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Designation: ~~E2108 – 10~~ E2108 – 16

Standard Practice for Calibration of the Electron Binding-Energy Scale of an X-Ray Photoelectron Spectrometer[1]

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 (ε) 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 Kα X-rays or by monochromated aluminum Kα 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~~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 ~~0–10000~~–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.~~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 ±0.03 eV or less.

1.7 On instruments equipped with a monochromated aluminum Kα 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 responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

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[1] 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.

Current edition approved ~~Nov. 1, 2010~~Nov. 1, 2016. Published ~~December 2010~~December 2016. Originally approved in 2000. Last previous edition approved in ~~2005~~2010 as ~~E2108 – 05.~~E2108 – 10. DOI: ~~10.1520/E2108-10.~~10.1520/E2108-16.

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2. Referenced Documents

2.1 *ASTM Standards:*[2]

E456 Terminology Relating to Quality and Statistics

E673 Terminology Relating to Surface Analysis (Withdrawn 2012)[3]

E902 Practice for Checking the Operating Characteristics of X-Ray Photoelectron Spectrometers (Withdrawn 2011)[3]

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:*[4]

ISO ~~9001:2000~~9001:2015 Quality ~~Management Systems—Requirements~~ management systems—Requirements

ISO ~~15472:2001~~15472:2010 Surface ~~Chemical Analysis—X-Ray Photoelectron Spectrometers—Calibration of Energy Scale~~schemical analysis—X-ray photoelectron spectrometers—Calibration of energy scales

ISO ~~18115:2001~~18115-1:2013 Surface ~~Chemical Analysis—Vocabulary~~ chemical analysis—Vocabulary—Part 1: General terms and terms used in spectroscopy

3. Terminology

3.1 *Definitions*—~~For definitions of~~Since Terminology E673 ~~terms used in X-ray photoelectron spectroscopy and surface analysis, see Terminology~~was withdrawn in 2012, definitions of terms used in Auger and ~~E673 and ISO 18115:2001.~~X-ray photoelectron spectroscopy are now based on ISO 18115-1:2013.[5] 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 Kα X-rays: magnesium (Mg) source; unmonochromated aluminum (Al) source; or monochromated Al source. This procedure is based on ISO ~~15472:2001.~~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**).[6] 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~~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.~~ 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 ~~standard.~~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**)

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the ~~standard's~~standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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

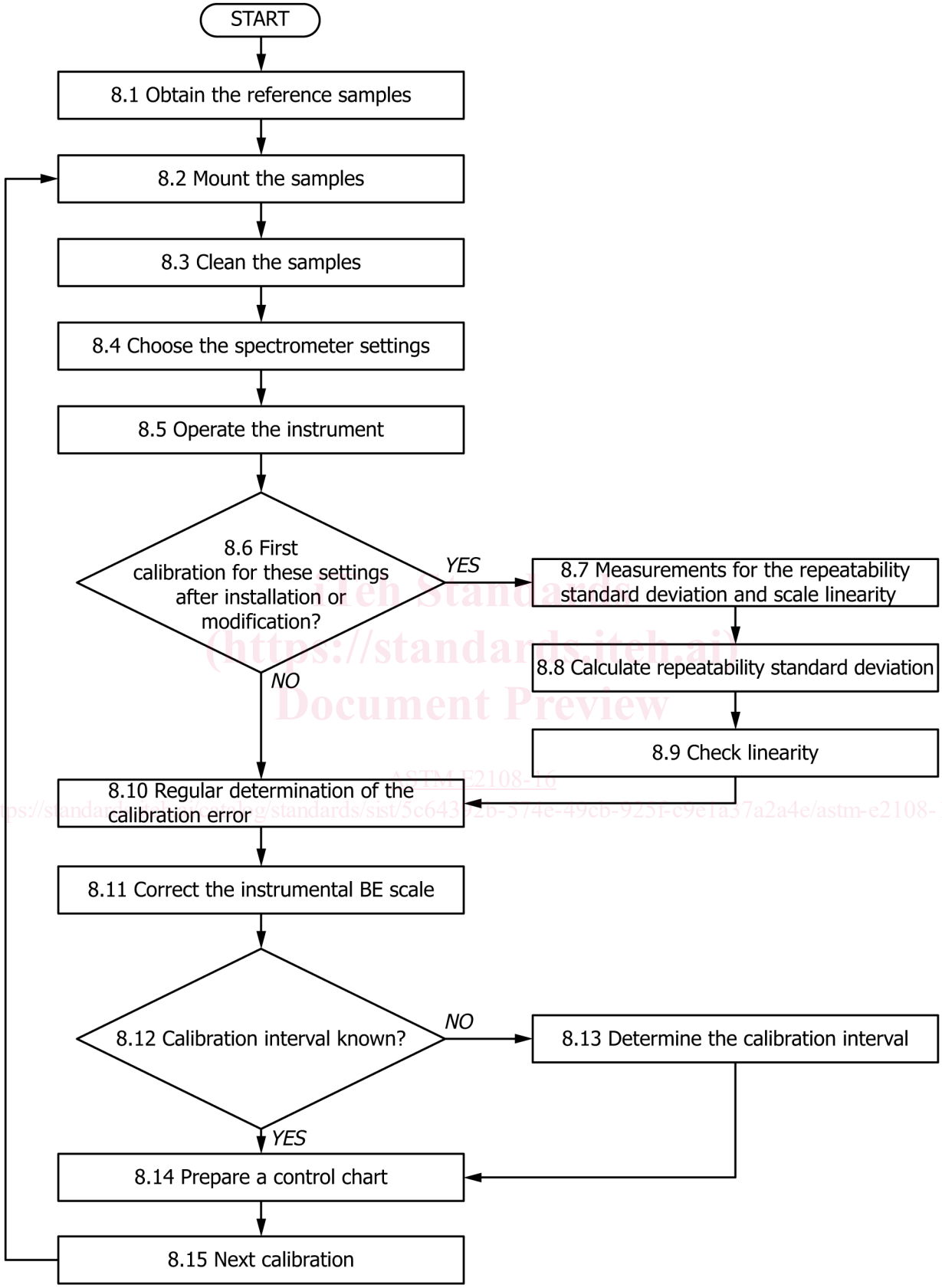
[5] https://www.iso.org/obp/ui/#iso:std:iso:18115:-1:ed-2:v1:en.

[6] 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 Table 3, in eV
$E_{meas\ ni}$	one of a set of measurements of binding energy for the peak, n, in Table 3, in eV
$E_{ref\ n}$	reference values for the position of peak, n, in Table 3, 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
hv_{Al}	effective X-ray energy from an unmonochromated Al X-ray source, in eV
~~hv_{Al}^{mon}~~	~~effective X-ray energy from a monochromated Al X-ray source, in eV~~
$h\vartheta_{Al}^{mon}$	effective X-ray energy from a monochromated Al X-ray source, in eV
hv_{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 $4f_{7/2}$, Cu $2p_{3/2}$ and Ag $3d_{5/2}$ or Cu L_3VV peaks in the repeatability standard deviation and linearity determinations
m	number of repeat measurements for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks in the regular calibrations
n	designation of the peak identifier in Table 3
~~p~~	~~parameter in Eq A1.1 and A1.1 defined in Eq A1.2 and A1.2~~
p	parameter in Eq A1.1, defined in Eq A1.2 and Section A1.2
~~q~~	~~parameter in Eq A1.1 and A1.1 defined in Eq A1.3 and A1.3~~
q	parameter in Eq A1.1, defined in Eq A1.3 and Section A1.2
~~r~~	~~parameter in Eq A1.1 and A1.1 defined in Eq A1.4 and A1.4~~
r	parameter in Eq A1.1, defined in Eq A1.4 and Section A1.2
~~t_x~~	~~Student's t value for x degrees of freedom of a two-sided distribution for a confidence level of 95 %~~
t_x	Student's t value for x degrees of freedom of a two-sided distribution for a confidence level of 95 %
U_{95}	total uncertainty of the calibrated energy scale at a confidence level of 95 %, in eV
$U_{95}^c(E)$	uncertainty at a confidence level of 95 % arising from the calibration using the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks at binding energy E, assuming perfect scale linearity, in eV
~~U_{95}^1~~	~~uncertainty of ε_2 or ε_3 at a confidence level of 95 % from Eq 7 and 7, in eV~~
U_{95}^l	uncertainty of ε_2 or ε_3 at a confidence level of 95 % from Eq 7 and Section 8.9.3, in eV
~~U_{95}^{cl}~~	~~uncertainty of the calibration at a confidence level of 95 % in the absence of a linearity error, from Eq 12 and 12 and Eq 13 and 13, in eV~~
U_{95}^{cl}	uncertainty of the calibration at a confidence level of 95 % in the absence of a linearity error, from Eq 12 or Eq 13 and Section 8.10.4, in eV
XPS	X-ray photoelectron spectroscopy
α	Auger parameter, in eV
α'	modified Auger parameter, in eV
Δ_n	offset energy, given by the average measured binding energy for a calibration peak minus the reference energy, in eV, for n = 1, 2, 3, 4 in Table 3, for a given X-ray source
ΔE_{corr}	correction to be added to E_{meas}, after calibration, to provide the corrected result for the binding energy, in eV
$\Delta E_{corr\ n}$	value of ΔE_{corr} for peaks 1 and 4 in Table 3, in eV
ΔE_n	drift of the binding-energy scale following a calibration for peaks 1 and 4 in Table 3, in eV
~~$\Delta\varphi$~~	~~the average of Δ_1 and Δ_4 from Eq 16 and 16, in eV~~
$\Delta\varphi$	the average of Δ_1 and Δ_4 from Eq 16 and Section 8.11.1.2, in eV
~~Δhv~~	~~difference between hv_{Al}^{mon} and hv_{Al}, in eV~~
Δhv	difference between $h\vartheta_{Al}^{mon}$ and hv_{Al}, in eV
δ	value for the tolerance limit of energy calibration at a confidence level of 95 % (set by the analyst), in eV
~~ε_2~~	~~measured scale linearity error at the Ag $3d_{5/2}$ peak from Eq 4 and 4, in eV~~
ε_2	measured scale linearity error at the Ag $3d_{5/2}$ peak from Eq 4 and Section 8.9.2, in eV
~~ε_3~~	~~measured scale linearity error at the Cu L_3VV peak from Eq 5 and 5 or Eq 6 and 6, in eV~~
ε_3	measured scale linearity error at the Cu L_3VV peak from Eq 5 or Eq 6 and Section 8.9.2, in eV
σ_R	maximum of σ_{R1}, σ_{R2} or σ_{R3}, and σ_{R4}, in eV
σ_{Rn}	repeatability standard deviation for the seven measurements of the binding energy of peak, n, in Table 3, in eV
σ_{Rnew}	repeatability standard deviation for a new peak, in eV

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 ~~9001:2000,~~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.



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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.

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 ±δ (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 ~~15472:2001).~~15472:2010). A user should select a value of δ 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 δ 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 ±δ. 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

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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 δ as a result of poor counting statistics, large peak widths, uncertainties associated with peak ~~synthesis,~~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 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 ±δ 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,~~ 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.~~ 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.~~ 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 ~~Practice~~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 compatible with the specimen holder of the X-ray photoelectron spectrometer, and typically are 10 ~~mm~~ 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° and 56° 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 σ_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.

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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 $3d_{5/2}$ 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_3VV Auger peak because the copper foil is already required for measurement of the Cu $2p_{3/2}$ 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 $4f_{7/2}$ and Cu $2p_{3/2}$ 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_{95} 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 δ 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 δ 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_{95} for values of δ of 0.1 eV and 0.2 eV and for values of m of 1 or 2. The difference between δ and U_{95} is the maximum drift of the instrumental BE scale that should be allowed between calibration checks. 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 δ, and it is suggested that a value of 0.1 eV be chosen. To decide whether the selected value of δ is realistic, this practice should be followed and a version of Table 2 should be completed. In general, the value of δ 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 δ versus the cost in instrument and staff time in performing calibrations. For example, if δ 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, δ may need to be increased to an acceptable value.

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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 ~~mm~~ by 10 mm and with thicknesses between 0.1 ~~mm~~ 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.~~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.~~ 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.

TABLE 2 Contributions to an Error Budget for Calibration of the BE scale (from ISO ~~15472:2001)~~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 δ and m) on the uncertainty of the calibration U_{95} and the required interval between calibrations for assumed values of σ_r, ε_2, or ε_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~~	~~± δ~~	~~You choose~~	~~± 0.1~~		~~± 0.2~~		~~(Your choice is dictated by the accuracy you require and the number of spectra you have time to acquire in regular calibrations.)~~
Tolerance limits, eV	± δ	You choose	±0.1		±0.2		(Your choice is dictated by the accuracy you require and the number of spectra you have time to acquire in regular calibrations.)
~~Repeatability standard deviation, eV~~	~~σ_R~~	~~Eq 1 and 1~~	~~0.020~~		~~0.020~~		~~(Characteristic of your spectrometer measured at first calibration (see 8.7)).~~
Repeatability standard deviation, eV	σ_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~~	~~m~~	~~You choose m= 1 or 2~~	~~m = 1~~	~~m = 2~~	~~m = 1~~	~~m = 2~~	
Number of times each pair of spectra is acquired	m	You choose m= 1 or 2	m = 1	m = 2	m = 1	m = 2	
~~Uncertainty of calibration measurements, eV~~	~~U_{95}^{c1}~~	~~Eq 12 and 12 or Eq 13 and 13~~	~~0.074~~	~~0.052~~	~~0.074~~	~~0.052~~	
Uncertainty of calibration measurements, eV	U_{95}^{c}	Eq 12 or Eq 13 and Section 8.10.4	0.074	0.052	0.074	0.052	
~~Measure of scale nonlinearity, eV~~	~~ε_2 or ε_3~~	~~Eq 4 and 4, Eq 5 and 5 or Eq 6 and 6~~	~~0.020~~	~~0.020~~	~~0.020~~	~~0.020~~	~~(Characteristic of your spectrometer measured at first calibration (see 8.7)).~~
Measure of scale nonlinearity, eV	ε_2 or ε_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~~	~~U_{95}~~	~~Eq 11 and 11~~	~~0.078~~	~~0.057~~	~~0.078~~	~~0.057~~	
Uncertainty of energy scale after calibration, eV	U_{95}	Eq 11 and Section 8.10.4	0.078	0.057	0.078	0.057	
~~Maximum allowable drift between calibrations, eV~~	~~± (δ-U_{95})~~	~~δ and U_{95}~~	~~± 0.022~~	~~± 0.043~~	~~± 0.122~~	~~± 0.143~~	~~(Define the drift allowable before you are in danger of exceeding your chosen limits ±δ eV.)~~
Maximum allowable drift between calibrations, eV	± (δ-U_{95})	δ and U_{95}	±0.022	±0.043	±0.122	±0.143	(Define the drift allowable before you are in danger of exceeding your chosen limits ±δ 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.)

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NOTE 2—Suitable sputtering conditions with an inert gas are 1 min of a 30 μA beam of argon ions covering 1 cm^2 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 ~~only~~ 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~~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.

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8.7 *Measurements for the Repeatability Standard Deviation and Scale Linearity:*

8.7.1 The repeatability standard deviation for the peak BE, σ_R, is determined from repeated measurements of the Au $4f_{7/2}$, Ag $3d_{5/2}$ or Cu L_3VV, and Cu $2p_{3/2}$ peaks as described in this section and in 8.8. The value of σ_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~~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 σ_R.

8.7.2 The BE-scale linearity error, ε_2 or ε_3, is determined from measurements of the Cu L_3VV Auger-electron peak for unmonochromated Mg or Al X-ray sources and from measurements of the Ag $3d_{5/2}$ 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 $4f_{7/2}$, Cu $2p_{3/2}$, Cu L_3VV, with this sequence repeated six additional ~~times~~times.

8.7.3.2 *Monochromated Al X-rays:* Au $4f_{7/2}$, Cu $2p_{3/2}$, Ag $3d_{5/2}$, with this sequence repeated six additional ~~times~~times.

NOTE 8—The Au $4f_{7/2}$ peak is often the weakest peak although, depending on the spectrometer, sometimes the Cu L_3VV peak may be weaker. Initial measurements with the Au $4f_{7/2}$ 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 $4f_{7/2}$ 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 $4f_{7/2}$ peak, peak 1, is given in Table 3.

NOTE 9—The reference BE values for the calibration peaks vary with 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 $2p_{3/2}$ 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 $2p_{3/2}$ 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_3VV 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_3VV peak or the Ag $3d_{5/2}$ 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 $3d_{5/2}$ peak, peak 2, and the Cu L_3VV peak, peak 3, are given in Table 3.

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 ~~used~~ normally used in the calibration.

Peak Number, *n*	Assignment	$E_{ref\ n}$ (eV)		
		Al Kα	Mg Kα	Monochromatic Al Kα
1	Au $4f_{7/2}$	83.95	83.95	83.96
2	Ag $3d_{5/2}$	(368.22)	(368.22)	368.21
3	Cu L_3VV	567.93	334.90	-
4	Cu $2p_{3/2}$	932.63	932.62	932.62