
**Surface chemical analysis — Medium-
resolution Auger electron spectrometers —
Calibration of energy scales for elemental
analysis**

*Analyse chimique des surfaces — Spectromètres d'électrons Auger à
résolution moyenne — Étalonnage des échelles d'énergie pour l'analyse
élémentaire*



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Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 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 17973 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *X-ray photoelectron spectroscopy*.

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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 peak energies and peak shapes, with tabulations of peak energies and data in handbooks of spectra for the different elements. To identify the peaks, calibration of the energy scale with an uncertainty of 3 eV is generally adequate, and this International Standard is only intended for work at that level of accuracy (for greater accuracy, see ISO 17974 [1]).

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). It does not include tests for defects in the instrument, since few defects are significant at the level of accuracy concerned.

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 user is free to choose the reference appropriate to his or her work.

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Surface chemical analysis — Medium-resolution Auger electron spectrometers — Calibration of energy scales for elemental analysis

1 Scope

This International Standard specifies a method for calibrating the kinetic energy scales of Auger electron spectrometers with an uncertainty of 3 eV, for general analytical use in identifying elements at surfaces. In addition, it specifies a method for establishing a calibration schedule. It is applicable to instruments used in either direct or differential mode, where the resolution is less than or equal to 0,5 % and the modulation amplitude for the differential mode, if used, is 2 eV peak-to-peak. It is applicable to those spectrometers equipped with an inert gas ion gun or other method for sample cleaning and with an electron gun capable of operating at 4 keV or higher beam energy.

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

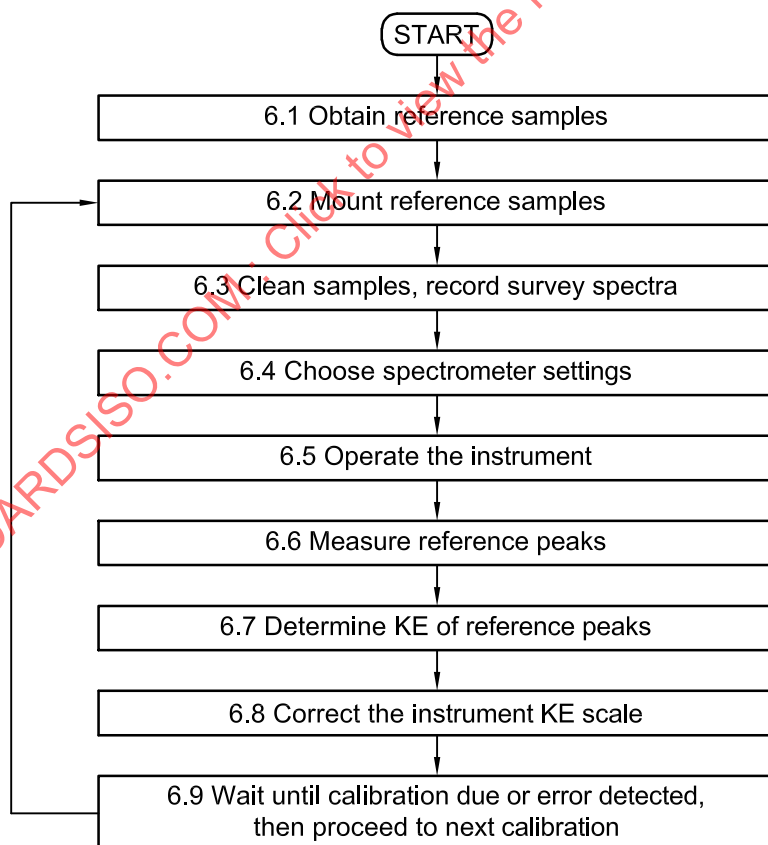
AES	Auger electron spectroscopy
a	measured energy scaling error
b	measured zero offset error, in electronvolts
E_{corr}	corrected result for kinetic energy corresponding to given E_{meas} , in electronvolts
E_{meas}	a measured kinetic energy, in electronvolts
$E_{\text{meas},n}$	measured kinetic energy for peak n (see Table 1), in electronvolts
$E_{\text{ref},n}$	reference values for kinetic energy position of peak n (see Table 1), in electronvolts
FWHM	full width at half maximum peak intensity above background, in electronvolts

W	FWHM of peak
Δ_n	offset energy, given by average measured kinetic energy for calibration peak minus reference kinetic energy, in electronvolts, for $n = 1, 2, 3, 4$ (see Table 1)
ΔE_{corr}	correction added to E_{meas} after calibration to provide corrected kinetic energy result
β	energy scale scan rate for analogue systems, in electronvolts per second
τ	time constant for analogue detector electronics, in seconds

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 one Auger electron peak in the high energy range, one in the middle range and one at low energies. The samples are cleaned and spectra are recorded in the direct mode, if that is available, or in the differential mode if not. The energies of the peaks are compared with reference values to provide an energy scale correction. How this correction is implemented depends on the facilities available with the spectrometer. Because this calibration may alter with time, a procedure is defined to enable the calibration to be established at regular intervals.

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



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

Figure 1 — Flowchart of method — Sequence of procedures

6 Energy scale calibration procedures

6.1 Obtaining reference samples

For the calibration of Auger electron spectrometers providing a high signal-to-noise ratio, as defined below, and able to scan the kinetic energy range up to 2 100 eV, use samples of Cu and Au. For spectrometers with a lower signal-to-noise ratio or those only able to scan to 2 000 eV, use samples of Cu and Al.

If, for the spectrometer used, the counts for the Cu L_{3VV} peak in the direct mode are less than 400 000 counts per second, or the root mean square noise in the differential spectrum exceeds 0,3 % of the Cu L_{3VV} peak-to-peak signal, or if the maximum electron beam energy is less than 5 keV, Cu and Al may be used instead of Cu and Au, since the recording of suitable Au data may be time consuming.

For instruments with higher signal intensities and for spectrometers able to scan to 2 100 eV, the use of Au could be found to be the more convenient and to provide a calibration over a wider energy range. The requirement for 400 000 counts per second for the Cu L_{3VV} peak may be relaxed to 100 000 counts per second if Savitzky and Golay smoothing is available at nine or more points in the smooth [2].

All 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 from 0,1 mm 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.

NOTE Better signal-to-noise ratios are often obtained for 10 keV to 20 keV beam energies rather than for lower beam energies.

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. Double-sided adhesive tape shall not be used.

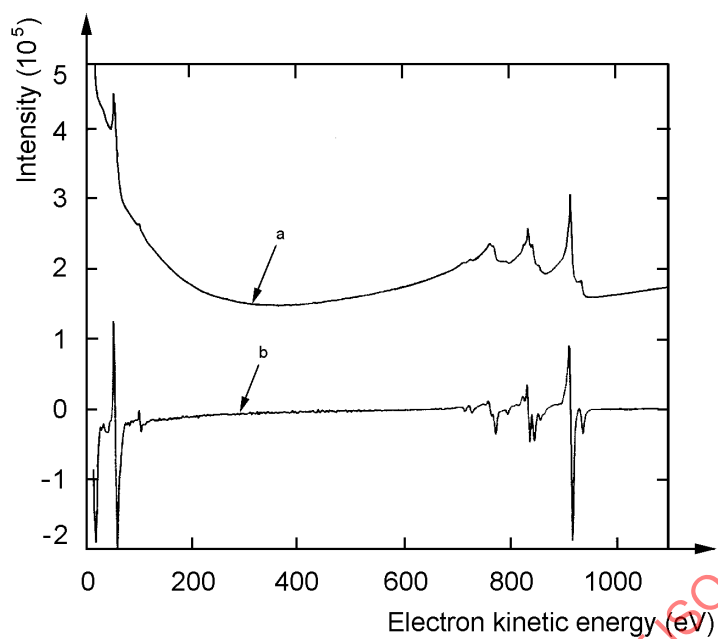
6.3 Cleaning samples

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 6.6 or at the end of the working day, whichever is the earlier.

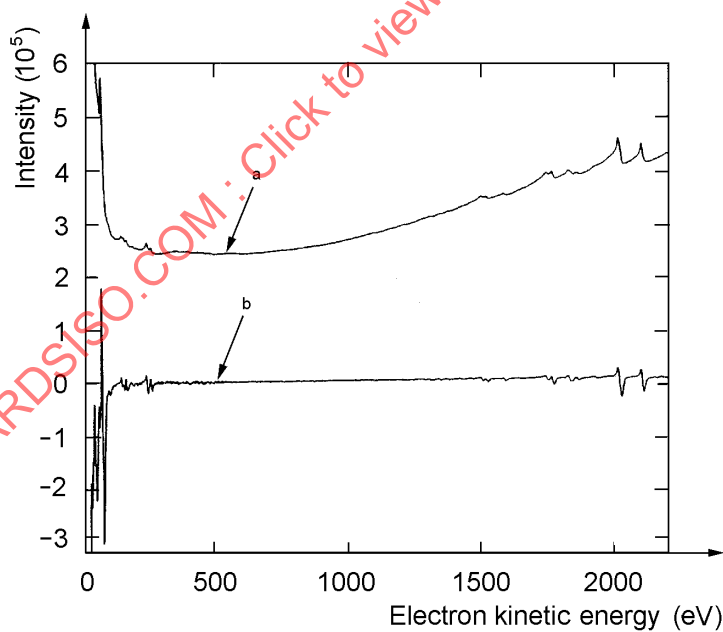
All relevant procedures of this International Standard should be completed in one working day. If more than one day is required, the cleanness of the samples shall be confirmed at the start of each day's work.

NOTE Inert gas ion sputtering conditions that have been found suitable for cleaning are 1 min of a 30 μ A beam of 5 keV argon ions covering 1 cm² of the sample.

For examples of direct and differential spectra, see Figure 2.

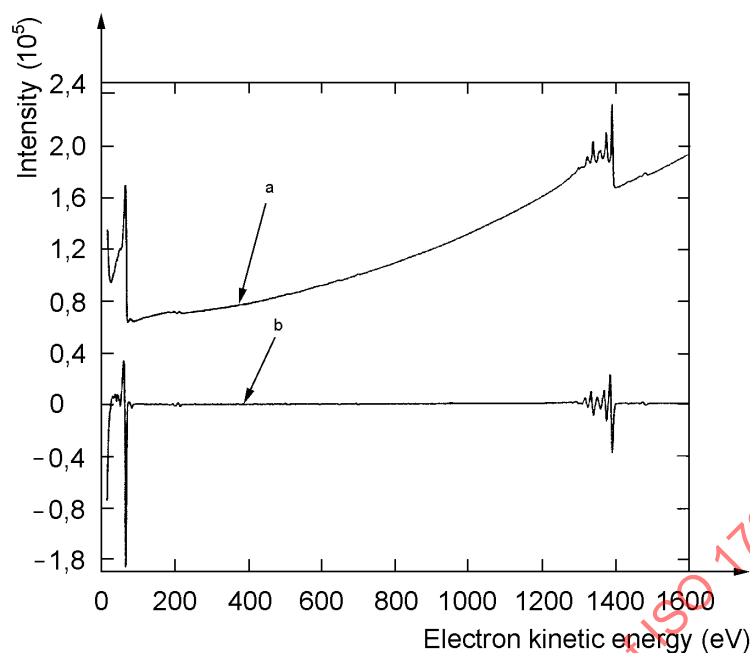


a) Cu



b) Au

Figure 2 — Survey spectra of clean copper, gold and aluminium



c) Al

- a Direct spectra.
- b Differential spectra.

Figure 2 (continued)

6.4 Choosing spectrometer settings for energy calibration

Set the spectrometer to acquire spectra in the direct mode, if possible. For spectrometers operating only in differential mode, set the amplitude of the differentiating function to 2 eV peak-to-peak. Choose the remaining spectrometer operating settings for which the energy calibration is required. Repeat the calibration procedure in accordance with 6.4 to 6.6 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.

6.5 Operating the instrument

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

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 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.

6.6 Measurement of reference peaks

6.6.1 Set the copper sample at the analytical position with the same angle of emission as normally used. The sample positioning procedure shall follow a documented protocol taking account of the manufacturer's recommendations. Record the Cu $M_{2,3}VV$ and L_3VV peaks [see Figure 3, a) and b)] for the direct or differential modes, using the settings chosen in accordance with 6.4.

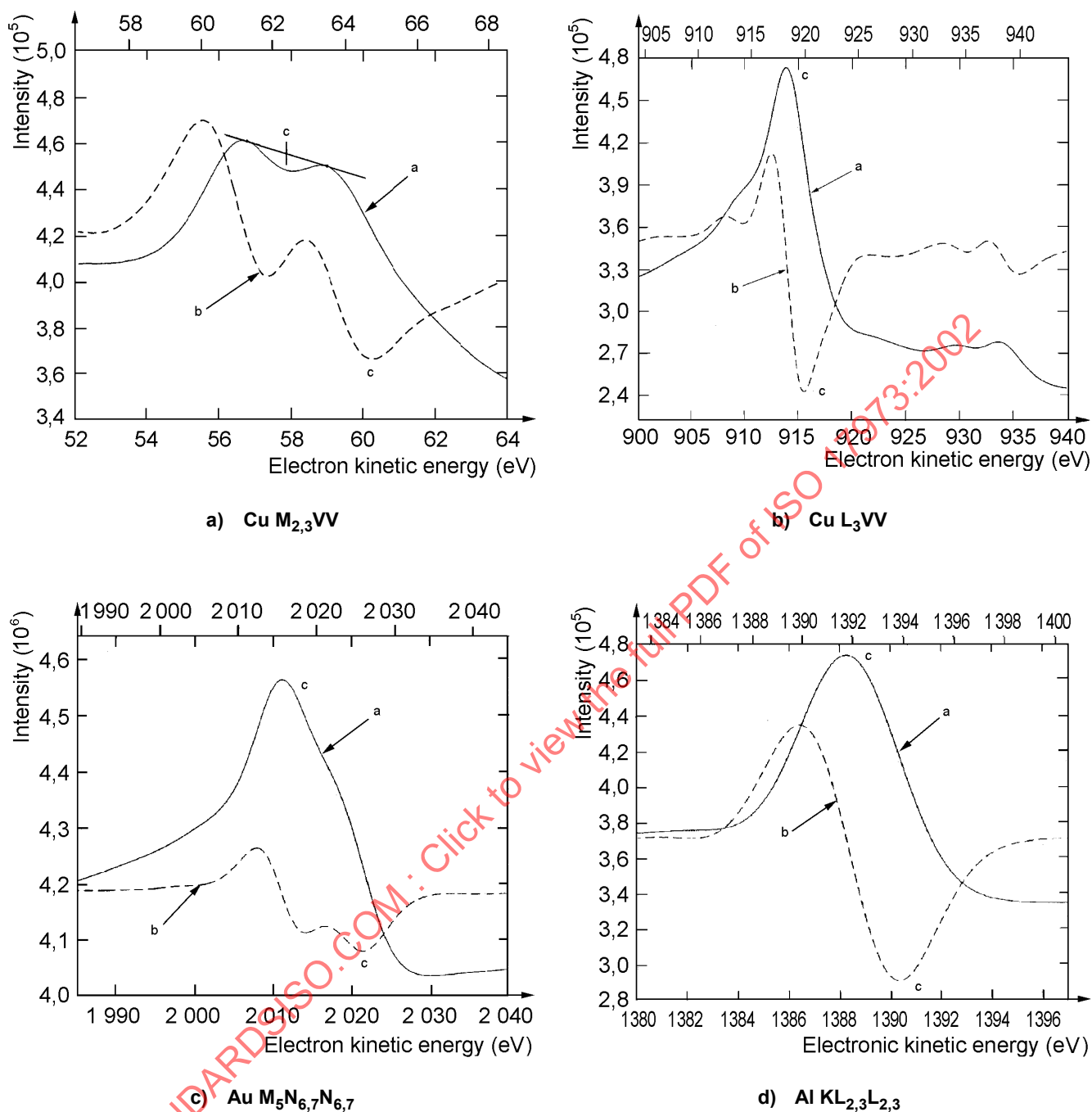
- a) If using a digital scan for the energy scale, set the increment at, or near, 0,1 eV.
- b) If using an analogue system, set the scan rate, β , at less than $0,07W\tau^{-1}$ eV/s, where W is the peak full width at half maximum (FWHM) and τ is the detecting amplifier time constant.

Record at least the signal levels in accordance with Table 1 by a suitable choice of total channel dwell time or τ/β . If Savitzky and Golay smoothing with nine or more points in the smooth is available, note that the minimum signal levels are lower (see Table 1).

6.6.2 Recording the Au $M_5N_{6,7}N_{6,7}$ peak takes approximately 10 times as long as the Cu L_3VV peak. If this time is unacceptable, or if the spectrometer only scans to 2 000 eV or if the electron beam energy is less than 5 keV, Cu and Al samples should be used instead of Cu and Au. Remove the Cu sample from the analytical position and replace it with the Au or Al sample. Using the same combination of analyser settings as for 6.6.1, except for the total channel dwell time or τ/β , which may be set as required, record the Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks shown in Figure 3, c) or d).

Table 1 — Signal intensities to be recorded

Peak number <i>n</i>	Assignment	Minimum counts per channel at the peak for direct mode ^a		Maximum acceptable root mean square noise as a percentage of peak-to-peak signal for differential mode	
		No smoothing	Savitzky and Golay ≥ 9 point	No smoothing	Savitzky and Golay ≥ 9 point
1	Cu $M_{2,3}VV$	400 000	100 000	1 %	2 %
2	Cu L_3VV	400 000	100 000	1 %	2 %
3	Al $KL_{2,3}L_{2,3}$	400 000	100 000	1 %	2 %
4	Au $M_5N_{6,7}N_{6,7}$	4 000 000	1 000 000	1 %	2 %
^a No backgrounds are to be subtracted.					



NOTE The differential spectra have been displaced vertically for clarity. The energy scale at the bottom of the figures is vacuum level referenced and that at the top is Fermi level referenced. These spectra have had the noise level reduced for clarity.

- a Direct mode.
- b Differential mode.
- c Calibration peak.

Figure 3 — Example narrow scan spectra of peaks at 0,3 % relative resolution

6.7 Determining measured kinetic energies of reference peaks

By observation of the peaks on a suitably expanded scale, determine, with one exception, the energies of the absolute peak maxima in the direct spectra, or the negative peak minima in the differential spectra, identified in Figure 3. The exception is the Cu $M_{2,3}VV$ direct spectral peak in Figure 3, a), where a tangent is drawn to the two peaks in the doublet to enable the kinetic energy mid-way between the points of contact to be determined. This procedure may be conducted using the directly acquired data if the intensities specified for the "No smoothing" condition (see Table 1) have been recorded. If less than this, but if at least the levels shown in the Savitzky and Golay ≥ 9 point condition have been acquired, smooth the data with a single application of a Savitzky and Golay cubic/quadratic smooth of at least 9 points, but not exceeding the values given in Table 2.

NOTE 1 Smoothing the data in accordance with Table 2 will also help with intensities higher than those given in Table 1.

NOTE 2 In the differential mode, the Au $M_{5,6,7}N_{6,7}$ peak has a triplet structure that is not resolved at resolutions poorer than 0,15 %. This triplet reduces to a doublet and, at resolutions worse than about 0,3 %, only the minimum [see c) in Figure 3, c] is visible.

Table 2 — Maximum number of points for Savitzky and Golay smoothing procedure for channel interval of 0,1 eV and indicated values for maximum spectrometer relative resolution

Peak number <i>n</i>	Assignment	Maximum spectrometer relative resolution				
		0,1 %	0,2 %	0,3 %	0,4 %	0,5 %
1	Cu $M_{2,3}VV$	9	9	9	9	9
2	Cu L_3VV	9	15	19	25	29
3	Al $KL_{2,3}L_{2,3}$	9	19	29	39	49
4	Au $M_{5,6,7}N_{6,7}$	19	29	39	55	69

6.8 Determining correction of instrument kinetic energy scale

6.8.1 Calculate the measured instrument offset error, Δ_n , for the peak n given in Table 1 using the equation:

$$\Delta_n = E_{\text{meas},n} - E_{\text{ref},n} \quad (1)$$

where $E_{\text{meas},n}$ is the measured peak energy and $E_{\text{ref},n}$ is the reference peak energy given in Table 3.

Ensure that the reference energy is appropriate for the choice of mode — direct or differential — being used.

NOTE Reference values are provided for calibration of the spectrometer with energies referred to either the vacuum level or Fermi level. Traditionally, the vacuum level is used and examples of spectra referenced in this way are given in bibliographical references [5] to [8]. If work is also done involving X-ray photoelectron spectroscopy, it may be more convenient to refer the data to the Fermi level as in [9] and [10].

6.8.2 Review the three values Δ_1 , Δ_2 , and Δ_3 or Δ_4 . If the moduli (i.e. the magnitude, ignoring the sign) of these values are all ≤ 2 eV, the instrument is in calibration. If the moduli of some values are > 2 eV, the instrument shall either be recalibrated according to the manufacturer's instructions or the energy correction defined in 6.8.3 shall be applied. After the instrument has been recalibrated for the first time, the measurements defined in 6.6 shall be repeated and the values of Δ_1 , Δ_2 , and Δ_3 or Δ_4 shall be redetermined to ensure that their moduli after recalibration are < 2 eV.

NOTE If the values of Δ_n are all in the range 3 eV to 6 eV, the instrument may currently be calibrated with reference to the Fermi level and not the vacuum level. This is usual for instruments of high energy resolution more commonly calibrated in accordance with ISO 17974[1].