainty associated with the calibration, as discussed here, and additional random and systematic uncertainties arising from the fitting procedure, the counting statistics, and the extent to which the peak of interest overlaps other peaks (18, 19). The latter uncertainties, not discussed here, may substantially exceed 0.1 eV.

NOTE X1.1—Additional uncertainties may arise from possible limita-

tions of the fitting software (20).

X1.3 An important parameter for determination of the analytical uncertainty is the repeatability standard deviation for a new peak of interest,  $\sigma_{Rnew}$ . In principle, this repeatability standard deviation could be determined by the procedure of 8.7 and 8.8 (with measurements made on the new peak instead of the calibration peaks) or evaluated as described in Ref (18). For simplicity, it is assumed here that  $\sigma_{Rnew} = \sigma_R$  (with the value of  $\sigma_R$  determined in 8.8.3).

NOTE X1.2—For many peaks of practical interest,  $\sigma_{Rnew}$  will often be greater than  $\sigma_R$  because the measured peaks will often be broader and less intense than the calibration peaks.

X1.4 *Uncertainty of the Energy Difference Between Photoelectron Peaks Measured for Two Chemical States in One Spectrum*—Since spectrometers rarely have scale errors greater than 0.1 % and the differences of binding energies for an element in different chemical states are less than 10 eV, many of the uncertainties described in this practice may be ignored.

The value of the repeatability standard deviation (see 8.7) has a significant contribution from variations in sample position and, since this aspect is common to two chemical states for the same element in a material, it can be ignored. If the measured peak profiles do not overlap and there are more than 40 000 counts acquired for each peak maximum, the analytical uncertainty of the measured energy difference between the two peaks should approach 0.02 eV. For weaker peaks, the uncertainty will be larger (18). If the peaks overlap, the maxima of spectral intensity will not occur at the same energies as for the component peaks. In addition, the random and systematic uncertainties of peak locations determined from fits of selected lineshape functions to measured spectra will depend on the degree of peak overlap, the relative intensities of the component peaks, and the statistical noise in the recorded spectra (18, 19).

NOTE X1.3—It has been assumed here that there is no shift or distortion of the measured spectra due to surface charging of the sample. See Guide E1523 for information on charge-control techniques for XPS.

**X1.5 Uncertainty of the Energy Difference Between Photoelectron Peaks Measured for Two Chemical States in Two Spectra that Have Been Acquired Sequentially**—As in X1.4, many of the uncertainties described in this practice can be ignored. Since the spectra for two samples containing the same element are being analyzed, it is necessary to consider the repeatability standard deviation,  $\sigma_{Rnew}$ , for a spectral peak in each spectrum. If we assume  $\sigma_{Rnew} = \sigma_R$  (see X1.3), the analytical uncertainty, at the 95 % confidence level, for the energy difference between the two peak positions is given by:

$$\text{Analytical uncertainty} = t_{k-1} 2^{1/2} \sigma_R \quad (\text{X1.1})$$

If  $k = 7$ , then

$$\text{Analytical uncertainty} = 3.5 \sigma_R \quad (\text{X1.2})$$

If one of the materials is a nonconductor and a third peak is measured for charge referencing, for example, the carbon 1s peak for adventitious carbon), the analytical uncertainty will be equal to or larger than  $\sqrt{2}$  times the values given in Eq X1.1 and X1.2; it has been assumed here that  $\sigma_{Rnew}$  for the carbon 1s peak also is equal to  $\sigma_R$ . See also Note X1.3.

NOTE X1.4—The uncertainty in the assumed value for the binding energy of the reference peak, for example, the carbon 1s peak of

adventitious carbon) may be larger than the analytical uncertainty from Eq X1.1 and X1.2.

**X1.6 Uncertainty of an Energy for a Single Peak Measured Soon After a Calibration**—If measurements of peak energies are made sufficiently soon after a calibration that instrumental drift (see 8.14) can be ignored, the analytical uncertainty of the peak energy (for binding energies between 0 eV and 1100 eV) is given by:

$$\text{Analytical uncertainty} = \quad (\text{X1.3})$$

$$\{[U_{95}^c(E)]^2 + (1.2 |\varepsilon_2 \text{ or } \varepsilon_3|)^2 + (t_{j-1} \sigma_{Rnew})^2\}^{1/2}$$

The third term in Eq X1.3 represents the contribution to the analytical uncertainty from  $j$  measurements of the new peak to give the repeatability standard deviation,  $\sigma_{Rnew}$ . In practice, only one measurement of the new peak generally is made. In this case, if it is assumed that  $\sigma_{Rnew} = \sigma_R$ , the analytical uncertainty is given by:

$$\text{Analytical uncertainty} \leq [(3.6 \sigma_R)^2 + (1.2 |\varepsilon_2 \text{ or } \varepsilon_3|)^2]^{1/2} \quad (m = 2) \quad (\text{X1.4})$$

or

$$\text{Analytical uncertainty} \leq [(4.4 \sigma_R)^2 + (1.2 |\varepsilon_2 \text{ or } \varepsilon_3|)^2]^{1/2} \quad (m = 1) \quad (\text{X1.5})$$

where Eq X1.4 corresponds to a calibration based on two measurements of each of the Au 4f<sub>7/2</sub> and Cu 2p<sub>3/2</sub> peaks (see 8.10.2) while Eq X1.5 corresponds to a calibration based on single measurements of these peaks. If  $\sigma_{Rnew} > \sigma_R$ , the analytical uncertainty should be evaluated from Eq X1.3.

**X1.7 Uncertainty of an Energy for a Single Peak Measured Between Calibrations**—The analytical uncertainty for a new peak measured between calibrations is given by:

$$\text{Analytical uncertainty} \leq \delta + t_{j-1} \sigma_{Rnew} \quad (\text{X1.6})$$

where, as in X1.6, the repeatability standard deviation for the new peak,  $\sigma_{Rnew}$ , is obtained from  $j$  measurements. If  $\sigma_{Rnew} \leq \sigma_R$ , then the analytical uncertainty for a single measurement of the energy of the new peak is given by:

$$\text{Analytical uncertainty} \leq \delta + 2.5 \sigma_R \quad (\text{X1.7})$$

NOTE X1.5—For many new peaks,  $\sigma_{Rnew}$  may be larger than  $\sigma_R$ .

## X2. MEASUREMENTS OF MODIFIED AUGER PARAMETERS AND AUGER-ELECTRON KINETIC ENERGIES USING XPS INSTRUMENTS WITH A MONOCHROMATED Al X-RAY SOURCE

**X2.1** This appendix provides information for determining the modified Auger parameter and an Auger-electron kinetic energy on XPS instruments equipped with a monochromated Al X-ray source. For these instruments, the average X-ray energy on the sample will usually be in the range 1486.5 eV to 1486.8 eV; the optimum energy, corresponding to the maximum intensity, is 1486.69 eV (21). The average energy in a particular instrument will depend on the monochromator adjustments and may drift with time of operation as the temperature changes in significant parts of the instrument. This average energy will generally be different from the average energy for an unmonochromated Al X-ray source by up to 0.3 eV (4). As

a result, the energy separations between photoelectron and Auger-electron peaks, that is, the Auger parameters [Ref (22) and ISO 18115-1:2013], will vary with changes in the average X-ray energy from a monochromated Al X-ray source and will be different from the corresponding values for an unmonochromated Al X-ray source. It is often more convenient in surface chemical analysis to use the modified Auger parameter [Ref (23) and ISO 18115-1:2013], which is the sum of the Auger parameter and the effective X-ray energy used in a particular experiment. The procedure described in this appendix can be used to determine the effective X-ray energy on XPS instruments equipped with a monochromated Al X-ray source. This

effective energy is used to derive modified Auger parameters and Auger-electron kinetic energies.

**NOTE X2.1**—The modified Auger parameter and the Auger-electron kinetic energy can assist in the identification of chemical states for materials for which chemical shifts in measured binding energies are inadequate for this purpose. An advantage of the modified Auger parameter for identification of chemical state is that it can usually be measured reliably even in the presence of some surface charging.

**NOTE X2.2**—Most of the available measurements of modified Auger parameters have been made on XPS instruments with unmonochromated Al or Mg X-ray sources. These sources irradiate the sample with bremsstrahlung radiation that can ionize core levels with binding energies greater than 1486 eV. As a result, it is not possible to measure modified Auger parameters for elements in the three series Al to Cl, Br to Mo, and Yb to Bi, inclusive, with a monochromated Al X-ray source because the incident X-rays do not have sufficient energy to ionize the core levels that would lead to emission of the desired Auger electrons.

**X2.2** The effective energy of an x-ray source is the sum of the values, for any peak in a measured spectrum, of the measured binding energy and the kinetic energy (both referenced to the Fermi level).

**X2.3** The effective X-ray energy from an unmonochromated Al X-ray source,  $h\nu_{Al}$ , is given approximately by:

$$h\nu_{Al} = 1486.61 \text{ eV} \quad (\text{X2.1})$$

and the same energy from an unmonochromated Mg X-ray source,  $h\nu_{Mg}$ , is given approximately by:

$$h\nu_{Mg} = 1253.60 \text{ eV} \quad (\text{X2.2})$$

For these X-ray sources, the effective X-ray energies are only approximately constant because small relative peak shifts occur for the different spectrometer energy resolutions and different spectral lineshapes that may occur in the use of this practice (5). The effective X-ray energies may vary by up to  $\pm 0.02$  eV for spectrometer energy resolutions in the range 0.2 eV to 0.4 eV, and can vary by up to 0.02 eV and  $-0.06$  eV for an unmonochromated Al X-ray source and by up to 0.02 eV and  $-0.03$  eV for an unmonochromated Mg X-ray source for spectrometer energy resolutions up to 1.5 eV (5). In addition, there is a further associated standard uncertainty of 0.01 eV in the values shown in Eq X2.1 and X2.2 from the X-ray energy measurements of Ref (21).

**NOTE X2.3**—The effective X-ray energies from unmonochromated Al and Mg X-ray sources lie between the centroid energy for the X-ray spectral lineshape and the energy of the  $K\alpha$  component such that the Cu  $L_3VV$  Auger peak occurs at the positions on the BE scale indicated in Table 3.

**NOTE X2.4**—The effective X-ray energies given in Eq X2.1 and X2.2 are averages of values from two sets of data. One set of effective X-ray energies was derived from calculated shifts of Cu, Ag, and Au photoelectron kinetic energies for XPS with unmonochromated Al or Mg X-rays from the corresponding energies with monochromated Al X-rays (5); for these calculations, the X-ray energies reported by Schweppe et al. were used (21). These shifts, together with the reference binding energies in Table 3, give effective X-ray energies of 1486.60 eV and 1253.61 eV for Al and Mg X-ray sources, respectively. A second set of data, XPS data with unmonochromated Al and Mg X-ray sources, indicates a difference between the Al and Mg effective X-ray energies that is 0.04 eV larger than obtained from the just-quoted effective X-ray energies (5, 24). The effective X-ray energies given in Eq X2.1 and X2.2 are averages of the energies obtained from these two data sets.

**X2.4** The effective X-ray energy for a monochromated Al X-ray source is given by the centroid of the X-ray spectral

lineshape from the monochromator.

**NOTE X2.5**—The X-ray spectral lineshape often is assumed to be a Gaussian function.

**X2.5 Determine the Effective X-Ray Energy from a Monochromated Al X-Ray Source:**

**X2.5.1** While conducting the regular calibration (see 8.10.2), also measure the Cu  $L_3VV$  Auger peak following the Cu  $2p_{3/2}$  peak (as indicated in Note 24).

**X2.5.2** Measure the position of the Cu  $L_3VV$  peak on the BE scale as described in 8.8.1. If two measurements were made of the Cu  $L_3VV$  peak, calculate the average value,  $E_{meas\ 3}$ .

**X2.5.3** Calculate the corrected position of the Cu  $L_3VV$  peak on the BE scale,  $E_{corr\ 3}$ , using the values of the parameters  $a$  and  $b$  obtained in the calibration (see 8.10.3) and the relation:

$$E_{corr\ 3} = (1 + a) E_{meas\ 3} + b \quad (\text{X2.3})$$

The value of  $E_{corr\ 3}$  should be close to 567.93 eV, the reference position on the BE scale for the Cu  $L_3VV$  peak with an unmonochromated Al X-ray source (Table 3).

**X2.5.4** Calculate the energy difference,  $\Delta h\nu$ , between the effective X-ray energy from the monochromated Al X-ray source and the effective X-ray energy from an unmonochromated Al X-ray source (Eq X2.1) from:

$$\Delta h\nu = E_{corr\ 3} - 567.93 \text{ eV} \quad (\text{X2.4})$$

**NOTE X2.6**—Values of  $\Delta h\nu$  ranging from about 0.0 eV to 0.3 eV were found in an interlaboratory study (4) that utilized different methods of peak location than those recommended in this practice.

**NOTE X2.7**—It may be desirable to consult the instrument manufacturer if the value of  $\Delta h\nu$  lies outside the range 0.0 eV to 0.2 eV since adjustment of the monochromator crystal and the X-ray source may be required. In some imaging XPS instruments, values of  $\Delta h\nu$  may occur outside this range in certain regions of the image (5).

**X2.5.5** Calculate the effective energy of the X-rays from the monochromated Al x-ray source,  $h\nu_{Al}^{mon}$ , from

$$h\nu_{Al}^{mon} = h\nu_{Al} + \Delta h\nu = 1486.61 + \Delta h\nu \text{ eV} \quad (\text{X2.5})$$

**X2.5.6** The uncertainty at the 95 % confidence level in the value of  $h\nu_{Al}^{mon}$ , at the time it is measured, is given by Eq X1.4 (if  $m = 2$ ) or Eq X1.5 (if  $m = 1$ ) for which it has been assumed that  $\sigma_R$  is appropriate for the Cu  $L_3VV$  peak. If this assumption is not believed to be correct, separate measurements should be made of the repeatability standard deviation for the Cu  $L_3VV$  peak and used as the value of  $\sigma_{Rnew}$  to obtain the analytical uncertainty from Eq X1.3.

**NOTE X2.8**—For the examples of Table 2, the uncertainty of  $h\nu_{Al}^{mon}$  at the 95 % confidence level is 0.09 eV for  $m = 2$  repeats and 0.10 eV for  $m = 1$  repeat of the measurement of the Cu  $L_3VV$  peak position.

**X2.5.7** The uncertainty of  $h\nu_{Al}^{mon}$  at a time between calibrations may remain at the value determined in X2.5.4 in an ideal instrument or may drift with time as parts of the instrument, particularly the monochromator, change in temperature. To determine this drift, include measurements of the Cu  $L_3VV$  peak in the procedure in 8.13. Prepare a control chart showing measurements of  $h\nu_{Al}^{mon}$  at different times (calendar dates) as described in 8.14, and include the corresponding uncertainties of  $h\nu_{Al}^{mon}$  from section X2.5.4 as error bars on the plotted points. Calculate the sum of the uncertainty of  $h\nu_{Al}^{mon}$  and the largest

deviation of  $h\vartheta_{Al}^{mon}$  from its initial value during the period chosen in 8.13 as the calibration interval. This sum may be a useful estimate of the uncertainty of  $h\vartheta_{Al}^{mon}$  between calibrations.

## X2.6 Determine the Modified Auger Parameter:

X2.6.1 The Auger parameter,  $\alpha$ , is the kinetic energy of a narrow Auger-electron peak in a spectrum minus the kinetic energy of the most intense photoelectron peak from the same element (ISO 18115-1:2013). Equivalently, the Auger parameter is the binding energy of the most intense photoelectron peak for an element in a spectrum minus the binding-energy position of a sharp Auger peak from the same element in that spectrum. The modified Auger parameter,  $\alpha'$ , is the sum of the Auger parameter and the effective X-ray energy used in the XPS experiment.

X2.6.2 Determine the Auger parameter,  $\alpha$ , for the element of interest from a measured spectrum.

X2.6.3 For a monochromated Al X-ray source, determine the modified Auger parameter,  $\alpha'$ , from

$$\alpha' = \alpha + h\vartheta_{Al}^{mon} \quad (\text{X2.6})$$

using the value of  $h\vartheta_{Al}^{mon}$  from Eq X2.5.

NOTE X2.9—For XPS systems with unmonochromated Al or Mg X-ray sources, the modified Auger parameter is the sum of the Auger parameter and the relevant effective X-ray energy, (Eq X2.1 or Eq X2.2, respectively).

X2.7 Determine the Auger-Electron Kinetic Energy—If the measured position of an Auger-electron peak on the BE scale is  $E_p$ , then the corresponding kinetic energy,  $E_K$ , of this peak is given by:

$$E_K = h\vartheta_{Al}^{mon} - E_p \quad (\text{X2.7})$$

NOTE X2.10—For XPS systems with unmonochromated Al or Mg X-ray sources, the kinetic energy of an Auger-electron peak is given by the difference of the effective X-ray energy for each source (as given by Eq X2.1 or Eq X2.2, respectively) and the measured position of the Auger-electron peak on the BE scale.

## REFERENCES

- (1) Seah, M.P., Gilmore, I. S., and Beamson, G., “XPS: Binding energy calibration of electron spectrometers: 5 - Re-evaluation of the reference energies,” *Surface and Interface Analysis*, Vol 26, No. 9, 1998, pp. 642–649.
- (2) Seah, M. P., and Gilmore, I.S., “AES: Energy calibration of electron spectrometers: III—General calibration rules,” *Journal of Electron Spectroscopy*, Vol 83, Nos. 2, 3, 1997, pp. 197–208.
- (3) X-Ray Photoelectron Spectroscopy Database, Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, MD 20899.
- (4) Powell, C. J., “Energy Calibration of X-Ray Photoelectron Spectrometers: Results of an Interlaboratory Comparison to Evaluate a Proposed Calibration Procedure,” *Surface and Interface Analysis*, Vol 23, No. 3, 1995, pp. 121–132.
- (5) Seah, M. P., Gilmore, I. S., and Spencer, S. J., “XPS: Binding energy calibration of electron spectrometers: 4 – Assessment of effects for different X-ray sources, analyser resolutions, angles of emission and of the overall uncertainties,” *Surface and Interface Analysis*, Vol. 26, No. 9, 1998, pp. 617–641.
- (6) Powell, C. J., “Elemental Binding Energies for X-Ray Photoelectron Spectroscopy,” *Applied Surface Science*, Vol 89, No. 2, 1995, pp. 141–149.
- (7) Seah, M. P., Jones, M. E. and Anthony, M. T., “Quantitative XPS: the calibration of spectrometer intensity - energy response functions: 2 – results of interlaboratory measurements for commercial instruments,” *Surface and Interface Analysis*, Vol 6, No. 5, 1984, pp. 242–254.
- (8) Briggs, D. and Seah, M. P., *Practical Surface Analysis*, Vol 1 - Auger and X-ray Photoelectron Spectroscopy, Chichester: Wiley, 1990.
- (9) Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, F. and Muilenberg, G. E., *Handbook of X-ray Photoelectron Spectroscopy*, Eden Prairie, MN: Perkin Elmer Corp., 1979.
- (10) Ikeo, N., Iijima, Y., Niimura, N., Sigematsu, M., Tazawa, T., Matsumoto, S., Kojima, K. and Nagasawa, Y., *Handbook of X-ray Photoelectron Spectroscopy*, Tokyo: JEOL, 1991.
- (11) Moulder, J. F., Stickle, W. F., Sobol, P. E. and Bomben, K. D., *Handbook of X-Ray Photoelectron Spectroscopy*, Eden Prairie, MN: Perkin Elmer Corp., 1992.
- (12) Seah, M. P. and Tosa, M., “Linearity in electron counting and detection systems,” *Surface and Interface Analysis*, Vol 18, No. 3, 1992, pp. 240–246.
- (13) Seah, M. P., Lim, C. S. and Tong, K. L., “Channel electron multiplier efficiencies: the effect of the pulse height distribution on spectrum shape in Auger electron spectroscopy,” *Journal of Electron Spectroscopy and Related Phenomena*, Vol 48, No. 3, 1989, pp. 209–218.
- (14) Powell, C. J., “Energy Calibration of X-ray Photoelectron Spectrometers, II. Issues in Peak Location and Comparison of Methods,” *Surface and Interface Analysis*, Vol 25, No. 10, 1997, pp. 777–787.
- (15) Anthony, M. T. and Seah, M. P., “XPS: Energy calibration of electron spectrometers: 2 – results of an interlaboratory comparison,” *Surface and Interface Analysis*, Vol 6, No. 3, 1984, pp. 107–115.
- (16) Seah, M. P., “Measurement: AES and XPS,” *Journal of Vacuum Science and Technology A*, Vol 3, No. 3, 1985, pp. 1330–1337.
- (17) Cumpson, P. J., Seah, M. P. and Spencer, S. J., “Simple procedure for precise peak maximum estimation for energy calibration in AES and XPS,” *Surface and Interface Analysis*, Vol 24, No. 10, 1996, pp. 687–694.
- (18) Cumpson, P. J. and Seah, M. P., “Random uncertainties in AES and XPS: 1: Uncertainties in peak energies, intensities and areas derived from peak synthesis,” *Surface and Interface Analysis*, Vol 18, No. 5, 1992, pp. 345–360.
- (19) Conny, J. M., Powell, C. J., and Currie, L. A., “Standard Test Data for Estimating Peak-Parameter Errors in X-ray Photoelectron Spectroscopy. I. Peak Binding Energies,” *Surface and Interface Analysis*, Vol 26, No. 12, 1998, pp. 939–956.
- (20) Seah, M. P. and Brown, M. T., “Validation and accuracy of software for peak synthesis in XPS,” *Journal of Electron Spectroscopy and Related Phenomena*, Vol 95, No. 1, 1998, pp. 71–93.
- (21) Schweppe, J., Deslattes, R. D., Mooney, T., and Powell, C. J., “Accurate measurement of Mg and Al  $K\alpha_{1,2}$  X-ray energy profiles,” *Journal of Electron Spectroscopy*, Vol 67, No. 3, 1994, pp. 463–478.
- (22) Wagner, C. D., “Auger parameter in electron spectroscopy for the identification of chemical species,” *Analytical Chemistry*, Vol 47, No. 7, 1975, pp. 1201–1203.
- (23) Wagner, C. D., Gale, L. H., and Raymond, R. H., “Two-dimensional



chemical state plots: A standardised data set for use in identifying chemical states by X-ray photoelectron spectroscopy,” *Analytical Chemistry*, Vol 51, No. 4, 1979, pp. 446–482.

(24) Seah, M. P., “AES energy calibration of electron spectrometers: IV: A re-evaluation of the reference energies,” *Journal of Electron Spectroscopy*, Vol 97, No. 3, 1998, pp. 235–241.

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