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Surface chemical analysis — High-resolution Auger electron spectrometers — Calibration of energy scales for elemental and chemical-state analysis

Analyse chimique des surfaces — Spectromètres d'électrons Auger à haute résolution — Étalonnage des échelles d'énergie pour l'analyse élémentaire et de l'état chimique

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Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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

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

ISO 17974 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *X-ray photoelectron spectroscopy*.

Introduction

Auger electron spectroscopy (AES) is used extensively for the surface analysis of materials. Elements in the sample (with the exception of hydrogen and helium) are identified from comparisons of the kinetic energies of their Auger electron peaks (determined from the measured spectra) with tabulations of those energies for the different elements or with handbooks of spectra. Information on the chemical state of such elements can be derived from the chemical shifts of measured Auger electron features with respect to those for reference states. Identification of chemical states is based on measurements of chemical shifts with accuracies in the range down to 0,1 eV, making necessary individual measurements having and reference sources available with, the appropriate accuracies. Calibrations of the kinetic energy scales of AES instruments are therefore required, often with an uncertainty of $\leqslant$ 0,3 eV.

The method for calibrating kinetic energy scales specified in this International Standard uses metallic samples of pure copper (Cu), and either aluminium (Al) or gold (Au), and is applicable to Auger electron spectrometers measuring direct spectra with relative resolutions of 0,2 % or better. It is valid for the kinetic energy range 0 eV to 2 250 eV if gold is used, and 0 eV to 1 550 eV if aluminium is used.

Traditionally, kinetic energies of Auger electrons have been referenced to the vacuum level, and this reference is still used by many analysts. However, the vacuum level is ill-defined and can vary from instrument to instrument over a range of 0,5 eV. Although use of the vacuum level reference procedure will generally not cause ambiguity in elemental identification, it may cause uncertainty in measurements at high resolution relating to chemical states. Because of this, instruments designed for both Auger electron spectroscopy and X-ray photoelectron spectroscopy reference the kinetic energies to the Fermi level, giving values typically 4,5 eV higher than those referenced to the vacuum level. For the purposes of this International Standard, the kinetic energies are referenced to the Fermi level.

AES instruments calibrated for providing analyses within the scope of ISO 17025 [1] as well as for other purposes may need a statement of the estimated calibration uncertainty. These instruments are in calibration for kinetic energy measurements within certain defined tolerance limits $\pm \delta$. The value of δ is not defined in this International Standard since it will depend on the application and design of the AES instrument. The value of δ is selected by the user, based on experience in the use of this International Standard, the calibration stability of the instrument, the uncertainty required for kinetic energy measurements in the intended applications of the instrument and the effort incurred in conducting the calibration. This International Standard provides information by which a suitable value of δ may be chosen. Typically, δ is $\geqslant$ 0,2 eV and greater than about four times the repeatability standard deviation, σ_R.

For an instrument to be in calibration, the divergence from the reference kinetic energy values plus the expanded calibration uncertainty for a confidence level of 95 %, when added to the instrumental drift with time, must not exceed the chosen tolerance limits. Before it becomes likely that the instrument is out of calibration, it needs to be recalibrated: a calibration measurement made and action taken to reduce the difference between the measured and reference values. This difference may not necessarily be reduced to zero, but will normally come down to a small fraction of the tolerance limits required for the analytical work.

This International Standard does not address all possible defects of instruments, since the required tests would be very time consuming and would need both specialist knowledge and equipment. However, it does address the basic and common problems in the calibration of the kinetic energy scales of AES instruments.

Surface chemical analysis — High-resolution Auger electron spectrometers — Calibration of energy scales for elemental and chemical-state analysis

1 Scope

This International Standard specifies a method for calibrating the kinetic energy scales of Auger electron spectrometers used for elemental and chemical state analysis at surfaces. It also specifies a calibration schedule for testing the kinetic energy scale linearity at one intermediate energy, for confirming the uncertainty of the scale calibration at one low and one high kinetic energy value, for correcting for small drifts of that scale and for defining the expanded uncertainty of the calibration of the kinetic energy scale with a confidence level of 95 % (this uncertainty includes contributions for behaviours observed in interlaboratory studies but does not cover all possible defects).

It is applicable only to those instruments incorporating an ion gun for sputter cleaning. It is not applicable to instruments with kinetic energy scale errors significantly non-linear with energy. Neither it is applicable to those instruments operated at relative resolutions poorer than 0,2 % in the constant $\Delta E/E$ mode or 1,5 eV in the constant ΔE mode, those requiring tolerance limits of ± 0,05 eV or less, nor to those with an electron gun that cannot be operated in the energy range 5 keV to 10 keV. It does not provide a full calibration check for confirming the energy measured at each addressable point on the energy scale, this being performed according to the manufacturer's recommendations.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 18115, *Surface chemical analysis — Vocabulary*

3 Terms and definitions

For the purposes of this International Standard, the terms and definitions given in ISO 18115 apply.

4 Symbols and abbreviated terms

The following symbols and abbreviated terms are used throughout this International Standard (see also annex B)

AES	Auger electron spectroscopy
A	Analyser retardation factor
a	Measured energy scaling error
b	Measured zero offset error, in electronvolts
c	Coefficient of R
d	Coefficient of R^2
E_{corr}	Corrected result for kinetic energy corresponding to given E_{meas}, in electronvolts
E_{elem}	Kinetic energy of a frequently measured element at which the indicated kinetic energy scale is set, after calibration, to read correctly, in electronvolts
E_{meas}	A measured kinetic energy, in electronvolts
$E_{\text{meas},n}$	Average measured kinetic energy for peak n, in electronvolts
$E_{\text{meas},ni}$	One of a set of measurements of kinetic energy for peak n, in electronvolts
$E_{\text{ref},n}$	Reference values for position of peak n on kinetic energy scale, in electronvolts
$E^{\text{o}}_{\text{ref},n}$	Reference kinetic energy of peak n
FWHM	Full width at half maximum peak intensity above background, in electronvolts
i	Index of spectrum for the seven repeat measurements of a peak
j	Number of repeat measurements for new peak
k	Number of repeat measurements for Cu $M_{2,3}VV$, Cu L_3VV, and Au $M_5M_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks in repeatability and linearity determinations
m	Number of repeat measurements for Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks in regular calibrations
n	Designation of peak identifier
R	Relative resolution of a spectrometer, expressed as percentage
t_x	Student's t values for x degrees of freedom of two-sided distribution for confidence level of 95 %
U_{95}	Total uncertainty of calibrated energy scale at confidence level of 95 %, in electronvolts
$U^{\text{c}}_{95}(E)$	Uncertainty at confidence level of 95 % arising from calibration using Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks at kinetic energy, E, assuming perfect scale linearity, in electronvolts
U^{l}_{95}	Uncertainty of ε_2 at confidence level of 95 %, in electronvolts
U^{cl}_{95}	Uncertainty of calibration at confidence level of 95 %, in the absence of a linearity error
Δ_n	Offset energy, given by average measured kinetic energy for calibration peak minus reference kinetic energy, in electronvolts, for $n = 1, 2, 3, 4$
ΔE_{corr}	Correction added to E_{meas} after calibration to provide corrected kinetic energy result
$\Delta\phi$	Average of Δ_1 and Δ_4

δ	Value for tolerance limit of energy calibration at confidence level of 95 % (set by the analyst), in electronvolts
ε_2	Measured scale linearity error at Cu L_3VV peak, in electronvolts
σ_R	Maximum of σ_{R1}, σ_{R2}, and σ_{R3} or σ_{R4}
σ_{Rn}	Repeatability standard deviation for nth peak
σ_{Rnew}	Repeatability standard deviation for new peak, in electronvolts

See annex B for a list of symbols used only in that annex.

5 Outline of method

Calibration of an Auger electron spectrometer using this International Standard is performed by obtaining and preparing copper and gold or aluminium reference foils in order to measure the kinetic energies of selected Auger electron peaks. These reference materials are chosen as they provide Auger electron peaks near the high and low kinetic energy limits used in practical analysis. For kinetic energy scale linearity tests, an intermediate energy peak is used. These peaks are well established for this purpose and the relevant reference data exist.

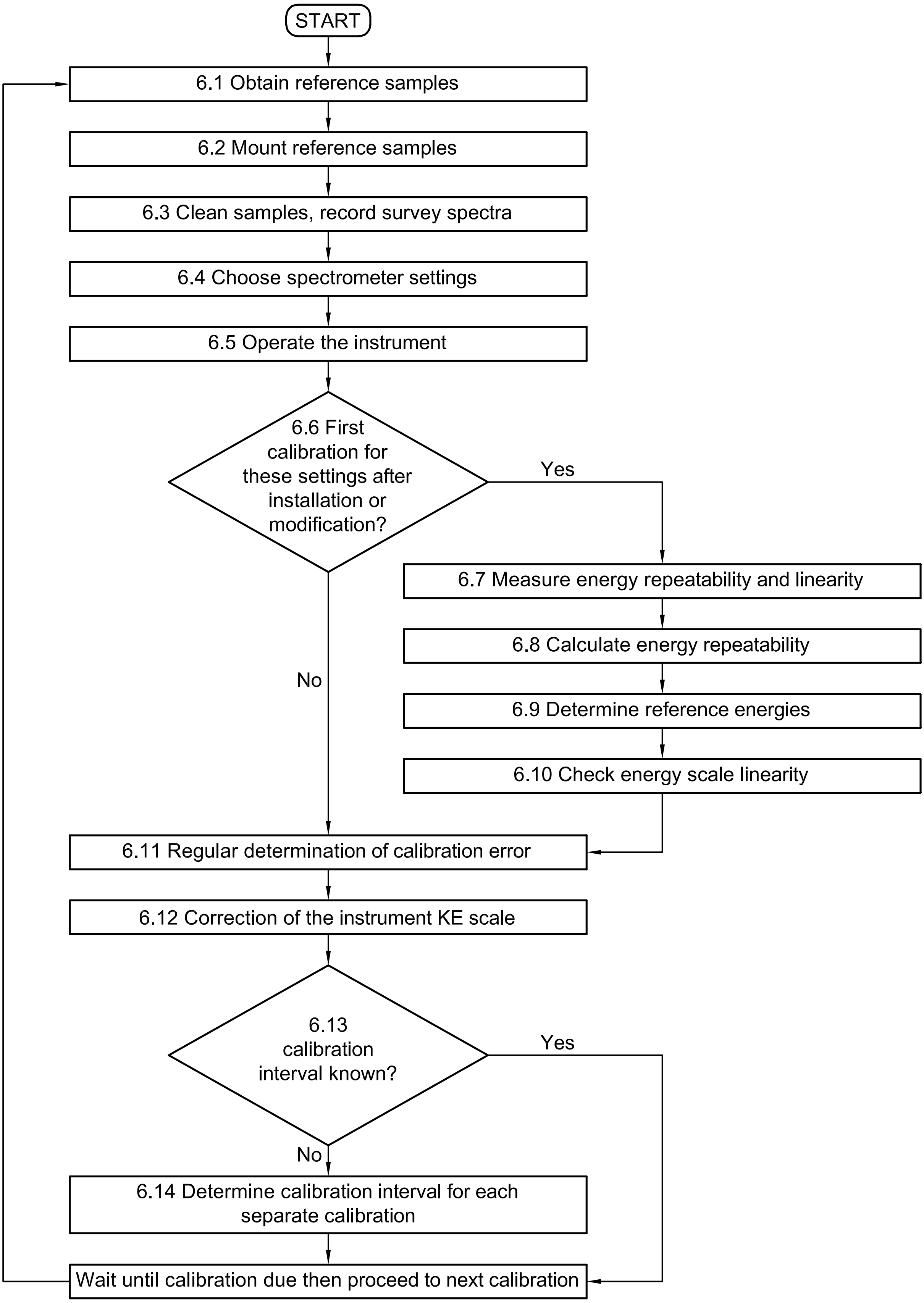
See Figure 1 for a flowchart showing the general structure of the work and the sequence of procedures.

The initial steps are given in 6.1 to 6.5. For the first calibration it is assumed that there has been no characterization of the spectrometer behaviour for the chosen instrument settings. Thus, in accordance with 6.7, measurements are made of the kinetic energies of the Cu $M_{2,3}VV$ and Cu L_3VV, and either Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$, peaks in a sequence repeated seven times. These data give the repeatability standard deviation, σ_R, of the kinetic energy of a peak. This repeatability has contributions from the stability of the spectrometer electronic supplies, from the sensitivity of the measured peak energy to the sample position and from the statistical noise at the peak. In the procedure, conditions are defined to ensure that the statistical noise is relatively small. The other two contributions may vary with the measured kinetic energy, and so σ_R is defined as the greatest of the values obtained for the three peaks used. The value of σ_R may depend on the sample positioning procedure. In 6.7.1, the use of a consistent sample positioning procedure is required and the final calibration is only valid for samples positioned using this positioning procedure.

The Au $M_5N_{6,7}N_{6,7}$ peak is weak, especially at 5 keV beam energy, and reference values for the peak energy are available only for incident beam energies of 5 keV and 10 keV. Thus, for instruments in which the signal-to-noise ratio is poor, or which cannot scan above 2 000 eV kinetic energy or do not operate at 5 keV or 10 keV beam energies, the Al $KL_{2,3}L_{2,3}$ peak is available as an alternative. Using the Au $M_5N_{6,7}N_{6,7}$ peak allows the calibration to cover the kinetic energy scale from 0 eV to 2 250 eV, whereas with Al $KL_{2,3}L_{2,3}$ the upper limit is restricted to 1 550 eV.

Studies of spectrometers show that, in general, any measured error in the peak energies varies approximately linearly with the peak kinetic energy. The equations presented in this International Standard are valid only for this most common situation and are based on the principle that the difference between the measured kinetic energies and the reference kinetic energies are both small and are linearly, or close to linearly, dependent on the kinetic energy. This linearity may fail if the instrument is defective and so a test is specified in 6.7 and 6.10 for confirming the closeness to linearity at an intermediate energy. For convenience, this test involves the Cu L_3VV peak.

If the linearity test is adequate, an energy scale correction may be derived using the simple regular calibration procedure given in 6.11. Exactly how the kinetic energy scale is corrected depends on practical details of the instrument being calibrated and so a number of strategies are given in 6.12. The analyst also needs to consider the uncertainty with which the peak kinetic energies need to be measured. Table 1 shows values of some of the typical parameters, defined in this International Standard, which lead to illustrative tolerance limits of ± 0,2 eV and ± 0,3 eV at a confidence level of 95 %. Note the importance of the allowable drift between calibrations in Table 1. Thus, as shown in Figure 1, the calibration interval is determined from measurements of the instrument drift as given in 6.14. The regular calibration is then made at the appropriate calibration interval to maintain the instrument kinetic energy scale within the required tolerance limits.



NOTE The numbers refer to the corresponding subclauses of this International Standard.

Figure 1 — Flowchart of sequence of operations of method

Table 1 — Illustrative contributions to error budget for kinetic energy scale calibration

Item	Symbol	Calculated from	Examples				Comment
			If high accuracy required		If lower accuracy required		
Tolerance limits, eV	$\pm \delta$	User's choice	± 0,2		± 0,3		User's choice dictated by accuracy required and number of spectra there is time to acquire in regular calibrations
Repeatability standard deviation, eV	σ_R	Equation (1)	0,050		0,050		Characteristic of spectrometer measured at first calibration (see 6.7)
Number of times, each pair of spectra is acquired	m	User's choice $m = 1$ or 2	$m = 1$	$m = 2$	$m = 1$	$m = 2$	
Uncertainty of calibration measurements, eV	U_{95}^{cl}	Equation (12) or (13)	0,185	0,130	0,185	0,130	
Measure of scale non-linearity, eV	ε_2	Equation (5) or (6)	0,050	0,050	0,050	0,050	Characteristic of spectrometer measured at first calibration (see 6.7)
Uncertainty of energy scale after calibration, eV	U_{95}	Equation (11)	0,192	0,139	0,192	0,139	
Maximum allowable drift between calibrations, eV	$\pm (\delta - U_{95})$	δ and U_{95}	± 0,008	± 0,061	± 0,108	± 0,161	Define drift allowable before danger of exceeding the chosen limits $\pm \delta$ eV
Maximum calibration interval (for an illustrative instrument that exhibits a steady drift rate of 0,025 eV per month), months	—	See 6.14	0,3	2,4	4,3	6,4	Choose convenient interval below this maximum, and less than four months, with safety margin for any erratic behaviour
Choice of calibration interval, months	—	User's choice, based on observed drift behaviour	Option impractical	1	3	4	

NOTE The uncertainties are for a confidence level of 95 %. The examples illustrate the effect of user choices on the uncertainty of calibration and the required interval between recalibrations.

In this International Standard, measurements are given to establish the uncertainty of the calibration at a confidence level of 95 %, directly after the calibration. The error of the kinetic energy scale will generally increase with time and, during the interval between calibrations, must not exceed the tolerance limits of $\pm \delta$ chosen by the analyst to define the quality of their measurements. Completing a table such as in Table 1 will assist the user in defining a suitable value for δ. If the user has little or no idea of the capability of his or her instrument, if the manufacturer's data give no assistance and if there is no clear idea of the requirements, start with Table 1 with δ set at 0,2 eV. Go through the procedure specified, filling in the rows, and finally check if this value of δ is feasible for the instrument being used. If not, review the operating procedures and either reduce one or more of the terms contributing to U_{95} or increase the value of δ to one that is acceptable.

It is important to note that δ is the tolerance limit for the accuracy of the calibration of the instrumental energy scale. Subsequent energy measurements can have uncertainties greater than δ as a result of peak breadth, poor counting statistics, peak synthesis or charging effects. For guidance on reporting the uncertainty of subsequent measurements, see annex D.

6 Procedure for calibrating the energy scale

6.1 Obtaining reference samples

For the calibration of Auger electron spectrometers able to scan to at least 2 050 eV and with beam energies of 5 keV or 10 keV available, use samples of Cu and of Au. For other instruments use Cu and Al. The samples shall be polycrystalline and of at least 99,8 % purity metals which, for convenience, are usually in the form of foils typically of an area 10 mm by 10 mm and 0,1 to 0,2 mm thick.

If the samples appear to need cleaning, a short dip in 1 % nitric acid may be used for Cu with subsequent rinsing in distilled water. If the Cu sample has been stored in the air for more than a few days, the dip in nitric acid will make the sample cleaning (see 6.3) much easier.

6.2 Mounting samples

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

6.3 Cleaning samples

Achieve ultra-high vacuum and clean the samples by ion sputtering to reduce the contamination until the heights of the oxygen and carbon Auger electron peaks are each less than 2 % of the height of the most intense metal peak in each survey spectrum. Record a survey (widescan) spectrum for each of the samples to ensure that the only significant peaks are those of the required pure elements. The quality of vacuum necessary here is such that the oxygen and carbon peak heights shall not exceed 3 % of the heights of the most intense metal peaks by the completion of the procedure in accordance with 6.11 or at the end of the working day, whichever is the earlier.

All relevant procedures of this International Standard should be completed in one working day. If more than one day is required, the cleanness of the samples shall be confirmed at the start of each day's work.

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

NOTE 2 Contamination effects are generally least for Au and greatest for Al.

See Figure 2 for example AES survey spectra.

6.4 Choosing spectrometer settings for energy calibration

Choose the combination of spectrometer operating settings for which the energy calibration is required. Repeat the calibration procedure in accordance with 6.4 to 6.14 for each combination of analyser settings of pass energy, retardation ratio, slits, lens settings etc., for which a calibration is required. Record the values of these settings in the spectrometer calibration log.

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

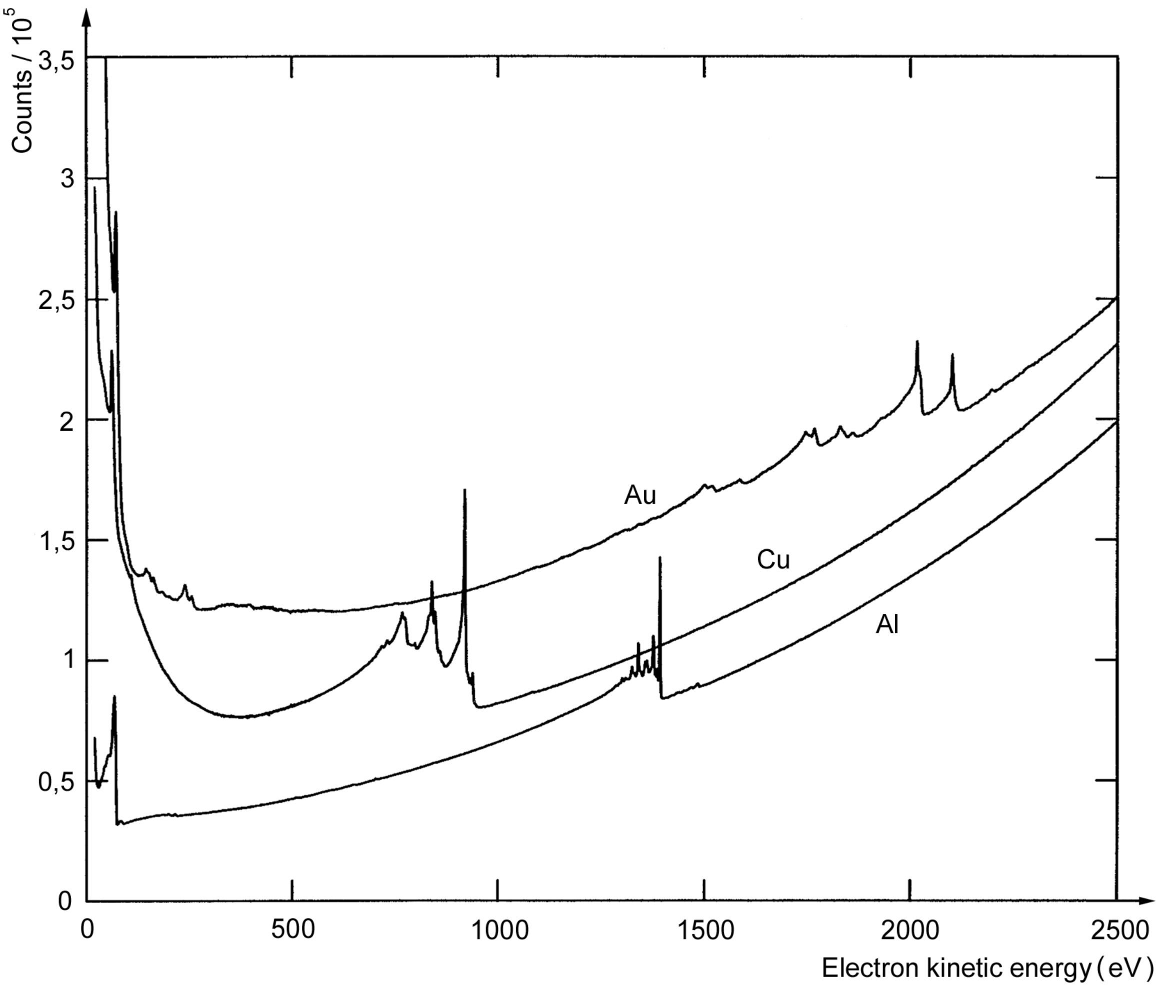


Figure 2 — Widescan (survey) direct spectra for clean Cu, Au and Al measured in constant $\Delta E/E$ mode

6.5 Operating the instrument

6.5.1 IMPORTANT — High counting rates [3] or incorrect detector voltages [3, 4] can cause peak distortions leading to erroneous peak energy assignments.

Set the electron beam energy to 5 keV or 10 keV when using the Au sample, and in the range 5 keV to 10 keV if Al is used. Operate the instrument in accordance with the manufacturer's documented instructions or local documented procedure. The instrument shall have fully cooled following any bakeout. Ensure that the operation is within the manufacturer's recommended ranges for cathode emission, counting rates, spectrometer scan rate and any other parameter specified by the manufacturer. Check that the detector multiplier settings are correctly adjusted. For multidetector systems ensure that any necessary optimizations or checks described by the manufacturer are conducted prior to this calibration.

NOTE Many manufacturers recommend that the control and high voltage electronics be switched on for at least 4 h before conducting any work where accurate energy referencing is important.

6.6 Options for initial or subsequent calibration measurements

In order to maintain the kinetic energy scale of an instrument in calibration, the kinetic energy repeatability, scale linearity error and the calibration interval all need determination. If any of these have not been determined, proceed as follows. If all of these have been determined for the relevant spectrometer settings through prior use of this

International Standard, and if the instrument has not been modified, undergone significant repair or been moved, proceed directly to 6.11, as shown in Figure 1.

6.7 Measurements for peak kinetic energy repeatability standard deviation and scale linearity

6.7.1 The repeatability standard deviation of the peak kinetic energy, σ_R, is measured, in accordance with 6.7.4 to 6.7.6, using the Cu $M_{2,3}VV$, Cu L_3VV, and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks and need usually only be done for the first energy calibration for a given combination of settings. The value of σ_R is valid only for the selected set of conditions and involves a significant contribution from the sample positioning procedure used for the analysis. For consistency, this sample positioning procedure shall follow a documented protocol which takes account of the manufacturer's recommendations. This procedure shall be conducted for each choice of spectrometer operating settings requiring energy calibration, chosen in accordance with 6.4. It could also need to be repeated after any substantive modifications to the instrument.

The sample positioning procedure will depend on the instrument design, the type and shape of the samples and the requirements for analysis. In many cases the correct sample position is determined by maximizing a spectral intensity. Where optimization involves setting two or more interacting parameters, a consistent strategy of optimization is necessary. For spectrometers operated in the constant $\Delta E/E$ mode, the recorded peak energy could be found to be more sensitive to the sample position at high, rather than at low, kinetic energies. It might be useful to conduct the procedure of 6.7 several times in order to refine the sample positioning procedure and obtain low values of the repeatability standard deviations.

NOTE In many spectrometers, setting the sample with its surface normal along the direction of the incident electron beam reduces the sensitivity of the measured peak energies to the sample position.

6.7.2 The kinetic energy scale linearity is determined (see 6.7.4), using the Cu L_3VV Auger electron peak. It is conducted at the same time as the repeatability measurements to reduce both the effort and the measurement uncertainty.

6.7.3 The order of the data acquisition is Cu $M_{2,3}VV$, Cu L_3VV, Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$, with the sequence (see 6.7.4 to 6.7.6) repeated a further six times.

See Figure 3 for details of these peaks.

6.7.4 Set the copper sample at the analytical position with an angle of emission of the detected electrons in the range 0° to 56° from the sample surface normal. Use the documented sample positioning procedure and record the Cu $M_{2,3}VV$ and L_3VV peaks using the set of conditions given in 6.4 with an appropriate electron beam current and channel dwell time to achieve more than 10^6 counts per channel for each of the peaks. Scan with the channel energy interval set at approximately 0,1 eV or less, depending on the chosen manner of determining the peak kinetic energy (see 6.8.1). Scan from at least 2 eV below the lower peak energy to 2 eV above the higher peak energy for the $M_{2,3}VV$ peak, and 2 eV below the peak energy to 2 eV above the peak energy for the L_3VV peak. Ensure that the correct peak has been identified in accordance with Figures 2 and 3.

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

NOTE The reference kinetic energy values for the calibration peaks can vary with the angle of emission. The reference values in this International Standard are only valid for angles of emission in the range 0° to 56° from the surface normal and so the method has been restricted to this angular range [4]. For greater emission angles, the larger shift of the peaks leads to significant errors in the calibration.

6.7.5 Remove the copper sample from the analysis position and replace it with the gold or aluminium samples with the same angle of emission, using the chosen sample positioning procedure. Record the Au $M_5N_{6,7}N_{6,7}$ peak while maintaining the same chosen set of spectrometer settings as for the copper sample and sufficient acquisition time to provide more than 10^7 counts per channel at the peak for Au $M_5N_{6,7}N_{6,7}$, and more than 10^6 counts per channel at the peak for Al $KL_{2,3}L_{2,3}$. Scan from at least 2 eV below the peak energy to 2 eV above the peak energy. Ensure that the correct peak has been identified in accordance with Figures 2 and 3.

The same spectrometer settings as those given in 6.7.4 are to be used, i.e. the same pass energy, retardation ratio, slit sizes, lens settings, multiplier settings, energy interval and energy scan rate. Usually, only the start energy, stop energy and data acquisition time need to be changed.

6.7.6 Repeat 6.7.4 and 6.7.5, in the given sequence, a further six times to obtain seven independent records of each of the three peaks. To save time, the scan widths for these spectra may be reduced, unless a wider interval is made necessary by the choice of a method for determining the peak kinetic energy in accordance with 6.8.1 a).

a) Cu $M_{2,3}VV$

b) Cu L_3VV

c) Au $M_5N_{6,7}N_{6,7}$

d) Al $KL_{2,3}L_{2,3}$

[a] Reference spectra.

[b] Regions of the spectra near the peak maximum on expanded energy scales, with the expansion factor shown beside each spectrum.

Figure 3 — Reference spectra for Auger electron peaks

6.8 Calculating peak kinetic energy repeatability standard deviation

6.8.1 Determine the measured peak kinetic energies for Cu $\mathrm{M}_{2,3}\mathrm{VV}$ by the method given in a) and for the other peaks by either the method given in a) or b).

a) By the first method for the Cu $\mathrm{L}_3\mathrm{VV}$ and Au $\mathrm{M}_5\mathrm{N}_{6,7}\mathrm{N}_{6,7}$ or Al $\mathrm{KL}_{2,3}\mathrm{L}_{2,3}$ peaks, determine the mid-point of the chords drawn horizontally across the peak at an intensity close to, but greater than, 80 % of the peak height above the background, and at three or more further intensities spaced approximately equally in the range 80 % to 100 % of the peak intensity above the background. The mid-points of these chords are then projected to a value at the peak to give the peak energy. See Figure 4, d) and f). This may be done either graphically or computationally using a best fit line for the four or more mid-points.

   For the Cu $\mathrm{M}_{2,3}\mathrm{VV}$ peak, draw a tangent to the peaks as shown in Figure 4, c) and e). Next, draw the chords parallel to this tangent at an intensity of approximately 50 % of the tangent height above a parallel line passing through the valley between the peaks, and at three or more further intensities equally spaced between this 50 % line and the tangent to the peaks. Find the mid-point of each chord across each of the peaks A and B. See Figure 4, c) and e). These mid-points, A_i and B_i for the ith spectrum, will be at approximately 61,3 eV and 63,4 eV, respectively. Next, determine the mid-points, M_i, of A_i and B_i for each tangent line. The M_i positions are then projected to a value at the highest tangent line either graphically or computationally using a best fit line for the four or more overall M_i positions. This value gives the measured energy appropriate to the reference value for the Cu $\mathrm{M}_{2,3}\mathrm{VV}$ peaks.

   The precision for this method of peak location may be improved by first smoothing the spectra with a single application of a Savitzky and Golay cubic/quadratic routine [5] with a width less than or equal to 0,5 of the full width at half the maximum intensity (FWHM) intensity of the peak above background, as shown by the nine-point and seven-point smoothing in Figure 4, e) and f), respectively. The widths of the constituent peaks of the Cu $\mathrm{M}_{2,3}\mathrm{VV}$ doublet are each taken to be 2,0 eV. See annex A for the maximum number of points to be used in the Savitzky and Golay smoothing procedure for different spectrometer relative resolutions.

b) By the second method for the Cu $\mathrm{L}_3\mathrm{VV}$ and Au $\mathrm{M}_5\mathrm{N}_{6,7}\mathrm{N}_{6,7}$ or Al $\mathrm{KL}_{2,3}\mathrm{L}_{2,3}$ peaks, use a least-squares fit of a parabola to the data around the top of the peak. The data points selected shall be approximately equal in number above and below the energy of the maximum intensity, and they shall start and finish at intensities in the range 80 % to 85 % of the peak intensity above the background. If this least squares fitting is unavailable in software, the simple least squares calculation procedure given in annex B may be used.

   NOTE The energy interval for use in the procedure given in annex B is 0,1 eV.

6.8.2 Tabulate the seven values of the measured kinetic energies for each of the three peaks.

6.8.3 Calculate the average kinetic energy, $E_{\mathrm{meas},n}$, from the set of seven measurements $E_{\mathrm{meas},ni}$ for each peak n. Next, calculate the repeatability standard deviation, $\sigma_{\mathrm{R}n}$, of the seven measurements of the nth peak, $E_{\mathrm{meas},ni}$, from 6.7 using the equation:

$$\sigma_{\mathrm{R}n}^2 = \sum_{i=1}^{7} \frac{\left(E_{\mathrm{meas},ni} - E_{\mathrm{meas},n}\right)^2}{6} \qquad (1)$$

The repeatability standard deviation is calculated in this way for $n = 1$, 2 and 4, if using Au, and $n = 1$, 2 and 3, if using Al. The overall repeatability standard deviation, σ_{R}, is taken as the greatest of $\sigma_{\mathrm{R}1}$, $\sigma_{\mathrm{R}2}$, and either $\sigma_{\mathrm{R}4}$ or $\sigma_{\mathrm{R}3}$.

NOTE It is helpful to record the values of σ_{R} in the user's version of Table 1.

6.8.4 Review the peak energies for any systematic changes with time through their order of acquisition. Such systematics may indicate an inadequate warm-up period, a change in the laboratory temperature or another source of drift. If this appears to be the case, take appropriate action (e.g. increase the warm-up period) and repeat 6.7.

a) Cu $M_{2,3}VV$

b) Cu L_3VV

c) Unsmoothed

d) Unsmoothed

e) Smoothed

f) Smoothed

The peaks shown in a) and b) are shown expanded and unsmoothed in c) and d), and smoothed in e) and f) by a single application of a nine-point and seven-point Savitzky and Golay function [5], respectively. The lower four plots show the bisected chord method of finding the peak kinetic energy.

Figure 4 — Spectra of Cu $M_{2,3}VV$ and Cu L_3VV peaks using 5 keV electron beam, relative resolution of 0,1 % and 0,1 eV energy steps

6.8.5 The values of the repeatability standard deviation for peaks with sufficient counts should be less than 0,05 eV for an instrument in good working condition. If σ_{R1}, σ_{R2}, σ_{R4} or σ_{R3} exceeds this value, check the stabilities of the voltage supplies to the instrument, the adequacy of the system ground and the sample positioning procedure. If $\sigma_R > \delta/4$, it will be necessary to increase the proposed value of δ or to find a way of reducing σ_R.

NOTE 1 For the 10^6 counts shown in Figure 3 for Cu and Al and 10^7 counts for Au, the value of σ_R arising from the statistics of counting will contribute a standard uncertainty of less than 0,025 eV using least squares fitting to the data in accordance with annex B.

NOTE 2 In an interlaboratory study [6] in which copper samples were repositioned each time after analysing a different sample, the average results gave $\sigma_{R2} = 0{,}06$ eV for graphically recorded data from high-resolution instruments.

6.9 Determining relevant reference kinetic energies

6.9.1 For instruments with a relative resolution value of below 0,04 %, if Al is used, or below 0,07 %, if Au is used, the reference kinetic energies shall be in accordance with Table 2.

Table 2 — Reference values for peak positions on kinetic energy scale [7]

Peak number n	**Assignment**	$E^{\mathrm{o}}_{\mathrm{ref},n}$ eV
1	Cu $M_{2,3}VV$	62,37
2	Cu L_3VV	918,69
3	Al $KL_{2,3}L_{2,3}$	1 393,09
4	Au $M_5N_{6,7}N_{6,7}$	2 015,80

NOTE 1 These kinetic energies are referenced to the Fermi level.

NOTE 2 This table is a refinement of tables already published in [8,9,10].

6.9.2 For instruments with a value of relative resolution, R %, higher than required for 6.9.1 and Table 2, but less than 0,2 %, the reference energies, $E_{\mathrm{ref},n}$, are given by

$$E_{\mathrm{ref},n} = E^{\mathrm{o}}_{\mathrm{ref},n} + cR + dR^2 \qquad (2)$$

where c and d are in accordance with Table 3.

Table 3 — Corrections to reference kinetic energies

Peak number n	**Assignment**	c eV	d eV
1	Cu $M_{2,3}VV$	0,0	0,0
2	Cu L_3VV	0,2	− 2,0
3	Al $KL_{2,3}L_{2,3}$	− 0,3	− 1,8
4	Au $M_5N_{6,7}N_{6,7}$:		
	5 keV n(E)	0,0	0,0
	5 keV En(E)	− 0,3	4,4
	10 keV n(E)	− 0,2	0,0
	10 keV En(E)	− 0,1	0,0

NOTE This simplification of a more complex table [10] is consistent with that table for relative resolutions in the range 0 % $< R <$ 0,2 % to within 0,015 eV.

6.10 Checking kinetic energy scale linearity

6.10.1 Subtract the reference energies $E_{\text{ref},n}$, given in Table 2 and Equation (2), from the corresponding values of the average measured kinetic energies $E_{\text{meas},n}$, determined in accordance with 6.8.3, and where n identifies the peak given in Table 2, to obtain the measured instrument offset energies, Δ_n, for each peak, n. Thus:

$$\Delta_n = E_{\text{meas},n} - E_{\text{ref},n} \tag{3}$$

6.10.2 To determine whether the kinetic energy scale is sufficiently linear for the intended application, it is necessary to calculate the measured kinetic energy scale linearity error, ε_2, at the Cu L_3VV peak energy using Equations (5) or (6). This error is the difference between the measured instrument offset energy, Δ_2, and that deduced from the measured Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peak kinetic energies, assuming the scale to be linear. For the use of Au $M_5N_{6,7}N_{6,7}$:

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

For the use of Al $KL_{2,3}L_{2,3}$, ε_2 is given by a similar equation, with Δ_4 and E_{ref4} replaced by Δ_3 and E_{ref3}, respectively. Numerically, these equations reduce to

$$\varepsilon_2 = \Delta_2 - 0{,}562\,\Delta_1 - 0{,}438\,\Delta_4 \tag{5}$$

for Au $M_5N_{6,7}N_{6,7}$

and

$$\varepsilon_2 = \Delta_2 - 0{,}356\,\Delta_1 - 0{,}644\,\Delta_4 \tag{6}$$

for Al $KL_{2,3}L_{2,3}$

Calculate the value of ε_2 from Equations (5) or (6) for the Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks, respectively.

NOTE 1 It is helpful to record the value of ε_2 in the user's version of Table 1.

NOTE 2 Non-linearities of the energy scale may arise through uncorrected relativistic effects [10,11,12]. For a cylindrical mirror analyser with no retardation, relativistic effects will add a contribution to ε_2 of 0,398 eV for calibration with the Au $M_5N_{6,7}N_{6,7}$ peak and of 0,172 eV for calibration with the Al $KL_{2,3}L_{2,3}$ peak. For a spherical sector analyser, these figures are higher at 0,920 eV and 0,398 eV, respectively. Few commercial analysers operate at relative resolutions of 0,2 % or better without pre-retardation of the electron energy, usually by a factor, A, of 4 or 10. This reduces the above non-linearity by A^2, i.e. by 16 or 100, respectively. The largest non-linearity above, for the spherical sector analyser, is thus reduced to 0,058 eV or 0,009 eV, respectively. These effects are often small enough to be ignored in practice; however, where very high accuracy or low retardation values are to be used and the magnitude of the contribution to ε_2 is calculated to exceed δ/4, the analyst is advised to consult the literature [10,11,12].

6.10.3 The uncertainty of ε_2 for a confidence level of 95 %, in electronvolts, is less than U_{95}^{l}, where U_{95}^{l} is given by the equation:

$$U_{95}^{\mathrm{l}} = \left[\left(1{,}2\sigma_{\mathrm{R}}\right)^2 + \left(0{,}040\right)^2 \right]^{1/2} \tag{7}$$

6.10.4 Calculate U_{95}^{l}. The kinetic energy scale may be considered as being linear for practical purposes if $|\varepsilon_2|$ is less than U_{95}^{l}. If the value of $|\varepsilon_2|$ is greater than U_{95}^{l}, the scale is non-linear. This non-linearity may be acceptable, however, if $|\varepsilon_2|$ is less than $\delta/4$, i.e. the linearity error may be regarded as sufficiently small compared to the chosen tolerance limit δ.

EXAMPLE If σ_{R} is 0,050 eV (the illustrative value in Table 1), the uncertainty U_{95}^{l} is 0,072 eV.

See Annex C for the derivation of Equation (7).

NOTE In an interlaboratory study [6] using spectra presented graphically, the average value of σ_{R2} was found to be 0,06 eV for high-resolution instruments.

6.10.5 If $|\varepsilon_2|$ is greater than $\delta/4$, it is recommended that corrective action be taken. This could require a revision of operating procedures followed by a repeat of 6.7, contact with the instrument vendor or an upward revision of δ.

NOTE This is not a full test of linearity, which would need extensive test equipment and is beyond the scope of this International Standard.

6.11 Procedure for regular calibration error determination

6.11.1 The calibration error shall be determined at regular intervals for each combination of spectrometer operating settings for which energy calibration of the spectrometer is required, after σ_{R} and ε_2 have been determined for those settings. Each determination of the calibration error shall be made prior to the expiration of the calibration interval established by previous use of the calibration procedure in accordance with 6.14.

6.11.2 For the regular calibration, only the Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks need be used. The order of measurement shall be Cu $M_{2,3}VV$, followed by Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$, with this sequence repeated one further time unless previous calibrations using this procedure have shown that $\sigma_{\mathrm{R}} < \delta/8$, in which case repetition is unnecessary. The number of repeat measurements for the regular calibration, m, is thus 1 or 2. For each measurement, the sample shall be set at the same angle of emission, with that angle being in the range 0° to 56° from the surface normal. The sample positioning procedure shall be used. Determine the peak kinetic energies in accordance with 6.8.1, and calculate the measured instrument offset energies, Δ_1 and Δ_4 from Equation (3).

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

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

The energy scaling error, a, is given by

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

and the zero offset error, b, by

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

where E_{ref1} and E_{ref4} are determined from Tables 2 and 3.

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

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

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

where, for kinetic energies in the range 0 eV to 2 250 eV using the Au $M_5N_{6,7}N_{6,7}$ peak, or 0 eV to 1 550 eV using the Al $KL_{2,3}L_{2,3}$ peak, U_{95}^{cl} is given by

$$U_{95}^{\text{cl}} = 2{,}6\ \sigma_{\text{R}} \tag{12}$$

for $m =$ two measurements

or

$$U_{95}^{\text{cl}} = 3{,}7\ \sigma_{\text{R}} \tag{13}$$

for $m =$ one measurement

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

See annex C, for the derivations of Equations (11) to (13).

6.12 Procedures for correction of instrument kinetic energy scale

6.12.1 Implementation of the calibration of the spectrometer now depends on the instrument, its software, the magnitudes of the instrument offset energies, Δ_n, the repeatability standard deviation, σ_{R}, and the tolerance limits, $\pm\,\delta$, to which it is desired that it work. If the values of $(|\Delta_n| + U_{95})$ for peaks 1 and 3 or 4 are less than $\delta/4$, recalibration of the instrument after the calibration check could be unnecessary. It is, of course, best to recalibrate the instrument after each calibration check, but whether to do so must be judged in terms of the effort and required uncertainty. The manufacturer's calibration instructions to the analyst should now be followed to implement the calibration. For many systems, these permit the analyst to change only the spectrometer work function, ϕ. The strategy chosen will depend on the facilities available on the instrument. For instruments in which changing the spectrometer work function is the only practical option, three simple optional strategies are provided [see a) to c), below]. In these options, the corrected value for the kinetic energy, E_{corr}, is given by

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

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

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

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

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

b) Option 2 minimizes the post-acquisition correction to be applied over the kinetic energy range 0 eV to 2 250 eV if the Au $M_5N_{6,7}N_{6,7}$ peak has been used or 0 eV to 1 550 eV if the Al $KL_{2,3}L_{2,3}$ peak has been used. If the Au $M_5N_{6,7}N_{6,7}$ peak has been used, an increase of $\Delta\phi$ is applied to the spectrometer work function, where

$$\Delta\phi = -\tfrac{1}{2}\left(\Delta_1 + \Delta_4\right) \tag{16}$$

The post-acquisition correction for subsequently measured kinetic energies is then given by

$$\Delta E_{\text{corr}} = a\left(E_{\text{meas}} - \frac{E_{\text{ref1}} + E_{\text{ref4}}}{2}\right) \tag{17}$$

If the Al $KL_{2,3}L_{2,3}$ peak has been used, subscript 4 is replaced by subscript 3 in Equations (16) and (17). Use of this option causes ΔE_{corr} to be zero at 1 039 eV if the Au $M_5N_{6,7}N_{6,7}$ calibration peak has been used, or 728 eV if the Al $KL_{2,3}L_{2,3}$ peak has been used, so that the post-acquisition corrections to the measured kinetic energies are minimized over the kinetic energy ranges 0 eV to 2 250 eV or 0 eV to 1550 eV, respectively.

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

$$\Delta\phi = a\,E_{\text{elem}} + b \tag{18}$$

where E_{elem} is the Auger electron peak energy for the frequently measured element. Now the post-acquisition correction for subsequently measured kinetic energies is given by

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

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

6.12.2 If, following 6.12.1, in the full, or chosen restricted, range of kinetic energies required for analysis, the subsequent sum $|\Delta E_{\text{corr}}| + U_{95}$ remains below δ over the calibration interval, the post-acquisition correction, ΔE_{corr} defined in the three options given in a), b) and c) of 0, may be ignored. However, the calibration, is now valid only for the chosen restricted range of kinetic energies.

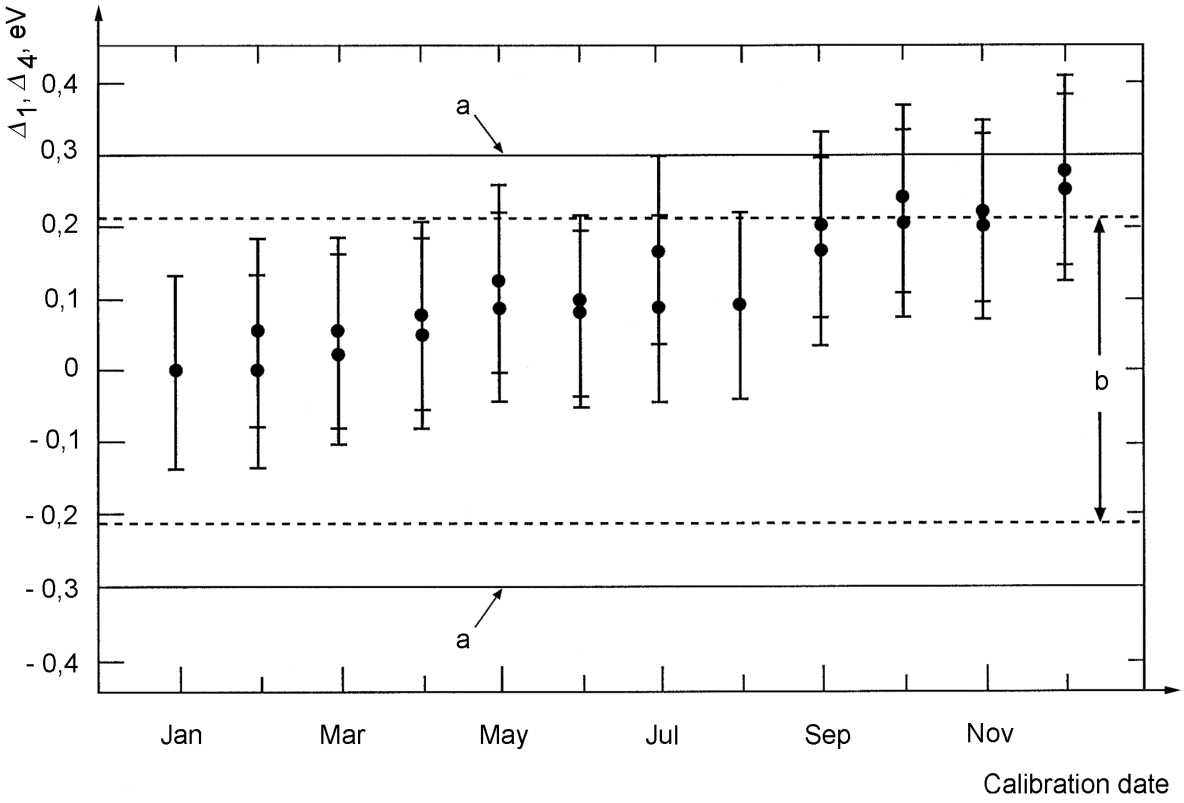
6.12.3 The corrective procedure chosen shall be documented together with the values of Δ_1, Δ_4, a, b, the valid kinetic energy range and $\Delta\phi$, if used. The corrective procedure shall be checked the first time the procedure is used by repeating the calibration to ensure that all actions have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

6.12.4 If this is the first calibration for the chosen conditions, prepare an energy calibration control chart as in Figure 5, to show the calibration data as a function of the calibration date. On the chart, also draw the tolerance limits, $\pm\,\delta$, and the warning limits at $\pm\,0{,}7\delta$ to indicate when recalibration is necessary.

6.12.5 On the energy calibration control chart, if post-acquisition corrections to the kinetic energy scale are not applied, plot the measured values of Δ_1 and Δ_4. However, if post-acquisition corrections to the kinetic energy scale are applied, also plot the values of [$\Delta_1 + \Delta E_{\text{corr}}$(evaluated at E_{ref1})] and [$\Delta_4 + \Delta E_{\text{corr}}$(evaluated at E_{ref4})]. Uncertainty limits, U_{95}, shall be plotted for each measurement on the control chart, as shown in Figure 5.

6.12.6 If post-acquisition corrections to the kinetic energy scale are not applied, check that ($|\Delta_1| + U_{95}$) and ($|\Delta_4| + U_{95}$) are both less than δ. If post-acquisition corrections to the kinetic energy scale are applied, check that [$|\Delta_1 + \Delta E_{\text{corr}}$(evaluated at E_{ref1})$| + U_{95}$] and [$|\Delta_4 + \Delta E_{\text{corr}}$(evaluated at E_{ref4})$| + U_{95}$] are both less than δ. If these conditions are not met and this is the first calibration, check for arithmetical errors. If these conditions are not met and this is not the first calibration, the calibration interval could need to be shortened or the value of δ increased to an acceptable one.

NOTE Plotting the values Δ_1 and Δ_4 on the control chart, where post-acquisition corrections to the kinetic energy scale are applied, is not important for confirming if the instrument is within calibration for this procedure, but is helpful in monitoring the cumulative drift of the instrument and, consequently, for optimizing the calibration interval.



The plotted values for Δ_1 and Δ_4 illustrate an instrument that has not been recalibrated since the start in January and in which no post-acquisition kinetic energy scale correction is applied. It is first out of calibration in September and should, since it has both passed the upper warning limit and reached the four-month time limit, have been recalibrated in May. The uncertainties shown for each plotted value, U_{95}, are for a confidence level of 95 % and include the scale linearity error and its uncertainty. This illustrates the example in Table 1 with $m = 2$ and $\delta = 0{,}3$ eV.

[a] 95 % tolerance limit.

[b] Warning limits.

Figure 5 — Control chart [13,14] for monitoring instrument calibration status — Example

6.13 Next calibration

6.13.1 The next calibration is made before the sum of the calibration uncertainty, U_{95}, and the instrumental drift causes the total uncertainty in the calibration at a confidence level of 95 % to exceed $\pm\,\delta$. The calibration is therefore made at or before the calibration interval defined by the work in 6.14. If the interval is not known, proceed to 6.14, determine the interval and then return to 6.12.2 while retaining that interval.

6.13.2 Repeat the procedure from 6.2 to 6.6 and 6.11 to 6.12 at the calibration interval defined in 6.14 unless the instrument has been modified or undergone significant change. Each time, note any change made to the instrument calibration (e.g. settings of electrode voltages or the spectrometer work function) and the cumulative change since the calibrations started. Ensure that the cumulative change does not exceed any figure advised by the manufacturer. In all cases, record the instrument settings for the calibration, including the pass energy or retardation ratio, slits or aperture settings, lens settings and the electron beam energy used.

6.14 Establishing calibration intervals

6.14.1 With the equipment running throughout the day, measure the Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ kinetic energies at hourly intervals. Any drift shows that it may be necessary to leave some of the electronic units on for some specified minimum time (or perhaps to leave the units on continuously) to achieve adequate stability. Note the ambient temperature with each measurement and check for any correlation. The procedure used for the calibration, in terms of warm up times etc., shall also be used during analysis where conformance with this International Standard is required.

NOTE 1 Drift is most likely to arise from temperature changes in the voltage supplies for the spectrometer. These drifts often occur as a function of the time of operation and so can, for example, be repeated similarly each day. Thus, tests at 9:00 each day miss any diurnal drift. Drifts of the Au $M_5N_{6,7}N_{6,7}$ peak energy have been observed to be larger than those of the Cu $M_{2,3}VV$ peak.

If the stability during the first day is adequate, measure the Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ kinetic energies at progressively greater intervals of time such that U_{95} added to the greater of the changes in Δ_1 and Δ_4 between calibrations remains less than $\pm\, 0{,}7\delta$. The last interval becomes the maximum useful calibration interval until it is found that the data of drift rate indicates that a shorter or longer period is appropriate. This interval shall not exceed four months.

NOTE 2 For many instruments, a calibration interval of one or two months has been found adequate. A judgement of what is an adequate interval and what are appropriate tolerance limits depends on the analytical requirements and the instrument behaviour.

Annex A
(normative)

Maximum number of points for single application of Savitzky and Golay smoothing of peaks at 0,1 eV energy intervals

A single application of Savitzky and Golay cubic/quadratic smoothing [5] may be used to reduce the apparent noise in spectra without contributing significant distortion, provided the width of the Savitzky and Golay function is less than 0,5 of the full width at half maximum of any of the intrinsic peaks in the spectrum being smoothed. The maximum number of points in such smoothing, for evaluating the peak energy by the chord method when using 0,1 eV channel intervals, is given in Table A.1.

Table A.1 — Maximum number of points in Savitzky and Golay smoothing for each peak for different spectrometer relative resolutions

Peak number	Assignment	Spectrometer relative resolution				
n		0,01 %	0,05 %	0,1 %	0,15 %	0,2 %
1	Cu $M_{2,3}VV$	9	9	9	9	9
2	Cu L_3VV	5	5	7	7	9
3	Al $KL_{2,3}L_{2,3}$	5	5	7	11	15
4	Au $M_5N_{6,7}N_{6,7}$	13	13	15	19	23

Annex B
(normative)

Least squares determination of peak kinetic energy by a simple computational method

B.1 Symbols and abbreviated terms

The following symbols and abbreviations are used in this annex.

c_i	Count value in the ith channel
E_o	Kinetic energy for the first data channel at energy lower than the channel for the absolute maximum intensity in the peak, in electronvolts
E_p	Least squares estimate of the peak kinetic energy, in electronvolts
g	Channel separation, in electronvolts
i	Channel number with its origin for the first data channel at lower kinetic energy than the channel for the absolute maximum intensity in the peak
P	Coefficient of p dependent on the value of S
p	Sum of the counts over S channels about the peak
Q	Coefficient of q dependent on the value of S
q	First moment of the counts over S channels about the peak divided by g
r	Second moment of the counts over the S channels about the peak divided by g^2
S	Number of sequential data values used in this least squares determination

B.2 Least squares method

A least squares estimate of the energy of the peak may be conveniently determined by using 0,1 eV channel intervals and selecting S data values, evenly spaced in energy with half of the data values on each side of the estimated peak kinetic energy, where S is as given in Table B.1.

Table B.1 — Maximum value of S for optimum use of Equation (B.1)

Peak number, n	Assignment	Minimum spectrometer relative resolution				
		0,01 %	0,05 %	0,1 %	0,15 %	0,2 %
2	Cu L_3VV	6	6	6	10	10
3	Al $KL_{2,3}L_{2,3}$	6	6	10	14	14
4	Au $M_5N_{6,7}N_{6,7}$	14	14	18	22	26

The least squares estimation of the peak kinetic energy, E_p, is given by [15]

$$E_\mathrm{p} = E_\mathrm{o} + \frac{g}{2}\left(\frac{r - Qq - 3Pp}{r - q - 5Pp}\right) \tag{B.1}$$

where

E_o is the kinetic energy of the first data channel at kinetic energy lower than that for the maximum count;

g is the channel separation, in electronvolts.

The parameters p, q and r are defined by

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

$$q = \sum_{i=-2}^{3} ic_i \tag{B.3}$$

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

where

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

c_i is the count value for the ith channel

and the values of P and Q are as given in Table B.2.

Table B.2 — Coefficients P and Q for values of S

Coefficient	Value of S					
	6	10	14	18	22	26
P	8/15	8/5	16/5	16/3	8	56/5
Q	47/15	37/5	69/5	67/3	33	229/5

Table B.3 illustrates a completed version of a table for the evaluation of Equations (B.1) to (B.4) for the Cu L_3VV peak measured at 0,05 % relative resolution.

In bibliographic reference [15], equations are provided to show the uncertainty in the value of E_p arising from the uncertainty associated with the statistics of Poissonian counts in the peak. The standard uncertainty is less than 25 meV for the defined conditions.

Table B.3 — Example evaluation of Equations (B.1) to (B.4) for Cu L3VV peak measured at 0,05 % relative resolution and using six data values

i	**Energy** E	**Counts** c_i	$i\,c_i$	$i^2 c_i$
– 2	*918,3*	*972 889*	*– 1 945 778*	*3 891 556*
– 1	*918,4*	*997 619*	*– 997 619*	*997 619*
0	*918,5*	*1 002 390*	0	0
1	*918,6*	*993 814*	*993 814*	*993 814*
2	*918,7*	*968 876*	*1 937 752*	*3 875 504*
3	*918,8*	*935 287*	*2 805 861*	*8 417 583*
		SUM	SUM	SUM

E_o	p	q	r
918,5	*5 870 875*	*2 794 030*	*18 176 076*

$$E_p = E_o + \frac{g}{2}\left(\frac{r - 47q/15 - 8p/5}{r - q - 8p/3}\right) = 918{,}495$$

NOTE The numbers in italics are the data that have been entered into the table, a blank copy of which can be found in reference [15].

Annex C
(informative)

Derivation of uncertainties

C.1 Computation of uncertainty for energy scale linearity error

In defining the repeatability standard deviations, σ_{R1}, and σ_{R4} or σ_{R3}, for the Cu $M_{2,3}VV$, and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks, k measurements are made. In this International Standard, the value of k has been chosen as 7. The uncertainties with which instrument offset energies Δ_1 and Δ_4 or Δ_3 at $E_{\text{ref 1}}$ and $E_{\text{ref 4}}$ or $E_{\text{ref 3}}$ are then determined are given by ± $U_{95}^{c}(E_{\text{ref1}})$ and ± $U_{95}^{c}(E_{\text{ref4}})$ or ± $U_{95}^{c}(E_{\text{ref3}})$, for a confidence level of 95 %, where

$$U_{95}^{c}(E_{\text{ref 1}}) = t_{k-1}\sigma_{R1}/k^{1/2} \tag{C.1}$$

and

$$U_{95}^{c}(E_{\text{ref 4}}) = t_{k-1}\sigma_{R4}/k^{1/2} \tag{C.2}$$

and, similarly, for $E_{\text{ref 3}}$, where t_{k-1} is Student's t factor for a two-sided distribution for $k - 1$ degrees of freedom. In this annex, all uncertainties are for a confidence level of 95 %.

The uncertainty for the offset energy at a measured energy, E_{meas}, predicted from a straight line passing through the offset energies Δ_1 and Δ_4 at E_{ref1} and E_{ref4}, is given by [4]

$$U_{95}^{c}(E_{\text{meas}}) = t_{k-1}\left[\left(\frac{E_{\text{meas}} - E_{\text{ref1}}}{E_{\text{ref 4}} - E_{\text{ref1}}}\right)^2 \frac{\sigma_{R4}^2}{k} + \left(\frac{E_{\text{ref 4}} - E_{\text{meas}}}{E_{\text{ref 4}} - E_{\text{ref1}}}\right)^2 \frac{\sigma_{R1}^2}{k}\right]^{\frac{1}{2}} \tag{C.3}$$

If, at this point, σ_R is equated with the greater of σ_{R1}, and σ_{R4} or σ_{R3}, the uncertainty of the calibration at the energy of the linearity test, E_{ref2}, is $U_{95}^{c}(E_{\text{ref2}})$ where

$$U_{95}^{c}(E_{\text{ref 2}}) = t_{k-1}\frac{\sigma_R}{k^{1/2}}\left[\left(\frac{E_{\text{ref 2}} - E_{\text{ref1}}}{E_{\text{ref 4}} - E_{\text{ref1}}}\right)^2 + \left(\frac{E_{\text{ref 4}} - E_{\text{ref 2}}}{E_{\text{ref 4}} - E_{\text{ref1}}}\right)^2\right]^{\frac{1}{2}} \tag{C.4}$$

$$= 0{,}71\, t_{k-1}\frac{\sigma_R}{k^{1/2}} \tag{C.5}$$

The coefficient of 0,71 is calculated for the calibration using Au $M_5N_{6,7}N_{6,7}$. For Al $KL_{2,3}L_{2,3}$ this coefficient is 0,74. The uncertainty of the measurement of the linearity test peak energy is given by $t_{k-1}\sigma_{R2}/k^{1/2}$. The uncertainty of the measured kinetic energy scale linearity error, ε_2, is given by the quadrature sum of this term and two further terms:

- $U_{95}^{c}(E_{\text{ref2}})$ from Equation (C.5);
- the uncertainty of the linearity test peak's kinetic energy with respect to the Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peak kinetic energies, and has the value [7] 0,04 eV.

Thus, if σ_R is now equated with the greatest of $\sigma_{\mathrm{R}1}$, $\sigma_{\mathrm{R}2}$ and $\sigma_{\mathrm{R}4}$ or $\sigma_{\mathrm{R}3}$:

$$\left(U_{95}^{\mathrm{l}}\right)^2 = \left(1{,}24\,\frac{t_{k-1}\;\sigma_\mathrm{R}}{k^{1/2}}\right)^2 + \left(0{,}040\right)^2 \tag{C.6}$$

in electronvolts

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

$$U_{95}^{\mathrm{l}} \leqslant \left[\left(1{,}2\sigma_\mathrm{R}\right)^2 + \left(0{,}040\right)^2\right]^{1/2} \tag{C.7}$$

in electronvolts

as shown in Equation (7).

C.2 Computation of uncertainties for regular calibration

The errors in the kinetic energy scales of most instruments will be approximately linear with the kinetic energy E. Even if ε_2 has been shown to be less than U_{95}^{l}, so that the scale may be taken to be linear, this is only known at the energy $E_{\mathrm{ref}\ 2}$ to the uncertainty U_{95}^{l}. Analysis of this situation, where σ_R is equal to the greatest of $\sigma_{\mathrm{R}1}$, $\sigma_{\mathrm{R}2}$, $\sigma_{\mathrm{R}3}$ or $\sigma_{\mathrm{R}4}$, gives the overall uncertainty U_{95}^{cl} for the kinetic energy range 0 eV to 2 250 eV using the Au $\mathrm{M_5N_{6,7}N_{6,7}}$ peak, or 0 eV to 1550 eV using the Al $\mathrm{KL_{2,3}L_{2,3}}$ peak, where [7]

$$U_{95}^{\mathrm{cl}} \leqslant \frac{1{,}5 t_6 \sigma_\mathrm{R}}{m^{1/2}} \tag{C.8}$$

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

$$U_{95}^{\mathrm{cl}} \leqslant 2{,}6\sigma_\mathrm{R}, \qquad m = 2 \tag{C.9}$$

$$\leqslant 3{,}7\sigma_\mathrm{R}, \qquad m = 1 \tag{C.10}$$

as shown by Equations (12) and (13). If $|\varepsilon_2|$ is greater than U_{95}^{l} but less than $\delta/4$, calibrations are still valid. The value of ε_2 must now be included in the uncertainty of the calibration. If the energy scale error is assumed to have a second order dependence on E, the non-linearity contribution would maximize at 1,15 ε_2 and minimize at – 1,15 ε_2 in the kinetic energy range 0 eV to 2 250 eV using the Au $\mathrm{M_5N_{6,7}N_{6,7}}$ peak or 0 eV to 1 550 eV using the Al $\mathrm{KL_{2,3}L_{2,3}}$ peak. Again, a third-order energy scale error is contained within ± 1,2 ε_2. The total energy scale uncertainty, U_{95}, is thus usefully given by

$$U_{95} = \left[\left(U_{95}^{\mathrm{cl}}\right)^2 + \left(1{,}2\,|\varepsilon_2|\right)^2\right]^{1/2} \tag{C.11}$$

as shown by Equation (11).

Annex D
(informative)

Citation of uncertainties of measured kinetic energies

D.1 General

This International Standard specifies a method for determining the calibration uncertainty for the kinetic energy scale of an Auger electron spectrometer. Analysts might then wish to cite the uncertainty with which they can determine further (i.e. new) peak energies. For the purposes of this International Standard, this will be called the "analytical uncertainty" (U_A). There are three common situations to consider, as outlined below. All three involve the repeatability standard deviation of the new peak, σ_Rnew.

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

In this case, since spectrometers rarely have scale errors greater than 0,1 % and the energy differences of chemical states are less than 10 eV, many of the uncertainties of the present calibration may be ignored. The repeatability measurements given in 6.7 have a significant contribution from the effects of sample position and, since this aspect is common to both of the relevant peaks, it is ignored. If the peak profiles do not overlap, the uncertainty of the separation will be defined by the uncertainties of defining each peak [15]. If the peaks overlap, the maxima of the spectral intensity will not occur at the same energies as for the constituent peaks. It is customary then to use peak synthesis software that provides the kinetic energies for each constituent peak. The analytical uncertainties, for valid software, are then dominated by the statistics of the peak fitting [16,17], rather than any of the items discussed in the present calibration.

D.3 Energy difference between Auger electron peaks measured for chemical state in two samples analysed sequentially

As in D.2, most of the calibration uncertainties may be ignored, but the analytical uncertainty depends on the repeatability standard deviations for the two peaks. If the repeatability standard deviation, σ_Rnew, for a new peak being measured is equal to the value of σ_R determined in the calibration, the analytical uncertainty at a confidence level of 95 % for the energy difference for conductors is given by

$$U_\mathrm{A} = t_{k-1} 2^{1/2} \sigma_\mathrm{R} \tag{D.1}$$

if $k = 7$, then

$$U_\mathrm{A} = 3{,}5 \sigma_\mathrm{R} \tag{D.2}$$

For insulators, the uncertainty of the charge referencing needs inclusion. This uncertainty may dominate the other terms.

It should be noted that, for many peaks of interest, σ_Rnew will be greater than σ_R, since the peaks will often be broader and less intense than the relevant metal peaks used for calibration.

D.4 Energy of single peak measured soon after calibration

If measurements of peak energies are made sufficiently soon after a calibration such that the instrumental drift can be ignored (see 6.14), the uncertainty is then as given in Equations (11) and (C.11) but includes a term for the new peak. For the conditions of Equations (11) and (C.11):

$$U_{\mathrm{A}} = \left\{ \left[U_{95}^{\mathrm{cl}}(E) \right]^2 + \left(1{,}2 \left| \varepsilon_2 \right| \right)^2 + \left(t_{j-1}\ \sigma_{\mathrm{Rnew}} \right)^2 \right\}^{1/2} \qquad \text{(D.3)}$$

This assumes that σ_{Rnew} has been derived from j measurements of the scatter for the new peak. In practice, of course, no measurement of σ_{Rnew} is generally made. If σ_{Rnew}, σ_{R1}, σ_{R2}, σ_{R4} or σ_{R3} are $\leqslant \sigma_{\mathrm{R}}$, Equation (D.3) may be evaluated. For two repeats or one repeat for the Cu $M_{2,3}VV$ and Au $M_5N_{6,7}N_{6,7}$ peaks in the regular calibration and for one measurement of the spectrum for the new peak:

$$U_{\mathrm{A}} \leqslant \left[\left(3{,}6\ \sigma_{\mathrm{R}} \right)^2 + \left(1{,}2 \left| \varepsilon_2 \right| \right)^2 \right]^{1/2} \qquad (m = 2) \qquad \text{(D.4)}$$

and

$$U_{\mathrm{A}} \leqslant \left[\left(4{,}4\ \sigma_{\mathrm{R}} \right)^2 + \left(1{,}2 \left| \varepsilon_2 \right| \right)^2 \right]^{1/2} \qquad (m = 1) \qquad \text{(D.5)}$$

As noted in D.3, for many new peaks, σ_{Rnew} may be greater than σ_{R} , when Equation (D.3) is used.

D.5 Energy of single peak between calibrations

For a new peak measured between calibrations:

$$U_{\mathrm{A}} \leqslant \delta + t_{j-1} \sigma_{\mathrm{Rnew}} \qquad \text{(D.6)}$$

where, as in D.4, the repeatability standard deviation of the new peak, σ_{Rnew}, is defined by j measurements.

If, as above, σ_{Rnew} is less than or equal to the value of σ_{R} determined in the calibration by previous recording of the new peak seven times, then for one measurement of the spectrum of the new peak:

$$U_{\mathrm{A}} \leqslant \delta + 2{,}5\ \sigma_{\mathrm{R}} \qquad \text{(D.7)}$$

As noted in D.3, for many new peaks, σ_{Rnew} may be greater than σ_{R}.

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